

**Volume IV**

**SCIENTIFIC PAPERS OF C V P**

**OPTICS OF MINERALS  
AND DIAMOND**



To C. V. Raman (1888 – 1970) colour in nature was an obsession. The visual impact that the blue of the Mediterranean had on him culminated in his discovery of the Raman effect. *Volume IV of the Scientific Papers of C. V. Raman* contains 79 papers he published on a variety of topics, 39 of which deal with colour in Nature. All the optical phenomena in his repertoire were necessary to explain the flashing rainbow colours of the plumage of birds. The hues of limestone and marble, the brilliant iridescence of feldspars of the labradorite variety, the pure spectral colours of the specular reflections from potassium chlorate, the schiller of the moonstones, fire of opals, and the silky lustre of the pearls which no lapidary can ever reproduce and hundred other topics are discussed in this volume. Raman was amongst the earliest to worry about what are now called periodic modulated structures.

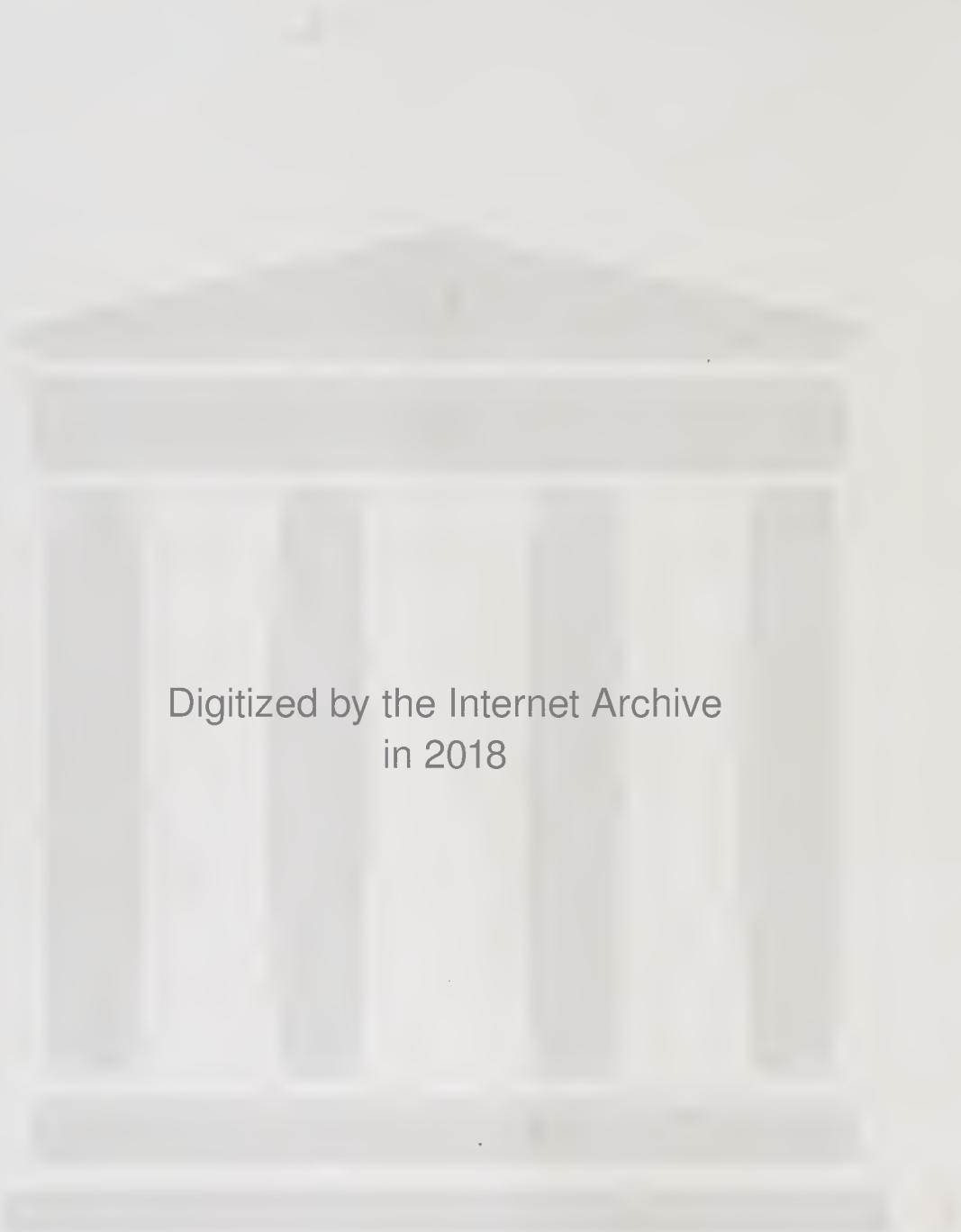
Sixteen papers deal with diamonds. The beauty of their geometric form, and their lustrous curved faces, bring out clearly that many specimens exhibit a symmetry lower than the highest in the cubic class. Raman required an interplay and intermingling of these lower and higher symmetries to explain many properties like Raman activity, infra-red absorption, fluorescence, birefringence, X-ray topography etc. Raman therefore attributed a lower intrinsic symmetry to the carbon atom. But it was found much later that the real lowering of the symmetry was due to the presence of impurities. The papers deal with this very controversial object.

OUP  
INDIA

Rs 375.00

(See on back flap)





Digitized by the Internet Archive  
in 2018

Scientific Papers of  
**C V RAMAN**

**Volume IV**

**OPTICS OF MINERALS  
AND  
DIAMOND**



**Scientific Papers of  
C V RAMAN**

**Volume IV  
OPTICS OF MINERALS  
AND  
DIAMOND**

Edited by

**S Ramaseshan**



**INDIAN ACADEMY OF SCIENCES  
BANGALORE  
1988**

*Published by*

Indian Academy of Sciences  
P.B. No. 8005, Sadashivanagar  
Bangalore 560 080, INDIA

Telephone: 342546 Telex: 0845-2178 ACAD IN  
Telefax: 0812 340492

*Distributed by*

Oxford University Press  
YMCA Library Building, Jai Singh Road, New Delhi 110001  
Bombay Calcutta Madras  
Oxford New York Toronto  
Melbourne Tokyo Hong Kong

© 1988 INDIAN ACADEMY OF SCIENCES, BANGALORE

The copyright of individual papers rests with  
the original publishers viz., American Physical Society,  
New York; Calcutta University Press, Calcutta; Chemical Society,  
London; Current Science Association, Bangalore; Gauthier-  
Villars, Paris; Indian Association for the Cultivation of  
Science, Calcutta; Institute of Physics, Bristol; Macmillan and  
Company Ltd., London; Nobel Foundation, Stockholm; Optical  
Society, London; Optical Society of America, Washington;  
The Physical Society, UK; Physikalisches Institut der  
Universität, Heidelberg; The Royal Society, London; Springer-  
Verlag, Heidelberg; Taylor & Francis Ltd., UK; University of  
Chicago Press, Chicago.

Typeset and printed at Thomson Press (I) Ltd., New Delhi, India.

## TABLE OF CONTENTS

1. Acknowledgements . . . . .	vii
2. Introduction . . . . .	ix
3. Contents . . . . .	xvii
4. The papers . . . . .	1-708
5. Index to co-authors . . . . .	709
6. Subject index . . . . .	709
7. Name index . . . . .	711
8. Papers published from C V Raman's laboratory on the subjects covered in this volume	
a) list of papers . . . . .	715
b) author index . . . . .	725
9. Consolidated list of C V Raman's scientific papers— Volumes I-VI . . . . .	727



## ACKNOWLEDGEMENTS

In bringing out the six volumes of the scientific papers of C V Raman many individuals and institutions have contributed.

I should like to express my thanks to the following learned societies, institutions and publishing houses for permission to reprint the papers which C V Raman published in their journals: American Physical Society, New York; Calcutta University Press, Calcutta; Chemical Society, London; Current Science Association, Bangalore; Gauthier-Villars, Paris; Indian Association for the Cultivation of Science, Calcutta; Institute of Physics, Bristol; Macmillan and Company Ltd., London; Nobel Foundation, Stockholm; Optical Society, London; Optical Society of America, Washington; The Physical Society, UK; Physikalisches Institut der Universität, Heidelberg; The Royal Society, London; Springer-Verlag, Heidelberg; Taylor & Francis Ltd., UK; University of Chicago Press, Chicago. I thank the President of the Indian Academy of Sciences, the Chairman of the Raman Research Institute Trust, and the Director of the Raman Research Institute for their generous help.

These volumes could not have been brought out without the invaluable support of the publication staff of the Indian Academy of Sciences and the staff of the Raman Research Institute Library. I wish to record my indebtedness to them and also to many others who so willingly helped. Special thanks are due to Thomson Press (I) Ltd for their efficient printing and prompt delivery of the volumes.

Thanks are also due to the Jawaharlal Nehru Foundation for a Fellowship during the tenure of which much of the preliminary planning of these volumes was done and to Rajaram Nityananda of the Raman Research Institute for his continual help.

*S RAMASESHAN*



## INTRODUCTION

### The background

Volume 4 of the *Scientific Papers of C V Raman* contains 76 papers on a variety of topics. The first 21 are on a medley of subjects ranging from surface tension to zonal winds—subjects which interested Raman from time to time (from 1905 to 1968!). The second set of 39 papers deals mainly with the colour displayed by objects in nature (mostly minerals) whose visual beauty had a strange fascination for Raman. The last set of 16 papers are again on a mineral for which Raman had a special affection, *the diamond*. As in the introductory essays for the previous volumes, we shall comment on some of the topics touching on historical details where appropriate.

### Miscellaneous papers

*Surface tension:* The experimental work reported in the first paper of this volume was started sometime in 1905. It is a neat piece of research, executing a casual suggestion made by Kelvin in his *Popular Lectures and Addresses* that the surface tension of a liquid can be determined by measuring the curvature of a suspended drop. The young Raman displayed skill and ingenuity in rigging up a spark generator to illuminate the suspended drop to take instantaneous photographs of its shadow, correct for any errors that diffraction of light may introduce, etc.

*Viscosity:* Raman's phenomenological theory of viscosity is based on the hypothesis that the liquid state is composite in character consisting in part of molecules rigidly attached to each other (as in a solid) and in part of molecules which are relatively mobile (as in the gaseous state). Taking the energies required to separate a pair of molecules of each type and applying the Boltzmann distribution law, Raman derived a simple formula connecting the viscosity of a liquid with that of its vapour. From this he computed the viscosity of liquid benzene at different temperatures. The calculated values agreed with the experimental ones to within 2 parts in a thousand! Staudinger, the pioneer in polymer chemistry later found Raman's model eminently suited to correlate the viscosity of solutions of molecules in various states of polymerization.

*Impact:* Raman's interest in struck strings led him to investigate the problem of impact where he made some significant advances both in theory and experiment.

While using Hertz's theory, Raman considered all the possible modes of dissipation of energy which could affect the coefficient of restitution when two spheres collide. These were (a) the sound waves and (b) the stresses occurring during impact when they exceed the limits of perfect elastic recovery. His group had shown that the sound waves were generated by the impulses communicated to the atmosphere due to the sudden reversal of the motion of the spheres and the energy thus dissipated is negligible; the dissipation due to imperfect elasticity would also be negligible for small velocities of impact. Therefore Raman argued, the coefficient of restitution at extremely low velocities must tend to unity irrespective of the nature of the material of the balls or their elastic properties. This result was verified by a series of beautiful experiments on balls made of different materials with a wide range of elastic and other properties. Raman also used the idea that part of the translational energy is transformed into elastic wave motion in the substance of the solid to calculate the coefficient of restitution in the case of the sphere and a flat plate. Assuming annular flexural waves to be set up in the plate, the coefficient of restitution was calculated and found to agree well with the experiment.

Many concepts of the manner and mechanism by which a solid breaks down under impact came out of these early researches. When a sphere impacts a plate the stresses in the centre are compressive and the fracture does not start there. The fracture is initiated as a circular crack near the margin and it travels inwards into the plate obliquely at  $45^\circ$  along the surface of maximum shearing stress set up during impact. Raman was also amongst the earliest to use interferometric methods to study the nature of the deformation after breakdown.

### The plumage of birds

The striking colours of the plumage of birds fascinated Raman and were the subject of many of his studies. The interest was all the more as the optical characters and distribution of colours were so different in different parts of the same bird, in different specimens and in different species that no single explanation would suffice. Every phenomenon known to the optical scientist—interference, diffraction and scattering of light—had to be invoked. Interference due to thin films on the surface, selective spectral reflection from stratified films, the diffraction of light by discontinuities not small compared to the wavelength of light, the Tyndall effect due to minute air cavities, the anisotropic scattering due to elongated holes and particles, all contribute to these colours. Further the delicate interplay of these physical effects with the chemical colours enhances the spectacular chromatic display seen in birds.

Raman published only one paper on this subject but gave dozens of lectures to large audiences. His favourite title was *Birds, Beetles and Butterflies* but each lecture was unique and usually contained an account of a study he made of a

specific object from his remarkable collection. He was particularly fond of the iridescence displayed by the magnificent tail feathers of the peacock and the gorgeous plumage that covers the head and neck of the Himalayan pheasant. The ubiquitous kingfisher and the plebian parrot were also subjects of his study. Those were days when colour slides were not yet in vogue. For his lectures he did use well mounted museum specimens. At one of these lectures on the commoner garden Indian jay Raman painted word pictures of this bird and its colourful feathers so graphically that the listener could see in his mind's eye the succession of coloured bands of alternating deep indigo blue and light greenish blue, changing dramatically when the bird was in flight; dull and drab when the light is from behind and turning to a brilliant green with almost enamel lustre when lit from the front. The feathers display transient colours after a shower when damp—the blue indigo becoming shimmering green or a dark blue or even a dramatic deep violet depending on the position of the sun and the observer. To Raman birds were beautiful and hence fit subjects for serious study.

### **Colours exhibited by minerals**

In the new Institute he built for himself to work in peace after he formally retired, he started by arranging his magnificent now famous, collection of minerals; specimens he had gathered from all over the world for the extraordinary optical phenomena they exhibited—(limestones, marbles, alabaster, gypsums, tourmalines, agates, quartzites, jades, amethysts, fluorites, micas and serpentines, iolites, malachites, lapis lazuli and feldspars).

Feldspars were truly intriguing—labradorite, a special variety, displayed, brilliant colours; another group, moonstones, found use in jewellery because of the beautiful optical effect called *schiller*. He continuously leaned on his old experiences with scattering of light in liquids. For example he compared the blue schiller from the best moonstones he had with the blue opalescence in binary liquid mixtures as the critical temperature is approached; or the spectacular blue colour exhibited by many labradorites with the blue opalescence when water is added to methanol containing benzene in solution (when benzene tends to separate). He concluded that although in a common macroscopic sense these substances, moonstones and labradorites, were monocrystals they had optical heterogeneities in them.

To begin with, the basic facilities had not yet been established at his Institute. There was as yet no electric power and so he had to revert to the use of his old trusted technique of using a beam of sunlight (the technique he had used to discover the Raman Effect) to explore and understand the optics of these substances. He felt that the passage of light through the mineral and its diffusion would reveal the existence and nature of optical heterogeneities, i.e., the local variations in composition and refractive index. These optical inhomogeneities

could be embedded in a matrix. But there were a large number of possibilities. The inhomogeneities could be cavities or crystallites or just variations of composition. They could be isotropic or birefringent, oriented randomly or with a preferred direction; they could show periodicities in one, two or three dimensions. The medium itself could be amorphous or crystalline, polycrystalline or a monocrystal, isotropic or birefringent. All these variations Raman wanted to probe with just a beam of light. He knew that it would be best to generalise the Raman–Nath theory considering not only the phase corrugations due to these random optical inhomogeneities but also the states of polarisation. But being pragmatic Raman (with Viswanathan) developed a theory based on simpler models. The character of the diffused light, its spectral nature, its intensity, and state of polarisation, and its distribution in different directions and the variation with setting of the crystal and the direction of the passage of light furnished him with the data needed to infer the nature and distribution of the local heterogeneities.

He studied a variety of minerals, iridescent potassium chlorate, iridescent shells, feldspars, moonstones, fiery opals, iridescent agates, iridescent calcite, iridescent quartz, jadeite, cryptocrystalline quartz, polycrystalline gypsum (and also a variety of natural and synthetic fibres). It is remarkable how much detailed information he could extract from this simple means of sending a beam of sunlight through the mineral. Many of his conclusions were right but some wrong as well. For example, Raman (with Jayaraman) deduced that in opal the fiery colour was due to isotropic inhomogeneities with a refractive index lower than that of the surrounding medium but segregated periodically. Later electron microscopic studies showed that they were isotropic and of lower refractive index and also periodically distributed in the lattice but were really submicroscopic air bubbles!

He was amongst the earliest to worry about the existence of periodic compositional segregation in minerals which he felt was much more common than usually supposed. This phenomenon underlies the modulated structures which are widely studied today.

*Pearls:* A special word about the pearl; the gemstone which does not need the services of a lapidary to enhance its natural beauty. The precise understanding of the optics behind its loveliness was a matter of more than ordinary interest to Raman. He (with Krishnamurti) discovered that light falling normally on the rear surface does not travel through the pearl but around it (as does sound in a whispering gallery—a subject in which he had done much research), following the lamination of its structure. The beauty of the pearl is to be found in this effect, together with the superposition of the chromatic diffusion halo and also the reflected light.

### The diamond

Soon after the discovery of the Raman Effect, C. Ramaswamy, Raman's younger brother, asked him to suggest a research problem which he could pursue. Seeing

the diamond ring that the newly wed Ramaswamy sported on his finger, Raman suggested the study of *the modified scattering* in diamond. Ramaswamy discovered the famous  $1332\text{ cm}^{-1}$  Raman line of diamond. This was followed by the work of Bhagavantam, one of Raman's star pupils recording the Raman spectrum of a 140 carat diamond that was borrowed from the Maharaja of Dharbhanga. Bhagavantam graphically describes how he spent two days and two nights in the dark spectroscopy room in trepidation praying that nothing untoward should happen to the precious gem. He confirmed Ramaswamy's discovery and also recorded the complex luminescence spectrum around  $4152\text{ \AA}$ . Raman must have had this in mind when he relates how he was "reduced to the expedient of borrowing diamond rings from wealthy friends who, though willing to oblige, were slightly apprehensive about the fate of their property". Raman later visited another of his wealthy friends when he was "graciously permitted by His Highness the Maharaja of Panna to examine his famous garland of fifty two large (Panna) diamonds of exquisite beauty, all in their natural uncut state as crystals ranging from 25 carats to 2 carats strung into the form of an exquisite necklace". He then wrote: "With their perfect geometric forms and their smooth lustrous beauty they look absolutely fresh from nature's crucible, although actually taken from sedimentary formations a thousand million years old. The strongly marked curvature of the crystal faces and the smoothly rounded edges are a surprising feature of these crystals". These diamonds as seen now, according to Raman, are exactly in the same state as they were when first formed. The love affair with diamond had begun.

Obtaining the material in the form suitable for study was his first obstacle. He discovered that flat pieces of diamond of excellent quality, not too expensive could be purchased in useful sizes from many jewellers in India. The diamond auctioneers in remote corners of India were very accommodating. They had never seen such a colourful personality, that too a scientist, sitting crosslegged in their midst. Contrary to all their usual custom they obligingly permitted him to examine each specimen under a microscope, a fluoroscope and a strain viewer (which he carried with him) and permitted him to form his own "lots" wondering why anyone should mix such expensive stones with such utterly worthless ones! Raman purchased hundreds of representative specimens, euhedral crystals, cut gems, or plates. They were bought for their beauty of form, colour, fluorescence or birefringence.

The results of the X-ray analysis of the crystal structure of diamond by W H Bragg and W L Bragg (1913) were regarded as demonstrating that diamond possesses the highest holohedral cubic symmetry. This was in conflict with the view of all the earlier crystallographers. Raman had in his personal library the works of some of the recognised authorities on mineralogy from all over the world—Groth, Liebisch, Hintze, Dana, Lewis, Miers etc. It was his custom to read these regularly—particularly those with painted illustrations. Without exception diamond was assigned to the ditessaral polar class i.e. the hemihedral tetrahedral class of the cubic system. The assignment was based on the fact that

although crystals of diamond exhibiting octahedral symmetry of form were seen in numbers, specimens showing only the tetrahedral symmetry were also forthcoming. It was the view of these crystallographers that the highest symmetry when observed was the result of supplementary twinning of positive and negative tetrahedral forms. The manifestation of grooves in many octahedral crystals was a clear proof of this. Raman was, of course, familiar with Van der Veen's work that diamond does not exhibit any pyroelectric properties, which was considered irreconcilable with the assignment of tetrahedral symmetry.

Much controversy had taken place upon the question whether diamond is actually octahedral or tetrahedral. Raman was very troubled by all this. In the twenties when he represented India at the bicentenary celebrations of the Academy of Sciences of the U.S.S.R. he discussed this with many Russian crystallographers as also Sir Henry Miers, the reputed British mineralogist (who represented the United Kingdom and the Royal Society) at these celebrations. Miers reiterated the statement he had made in his book "The problem is now regarded as decided in favour of the tetrahedrite class". Raman paid much credence to the conclusions of the older scholars and felt that the evidence they had gathered after careful study must not so easily be brushed aside. He also believed that while the structure as determined by X-rays was essentially right, the symmetry itself was open to question because of the basic ambiguity of X-ray methods in symmetry determination.

In 1934 many things happened. Nagendra Nath at Raman's instance studied the dynamics of the diamond lattice and published a series of papers in which he showed that the fundamental frequency of the diamond structure ( $1332\text{ cm}^{-1}$  frequency) is a triply degenerate oscillation of the two face-centred cubic lattices of carbon atoms with respect to each other. In the same year the celebrated article of G. Placzek *Rayleigh-Streuung und Raman Effekt* appeared. In this he discussed the relation between the symmetry class of a crystal and the activity of its vibration in infrared absorption and the Raman Effect. He showed that for groups which contain a centre of symmetry the selection rules for the two are complementary; but for groups that do not have a centre of symmetry there is a possibility that the same vibration may appear both in Raman Effect and in infrared absorption. In the case of the triply degenerate vibration in a crystal having octahedral symmetry it can manifest itself *only* in the infra-red absorption *or* in scattering of light but *not in both*. On the other hand, in a crystal with tetrahedral symmetry, such a vibration must appear *both* in infra-red absorption and Raman Effect or *can appear in neither*.

Again in 1934, Robertson, Fox and Martin showed that diamonds are not identical in their behaviour in infra-red absorption—one group which represents the majority of cases showing strong absorption in the  $1300\text{--}1350\text{ cm}^{-1}$  region which is wholly absent in a second and rarer variety.

When his collection of diamonds had expanded Raman decided to examine (along with a student) a large number of diamonds in their natural form—

obtained from various sources—many of them from India. There was no doubt whatsoever that many of these exquisite clear, water white crystals displayed the symmetry of the tetrahedral class. To Raman it appeared that the view of the earlier crystallographers in assigning the hemihedral or lower symmetry to diamond was justified and it was vindicated by the infra-red absorption data and the selection rules so far as the common variety of diamond was concerned. He was also certain that the rarer variety *must* be credited with the full holohedral symmetry. Here was the enigma. It was quite confusing.

Raman was convinced that the intensive study of diamond itself would surely not only provide the answer but could be of import to physics and chemistry. He felt history had a way of repeating itself. For, did not diamond exhibit in a striking fashion many phenomena which are scarcely noticeable in other solids under ordinary circumstances? The variation of specific heat with temperature was known as an experimental fact in the case of diamond at least 50 years before it was recognised as a universal property of the solid state. Weber's data published in 1875 formed the basis of Einstein's epoch-making paper introducing the quantum theory of specific heat.

So experimental activity was mounted at a rate never before undertaken in India and results and techniques began to pour out.

Even if it is conceded that diamond has tetrahedral symmetry, the two variant subclasses, the positive and negative tetrahedral structures, would be identical in respect to energy of formation. It is therefore possible to have both of these in the same structure but this cannot give a crystal which has a centre of symmetry at a microscopic level.

To explain the existence of diamond with octahedral symmetry Raman was obliged to give symmetry properties to the atom itself—that the carbon atom *itself* had a tetrahedral symmetry (as distinct from the symmetry of its bonds). If the structure had either positive tetrahedral carbon atoms or negative ones *only* and they were all oriented in the same direction, a diamond structure with positive or negative tetrahedral symmetry will result giving two tetrahedral forms of diamond. A positive tetrahedral carbon atom can combine with a negative one in two ways to get a centre of symmetry between the two atoms—with their apices pointing to each other or away from each other—giving two more forms of octahedral diamond structure. He then considered the effect of these four types intermingling in the same crystal, the strains they would generate, their imperfections as seen in X-ray topography, their infra-red absorption, the fluorescence they would exhibit under ultraviolet light and X-rays, the ultraviolet absorption and many other properties. He tested these in his diamond plates—and the correlations were striking. He could look at the birefringence patterns of a plate and predict the patterns they would show in regard to other properties. It was almost uncanny. Raman therefore thought he was right. It is now believed that all this was based on a wrong premise and the accepted explanation of these variations is that they are caused by impurities.

The possible role of impurities had in fact been suggested to Raman but it went against his intuition and he rejected it.

It is interesting how intuition played a vital role in his earlier important discoveries. The discovery of the Raman Effect owed much to his intuitive belief, dating from 1923, that the “weak fluorescence” that he and his students observed in light scattering was not due to impurities but originated from the molecules that constituted the liquid. It must have been this unshakable conviction that made him drive his student collaborators into purifying and repurifying scores of liquids to look for specific characteristics in the scattered light which would distinguish it from the molecular scattering or fluorescence due to impurities. However, the same intuition seems to have played him false in the case of diamond. Unable to purify his diamonds, he studied hundreds of specimens. All the while he was unwilling to believe that the “prince of crystalline solids” could be flawed by major impurities. Years later it was established that many of the phenomena he and his students discovered arose due to impurities (like nitrogen) in the diamond lattice. It is ironic that the symmetry changes induced by these are similar to those Raman proposed to explain the observed phenomena and which he considered intrinsic to the carbon atom.

We have pointed out that Raman’s vision of intrinsic tetrahedral symmetry in diamond did not prove correct. But the number of new ideas and techniques which came out of the extensive studies of this crystal is truly remarkable. The use of X-ray topography for the study of crystal imperfection was discovered independently in Raman’s laboratory. The application of the Jamin effect (now called ellipsometry) for the study of thin surface films was introduced. The cleavage properties and energies and hardness anisotropy of crystal surfaces were studied and ideas such as dangling bonds discussed. The fluorescence and phosphorescence of crystals was studied and a whole range of optical effects such as second order Raman scattering, Brillouin scattering, photoelastic properties of solids, and many others were systematically investigated, many for the first time. It would be no exaggeration that a whole school of crystal physics grew and flourished in that period with its roots in Raman’s fascination for the diamond. Even though the tetrahedral symmetry that Raman sought proved elusive, the tools and results of his quest came to be of lasting value to the physics of solids.

*S RAMASESHAN*

## CONTENTS

### 1. Miscellaneous Papers

1. The curvature method of determining the surface-tension of liquids, 1907, <i>Philos. Mag.</i> , <b>14</b> , 591–596.	1
2. Some new methods in kinematical theory, 1912–1913, <i>Bull. Calcutta Math. Soc.</i> , <b>4</b> , 1–4.	7
3. On the summation of certain Fourier series involving discontinuities, 1913–1914, <i>Bull. Calcutta Math. Soc.</i> , <b>5</b> , 5–8.	11
4. A theory of the viscosity of liquids, 1923, <i>Nature (London)</i> , <b>111</b> , 532–533.	15
5. The viscosity of liquids, 1923, <i>Nature (London)</i> , <b>111</b> , 600–601.	18
6. The photographic study of impact at minimal velocities, 1918, <i>Phys. Rev.</i> , <b>12</b> , 442–447.	20
7. Percussion figures in isotropic solids, 1919, <i>Nature (London)</i> , <b>104</b> , 113–114.	26
8. On some applications of Hertz's theory of impact, 1920, <i>Phys. Rev.</i> , <b>15</b> , 277–284.	28
9. The optical study of percussion figures, 1926, <i>J. Opt. Soc. Am.</i> , <b>12</b> , 387–390.	37
10. Percussion figures in crystals, 1958, <i>Proc. Indian Acad. Sci., A</i> <b>48</b> , 307–316.	41
11. Percussion figures in crystals, 1959, <i>Curr. Sci.</i> , <b>28</b> , 1–3.	55
12. India's debt to Faraday, 1931, <i>Nature (London)</i> , <b>128</b> , 362–364.	59
13. Newton and the history of optics, 1942, <i>Curr. Sci.</i> , <b>11</b> , 453–455.	63
14. Astronomical research in India: I, 1943, <i>Curr. Sci.</i> , <b>12</b> , 197–198.	65
15. Astronomical research in India: II, 1943, <i>Curr. Sci.</i> , <b>12</b> , 289–291.	67
16. Astronomical research in India: III, 1943, <i>Curr. Sci.</i> , <b>12</b> , 313–314.	71
17. Centenary of the Faraday effect, 1945, <i>Curr. Sci.</i> , <b>14</b> , 281–283.	73
18. Science in Eastern Europe: I, 1958, <i>Curr. Sci.</i> , <b>27</b> , 371–375.	77
19. Science in Eastern Europe: II, 1958, <i>Curr. Sci.</i> , <b>27</b> , 421–426.	83
20. Zonal winds and jet-streams in the atmosphere, 1967, <i>Curr. Sci.</i> , <b>36</b> , 593–595.	91
21. The atmosphere of the earth, 1968, <i>Curr. Sci.</i> , <b>37</b> , 151–155.	95

## 2. The Colour and Optics of Minerals

<p>22. The origin of the colours in the plumage of birds, 1934, <i>Proc. Indian Acad. Sci.</i>, <b>A1</b>, 1–7.</p> <p>23. On iridescent shells—Part I. Introductory, 1934, <i>Proc. Indian Acad. Sci.</i>, <b>A1</b>, 567–573.</p> <p>24. On iridescent shells—Part II. Colours of laminar diffraction, 1934, <i>Proc. Indian Acad. Sci.</i>, <b>A1</b>, 574–589.</p> <p>25. On iridescent shells—Part III. Body-colours and diffusion-haloes, 1934, <i>Proc. Indian Acad. Sci.</i>, <b>A1</b>, 859–870.</p> <p>26. The structure and optical behaviour of iridescent shells, 1954, <i>Proc. Indian Acad. Sci.</i>, <b>A39</b>, 1–13 (with D Krishnamurti).</p> <p>27. The structure and optical characters of iridescent glass, 1939, <i>Proc. Indian Acad. Sci.</i>, <b>A9</b>, 371–381 (with V S Rajagopalan).</p> <p>28. Colours of stratified media—I. Ancient decomposed glass, 1940, <i>Proc. Indian Acad. Sci.</i>, <b>A11</b>, 469–482 (with V S Rajagopalan).</p> <p>29. The iridescent feldspars, 1950, <i>Curr. Sci.</i>, <b>19</b>, 301–305.</p> <p>30. The structure of labradorite and the origin of its iridescence, 1950, <i>Proc. Indian Acad. Sci.</i>, <b>A32</b>, 1–16 (with A Jayaraman).</p> <p>31. The structure and optical behaviour of the Ceylon moonstones, 1950, <i>Proc. Indian Acad. Sci.</i>, <b>A32</b>, 123–140 (with A Jayaraman and T K Srinivasan).</p> <p>32. The diffusion haloes of the iridescent feldspars, 1953 <i>Proc. Indian Acad. Sci.</i>, <b>A37</b>, 1–10 (with A Jayaraman).</p> <p>33. On the iridescence of potassium chlorate crystals—Part I. Its spectral characters, 1952, <i>Proc. Indian Acad. Sci.</i>, <b>A36</b>, 315–320 (with D Krishnamurti).</p> <p>34. On the iridescence of potassium chlorate crystals—Part II. Polarisation effects, 1952, <i>Proc. Indian Acad. Sci.</i>, <b>A36</b>, 321–329 (with D Krishnamurti).</p> <p>35. On the iridescence of potassium chlorate crystals—Part III. Some general observations, 1952, <i>Proc. Indian Acad. Sci.</i>, <b>A36</b>, 330–334 (with D Krishnamurti).</p> <p>36. On the polarisation and spectral character of the iridescence of potassium chlorate crystals, 1952, <i>Proc. Indian Acad. Sci.</i>, <b>A36</b> 419–424 (with D Krishnamurti).</p> <p>37. The structure and optical behaviour of iridescent crystals of potassium chlorate, 1953, <i>Proc. Indian Acad. Sci.</i>, <b>A38</b>, 261–270 (with D Krishnamurti).</p>	<p>101</p> <p>108</p> <p>119</p> <p>140</p> <p>158</p> <p>175</p> <p>201</p> <p>222</p> <p>228</p> <p>248</p> <p>265</p> <p>278</p> <p>292</p> <p>303</p> <p>310</p> <p>318</p>
---	---

38. The structure of opal and the origin of its iridescence, 1953, <i>Proc. Indian Acad. Sci.</i> , <b>A38</b> , 101–108 (with A Jayaraman).	335
39. The structure and optical behaviour of iridescent opal, 1953, <i>Proc. Indian Acad. Sci.</i> , <b>A38</b> , 343–354 (with A Jayaraman).	346
40. The structure and optical behaviour of pearls, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A39</b> , 215–222 (with D Krishnamurti).	363
41. Optics of the pearl, 1954, <i>Curr. Sci.</i> , <b>23</b> , 173–176 (with D Krishnamurti).	377
42. On the chromatic diffusion halo and other optical effects exhibited by pearls, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A39</b> , 265–271 (with D Krishnamurti).	383
43. The structure and optical behaviour of iridescent agate, 1953, <i>Proc. Indian Acad. Sci.</i> , <b>A38</b> , 199–206 (with A Jayaraman).	394
44. The structure and optical behaviour of iridescent calcite, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A40</b> , 1–7 (with A K Ramdas).	406
45. The structure and optical behaviour of jadeite, 1955, <i>Proc. Indian Acad. Sci.</i> , <b>A41</b> , 117–120 (with A Jayaraman).	415
46. Crystals of quartz with iridescent faces, 1950, <i>Proc. Indian Acad. Sci.</i> , <b>A31</b> , 275–279.	420
47. The optical anisotropy and heterogeneity of vitreous silica, 1950, <i>Proc. Indian Acad. Sci.</i> , <b>A31</b> , 141–148.	426
48. Structural birefringence in amorphous solids, 1950, <i>Proc. Indian Acad. Sci.</i> , <b>A31</b> , 207–212.	436
49. The lamellar structure and birefringence of plate glass, 1950, <i>Proc. Indian Acad. Sci.</i> , <b>A31</b> , 359–364.	445
50. "Smoky" quartz, 1921, <i>Nature (London)</i> , <b>108</b> , 81.	451
51. The structure of amethyst quartz and the origin of its pleochroism, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A40</b> , 189–195 (with A Jayaraman).	452
52. The birefringence patterns of crystal spheres, 1956, <i>Proc. Indian Acad. Sci.</i> , <b>A43</b> , 1–3.	460
53. Amethyst—its nature and origin, 1954, <i>Curr. Sci.</i> , <b>23</b> , 379–383.	469
54. On the structure of amethyst and its genesis in nature, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A40</b> , 221–229 (with A Jayaraman).	475
55. On the optical behaviour of crypto-crystalline quartz, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A41</b> , 1–6 (with A Jayaraman).	487
56. X-ray study of fibrous quartz, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A40</b> , 107–109 (with A Jayaraman).	497
57. On the polycrystalline forms of gypsum and their optical behaviour, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A39</b> , 153–161 (with A K Ramdas).	501

58. X-ray studies on polycrystalline gypsum, 1954, <i>Proc. Indian Acad. Sci.</i> , <b>A40</b> , 57–60 (with A Jayaraman).	512
59. The luminescence of fluorspar, 1962, <i>Curr. Sci.</i> , <b>31</b> , 361–365.	518
60. The two species of fluorite, 1962, <i>Curr. Sci.</i> , <b>31</b> , 445–448.	525

### 3. The Diamond

61. The physics of the diamond, 1942, <i>Curr. Sci.</i> , <b>11</b> , 261–268.	531
62. The structure and properties of diamond, 1943, <i>Curr. Sci. (Suppl.)</i> , <b>12</b> , 33–42.	540
63. The four forms of diamond, 1944, <i>Curr. Sci.</i> , <b>13</b> , 145–148.	551
64. The crystal symmetry and structure of diamond, 1944, <i>Proc. Indian Acad. Sci.</i> , <b>A19</b> , 189–198.	558
65. The nature and origin of the luminescence of diamond, 1944, <i>Proc. Indian Acad. Sci.</i> , <b>A19</b> , 199–215.	567
66. Birefringence patterns in diamond, 1944, <i>Proc. Indian Acad. Sci.</i> , <b>A19</b> , 265–273 (with G R Rendall).	587
67. The crystal forms of diamond and their significance, 1946, <i>Proc. Indian Acad. Sci.</i> , <b>A24</b> , 1–24 (with S Ramaseshan).	599
68. The diamond and its teachings, 1946, <i>Curr. Sci.</i> , <b>15</b> , 205–213.	625
69. New concepts of crystal structure, 1946, <i>Curr. Sci.</i> , <b>15</b> , 329–331.	638
70. The luminescence of diamond and its relation to crystal structure, 1950, <i>Proc. Indian Acad. Sci.</i> , <b>A32</b> , 65–73 (with A Jayaraman).	642
71. The luminescence of diamond—I, 1950, <i>Curr. Sci.</i> , <b>19</b> , 357–363.	659
72. The luminescence of diamond—II, 1951, <i>Curr. Sci.</i> , <b>20</b> , 1–7.	667
73. The luminescence of diamond—III, 1951, <i>Curr. Sci.</i> , <b>20</b> , 27–31.	676
74. The luminescence of diamond—IV, 1951, <i>Curr. Sci.</i> , <b>20</b> , 55–60.	682
75. The diamond, 1956, <i>Proc. Indian Acad. Sci.</i> , <b>A44</b> , 99–110.	689
76. The tetrahedral carbon atom and the structure of diamond, 1957, <i>Proc. Indian Acad. Sci.</i> , <b>A46</b> , 391–398.	702

THE PAPERS



## The curvature method of determining the surface-tension of liquids

C V RAMAN, M.A.\*

[Plate I]

Lord Kelvin, in his lecture on capillarity (published in his ‘Popular Lectures and Addresses’), describes this method as a practicable one for measuring the surface-tension of liquids. In the following account is described an arrangement by which this method is rendered a convenient and fairly accurate one, and the results of a series of determinations made by the method are tabulated.

### The theory of the method

Let ADB be the principal section of a drop hanging down from a tube, and  $\rho$  the radius of curvature of ADB at the point D. If T is the surface-tension, then

$$\frac{2T}{\rho} = \frac{g}{\sigma} \cdot CD,$$

$\sigma$  being the density of the liquid, since CD is the head at the point D. This is true, provided that the surface of the drop is one of revolution about CD.  $\rho$  can be determined by measuring the coordinates  $x$  and  $y$ , of points on the curve ADB.

$$\rho = \lim_{x=0} \frac{y^2}{2x}.$$

In practice, it is quite sufficient to make the measurements of  $x$  and  $y$  close to the vertex for two or more values of  $x$ . The value of the ratio  $y^2/2x$  at different points close to the vertex varies only very slightly, and any variation shown can be corrected for, by calculating the value of the ratio for the point  $x = 0$  from the observed values of the ratio. The reason why the ratio  $y^2/2x$  varies very little can easily be seen. As we go up along the surface from the vertex D the head diminishes, and therefore also the sum of the principal curvatures. The section of the surface is therefore nearer being a parabola than a circle, for the sum of the principal curvatures of a paraboloid of revolution diminishes as we recede from the vertex.

---

\*Communicated by the author.

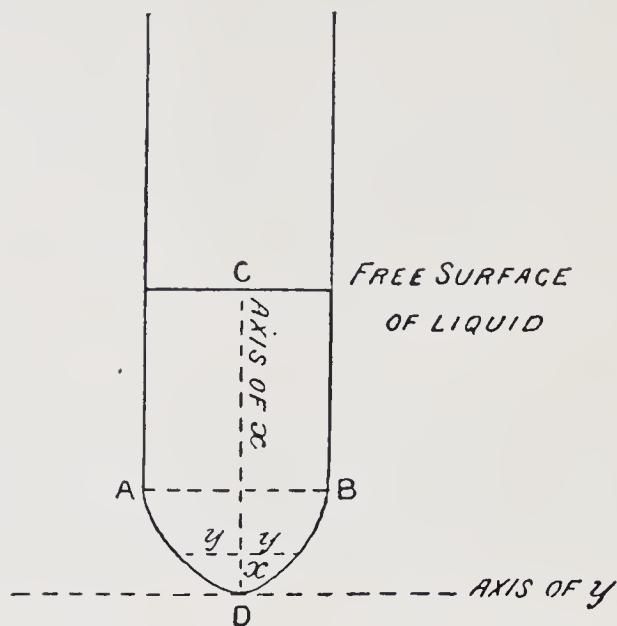


Figure 1

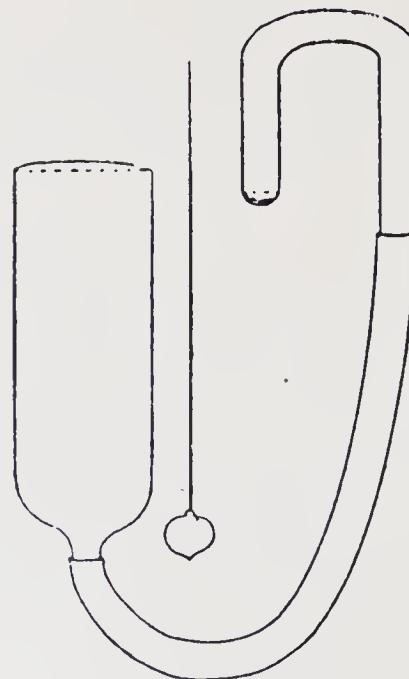


Figure 2

The measurements of  $x$  and  $y$  were not made on the drop, but, adopting a more accurate and convenient method, on a photograph of the surface. The apparatus designed for the purpose is shown in figure 2.

A tube 2 cm diameter is connected up with a tube 6 mm diameter by caoutchouc tubing. The arrangement shown in the figure is filled up with the liquid. The small tube can easily be adjusted so that the liquid bulges out of both tubes, the concavity being in opposite directions in the two. A plumb-line hanging between the two gives the direction of the vertical. The apparatus is then photographed in the following manner:

A horizontal beam of parallel light is produced by an electric spark placed at the focus of an achromatic lens of long focal length (about 1·5 metres), and is thrown on the apparatus. The shadow cast by the tubes is then photographed on a plate held vertically as near to them as possible.

The negative is then measured under a sliding microscope. It is coupled, film to film, with a "réseau" plate on which is ruled a set of squares (side = 0·5027 cm), and placed on an inclined plane so that it has freedom of up and down movement. The microscope, which is capable of motion sideways, has two scales at right angles to each other in its focal plane. The glass plate on which these scales are ruled can be moved in the focal plane by a micrometer-screw. The réseau plate is first adjusted so that the rulings on it are parallel and perpendicular to the shadow of the plumb-line on the plate. By rotating the eyepiece and the photographic plate on the stage, the scales in the focal plane are adjusted parallel to the rules on the réseau plate and to the lines of travel of the microscope and the photographic plate.

The objective of the microscope (which is a small one) produces very little magnification, but the eyepiece is a fairly powerful one. The scales in the focal plane ( $1$  division =  $\frac{1}{10}$  mm) serve only as auxiliaries, for the readings made on them can easily be expressed in terms of the side of the squares on the réseau plate, the absolute value of which is known. The  $x$  and  $y$  coordinates of any point on the meniscus can thus be measured and reduced to centimetres. What was directly read off was not the  $y$  coordinate but  $2y$ . From these measurements the radius of curvature at the vertex of the curve can be deduced in the manner mentioned above. If the variation of  $y^2/2x$  is not negligible, then  $x$  is written equal to

$$ay^2 + by^4,$$

since the curve is symmetrical about the axis of  $x$ . From the observational equations

$$x_1 = ay_1^2 + by_1^4, \text{ &c.,}$$

two normal equations for the constants  $a$  and  $b$  can be deduced and  $a$  determined; and

$$a = \frac{1}{2\rho}.$$

Further, by means of the ruling on the réseau plate, the difference of level between the vertices of the two curves can be measured. This gives the pressure corresponding to the observed curvature.

In practice, it was found that the curvature of the larger meniscus could not altogether be neglected. It amounted to from 2 to 4 per cent of the curvature of the smaller. This could be measured and allowed for. If  $1/\rho$  is the curvature of the smaller and  $1/R$  that of the larger meniscus, then

$$2T\left(\frac{1}{\rho} - \frac{1}{R}\right) = g\sigma h,$$

$h$  being the difference of level between the vertices.

The liquid used in the experiments was clean distilled water. Precautions were taken that in transferring the liquid into the apparatus no contamination occurred. That the surface whose tension was measured was free from greasy contamination was ensured by allowing the water to run down from the small tube for some time. The surface of the drop that was finally left hanging was, therefore, an absolutely fresh one, and any oily film originally on the surface would have been reduced in thickness to a very great extent. The parallelism of the beam used to photograph the drop was tested by a telescope adjusted for infinity. To have the photograph as sharp as possible, the plate was held only 3 cm behind the apparatus. It was found that it was necessary to adjust the wide tube so that it might be approximately vertical. If not, there was reason to think that the two principal curvatures at the highest point of the large meniscus would not be equal. This was really the weakest point in the whole work. The writer hopes to repeat the work with a tube so wide that the curvature of the meniscus above it can entirely be neglected.

As an illustration of the method, I give a table of the measurements made on one of the plates (see plate I).

Difference of level between the vertices

$$\begin{aligned} &= 44.37 \text{ divisions of the microscope scale;} \\ &= 0.2826 \text{ cm.} \end{aligned}$$

Difference of level	x	y	$y^2/2x$
44.37	3.00	45.80	87.06
divisions	4.00	52.78	87.05
	5.00	58.92	86.79
	6.00	64.71	87.24
Mean			87.03

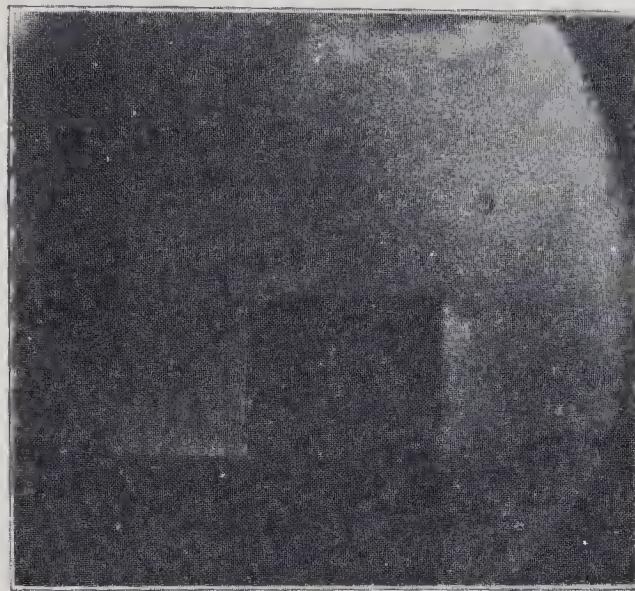


Plate I

From this it appears that for this plate  $y^2/2x$  is very nearly indeed a constant = 87·03 divisions.

Of course, the edge of the shadow was not a sharp line but a series of very narrow diffraction-fringes. In measuring the difference of level, the position of the geometrical edge of the shadow (G in figure 3) was estimated and used. But in making the measurement of curvature, a better-defined point (B in figure 3) in the curve of illumination was used.

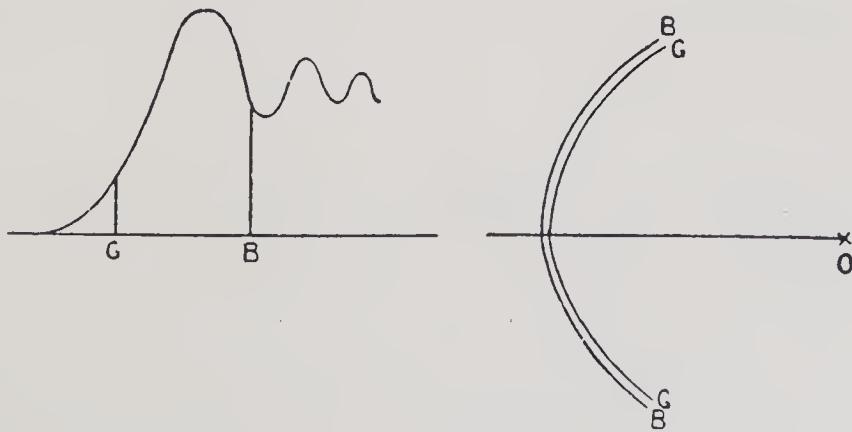


Figure 3

GB was carefully measured and found to be 1·16 divisions.

$$\rho = 87\cdot03 - 1\cdot16 = 85\cdot87 \text{ divisions.}$$

R, by measurement (in a similar fashion) was found to be 3400 divisions.

The surface-tension calculated from these measurements was (temp = 30° C) found to be 77·0 dynes per cm.

Another plate, not so sharp, gave 76·3 dynes per cm.

A third, in taking which the wide tube happened to be out of the vertical, gave no definite result on account of the uncertainty of the value of the curvature of the large meniscus. The value of the surface-tension was, however, estimated to lie between 75 and 77 dynes per cm.

The accepted value for the surface-tension of clean distilled water at 30° C = 71·3 dynes per cm (T P Hall, *Philos. Mag.* 1893). The method described in this article gives results which are fairly self-consistent. The cause of the difference has as yet not been found and is under investigation.

The experiments and observations recorded in this note were made at the Physical Laboratory of the Presidency College, Madras.

## Some new methods in kinematical theory

C V RAMAN

In the course of my recent experimental work on the vibrations of bowed strings,\* it occurred to me that the ordinary Fourier analysis which has been used by previous investigators<sup>†</sup> is not a convenient or suitable method of considering the kinematics of this class of vibrations. In fact, the nature of the case is such that the Fourier analysis obscures instead of elucidating the physical processes set up in the string by the action of the bow. I have therefore developed a new method of treatment which has the great advantage of enabling the subject to be considered entirely from first principles *i.e.*, without any appeal to experiment except for confirming the fully-worked-out predictions of theory. I am using this method in a monograph on the 'Mechanics of Bowed Strings' which is under preparation and which I intend to contribute to one of the regular periodicals for physics. The brief account of this method which I propose to give here may perhaps be of some interest to mathematicians.

The general solution of the equation of wave-propagation on an infinite string not subject to damping is

$$Y = f(x - at) + F(x + at). \quad (1)$$

It is well-known that this solution for the case of an infinite string can be used to represent the configuration at any instant of a vibrating string of finite length by arranging the form of the *displacement* waves in such manner that the motion is periodic and satisfies the terminal condition  $y = 0$  at the two ends of the string.

Similarly, the solution obtained by differentiating (1) with respect to time, *viz*

$$\frac{dy}{dt} = - af'(x - at) + aF'(x + at) \quad (2)$$

can be applied to represent the *velocity-diagram* of a finite string at any instant during its vibration, if the periodicity of the motion and the terminal conditions of velocity are secured. It is obvious that solution (2), as it stands, represents

\* Bulletin No. XI of the Indian Association for the Cultivation of Science, pp. 43-52, May 1914. Also, 'Nature', page 622, August 1914, and Science Abstracts, February 1915.

† Helmholtz, 'Sensations of Tone' English Translation by Ellis, Chapter V and Appendix VI.

Krieger-Menzel and Raps, Über Saitenschwingungen, *Sitzungberichte* of the Berlin Academy, 1891.  
A. Stephenson, "On the Maintenance of Periodic Motion by Solid Friction," *Philosophical Magazine*, January 1911.

the velocity-waves that travel on an infinite string without change of form in the positive and negative directions respectively. In the case of a finite string of length  $l$ , the reflexions that take place at the two ends have to be taken into account, and we may write

$$\frac{dy}{dt} = \theta(x - at) + \phi(x + at). \quad (3)$$

The two functions  $\theta(x - at)$  and  $\phi(x + at)$  represent the velocity-waves which must be imagined as extending to infinity in both directions, and as being perfectly periodic with wavelength equal to twice the length of the string. To satisfy the terminal conditions  $dy/dt = 0$ , we must assume that the positive wave from  $x = 0$  up to  $x = l$  in its initial position is an inverted and reflected image of the negative wave from  $x = l$  up to  $x = 2l$ , and vice-versa.

The next step in the argument is to consider the changes of velocity that take place at individual points on the string. Obviously the form of the positive and negative velocity waves must be such that by their movement and superposition they reproduce the changes of velocity at any given point on the string.

If now, some point on the string (say the point  $x = x_b$ ) has the characteristic property of always moving with a succession of constant velocities during each period of vibration, the velocity passing in a discontinuous manner from each value to the next, we must have, at that point, the condition  $d^2y/dt^2 = 0$  always satisfied, except at certain instants in each period of vibration when it becomes  $\pm$  infinity. Differentiating (3) with respect to time, we have

$$\frac{d^2y}{dt^2} = -a\theta'(x - at) + a\phi'(x + at). \quad (4)$$

Since, at the point  $x_b$ ,  $d^2y/dt^2$  is generally zero, we must have

$$\theta'(x_b - at) = \phi'(x_b + at). \quad (5)$$

If the velocity-waves  $\theta(x - at)$  and  $\phi(x + at)$  are represented graphically, equation (5) may be given a geometrical significance. If any two points are taken, one on the positive wave and one on the negative wave, the distances of which from the point  $x_b$  measured along the string are equal but in opposite directions, we should find the slopes of the waves at the two points to be equal. As already mentioned, the form of the velocity-waves must satisfy certain other conditions, viz., that they are periodic with wavelength  $2l$ , and that initially the form of the positive wave from  $x = 0$  up to  $x = l$  is an inverted and reflected image of the negative wave from  $x = l$  up to  $x = 2l$ , and *vice-versa*. It is a simple geometrical problem to find the form of the positive and negative waves which would simultaneously satisfy these three conditions. By inspection, the following remarkably simple and significant solution is obtained: if the point  $x_b$  divides the string in an *irrational* ratio, the only possible form of the velocity-waves is

that in which the slope is everywhere the same, *i.e.* they are representable by a number of straight lines that are all parallel to one another, a discontinuity intervening wherever one straight line leaves off and the next begins.

The next step in the argument is to show that the *modus operandi* of the bow requires that  $d^2y/dt^2$  should be generally zero at the bowed point except at certain instants in each period of vibration when it becomes  $\pm$  infinity. This can be proved from dynamical considerations, for which I must refer the reader to my forthcoming monograph, and it is also shown there that the velocity at the bowed point must alternate between two and only two constant values. The preceding theory is thus applicable when the velocity-waves travel on the string without any appreciable change of form, and the discussion shows the form of the velocity-waves to be representable by a number of parallel straight lines with intervening discontinuities, when the bow is applied at a point dividing the string in a rational ratio, as well as in the cases in which it divides the string in an irrational ratio. The condition that the velocity at the bowed point alternates between two and only two constant values is then used to find the form of the velocity-waves. When the bowed point divides the string in an irrational ratio, the discontinuities in the velocity-waves are all numerically equal in magnitude to one another, and to the arithmetical sum of the two speeds possible at the bowed point. The types of vibration may then be classified according to the *number* of the discontinuities (one, two, three or more) per wave-length, in each wave. In the detailed discussion of these cases, the conditions under which they are excited and the kinematical relations involved therein are investigated, and the modifications that occur when the bow is applied at a *rational* point are also worked out. The general procedure adopted is very simple. If there are  $n$  equal discontinuities in each velocity-wave, the lines in the velocity-graph of the string being parallel to one another must evidently all pass through the nodes of the  $n$ th harmonic or the ends of the string (there being situated at equal intervals along the string). The position of the intervening discontinuities is, in general, arbitrary. From this we get at once, the general kinematical relation

$$w = \frac{nx_n}{l} \quad (6)$$

where  $w$  is the ratio of the time during which the bowed point moves with the larger of the two speeds, to the total period of a complete vibration,  $n$  is an integer, and  $x_n$  is the distance of the bowed point from the *nearest* node of the  $n$ th harmonic. This relation holds good both for 'rational' and 'irrational' points of application of the bow. When  $n = 1$ , we have the well-known kinematical relation  $w = x/l$  discovered by Helmholtz. The relation has been verified by me for the other cases in which  $n = 2, 3$ , or  $4$  etc.

It is impossible here to enter into further detail of the various developments of the theory outlined above, and I must therefore content myself with summarising briefly the main results of the research which are as follows:

- (a) The theory gives a completely satisfactory account of the observed types of vibration, proceeding from first principles and including the so-called 'complicated' types of motion.
- (b) It predicts the general kinematical relation (6) given above, of which only the first case ( $n = 1$ ) was known previously through the work of Helmholtz. The general relation has since been verified by me experimentally.
- (c) It predicts the effect to be observed by varying the pressure or velocity of bowing at any given point, rational or irrational, and has an important bearing on the musical applications of the subject.
- (d) The actual form of the vibration-curve for any given point on the string for any one of the possible or actual types of vibration can be readily traced by a very simple graphical process which dispenses entirely with the tedious methods of harmonic analysis, and the curve thus traced from purely theoretical principles, can be compared directly with that observed in experiment. A large number of examples will be given in my complete monograph.
- (e) Many of the conclusions arrived at by Krigar-Menzel and Raps as the result of their work require to be largely modified.
- (f) The whole treatment gives a far more vivid idea of the kinematics of bowed strings than can possibly be conveyed by the Fourier analysis.

## On the summation of certain Fourier series involving discontinuities

C V RAMAN

In a previous communication published in the Bulletin,\* I gave a brief outline of a method which I had adopted for discussing the kinematics of a bowed string in a detailed memoir on the subject which I had under preparation. Subsequently, whilst the memoir was being written, I noticed some points which were of great importance in the theory of the subject and which were not alluded to in the note published in the Bulletin of the Society. I propose now to supplement the first note by referring to the fresh results thus obtained.

The treatment adopted for discussing the motion of a bowed string in detail is based on the following two dynamical principles:

(1) The frictional force at the point of contact is a function of the relative velocity which decreases when the relative velocity is increased and becomes indeterminate when the relative velocity is zero.

(2) The force required to maintain any given harmonic component of the motion with a specified amplitude is a function of the damping coefficient and may thus be regarded as small compared with the variation of frictional force due to a finite change of relative velocity; this statement is however subject to the qualification that the point of application of the force should not coincide with a node of the given harmonic, and that the pressure with which the bow is applied is sufficiently large.

When a steady state of vibration is reached under the action of the bow, the harmonic components in the frictional force at the point of contact and the forces actually required to maintain the motion must balance one another. This can only be reconciled with the principles set out in (1) and (2) above on the assumption that during a part of the motion, the relative velocity at the point

---

\*C V Raman, 'On some new methods in kinematical theory' 4, pages 1–4.

To the references cited in the note may be added the following:

A Harnack, *Mathematische Annalen*, Bd. 29, S. 486, 1887.

F Lindemann, *Philosophical Magazine*, March 1880.

Carslaw, *Proceedings of Edin. Math. Soc.* 1902.

of contact actually becomes zero, so that the frictional force in those stages falls below the maximum statical value.

It is also seen from principle (2) that during those stages of the motion during which the relative velocity at the point of contact is not actually zero, its value would in any case be practically a constant quantity. But this result would not hold good with the same universality as the constancy of the velocity of the bowed point during the stages in which its movement is in the same direction as that of the bow. In fact, except in special cases, the velocity in the backward movement would be rigorously constant only when the damping coefficients of all the harmonics are vanishingly small compared with the other quantities involved.

Assuming the rigorous constancy of the velocities of motion at the bowed point both in the forward and backward movements, we see that the condition  $(d^2y/dt^2) = 0$  is satisfied generally at the bowed point. The kinematics of the motion can then be discussed on the lines indicated in my first note. If the bowed point divides the string in an irrational ratio, all the discontinuities in the velocity-diagram of the string are equal to one another and to  $(v_a - v_b)$ , where  $v_a$  and  $v_b$  are the two velocities possible at the bowed point. If there are  $n$  such discontinuities on the velocity diagram of the string during the motion, the mode of vibration may be classified as belonging to the  $n$ th type. It is readily seen that the lines in the velocity-diagram are not more than  $(n + 1)$  in number at any instant, and that they always pass or would pass, if produced, through the  $(n + 1)$  nodes of the  $n$ th harmonic. These nodes are then points alternately of rest and of motion in one direction or the other.

When the bowed point divides the string in a rational ratio, the form of the velocity-diagram may be derived from that of the corresponding irrational type by the following process: Taking the form of the velocity-diagram at any specified epoch in the irrational case, we have to analyse it into its Fourier components and then effect a summation of the series of components which have a node at the bowed point in the form of a subsidiary velocity-diagram for the specified epoch. Subtracting the ordinates of this diagram from the other, we get the actual velocity-diagram in which the harmonics having a node at the bowed point are non-existent.

Let the velocity-diagram of the string at a certain epoch in the corresponding irrational type of vibration consist of parallel straight lines inclined to the x-axis at an angle  $a$ , with discontinuities  $d_1, d_2, d_3$ , etc., intervening at the points  $x = c_1, c_2, c_3$ , etc., respectively. Let this diagram be represented by the function  $\phi(x)$ . Then

$$\phi(x) = \sum_{n=1}^{n=\infty} A_n \sin \frac{n\pi x}{l},$$

where the value of  $A_n$  is determined by the equation.

$$A_n = \frac{2}{l} \int_0^l \phi(x) \sin \frac{n\pi x}{l} dx.$$

$\phi(x)$  is equal to  $x \tan a$  between the limits  $x = 0$  and  $x = c_1$ . From  $x = c_1$  up to  $x = c_2$ ,  $\phi(x)$  is equal  $(x \tan a - d_1)$ , and then changes to  $(x \tan a - d_1 - d_2)$ , retaining this value up to  $x = c_3$ , and so on. Integrating by parts, we have

$$A_n = -\frac{2}{n\pi} \left[ \phi(x) \cos \frac{n\pi x}{l} \right]_0^l + \frac{2}{n\pi} \int_0^l \tan a \cos \frac{n\pi x}{l} dx.$$

Since  $\tan a$  is a constant, the second integral reduces to zero, and the equation may be written in the form

$$A_n = -\frac{2}{n\pi} \left[ d_1 \cos \frac{n\pi c_1}{l} + d_2 \cos \frac{n\pi c_2}{l} + \text{etc.} \right].$$

When  $n = 1$ , we have

$$A_1 = -\frac{2}{\pi} \left[ d_1 \cos \frac{\pi c_1}{l} + d_2 \cos \frac{\pi c_2}{l} + \text{etc.} \right].$$

When  $n = s$ ,  $A_s$  may be written in the form

$$A_s = \frac{2}{\pi} \left[ \frac{d_1}{s} \cos \frac{\pi c_1}{l/s} + \frac{d_2}{s} \cos \frac{\pi c_2}{l/s} + \text{etc.} \right].$$

The summation of the series  $\sum_{n=1}^{\infty} A_n \sin(n\pi x)/l$  of which  $A_1 \sin(\pi x)/l$  is the leading term gives us the original velocity-diagram  $\phi(x)$  which consists of parallel straight lines inclined to the x-axis at an angle  $a$  and has a discontinuity  $d_1$  at the point  $x = c_1$ , a discontinuity  $d_2$  at the point  $c_2$ , and so on. From this, it follows that the series

$$\sum_{n=1}^{\infty} A_{ns} \sin \frac{n\pi x}{l/s}$$

of which  $A_s \sin(s\pi x)/l$  is the leading term would similarly give us when summed, a diagram also consisting of straight lines inclined to the x-axis at the same angle  $a$ , the magnitude of the discontinuities in it being  $d_1/s$ ,  $d_2/s$ ,  $d_3/s$ , etc., and the series being periodic for increments of  $x$  by the length  $2l/s$  instead of by  $2l$  as with the original series. The positions of the discontinuities in the diagram thus derived are given by the abscissae obtained by subtracting from  $c_1$ ,  $c_2$ ,  $c_3$ , etc., the nearest multiples of the length  $l/s$ .

Subtracting the ordinates of the diagram thus derived from the ordinates  $\phi(x)$  of the original diagram, the resulting figure in which the sth, 2sth, 3sth harmonics, etc. are all absent is seen to consist of straight lines *parallel* to the x-axis with intervening discontinuities. From the graph thus derived, the motion at any given point on the string can be drawn as a time-displacement diagram

with the greatest ease and simplicity by noting the times at which the successive changes of velocity occur at the point by the passage of the discontinuities over it. In the special cases in which the motion at the bowed point is a simple two-step zig-zag, the quantities  $c_1, c_2, c_3$ , etc., are found to be merely multiples of the length  $l/s$  and the construction becomes particularly elegant.

The treatment of the cases in which the velocity at the bowed point has a continuous variation, particularly during the stages of backward motion, is naturally far more complicated. It is however of great importance in regard to the musical applications of the subject. These variations of velocity occur owing to the harmonics not being elicited in the normal strength in which they are present in any of the standard types of vibration referred to in this note. It is not within the scope of this note to consider such cases in detail.

## A theory of the viscosity of liquids

As is well-known, the viscosity of gases and its variation with temperature has received a satisfactory explanation on the basis of molecular theory. Little progress has, however, been made towards explaining the phenomena of the viscosity of *condensed media*—that is, of liquids and solids from a molecular point of view. What is evidently required is a working hypothesis which will indicate why, when a substance passes from the state of vapour to that of liquid, its absolute viscosity is greatly increased but *diminishes* with rising temperature, while that of the vapour *increases* in the same circumstances. I propose in this note to put forward briefly the outline of a theory which appears to have claims to serious consideration, as it indicates a quantitative relation between the viscosity of a liquid and of the corresponding vapour which is supported by the experimental data.

The manner in which transverse stress is propagated through a material medium is known in the cases in which the substance is in the state of vapour and in that of a crystalline solid. In the former case, momentum is transferred through the diffusion of the molecules between parts of the medium in relative motion, and this is a relatively slow process. In the crystal, on the other hand, the stress is transmitted in the form of transverse elastic waves, and the latter process, at least for ordinary displacements, is extremely rapid. We may conceive that in a liquid, momentum is transported partly by the first process and partly by the second, and that the effective viscosity depends on their relative importance. The ratio in which the two modes of propagation are operative may be determined from thermodynamical considerations, combined with certain simple suppositions regarding the constitution of a liquid.

We shall assume that the state of aggregation of the molecules in a liquid is of a composite character; some of the molecules are quite free to move, and may be termed “vapour” molecules; the others are attached to each other somewhat as in a crystal, and may be termed “crystalline” molecules. In determining the proportion of the two types, we shall consider only binary encounters between molecules. Let  $E_1$  be the work required to separate a pair of molecules of the first type, and  $E_2$  those of the second type. Then applying Boltzmann’s distribution law, we may, as a first approximation, take the relative proportion of the two types of aggregation in the dissociation equilibrium to be as  $e^{E_1/RT}$  to  $e^{E_2/RT}$ , where R is the gas-constant and T the absolute temperature. The next step is to determine the rate of transport of momentum through the medium. In the “vapour” part of the aggregation, the transport occurs by bodily movements. In

the "crystalline" part, the rate of transport may be considered to be practically infinite. The effective rate of transport in the liquid is therefore greater than in the vapour at the same temperature and pressure in the ratio  $e^{E_2/RT}/e^{E_1/RT}$ . The viscosity of the liquid is therefore given by the formula  $\eta_{\text{liquid}} = \eta_{\text{vapour}} e^{(E_2 - E_1)/RT}$ . Since  $E_2 > E_1$  it follows that the viscosity of the liquid will diminish with rising temperature.

The next step is to determine the absolute magnitudes of the energy constants  $E_1$  and  $E_2$ . As was first pointed out by Sutherland, in the cases of gases and vapours the attractive forces between the molecules tend to increase the frequency of collisions and thus diminish the viscosity. The matter has been further examined by Chapman, who has shown that Sutherland's constant is one-sixth of the mutual potential energy of the molecules when in contact. It is convenient to use an amended form of Sutherland's formula and write

$$\eta_{\text{vapour}} \propto T^{\frac{1}{2}} e^{-E_3/RT},$$

where  $E_3$  is another energy-constant. From Chapman's work it would appear that  $E_2 = 6E_3$ , and we may also take  $E_1 = E_3$ . Hence, finally, we have

$$\eta_{\text{liquid}} = \eta_{\text{vapour}} e^{5E_3/RT}.$$

$E_3$  may be found from the data for the viscosity of vapour at different temperatures, and the formula thus enables the viscosity of the liquid to be calculated *a priori*.

To illustrate the matter, it will suffice to take the case of benzene as an example. The table shows the viscosity of liquid benzene at different temperatures as

Viscosity of benzene liquid			
	A = 0.0000951	B = 1237	
Temperature	Calculated viscosity	Observed viscosity	Difference
7.67°	0.00781	0.00789	+8
13.46	0.00714	0.00717	+3
19.39	0.00654	0.00654	0
25.96	0.00595	0.00595	0
32.07	0.00549	0.00547	-2
38.47	0.00504	0.00502	-2
45.35	0.00464	0.00461	-3
51.66	0.00429	0.00429	0
57.37	0.00403	0.00402	-1
63.29	0.00377	0.00377	0
69.41	0.00353	0.00354	+1
73.36	0.00332	0.00333	+1

Viscosity of benzene vapour at 100° C = 0.0000930.

5E<sub>2</sub> calculated from the value at 212.5° C is 1300.

determined by Thorpe and Rodgers, and also as calculated from an empirical equation of the type  $\eta = Ae^{B/T}$ .

It will be seen that the formula represents the viscosity of the liquid within an average error of 2 parts in a thousand; and that the constants A and B are in fair agreement with the values calculated from the data for the viscosity of the vapour. An empirical formula of the type  $Ae^{B/T}$  is found to represent closely the variation of the viscosity of many liquids, especially at the higher temperatures. As we have assumed that the "vapour" molecules are identical with those actually found in the gaseous state, we cannot expect the experimental constants A and B to agree exactly with those indicated by the theory outlined in this note in all cases. Considerable deviations actually occur in the case of "associated" liquids, in which presumably the effect of the molecular fields of force cannot be handled so simply.

The further discussion of this question and of the extension of the theory to the case of dense vapours on one hand, and to supercooled liquids and amorphous solids on the other hand, offers a most interesting field of research. The treatment suggested can obviously be improved in several directions, especially in the discussion of the dissociation equilibrium between the two types of molecules, and the effect of high pressures on the viscosity of liquids could probably be explained by a more exact investigation.

C V RAMAN

210 Bowbazaar Street

Calcutta, India

March 1

## The viscosity of liquids

I wish very briefly to supplement the remarks made in a previous communication on this subject in which I have suggested that the viscosity of liquids and its variation with temperature may be explained on the hypothesis that the liquid state of aggregation is composite in character; that is, is composed in part of molecules “rigidly” attached to each other as in a solid, and in part of molecules which are relatively mobile as in the gaseous state (*Nature*, April 21, p. 532).

That the supposition made regarding the constitution of liquids is *prima facie* a reasonable one is, I think, clear from thermodynamical considerations. The liquid stands midway between the solid and the gas and has affinities to both. The volume of a liquid at temperatures slightly higher than the melting point is only moderately different from that of the solid, and hence the probability that many of the molecules are at any instant at the same distance from each other as in a solid is considerable. This probability may indeed be found from the latent heat of fusion of the substance. If  $W$  be the heat of fusion in ergs per mol, the number of molecules in the “rigid” and “mobile” states should be approximately, in the ratio  $e^{W/RT}$ .

The mechanism of viscous flow of a liquid is perhaps clearest if we consider the case of a thin layer enclosed between two parallel plates, one of which slides over the other. When a steady state is reached, the “rigid” parts of the liquid move practically as complete wholes, and hence the effect of their existence is to diminish the thickness of the layer through which momentum has to be transported by the “mobile” molecules, and thus to increase the viscosity. As a rough approximation, this increase is in the proportion of the numbers of the two types of molecules. A more exact theory should take into account also the volumes occupied by the two types of aggregation and their changes with temperature.

The effect of pressure on viscosity of liquids would arise in two distinct ways. In the first place, we have a change of volume on fusion, and hence, by the Le Chatelier–Braun principle, the assumed dissociation from the “solid” to the “mobile” aggregation would be retarded by pressure, so that the viscosity should be increased. With substances such as ice which contract on melting, we have the opposite effect. In the second place, pressure diminishes the volume occupied by the “mobile” molecules, and therefore also the distance through which they have to transport momentum. This would increase the viscosity. At temperatures not much higher than the melting point, the first effect would preponderate. This is

strikingly illustrated in the case of water, the pressure-coefficient of viscosity of which is negative up to 32° C, that is, even at temperatures much higher than that of maximum density.

*C V RAMAN*

210 Bowbazaar Street Calcutta  
March 15

# The photographic study of impact at minimal velocities

C V RAMAN

## 1. Introduction

Hertz's well known theory<sup>1</sup> treats the phenomena occurring during elastic impact practically as statical effects; the local compression at the place of contact is regarded as gradually produced and subsiding completely by reversal of the process by which it is produced. In the particular case of two solid spheres impinging on each other, the theory finds its own justification by showing that the duration of impact is large compared with the gravest period of vibration of either body. The results indicated by Hertz's theory for the duration of impact, for the radius of the area of contact, and for the approach of the centers of the spheres have been compared with those found in experiment by various investigators among whom may be mentioned Schneebeli, Hamburger,<sup>2</sup> and more recently, Lafay,<sup>3</sup> Kennelly and Northrup.<sup>4</sup> Hertz's theory is incomplete in that it entirely ignores the dissipation of energy that occurs during collision. Recently, however, Lord Rayleigh<sup>5</sup> has extended Hertz's work by investigating the circumstances of the first appearance of vibrations in the case of two impinging spheres, and has shown that the proportion of translational energy transformed into energy of vibration is negligibly small over a considerable range of velocities. The dissipation of energy that occurs in the impact of spheres has thus to be assigned principally to two causes, (a) the stresses occurring during impact exceeding the limits within which elastic recovery is immediate and perfect, and (b) the production of sound. The second of these causes has been recently investigated at Calcutta by Banerji,<sup>6</sup> who has shown that the sound waves produced by the

---

<sup>1</sup>Hertz's Miscellaneous Papers, English edition, p. 146, and Love's Treatise on Elasticity, 2nd edition, p. 195.

<sup>2</sup>Schneebeli, *Rep. Phys. Bd.* **22**, 1886, and Hamburger, *Tageblatt d. Nat. Vers.* in Wiesbaden, 1887.

<sup>3</sup>Lafay, *Comp. Rend.* p. 525, 1900, and *Ann. Chim. Phys.*, p. 241, 1901.

<sup>4</sup>Kennelly and Northrup, *Franklin Inst. J.*, July, 1911.

<sup>5</sup>Rayleigh, *Philos. Mag.*, **XI**, p. 283, 1906.

<sup>6</sup>Banerji, *Philos. Mag.*, July, 1916, and January, 1918.

impact of spheres are practically due to the impulse communicated to the atmosphere by the sudden reversal of the motion of the spheres. The energy thus lost may be evaluated mathematically, and being directly proportional to the density of the atmosphere, can be made as small as desired by sufficiently reducing the pressure. If we leave it out of consideration, the dissipation of energy has to be ascribed entirely to failure of perfect elasticity during impact. According to Hertz, if two steel spheres 2·5 cm radius meet with a relative velocity of only 1 cm per second, the maximum pressure developed during impact is 7,300 kilogrammes per sq. cm. Stresses of this order of magnitude would, in the case of most materials overstep the elastic limits and result in dissipation of energy. If the substance of the spheres be plastic, the energy of collision may even be dissipated entirely in the production of deformation. This is illustrated by some recent interesting experiments by Pochettino<sup>7</sup> who studied the elasticity, the viscosity, and the coefficient of restitution of pitch at different temperatures. The coefficient of restitution was 0·92 at 10° C, fell to 0·44 at 28·1° C, to 0·12 at 31° C, and was zero at 32° C.

The question naturally arises whether the coefficient of restitution can be connected in some definite manner with the magnitude of the stresses produced by impact. According to Hertz's theory, the maximum pressure developed per unit area is proportional to the two-fifths power of the velocity before impact, and is independent of the size of the balls. Accordingly, by reducing the velocity of impact sufficiently, it should be possible to keep the stresses developed below any definite value which may be assigned as the elastic limit, and the coefficient of restitution for such velocities should approach unity for all solids. That the coefficient becomes smaller with increasing velocity of impact has indeed been shown by Hodgkinson,<sup>8</sup> and more recently also by Vincent.<sup>9</sup> In view, however, of the bearing of the subject on the theory of impact, it appeared worthwhile to make a more detailed examination, and to push the observations to the smallest velocities up to which it is possible to obtain regular results. In order to make reliable measurements at such small velocities, it was decided to use the photographic method to record the relative motions of the spheres immediately before and after impact, and to determine the coefficient of restitution at leisure by measurements of the plates. The paper presents the first instalment of the results of the work in the form of graphs (figures 1 to 5) showing the relation between the coefficient of restitution and the velocity of impact for polished spheres of equal radius of (1) brass, (2) aluminium, (3) hard bronze, (4) white marble and (5) lead.

<sup>7</sup>Pochettino, *Nuovo Cimento*, Aug, 1914.

<sup>8</sup>Hodgkinson, *Report Britt. Assoc.*, 1834.

<sup>9</sup>Vincent, *Camb. Phil. Soc. Proc.*, August, 1900.

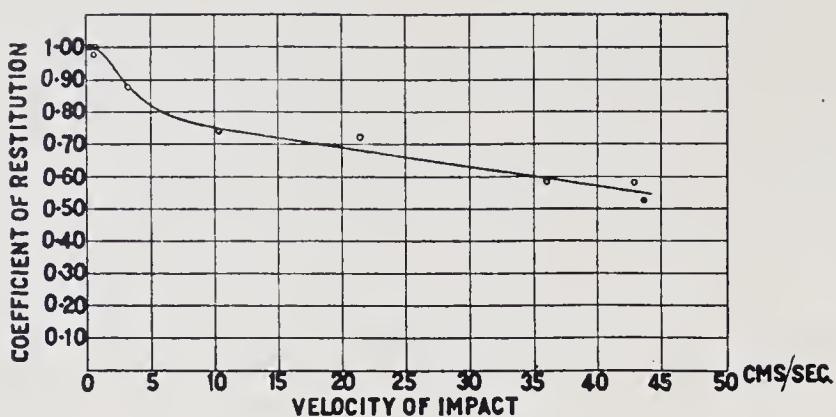


Figure 1. Brass spheres.

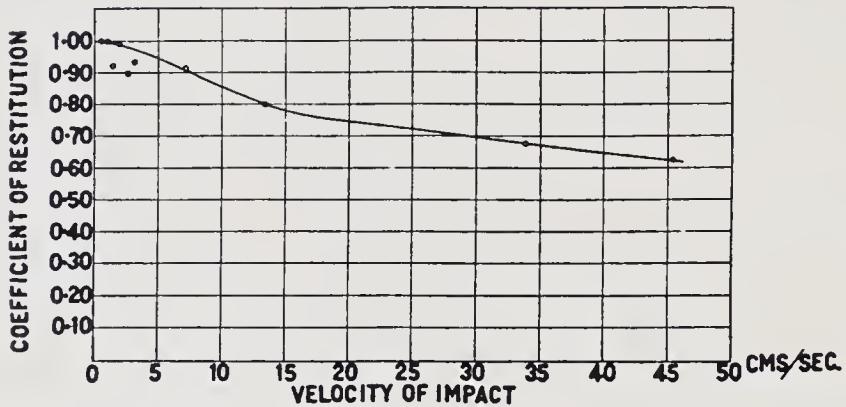


Figure 2. Aluminum spheres.

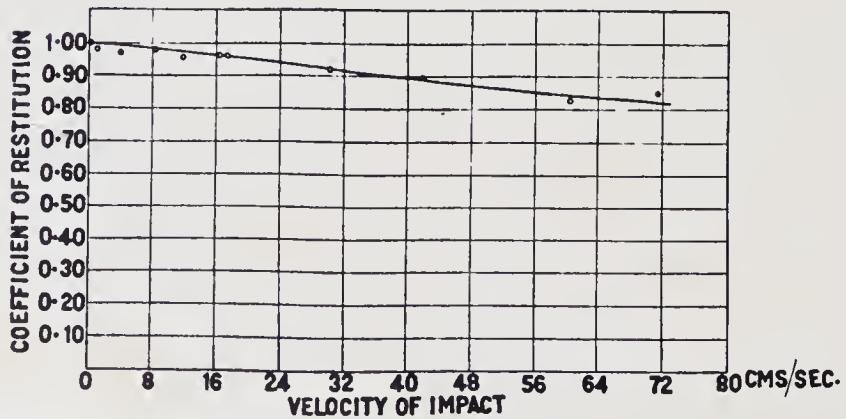


Figure 3. Hard bronze spheres.

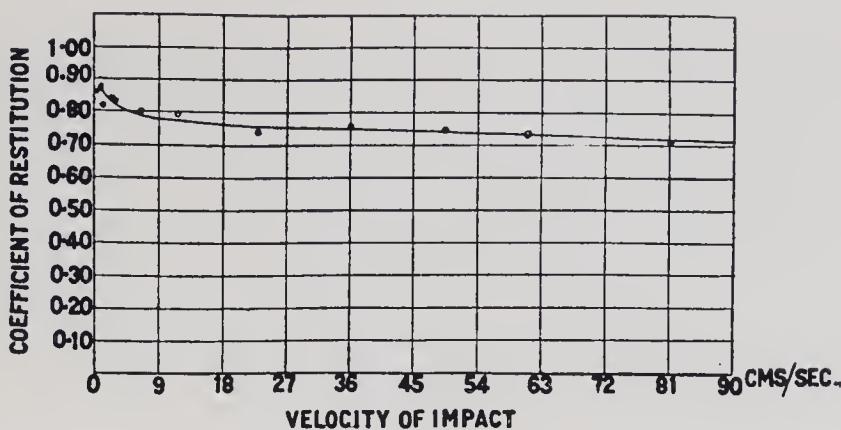


Figure 4. Marble spheres.

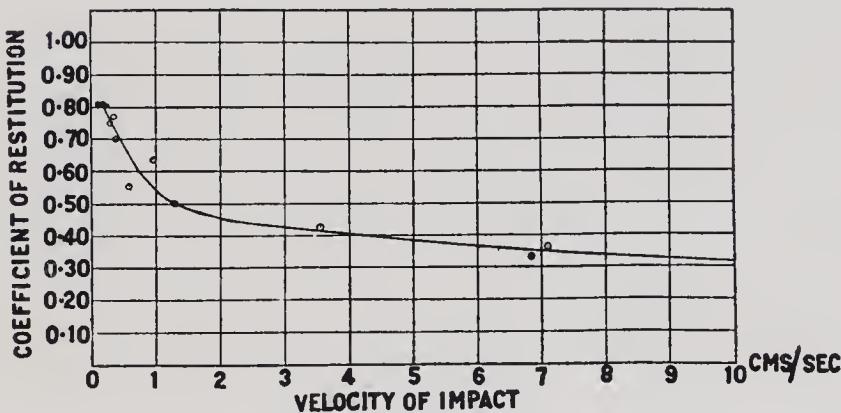


Figure 5. Lead spheres.

## 2. Experimental methods and results

The impinging spheres were hung by bifilar suspensions, and were held apart and dropped electromagnetically by the aid of small iron washers firmly fixed near the point of suspension. The motion of the balls before and after impact was recorded photographically in the following manner. A fine horizontal slit was illuminated by an electric arc, and an image of it was focused on the lowest point of the circle on which the centers of the balls move when dropped, and so adjusted that when the balls hang in the position of equilibrium, the image of the slit is just completely obscured, and appears only when the balls are drawn apart. A second lens refocuses the image of the slit seen between the balls, on a photographic plate which is caused to move vertically downwards when the balls are released. A fairly uniform vertical motion of the plate was obtained by suspending the dark

slide from a string wrapped round the axle of a small fly wheel, and setting the latter in rotation. The dark slide moves down in vertical grooves at the back of the camera which is completely covered up with the exception of a small slit through which the light falls on the plate. With this arrangement the photograph can be taken without any need for specially darkening the room. The vibration of a tuning fork of frequency 60 d.v. is simultaneously recorded on the photographic plate, and serves both as a check on the approximate uniformity of the motion and also as a scale of time against which the relative velocity of the balls is measured. A specimen photograph is reproduced as figure 6, see accompanying plate. The width of the wedges of light that appear immediately before and after the impact is measured at two or three points on each side, and gives directly the relative motion of the balls during the corresponding intervals of time. The ratio gives the coefficient of restitution. The magnification of linear dimensions on the plate is measured once for all by photographing a scale held in the plane containing the centers of the impinging spheres. By using long suspensions (2, and sometimes 5 meters length), very small velocities can be obtained without an undue diminution in the amplitude of motion of the balls.<sup>10</sup>

The method was found very simple and convenient in practice, as the record once secured could be studied and measured at leisure. The most rapid way of measuring the photographs was to project them on a screen with a lantern, and to read off the widths of the wedges with an ordinary millimeter scale. An alternative which, however, proved much less convenient was to measure the photographs on a cross-slide micrometer.

It was found impossible to obtain regular and consistent results at low velocities of impact unless the surfaces of the balls were clean and highly polished. The choice of materials for the work was somewhat restricted by this consideration. According to recent views, polishing results in the formation of a surface film whose elastic properties are somewhat different from those of the bulk of the substance, and the complication introduced by this fact though undesirable, could not be avoided. Nevertheless the results indicated in figures 1 to 5 are sufficient to show that the coefficient of restitution makes a decided approach towards unity for a very small velocity of impact. The most noteworthy case is that of lead, in which this rise is particularly rapid. With marble spheres, it was found difficult to obtain a thoroughly satisfactory polish to begin with, and the breaking up of the crystalline structure at the place of contact as the result of impact was very evident to inspection. It was not therefore surprising that in the case of marble somewhat irregular results were obtained when it was attempted

---

<sup>10</sup>In the course of the work, the curious observation was made that the suspensions of the spheres were set in oscillation as the result of impact in a mode which is initially the same as that of a bowed string observed by Helmholtz. (See the paper on Discontinuous Wave-motion by Raman and Appaswamaiyar, *Philos. Mag.* January, 1916).

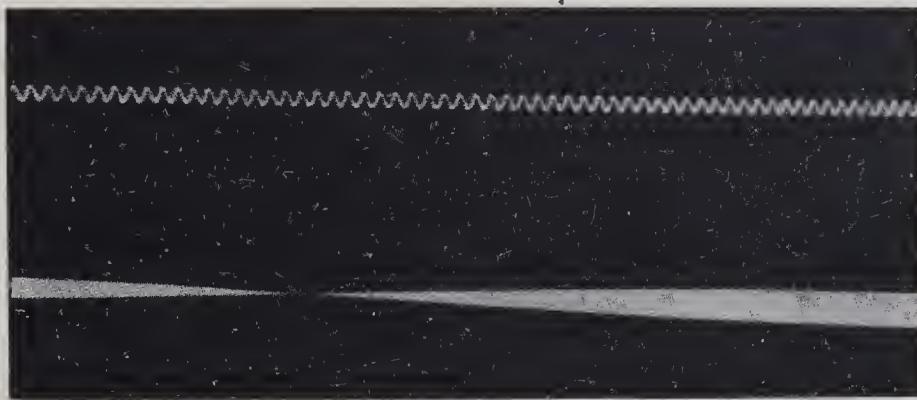


Figure 6

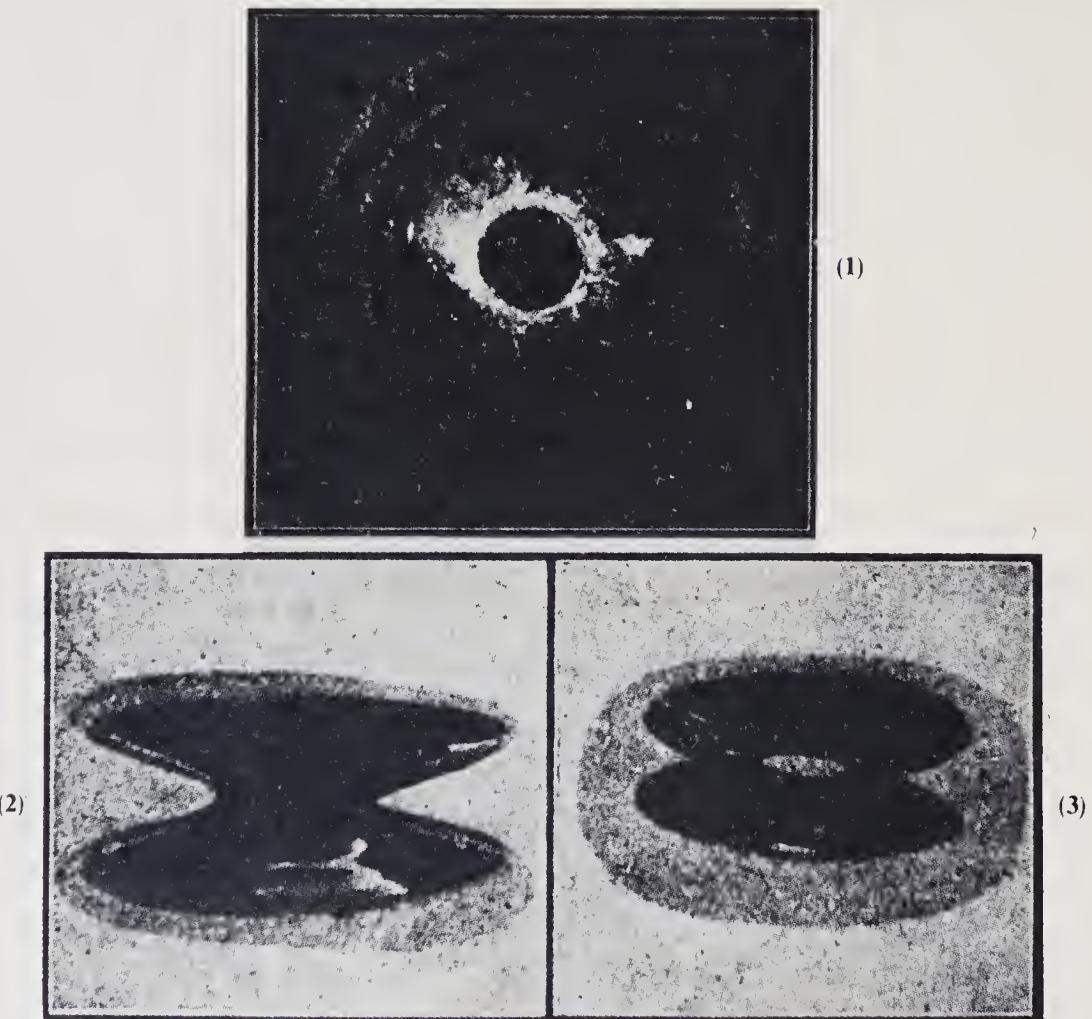
to push the observations down to very low velocities of impact. It is hoped when a suitable opportunity arises to continue this investigation in various directions, particularly as regards (a) the results obtained when the impinging spheres are of unequal diameters or of different materials; (b) to determine in what manner the apparent coefficient of restitution is affected by the density of the surrounding fluid, and (c) to give a fuller theoretical discussion of the results.

210, Bowbazaar Street  
Calcutta, India  
14 May 1918

## Percussion figures in isotropic solids

The accompanying photographs are of interest as illustrating the manner in which an isotropic solid breaks down under the stresses set up by impact when these exceed the limits of perfect recovery, and have a bearing on the theory of the collision of elastic solids developed mathematically by Hertz.

Figures 1, 2, and 3 are pictures of the percussion figure, taken from three different points of view, produced on the surface of a thick glass plate by the



Figures 1–3

impact of a polished hard steel ball. Near the centre of the region of contact between the sphere and the plate the stresses are mainly in the nature of a volume-compression, and fracture accordingly does not originate there, but occurs at or near the *margin* of the compressed area in the form of a fine circular crack which spreads inwards into the plate obliquely in the form of a surface of revolution. This is clearly shown in figure 1, which is a front view of the percussion figure by reflected light, the dark circle in the middle being the uninjured area of contact between ball and plate. The circular interference-rings seen in the picture are a measure of the separation of the surfaces of the internal fracture within the plate.

Figure 2 is a side view, and figure 3 an oblique view, of the internal fracture seen through the edge of the plate, the lower half of each picture being the image of the upper half formed by the reflection of light at the interior surface of the plate. The circular area of contact from the margin of which the fracture starts appears in figure 3 as an elliptic white disc at the centre. It seems clear that the internal fracture practically occurs along the surface of maximum *shearing* stress set up during the impact.

C V RAMAN

210 Bowbazaar Street, Calcutta

18 August

# On some applications of Hertz's theory of impact

C V RAMAN

## Synopsis

*Statement of the Theory:* One of the premises on which the mathematical theory of the collision of elastic solids given by Hertz is based is that the strains produced in the immediate neighborhood of the region of contact are determined by the pressure subsisting at any instant between the bodies, and are practically the same as under statical conditions. This premise is valid even when the impinging bodies do not move as rigid bodies, and the impact results in part of the translational kinetic energy being transformed into energy of elastic wave-motion in the substance of the solids. *Hertz's theory of impact* with suitable modifications may accordingly be applied under a very wide variety of conditions. In the present paper, an attempt is made to discuss the problem of *the transverse impact of a solid sphere on an infinitely extended elastic plate of finite thickness* and to calculate the theoretical *coefficient of restitution* which is a function of the elastic constants and densities of the materials, the diameter of the sphere and the thickness of the plate, and of the velocity of impact. As the result of the impact, annular waves of flexure are set up in the plate, and the sum of the kinetic and potential energies of the wave-motion may be determined in terms of the magnitude and duration of the impulse on certain simplifying assumptions. The calculation results in a *simple formula for the coefficient of restitution*.

*Experiments:* A series of *experiments* carried out in the author's laboratory by Mr A Venkatasubbaraman has furnished a quantitative confirmation of the formula within the limits of its applicability, that is for plates not thinner than about half the diameter of the sphere. For plates much thinner than this, theory and experiment agree in indicating a zero coefficient of restitution. The formula indicates that the coefficient of restitution should increase and approach unity for greatly diminished velocities of impact, and this is also confirmed in experiment. The paper concludes with indications of some *further applications and extensions* of Hertz's theory of impact.

## 1. Introduction

As is well known, Hertz<sup>1</sup> developed a solution of the problem of the collision of curved elastic solids on the following premises: (1) the elastic state of the two bodies near the point of impact during the whole duration of impact is very nearly the same as the state of equilibrium which would be produced by the total pressure subsisting at any instant between the bodies, supposing it to act for a long time; (2) it is further assumed that the time of impact is large compared with the time taken by elastic waves to traverse the impinging bodies from end to end, which consequently move practically as rigid bodies except in the immediate neighborhood of the region of contact. From these premises, it follows at once that the energy of the colliding bodies remains as translational energy after the impact, a deduction which is closely borne out in experiment, provided the impinging bodies are of appropriate shape, e.g. solid spheres, and the stresses set up do not transcend the limits of perfect elastic recovery.<sup>2</sup> The first of the two premises on which Hertz's theory is based is of very general validity, in as much as it depends for its truth on the consideration that the elastic deformations near the region of contact are determined mainly by the pressure subsisting between the bodies at the instant, and being of a local character and relatively large, are uninfluenced by any changes in the elastic deformations that might be developed elsewhere as the result of movements of the bodies. The second premise of Hertz is however purely an assumption<sup>3</sup> which is of comparatively restricted validity and may even fail completely. Indeed it is often the case that the colliding bodies *cannot* even approximately be considered to move as rigid bodies during and after the collision, and a considerable proportion of the energy is transformed into the energy of elastic wave-motion set up in the substance of the solids. Hertz remarked in his paper, though he did not fully develop the idea, that even in such cases, the first hypothesis (which remains valid) taken together with the equations of wave-motion in an elastic solid might enable the course of the impact to be traced. This suggestion of Hertz does not appear to have been generally followed up, though indeed in one case, that of the longitudinal impact of rods with rounded ends, its utility has been established.<sup>4</sup> It is proposed in the present paper to consider the application of the method suggested by Hertz to the problem of the *transverse* impact of a sphere or other solid of limited dimensions upon an infinitely extended elastic plate of finite thickness. It will be shown how the

<sup>1</sup>Hertz's Miscellaneous Papers, English edition, page 146, and Love's Theory of Elasticity, page 195 (1906 edition).

<sup>2</sup>C V Raman, *Phys. Rev.* December 1918, page 442.

<sup>3</sup>Except in the case of *extremely small* velocities of impact when it is true irrespective of the shapes of the impinging bodies.

<sup>4</sup>J E Sears, *Trans. Cambridge Phil. Soc.*, XXI (1908), page 49.

proportion of energy of impact transformed to energy of elastic wave-motion may be approximately calculated, in other words how the coefficient of restitution of the impinging body may be theoretically determined.

## 2. On the nature of the wave-motion set up by impact

The effect of an impulse of short duration applied at a point on the plane face of an infinite mass of elastic solid has been investigated by Lamb,<sup>5</sup> who found that the main shock produced by the impulse travels along the surface of the solid as a solitary wave (with one maximum and one minimum, both in the horizontal and vertical displacements), with its time-scale constant, and its amplitude decreasing in accordance with the usual law of annular divergence, so that its total energy remains undiminished. The velocity of this solitary wave is that of the free Rayleigh waves on the surface of the solid which is somewhat less than that of the equivoluminal waves in an unlimited medium. As the depth to which the Rayleigh waves penetrate is comparable with their wavelength, it may be readily shown that for the case of a sphere impinging on the plane face of an infinite solid, the fraction of the translational energy transformed to energy of elastic wave-motion is extremely small. When, however, the impact takes place on an unlimited elastic plate or bar of *finite* thickness, this is no longer true, and a considerable proportion of the energy (in some cases, the whole of it) may be so transformed. The theory of wave-motion on a cylindrical rod of infinite length has been discussed by Pochhammer in a well known memoir,<sup>6</sup> and for the case of an infinite elastic plate of finite thickness by Lamb<sup>7</sup> in a recent paper. Lamb finds that the types of wave-motion possible in an elastic plate may be divided into two classes, (a) the symmetrical modes, and (b) the asymmetrical modes. The former class travel with very high velocities ranging from a maximum equal to the highest value possible in an unlimited medium to a minimum equal to that of the Rayleigh surface-waves. The asymmetrical modes of wave-motion have relatively smaller velocities ranging from a maximum equal to that of the Rayleigh waves to a minimum value which tends to zero for very long flexural waves. *Prima facie*, it is clear that the modes of wave-motion excited by transverse impact would be chiefly of the asymmetrical class, and that, even of the latter, those chiefly concerned in taking up the momentum of the blow would be the relatively slowly-moving waves. Which particular type of wave-motion preponderates would obviously depend on the duration of impact and the manner in which the pressure exerted by the impinging body varies during impact.

---

<sup>5</sup>Philos. Trans. R. Soc. A, 203 (1904), pages 1–42.

<sup>6</sup>Crelle, 81, page 324, see also Love's Elasticity, 1906, page 275.

<sup>7</sup>Proc. R. Soc. (London), 93 (A series), 1917, page 114.

An approximate calculation of the energy taken up by the wave-motion excited in the plate may be founded on the simplifying assumption (which may be justified at least as a first approximation) that the disturbance set up by the impact travels outward in the plate with the velocity of flexural waves having a half-period equal to the duration of impact. Let  $2f$  and  $2b$  be the thickness of the plate, and the diameter of the sphere respectively,  $\rho_1, \rho_2$ , their densities,  $q_1, q_2$ , their Young's Moduli,  $\sigma_1, \sigma_2$  the values of Poisson's ratio, and  $\tau$  the duration of impact. The velocity  $V$  of long flexural waves of wavelength  $\lambda$  in the plate is given by the formula

$$V^2 = \frac{4}{3} \cdot \pi^2 \cdot \frac{f^2}{\lambda^2} \cdot \frac{q_1}{\rho_1(1 - \sigma_1^2)}. \quad (1)$$

On the foregoing assumption, the radius  $a$  of the circle on the plate over which the disturbance has spread at the termination of the impact is given by the relation  $a = V\tau = \lambda/2$ . Accordingly, we have

$$a^2 = \pi\tau f \sqrt{q_1/3\rho_1(1 - \sigma_1^2)}. \quad (2)$$

The next step is to find the kinetic and potential energies of the wave-motion in the plate. The kinetic energy may be determined if we know the transverse velocity of the plate at each point over the circle of radius  $a$  covered by the wave. The problem is one of two-dimensional wave-propagation analogous to that treated by Lamb,<sup>8</sup> who has discussed the configuration of the annular solitary wave diverging from a point at which a local pressure is applied, rising from zero to a maximum and falling again to zero. Lamb has given a sketch in the paper cited, showing the form of the wave when it has moved out to a considerable distance from the origin, from which it is seen that the wave consists of two parts: a rising part in which the transverse velocity of a point over which the wave passes increases quickly from zero to a maximum positive velocity and decreases again to zero, and a falling part which consists of an infinitely extended 'tail' in which the transverse velocity after reaching a certain maximum *negative* value (which is numerically less than in the first part) gradually drops down to zero again. The first part of the wave in Lamb's diagram passes over any specified point in about  $5/8$  of the duration of the original impulse. The form of the wave when near the origin just after the impulse has ceased would, of course, differ in details from that described above, but may be approximately represented as in figure 1 in which the ordinates represent transverse velocities, and the abscissae are the radial distances from the point of impact. The direction of the impact is shown in the figure by an arrow.

---

<sup>8</sup>Proc. London Math. Soc. 35 page 141 (1902).

### 3. Calculation of the coefficient of restitution

The kinetic energy contained in the wave is given by

$$E = \int_0^a \frac{1}{2} \cdot 2f \rho_1 \cdot 2\pi r v^2 dr, \quad (3)$$

where  $v$  is the transverse velocity at any point as given by the graph in figure 1. We may, without appreciable error, denote the sum of the potential and kinetic

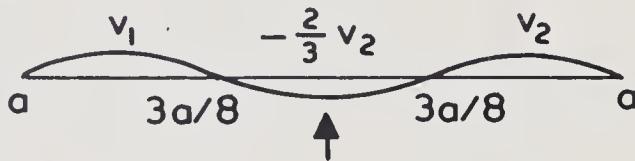


Figure 1.

energies in the wave by twice the integral in (3), that is by  $2E$ . The impulse given by the impinging body to the plate is given by

$$I = \int_0^a 2f \rho_1 \cdot 2\pi r v dv, \quad (4)$$

the integration in which is to be carried out having due regard to the sign of  $v$ . If  $M$  be the mass of the impinging body,  $v_1$  its velocity before impact, and  $e$  the coefficient of restitution, we have on the assumption that the energy is fully conserved, the two relations

$$\left. \begin{aligned} \frac{1}{2} M v_1^2 (1 - e^2) &= 2E \\ M v_1 (1 + e) &= I \end{aligned} \right\}. \quad (5)$$

On evaluating the integrals in (3) and (4), and substituting the same in (5), we get the value of coefficient of restitution,  $e$ . The necessary integrations are readily carried out by taking the graph of the transverse velocity in figure (1) to be made up of arcs of sine-curves. The formula finally obtained is

$$e = \frac{\int \rho_1 a^2 - 0.56M}{\int \rho_1 a^2 + 0.56M}. \quad (6)$$

The distribution of transverse velocity shown in figure (1) is, as explained above, based on Lamb's investigation of two dimensional wave-propagation, and has thus theoretical justification. It also appears to be that most closely agreeing with facts. Nevertheless, it is of interest to see how far other assumed distributions of velocity would modify the formula for  $e$  given in (6). If the distribution of

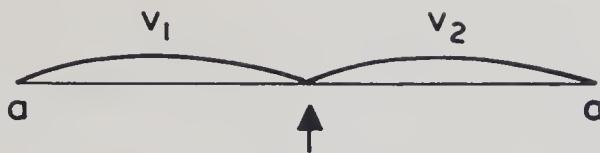


Figure 2a.

transverse velocity were that shown in figure 2(a), the formula for  $e$  is found to be

$$e = \frac{f\rho_1 a^2 - 0.39 M}{f\rho_1 a^2 + 0.39 M}. \quad (7)$$

For the distribution shown in figure 2(b), the formula is

$$e = \frac{f\rho_1 a^2 - 0.44 M}{f\rho_1 a^2 + 0.44 M}. \quad (8)$$

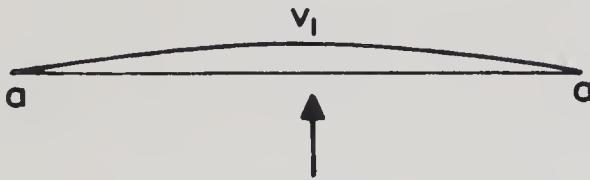


Figure 2b.

To make use of the formula given in (6), we have to substitute in it the value of  $a$  as given by (2), and to enable this is to be done, we have to ascertain the duration of the impulse  $\tau$ . It is obvious that to a first approximation, this may be taken to be the same as that given by Hertz's theory of impact, the mass of the impinging body being  $M$ , and the mass of the plate being taken to be infinitely great. If there is any deviation from this in actual practice, such deviation should be sensible only when the velocity of impact is very large or when the thickness of the plate is much smaller than the diameter of the impinging sphere. The duration of impact on Hertz's theory is given by the equation

$$\tau = 2.94\alpha/v_1, \quad (9)$$

where

$$\alpha = \left[ \frac{15}{16}v_1^2 \left( \frac{1-\sigma_1^2}{q_1} + \frac{1-\sigma_2^2}{q_2} \right) M \right]^{2/5} b^{-1/5} \quad (10)$$

and  $b$  is the radius of the impinging sphere. These values have to be substituted in equations (2) and (6) above.

#### 4. Comparison with experiment, and some concluding remarks

The correctness of the formula for the coefficient of restitution developed in (6) above has been tested in the author's laboratory in a very careful series of experiments carried out by Mr A Venkatasubbaraman to whom his best thanks are due. The impacts observed were those of polished hard steel spheres impinging on horizontally held glass plates of sufficient size to permit of the application of the theory, these materials being chosen as for moderate velocities of impact they very nearly satisfy the condition that the system is of the conservative type. As remarked above, the calculations assume that the duration of impact is the same as that given by Hertz's formulae which would be practically correct, provided the velocity of impact is not very great and that the thickness of the plate is not very small. Mr Venkatasubbaraman's experiments give results for the coefficient of restitution under these conditions closely agreeing with those found from (6).

The following facts emerge on an examination of the figures shown in the table of results. For the thicker plates, the experimental values for  $e$  are smaller by two or three per cent than the theoretical values. This is evidently due to various minor causes of dissipation of energy not being taken into account in the theoretical treatment. For moderate thicknesses of plate, the calculated and observed coefficients of restitution agree well. Theory and experiment also agree in the case of very thin plates in giving a zero coefficient of restitution. In other words, in such cases, the sphere on impact with the plate remains in contact with it. But in certain intermediate cases, where the thickness of the plate is less than about half the diameter of the impinging sphere, but not so small as to give a zero coefficient of restitution, the observed values of  $e$  are somewhat larger than the calculated values. These cases are shown enclosed in heavy lines in the columns of the table. It has already been remarked that in such cases, the assumption made that the duration of the impulse is given by Hertz's formula for impact with an infinite mass of solid would cease to be valid, and the discrepancy between the observed and calculated figures may possibly be due to this. An alternative explanation would be that in such cases, the configuration of the annular wave set up in the plate may slightly differ from that shown graphically in figure 1, and may approach more closely to that shown in figure 2(a). It is obvious then that the formula (6) would have to be modified for such cases by slightly decreasing the numerical constant 0.56 appearing in it to 0.50 or 0.45 for the thinnest plates. As a matter of fact, if this is done, the discrepancy between the observed and calculated values of  $e$  in these cases disappears.

Another noteworthy result indicated by formulas (2) and (6) and which is confirmed by some observations made by the writer is that the coefficient of restitution for impact on an elastic plate should depend on the velocity of impact, and should approach unity for very small values of this velocity. This is a consequence of the fact that the duration of impact as given by Hertz's formula

Table 1  
Coefficient of restitution,  $e$   
Velocity of impact = 234 cm per second

Thickness of plate in centimeters	Diameter of spheres in centimeters.																	
	0.791			0.714			0.637			0.555			0.396			0.314		
	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.
	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$	$e$
2.53	0.98	0.95	0.99	0.96	0.99	0.97	0.99	0.97	0.99	0.98	0.99	0.98	0.99	0.98	0.99	0.98	0.99	0.98
1.93	0.97	0.95	0.98	0.96	0.98	0.96	0.99	0.97	0.99	0.97	0.99	0.98	0.99	0.98	0.99	0.98	0.99	0.98
1.29	0.93	0.91	0.94	0.93	0.96	0.93	0.97	0.94	0.98	0.95	0.99	0.97	0.99	0.97	0.99	0.98	0.99	0.98
1.01	0.89	0.87	0.91	0.89	0.93	0.91	0.95	0.93	0.97	0.94	0.98	0.96	0.99	0.96	0.99	0.97	0.99	0.97
0.79	0.77	0.83	0.80	0.86	0.83	0.89	0.86	0.89	0.94	0.90	0.96	0.95	0.96	0.95	0.98	0.96	0.95	0.96
0.61	0.60	0.67	0.66	0.73	0.71	0.79	0.77	0.89	0.86	0.93	0.91	0.96	0.94	0.96	0.94	0.96	0.95	0.96
0.35	0.38	0.44	0.45	0.53	0.53	0.62	0.61	0.79	0.77	0.86	0.84	0.92	0.89	0.92	0.89	0.92	0.92	0.89
0.225	0	0	0.03	0.13	0.15	0.23	0.28	0.34	0.55	0.55	0.69	0.68	0.81	0.79	0.68	0.68	0.79	0.79
0.150	0	0	0	0	0	0	0	0	0.12	0.21	0.42	0.45	0.62	0.63	0.42	0.45	0.62	0.63
0.105	0	0	0	0	0	0	0	0	0	0.08	0.09	0.24	0.36	0.43	0.43	0.24	0.24	0.36

varies inversely as the one fifth power of the velocity, and the radial distance  $a$  covered by the annular wave diverging from the origin should therefore increase with decreasing velocity of impact. Fuller quantitative data showing the relation between the coefficient of restitution and the velocity of impact will be obtained and presented in due course in a further communication.

It may be remarked that much higher velocities of impact or larger spheres than those indicated in the table cannot be used, for the reason that the impact in such cases ceases to be of the conservative type, and results in internal fractures of a local character and of peculiar geometrical form in the glass plates. The character of these fractures bears an interesting relation to the distribution of stress in impact as given by Hertz's mathematical theory, and will be more fully discussed in a later paper.

The method used in the present paper can of course be applied also to the problem of transverse impact on an elastic bar, which is of a somewhat simpler character owing to the wave-propagation being in a single dimension instead of in two dimensions as in an elastic plate. The nature of the wave-motion set up by impact in this case is also capable of somewhat stricter analytical treatment if, following Boussinesq, we use Fourier's well known integral for the transverse vibration of an infinitely long bar to find the motion resulting from the initial impulse. In both cases also, it would be of interest to attempt a theoretical treatment (with experimental verification) of the manner in which the duration of impact varies with the thickness of the bar or plate, and also a direct experimental determination of the form of the wave at the instant at which the impact ceases.

210, Bowbazaar Street  
Calcutta, India

# The optical study of percussion figures

C V RAMAN

## ABSTRACT

The application of optical interference methods to the study of the small local deformations occurring in impact is indicated as likely to lead to an extension of our knowledge of such deformations. As an illustration of the usefulness of the method, interference photographs showing the surface deformations produced by the percussion of a polished steel ball on a thick glass plate are reproduced. The photographs show the percussion figure to consist of three distinct regions.

- a. A central area which remains plane and practically undisturbed except for a small permanent lowering of its level.
- b. A narrow annular region of fracture showing severe injury to the surface.
- c. A sudden elevation of the surrounding surface which slopes down gradually to the general level of the plate at the outer margin of the area of internal fracture.

As is well known, a theory of the elastic deformations produced when two solid bodies with curved surfaces are pressed into contact was developed by Hertz,<sup>1</sup> and applied by him to a consideration of the phenomena occurring during the impact of such bodies. The theory takes no account of the *irreversible* deformations such as actually occur in practice under sufficient static pressure or in elastic collision, and of the consequent dissipation of energy; it does not therefore completely describe the phenomena. Nevertheless the theory serves as a first approximation and is a useful guide in attempting to understand the behaviour of imperfectly elastic materials in hardness or impact tests. In special cases, as for instance when the impact velocities are very low,<sup>2</sup> or when no energy loss occurs except that due to production of vibrations in the impinging bodies,<sup>3</sup> Hertz's theory fits the facts tolerably well or at any rate can be suitably modified. It is more difficult adequately to take into account the effect of inelastic deformations on the course of the phenomena of impact, particularly because the element of time enters in the problem in a somewhat complicated way. Nevertheless it may be hoped that an exact experimental knowledge of the subject may pave the way for further developments in theory.

<sup>1</sup>Hertz, *Miscellaneous papers*, English Translation, p. 146.

<sup>2</sup>C V Raman, *Phys. Rev.*, 2nd Series, **12**, p. 442, 1918.

<sup>3</sup>C V Raman, *Phys. Rev.*, 2nd Series, **15**, p. 277, 1920. See also, J. Okubo, *Tohoku Univ. Sci. Rep.*, **11**, pp. 445–461, Dec. 1922.

It occurred to the writer that an application of optical interference methods might be useful in extending and making more precise the knowledge of the local deformations occurring in impact. The interference lines between the deformed surface and an optical flat would form an accurate contour map which could easily be measured up and interpreted, and the sensitivity of the method would be such that deformations as small as  $10^{-5}$  of a centimeter could be accurately determined. In the case of metallic surfaces, a difficulty which presents itself is that the reflecting power of a polished metallic surface is usually much higher than that of an optical flat of glass or fused quartz, and the visibility of the fringes between them is therefore somewhat low. This may however be overcome by half-silvering the lower face of the optical flat and thus making the reflecting power of the two boundaries of the air film nearly equal. Work on these lines has been undertaken by Mr Kedareswar Banerjee, a research student under the writer's direction, and the results obtained will be reported in due course. As an indication of the usefulness of the method suggested in the study of the deformations produced by elastic impact, the writer wishes to present three interference photographs obtained by him showing the effect of the collision of a polished steel ball 2 cm diameter on the surface of a thick glass plate. The percussion figure obtained in this case was described by the writer some five years ago in a communication to *Nature (London)*<sup>4</sup>. Its remarkable character is brought out in a striking way when an optical flat is laid on the deformed surface, and the interference fringes between the contiguous faces are observed in monochromatic light. Figures 1, 2 and 3 are photographs obtained in this way, (magnification



**Figure 1.** Percussion figure: interference pattern with test-plate nearly parallel to surface of glass block.

about five diameters), a quartz mercury lamp with quinine sulphate filter being the source of light used. In figure 1, the two surfaces were nearly parallel, in

<sup>4</sup>C V Raman, *Nature (London)* 9 October 1919.



Figure 2. As in figure 1, but with the test-plate not parallel to surface.

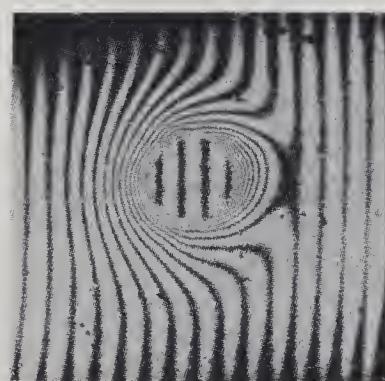


Figure 3. As in figure 2, but with still larger tilt of test-plate.

figure 2, somewhat more inclined to each other and in figure 3 further inclined still.

An inspection of the photographs shows three distinct regions in the percussion figures. Firstly, there is a central area, nearly circular which, apparently, is unaffected by the impact as is shown by the fringes passing through it in figure 3 being straight and parallel. Secondly, there is a narrow annular region of fracture full of a net-work of irregular fringes, showing severe injury to the surface. Thirdly, and just beyond this, there is a sudden elevation of the surface, of about four wavelengths, which slopes down first quickly, and then more slowly, to the original level of the surface at the edge of an area which sets the limit to the percussion figure. Closer examination reveals another remarkable feature, namely, that the central area of the percussion figure, though it remains plane and apparently undisturbed has, in reality, been *depressed below* the original level of the surface by an appreciable fraction of a wavelength, as shown by the fact that the course of the fringes outside the percussion area and within the central circle are distinctly out of register. This feature will be evident on a

scrutiny of all three photographs and has been found to be an invariable feature of the percussion figures produced even on very thick glass plates by the impact of steel balls.

An explanation of these features on Hertz's theory of impact may be ventured, though some points still remain obscure. The nature of the stress distribution in the case of a sphere resting on a plane has been worked out by S Fuchs<sup>5</sup> who has given a diagram of the lines of principal stress. Near the central compressed area both the principal stresses are pressures, and the glass stands the compression without giving way. There is a narrow annular region surrounding the central area where one set of principal stresses are pressures and the other set are tensions. The shearing stresses are a maximum in this region and the glass gives away, the circular crack spreading obliquely inwards into it for a considerable region. When the crack forms, the surface of the glass on its outer side is raised up and dips down slowly to the edge of the area covered by the extension of the internal fracture-surface. The small permanent depression of the central area remains, however, a mystery. It does not seem possible that it can be due to any actual flow of the glass during the impact, as the time available is all too short for such flow to occur, and as, moreover, there is no sign of the area in contact with the sphere acquiring any appreciable curvature, as could reasonably be expected if viscous flow occurred. Accepting the reality of the phenomenon, the only explanation of it that the writer can offer is that, at the instant the crack starts and spreads inwards, part of the material which has shifted its position outwards under the intense compressive forces remains outside it and is unable to return. The level of the central area is thus permanently lowered when the stress is removed. Further studies of the phenomenon under large static stresses would be of interest.

210 Bowbazaar Street  
Calcutta, India

---

<sup>5</sup>S Fuchs, 1913 *Phys. Zeit.*, p. 1282.

## Percussion figures in crystals

SIR C V RAMAN

(Memoir No. 111 from the Raman Research Institute, Bangalore-6)

Received November 29, 1958

### 1. Introduction

When a polished sphere of hard steel is dropped from a height on the plane smooth surface of a thick slab of glass and rebounds therefrom, the impact results in a beautiful effect which is seen within the glass around the region of contact between the sphere and the slab. The phenomenon was described and illustrated by a set of photographs in a communication published many years ago under the title "Percussion figures in isotropic solids" in *Nature* of 9th October 1919. When an optical test-flat is laid on the surface of the glass slab over the region of impact, the nature of the permanent deformations resulting from the impact is very clearly revealed by the interference patterns seen in monochromatic light between the two surfaces. Photographs of these patterns were published in an article by the author on "The optical study of percussion figures" which appeared in the *Journal of the Optical Society of America* of April 1926. A more detailed study of the phenomena including especially a quantitative comparison between the facts of observation and the consequences of Hertz's well-known theory of impact appeared shortly afterwards in a paper by one of the author's collaborators in the *Indian Journal of Physics*.

It had long been the author's intention to investigate by similar methods the results of the impact of a steel sphere on single crystals of various materials. Only recently however did it become possible for this programme to be taken up and the present communication reports the results. The materials investigated were quartz, calcite, barytes, and felspar, and to make the study more complete, a few polycrystalline solids found in nature were also investigated. Photographs of the percussion figures obtained in the various cases are reproduced with the paper. The cases studied most fully are those of quartz and calcite. The results obtained with quartz are illustrated by figures 1 to 6 in plate I and figures 1 to 6 in plate II. Plates III–V illustrate the results obtained with the other solids.

## 2. Percussion figures in glass

Three photographs reproduced as figures 1, 2 and 3 in plate III exhibit the results of the impact of a steel sphere on the surface of a thick glass plate. Simple inspection reveals that the external surface of the slab remains uninjured by the impact except along a ring or annulus with a sharply defined inner boundary. Within the annulus is a clear circular area which evidently represents the region where the sphere and plate come into contact during the impact. From the ring or annulus a fracture spreads obliquely inwards within the glass in the form of a surface of revolution. Figure 1 in the plate is a lateral view of the fracture seen through the edge of the plate; its mirror-image as seen by internal reflection at the surface of the plate also appears in the photograph. Interference rings are exhibited by the fracture both by reflected and by transmitted light; their configuration indicates that the separation between the two faces of the fracture is a maximum at the surface of the plate and diminishes progressively to zero at its termination in the interior (figure 2). The interference pattern which is observed when a test-plate is laid on the surface is reproduced as figure 3. It shows the area of the percussion figure to consist of three distinct regions: (a) a circular central area which remains plane and undeformed, but exhibits a small permanent lowering of its level; (b) an annular region of fracture showing severe injury and (c) a sudden elevation of the surrounding area which slopes gradually down to the general level of the surface at the outer margin of the percussion figure; the last-mentioned feature is clearly a consequence of the internal fracture.

While the above is a general description, there are also other subsidiary features deserving of mention. When the circumstances of the impact are such that the pressure exerted by the sphere on the plate just suffices to produce a fracture, the circular ring-crack is sharp and well defined. On the other hand, when the velocity of the impinging sphere in relation to its size exceeds the minimum needed to cause a fracture, we have instead of a single circular crack, several cracks forming an annulus, the external diameter of which corresponds to the maximum area of contact, while the inner diameter is noticeably smaller. Subsidiary cracks also spread out in various directions along the surface of fracture interrupting its smooth continuity. Several of these can be seen in figure 2 in plate III.

## 3. Percussion figures in polycrystalline solids

Several naturally occurring solids are known which are polycrystalline in texture and which by reason of their mechanical strength find useful applications as building materials. Marble is one of the best known of them. It is however rather coarsely crystalline in its texture. Of greater interest from our present point of view is a material which may be described as a fine-grained limestone exhibiting

varied colours and of which enormous quantities are quarried in Southern India for use as flooring tiles. According to the locality of its origin, the material is variously known as Cuddappah stone, Shahabad stone, Tandur stone, etc. It is easily split into slabs of the desired thickness and the surface of the slabs can be worked to any desired degree of perfection. Indeed, it can be polished so perfectly as to give regular interference fringes when a test-flat is laid on it.

Figures 4, 5 and 6 in plate III show the highly characteristic features of the percussion figures shown by the Tandur stones. Simple inspection by reflected light reveals a spherical dimple covering the area of contact between the sphere and the slab. A closer examination reveals a concentric set of sharply defined circular cracks lying on the slopes of the depression. One also observes a set of radial cracks spreading outwards from the edge of the cup-shaped depression. These features can be recognized in figure 4 of the plate. The interference patterns observed with a test-plate are of a totally different nature within the area of the depression and in the region outside it. They form a set of closely spaced circular rings within the depression (figure 6), while in the outer area they form a roughly hexagonal pattern the edges of which evidently correspond to the radial cracks spreading outwards (figure 5 in the plate).

A polished surface of marble shows very clearly the shallow depression produced by the impact of a steel sphere. Simultaneously also, the impact results in a visible breaking up of the texture of the marble, so much so that the entire area affected by it acquires a frosted appearance. We do not, however, observe either the circular or the radial cracks which are so conspicuous a feature in the case of the Tandur stones. The depressions in marble can also be made visible by laying a test-plate on the surface. This is shown in figures 3 and 4 in plate IV which refer to two different samples of marble.

Broadly speaking, it may be said that coarsely grained solids exhibit effects in impact which are similar to those exhibited by marble. This is illustrated by figures 5 and 6 in plate V which represent the deformations produced by impact as revealed by a test-plate. Figure 5 refers to the case of a black limestone akin to marble, while figure 6 represents the percussion figure in dolerite which is a hard and tough building stone capable of taking a high polish.

#### 4. Percussion figures in quartz

Quartz does not exhibit any regular cleavages and shows only irregular fractures when broken under a hammer. In this respect it resembles glass. *Prima facie* therefore, we may expect quartz to exhibit percussion figures broadly resembling those observed with glass but differing therefrom in detail by reason of the fact that quartz is a crystal with anisotropic physical properties. These expectations are borne out by the facts. There are however some additional features of a rather surprising and unexpected nature.

In studying the percussion figures of crystals, it is obviously necessary that the surface on which the impact occurs is optically plane and has a specified orientation in relation to the axes of crystal symmetry. It is also necessary that the specimen employed is sufficiently massive in relation to the size of the impinging sphere. These conditions are fortunately attainable without much difficulty in the case of quartz. Specimens of adequate size and of reasonably good quality are obtainable which admit of being cut and polished in any desired direction. Three specimens of quartz were employed in the present investigation. One of them was a massive crystal weighing several kilograms. On this, a large surface about  $20\text{ cm} \times 10\text{ cm}$  normal to the optic axis was cut and polished. A second face of nearly the same size parallel to a natural prismatic face was also ground and polished. Though the material was not of the highest optical quality, there were regions abutting on the two prepared surfaces which were quite clear and transparent and of sufficiently great extension in relation to the size of the percussion figures. The results observed are therefore worthy of confidence. The second specimen was a slab of crystal quartz about  $20\text{ cm} \times 15\text{ cm}$  and 5 cm thick, the faces of which were normal to the optic axis. One of the faces was carefully ground and polished. The third specimen employed was a crystal in its natural form exhibiting six prismatic faces, besides three large and three small rhombohedral faces. All these were ground and polished to perfection. The optical quality of the material was however rather poor.

Most of the detailed studies made refer to the case in which the surface on which the impact occurs is a basal section. Indeed, all the photographs reproduced in plates I and II refer to this situation. The reason for the choice made is obvious; for, since the impact in this case is along the optic axis of the crystal, we should expect the percussion figure to exhibit the maximum degree of symmetry. This expectation is borne out by the facts. Some visual observations were however also made for percussion figures on the prismatic and rhombohedral faces.

It is instructive to compare the photographs reproduced as figures 1 to 6 in plate I and as figures 1 to 6 in plate II which, as already stated, represent the percussion figures of quartz on a surface normal to the optic axis with figures 1 to 3 in plate III which show the percussion figures in glass. There are certain general similarities, but the differences are also striking and noteworthy. Alike in glass and in quartz, the impact results in the formation of cracks which commence on the surface around the margin of the area of contact and spread inwards into the material. But here all resemblance ends. The surface cracks in quartz are exceedingly fine and are seen under a magnifier as hair-lines clearly separated from each other, and there is otherwise no visible damage to the surface. The assembly of surface cracks is not circular in shape but resembles a hexagon with rounded edges. The fracture also spreads into the interior of quartz much more steeply than in the case of glass. This will be evident on a comparison of figure 4 in plate II which is an attempt to photograph the percussion figure in quartz as seen

laterally with figure 1 in plate III which is the corresponding figure for glass. The fracture-surface in the interior of quartz rarely shows any interference colours either by reflection or in transmission, from which it is clear that the two faces of fracture are very close to each other. By reason of its steepness, however, the fracture can cut off the transmitted light and then appears dark. This is clearly seen in figures 1, 2 and 3 of plate I and also figure 3 of plate II. A light tilt of the fracture-surface in relation to the direction of the incident light however makes a large change in this respect (see figures 2 and 3 in plate I). The fracture-surface can also be seen and photographed by reflected light (figures 1 and 2 in plate II).

As will be evident from the photographs reproduced in the two plates, the percussion figure inside quartz exhibits only trigonal symmetry, and not hexagonal symmetry. The photographs, however, do not adequately picture the actual configuration of the fracture. The shape of the latter is perhaps best described as resembling a three-cornered hat. In other words, the fracture takes the form of three ribs with three flaps separating them. The flaps are much more easily seen by transmitted and reflected light than the ribs. Another and most interesting feature is the fine structure exhibited by the fracture within the quartz. One observes a radial fibrous structure and crossing this we have also a circumferential ribbing consisting of a great number of concentric circles which run all the way down from the surface to the termination of the fracture. The circumferential ribbing is most clearly seen in figure 1 of plate I and not quite so clearly in figures 1 and 2 of plate II. The radial structure is very clearly manifest in the two latter photographs.

As the fracture within the quartz exhibits only trigonal symmetry, the elevation of the surrounding surface may naturally also be expected to exhibit the same symmetry. This is manifest from the interference patterns observed when a test-plate is laid on the surface (see figures 4, 5 and 6 in plate I and figures 5 and 6 in plate II). The trigonal symmetry is particularly clear in the second of the two patterns reproduced in figure 6 in plate I.

It would not be profitable to attempt here any explanation or interpretation of the various features set out above. That the percussion figure for impact on a basal plane, in other words along the optic axis of quartz, exhibits only trigonal symmetry and not hexagonal symmetry is interesting, but not altogether surprising. For, we know that the optic axis of quartz is a three-fold axis and not a six-fold axis of symmetry of the structure.

With regard to the observations which have been made of the percussion figures on the prismatic and rhombohedral faces, it will suffice here to remark that they do not exhibit the trigonal symmetry described and illustrated in plates I and II. In other respects, however, they exhibit features very similar to those set forth above. Each of the two cases exhibits special features of its own. But the observations made are not sufficiently numerous and trustworthy to justify a detailed description or discussion of the same.

## 5. Percussion figures in calcite

A calcite crystal in its natural form as a rhomb with edge-lengths 8 cm  $\times$  6 cm  $\times$  4 cm was employed in the study. Though the material was not of the highest optical quality throughout its volume, a region adjacent to one of the larger faces (8 cm  $\times$  6 cm) was clear and transparent to a considerable depth. Accordingly, this particular face was ground and polished and utilized for the production of the percussion figures. One of the adjacent faces (6 cm  $\times$  4 cm) was also ground and polished so as to permit of the interior of the crystal being viewed through it. In view of the small size of the specimen, the steel sphere employed was also small, about a centimetre in diameter. It had a highly polished surface and was dropped on the polished face of the rhomb from different heights at eight different points sufficiently remote from each other to ensure the absence of any mutual interference.

Percussion figures are observed around each of the chosen points of impact. They are conspicuous when the faces of the rhomb are viewed by reflected light, and they can also be seen to penetrate into the crystal when viewed longitudinally and also when observed laterally through the adjacent polished face. All the eight figures exhibit a general similarity with each other, though their sizes are different, since they diminish with the velocity of impact. They are all similarly orientated on the face of the rhomb and the configuration of each is symmetric about a plane normal to the face of the crystal which makes equal angles with its two rhombohedral edges. But they do not exhibit any symmetry with respect to a perpendicular plane and are indeed strikingly different on the two sides of it. The actual region of contact between the sphere and the crystal can be readily recognized by the fact that it appears relatively dark as seen by reflected light in comparison with the brilliant display of colours all round. It is also evident on a careful examination that it is slightly depressed in level below the original surface of the crystal.

Viewed by reflected daylight, the percussion figures exhibit a complex pattern of interference colours and fringes. The interferences are also conspicuously visible in monochromatic light. A photograph of the same is reproduced as figure 1 in plate IV. When an optical test-flat is laid on the calcite and allowed to settle down so that it comes into close contact with the crystal face, the interference pattern seen differs very little indeed from that observed without the test-plate. This fact is evident on a comparison of figure 1 in plate IV with figure 2 in the same plate, the latter representing the fringes seen when the test-plate has been laid on. If there are any fringes between the test-plate and the crystal, they are so faint and broad that their superposition on the closely spaced fringes in the interior makes little difference to what is actually observed.

It is well-known that calcite has three planes of easy cleavage parallel to the three faces of the rhombohedron and that it also possesses three glide planes each containing one of the rhombohedral edges and equally inclined to the other two.

An examination of the percussion figures in calcite reveals that the two cleavage planes intersecting the face on which the impact occurs play an important role in determining the results of the impact. It is observed that on either side of the area of contact between the sphere and the crystal, two cleavages making an acute angle with each other develop and extend outwards from the edges of that area. These cleavages are clearly visible on the face of the crystal, and they sharply limit the areas within which the fracture develops and spreads inwards into the crystal. Indeed, the pattern of reflected colours as seen in daylight and the interference pattern as seen by monochromatic light manifest themselves wholly within the limits set by these two cleavages. These features can be clearly recognized in figure 1 of plate IV. A further and most interesting feature is the appearance of a whole series of parallel lines outside the region of contact and on only one side of it and which extend over a considerable area of the pattern. These lines are equally inclined to the two sets of cleavages and cut across the curved interference bands exhibited by the fracture. We may explain them as due to glides occurring in the crystal along the direction of the third rhombohedral edge. The direction of the glide deviates greatly from the normal to the crystal face on which the impact occurs and hence also from the direction of impact. This may explain why the fracture-surface within the crystal extends much more in the forward direction than in the backward.

## 6. Percussion figures in barytes

The specimen of barytes employed was translucent with a faint bluish tinge. Its original shape as a crystal was that of a parallelopiped, four of whose faces were nearly rectangular, while the other two deviated sensibly from that shape. An artificial face of larger dimensions was obtained by cutting through the specimen in a direction making  $45^\circ$  with the rectangular faces; it was then ground and finely polished. In view of the small size of the specimen, the steel ball used had also to be quite small, only about 6 mm in diameter. It was dropped from various heights and the percussion figures thus obtained were critically examined.

The effects produced by the impact may be summed up as follows. Firstly, we have a visible dimple or depression left on the surface. There is also a general disturbance of the level of the crystal face around the point of impact, and this is not spherically symmetrical around the region of impact. We have also noteworthy changes in the interior of the crystal which result in a brilliant reflection appearing in certain directions, while it appears dark in other directions. This effect varies greatly with the direction of illumination and the direction of observation, some areas appearing dark in certain circumstances and others bright and *vice versa*. A remarkable lack of symmetry is exhibited by the effect. Merely turning round the specimen through  $180^\circ$  under oblique illum-

nation and normal observation results in all the areas which appear dark becoming bright and *vice versa*.

The internal reflections exhibited by one of the patterns is reproduced as figure 5 in plate IV. As both the illumination and the observation were normal, the special features mentioned above are not exhibited. Seen under oblique illumination, the figure resembles a butterfly with outstretched wings and tail, the head being bright and the tail and wings dark or *vice versa*. The changes in the interior—presumably in the nature of fractures—are accompanied by changes in the external level of the surface. These latter are revealed by the interference fringes observed when a test-plate is put on the specimen. This is illustrated by figure 6 in plate IV. This has the same orientation as figure 5, the latter being the figure as seen by reflected light.

## 7. The percussion figures in felspar

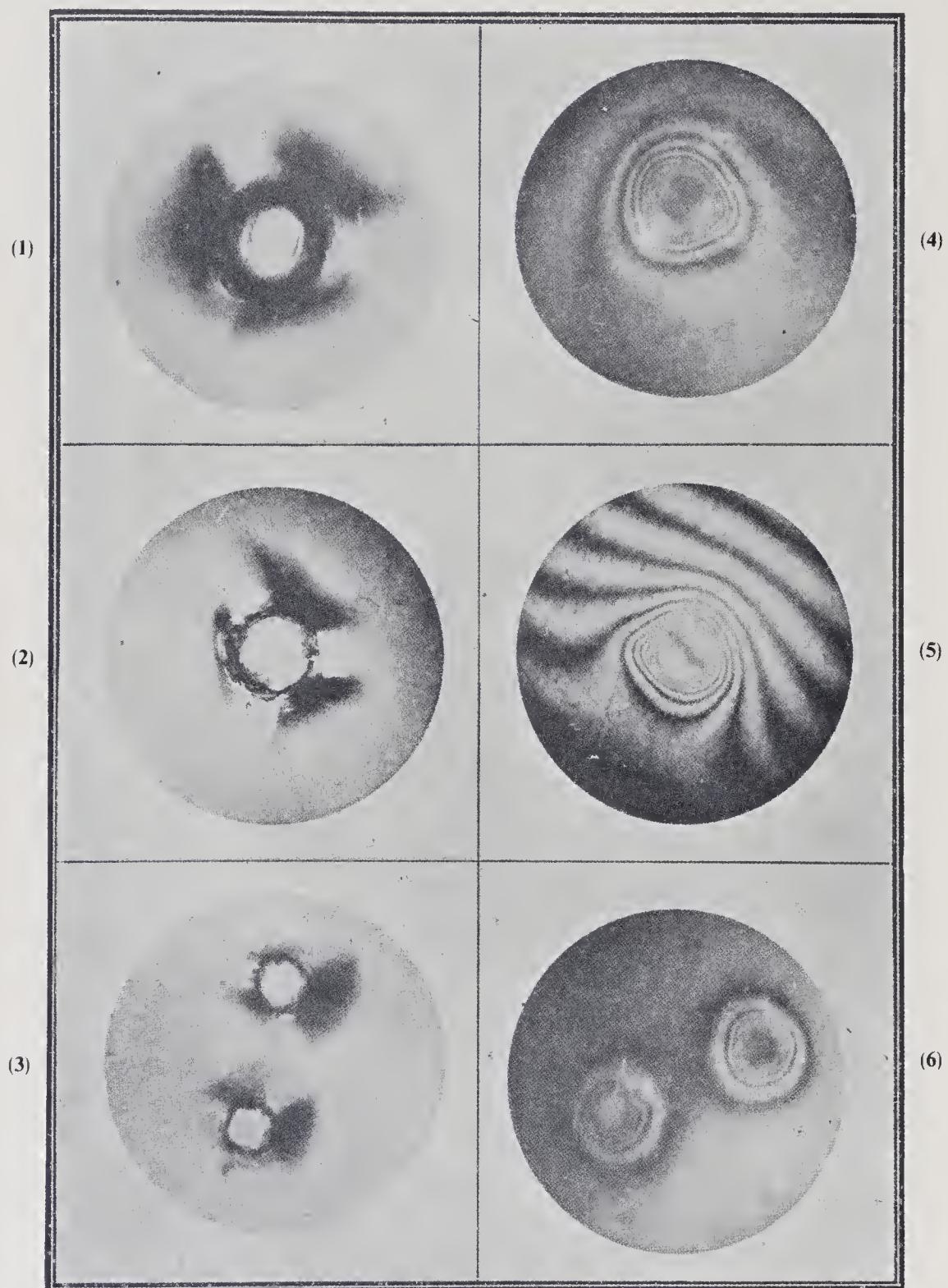
Specimens of felspar of large size are readily available exhibiting the natural faces of the crystal. These faces can be ground and polished so as to be optically plane. Thus, felspar lends itself readily to an exact study of the results of impact on crystal surfaces of known orientation. Unfortunately, however, it is not easy to obtain crystals of any appreciable size which are *optically clear*. The observations have accordingly to be confined to those features resulting from impact which are *externally observable*. This makes it rather difficult to make any detailed analysis of the results of impact in terms of crystal structure and orientation.

A highly characteristic effect exhibited by felspar and produced by the impact of a steel sphere on a natural crystal face is illustrated in figure 1 in plate V. Viewed by oblique illumination, the area of contact appears as a dark crescent surrounded by a bright crescent beyond it. Careful examination shows that the bright crescent is an internal reflection. Merely turning round the specimen through  $180^\circ$  causes the reflection to disappear. The reflection presumably arises from a fracture in the interior of the felspar produced by the impact. This naturally also results in an elevation of the surface and this is revealed by placing a test-plate on the surface. We then observe an asymmetric distribution of interference rings around the region of the impact. Five such patterns are seen in figures 2 and 3 in plate V. It will be noticed that the interference patterns are all similarly orientated, indicating that the phenomenon is definitely related to the crystal structure of the material. Figure 4 is a photograph of the interference pattern exhibited by the percussion figure on a different natural face of a felspar crystal. It will be seen that it has an altogether different character from those reproduced in figures 2 and 3 in the same plate.

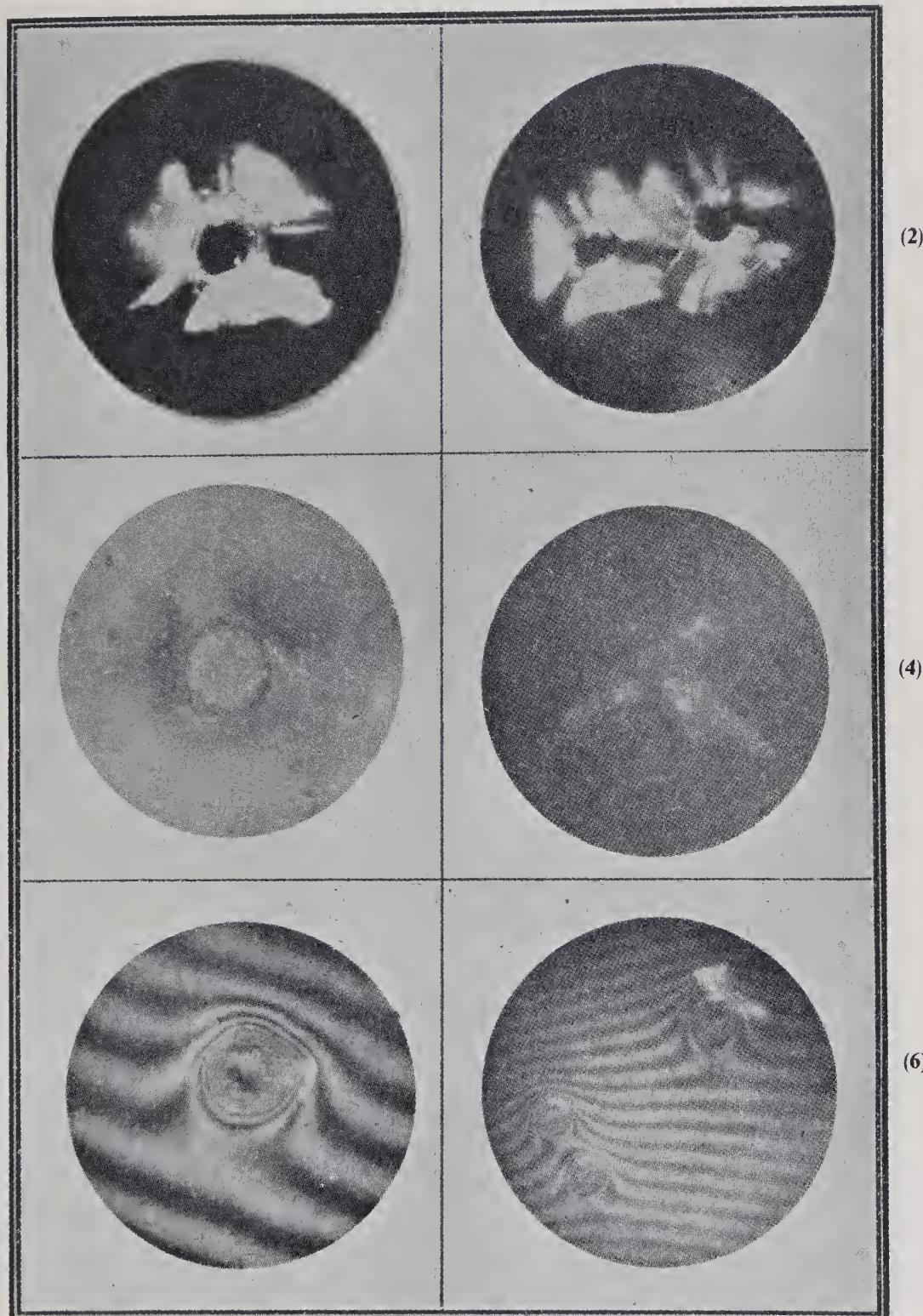
The preparation of the material employed in these studies and of the pictures which illustrate the paper required much painstaking labour. The work was undertaken and successfully carried out by my research assistant Mr J Padmanabhan.

### Summary

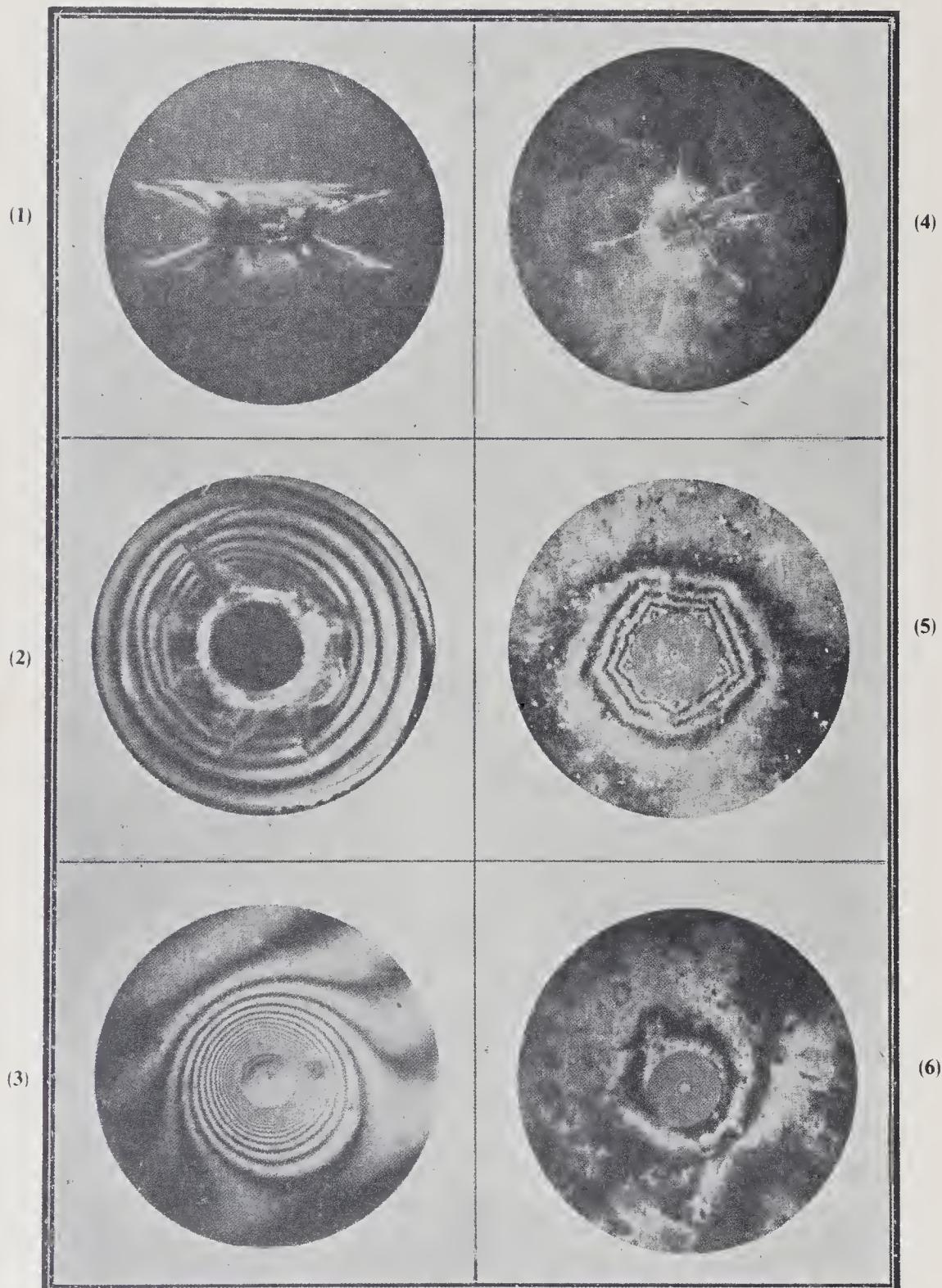
The impact of a hard steel sphere on the optically polished surface of a solid results in a permanent deformation of the surface and also produces fractures or rearrangements in the interior of the solid. These have been studied with crystals of quartz, calcite, barytes and felspar and also with a few polycrystalline solids. The results of the study show clearly that the nature of the percussion figure exhibited by a solid is a characteristic property of the material and is related to its inner structure and symmetry. The paper is illustrated by a series of photographs.



**Figures 1-6.**  
**Plate I.** Percussion figures in quartz.

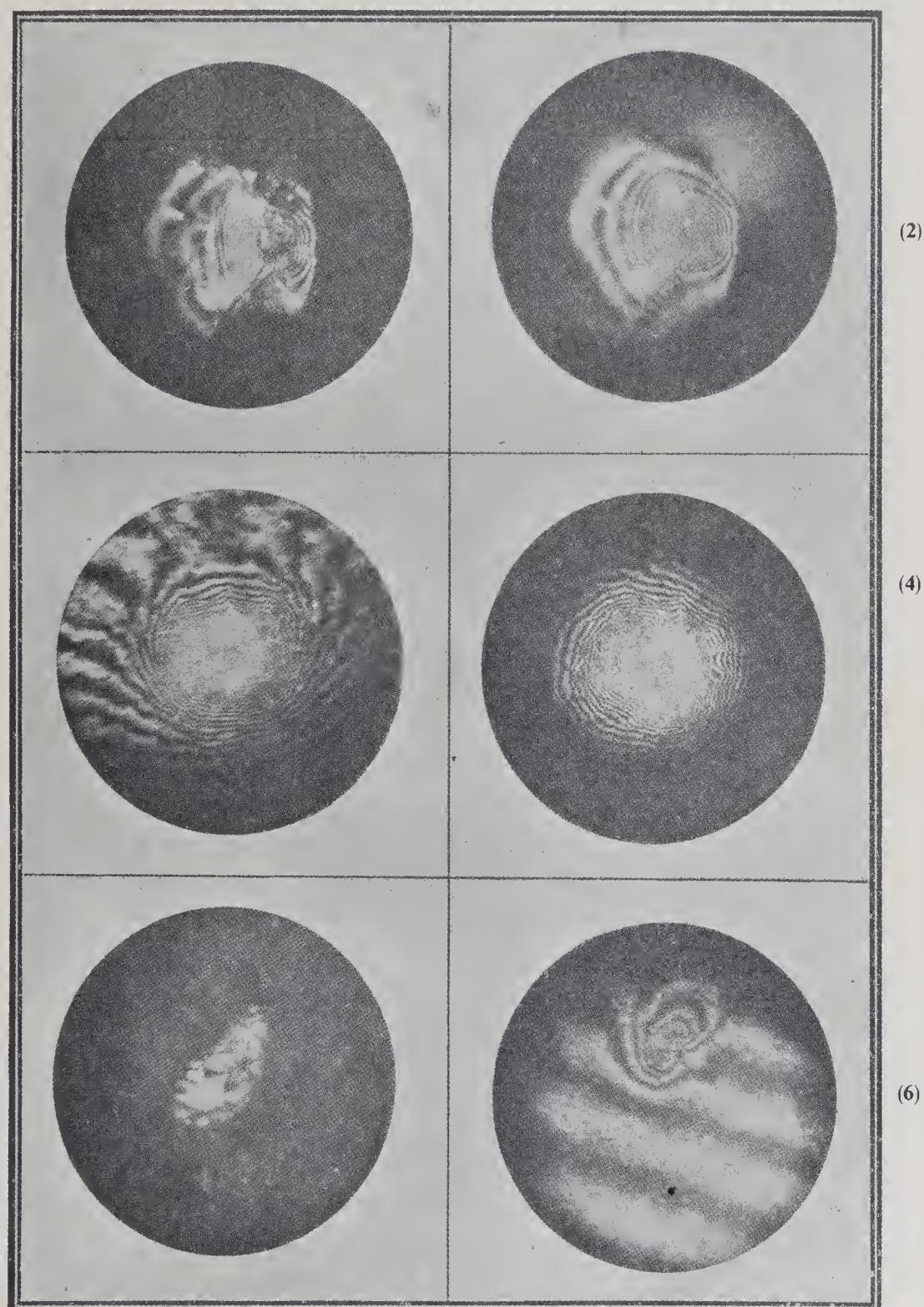


Figures 1-6.  
Plate II. Percussion figures in quartz.



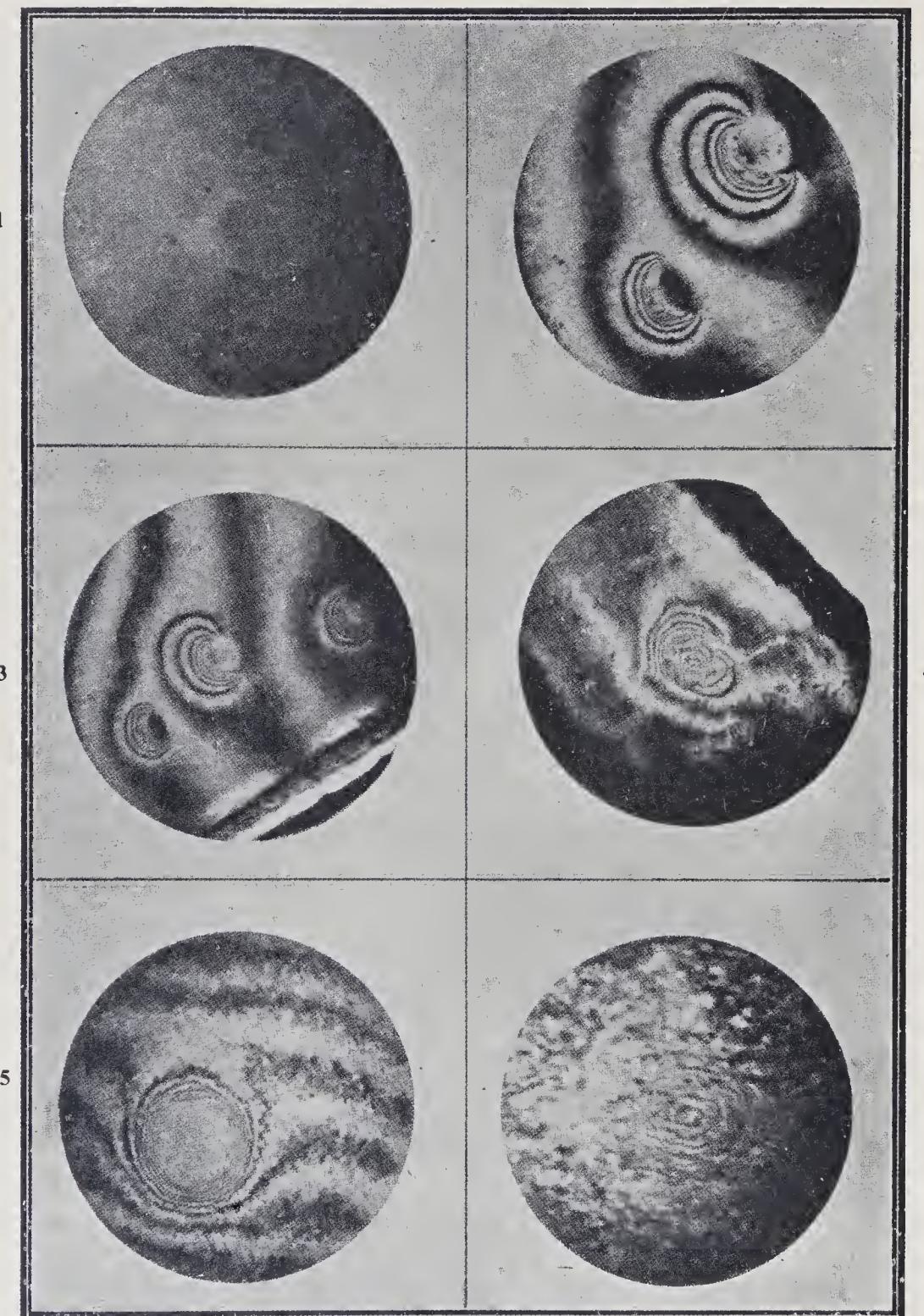
Figures 1-6.

Plate III. Percussion figures: figures 1, 2, 3 in glass and figures 4, 5, 6 in polycrystalline limestone.



Figures 1-6.

Plate IV. Percussion figures: figures 1 and 2 in calcite; figures 3 and 4 in marble; figures 5 and 6 in barytes.



Figures 1-6.

Plate V. Percussion figures: figures 1, 2, 3, 4 in felspar; figure 5, hard limestone; figure 6, dolerite.

## Percussion figures in crystals

SIR C V RAMAN

The impact of elastic solids was the subject of investigation by the author many years ago. The earliest of his publications on the subject which appeared in the *Phys. Rev.* for December 1918 recorded the discovery that the coefficient of restitution in the impact of elastic solid spheres tends to unity as the velocity of impact diminishes and becomes small, a result which could have been anticipated from theoretical considerations. His second paper which appeared in the *Phys. Rev.* for April 1919 considered the problem of the impact of spheres on elastic plates of finite thickness but of extended area. It was shown theoretically and confirmed experimentally that the kinetic energy of the impinging sphere is transferred to the elastic plate as energy of wave motion to an extent determined by the thickness of the plate and that as a consequence, the coefficient of restitution diminishes progressively from unity for thick plates to small values for thin ones.

In the course of the studies referred to above, the remarkable effects arising from the impact of a polished sphere of steel on the surface of a thick slab of glass came under the notice of the author. They were described and illustrated in a note published in *Nature (London)* of the 9th October 1919. Some further studies of the same effect were later reported in the *J. Opt. Soc. Am.* for April 1926. It had long been the intention of the author to return to the subject and investigate the effect of impact of spheres on crystal slabs. Only recently, however, did this intention materialize. Studies have been made of the results of the impact of polished steel spheres of appropriately chosen size on the optically polished surfaces of quartz, calcite, barytes and felspar. The results of the study show clearly that though the size of the sphere and the velocity of the impact are important factors, the general nature of the effects observed is a characteristic property of the crystal itself and is related both to the structure of the crystal and to the orientation of the face on which the impact occurs. The importance of the subject is thereby made evident and a wide field of research is opened up. It is proposed to give here a brief account illustrated by selected photographs of the results of the research. The interested reader will find a more detailed account and many more illustrations in the paper published by the author in the *Proc. Indian Acad. Sci.* for December 1958.

## 2. Percussion figures in glass

It is useful to commence with a brief account of the effects observed when a polished steel sphere is dropped on the smooth surface of a thick slab of glass from an appropriate height. The most striking feature of the percussion figures observed in the glass is a fracture which is symmetrical in shape and extends inwards from a ring-shaped crack on the surface to a sharply defined limit in the interior. The fracture exhibits interference colours both in transmission and by reflection, these being complementary to each other. A remarkable feature is that the area over which the sphere and the glass come into contact during the impact exhibits no visible damage, and indeed only with difficulty can one perceive by passing the finger over the surface of the glass that the impact has had any effect at all. The ring-crack from which the internal fracture spreads inwards is however readily visible at the surface, and a critical examination by reflected light also reveals a slight elevation of the surface round the crack, as is naturally to be expected from the presence within the glass of fracture surfaces which are separated from each other. This effect is however best exhibited by placing a test plate of glass over the percussion figure and observing the interferences between the lower surface of the test plate and the upper surface of the glass slab by reflected light. Monochromatic light, e.g. that of a sodium lamp should be used for the observations. The phenomenon of which a photograph is reproduced as figure 1(a) is then observed. At the centre of the figure is seen the undamaged area of the surface bounded by the circular ring crack. There is then a sudden elevation of the surface which is symmetrical around the area and slopes down gradually to the original level on all sides, as is shown by the configuration of the closely spaced circular interference rings.

## 3. Percussion figures in quartz

The nature of the results observed with quartz is found to depend notably on the orientation of the surface on which the impact occurs. The most interesting results are those noticed when this surface is perpendicular to the optic axis of quartz. Figures 1(b) and 1(c) reproduce photographs of the percussion figure observed in this case, figure 1(b) representing what is observed by transmitted light and figure 1(c) being the interference rings observed when a test plate is laid on the slab of quartz over the percussion figure. Figure 1(b) exhibits the very striking fact that the fracture surface inside the quartz exhibits only trigonal symmetry and *not* hexagonal symmetry. This feature is further evident from the nature of the elevation of the surface as revealed by figure 1(c). There are, of course, many other features noticeable in the photographs reproduced, but it is not possible to refer to them here in detail. They will be found fully set out and illustrated in the detailed paper referred to above.

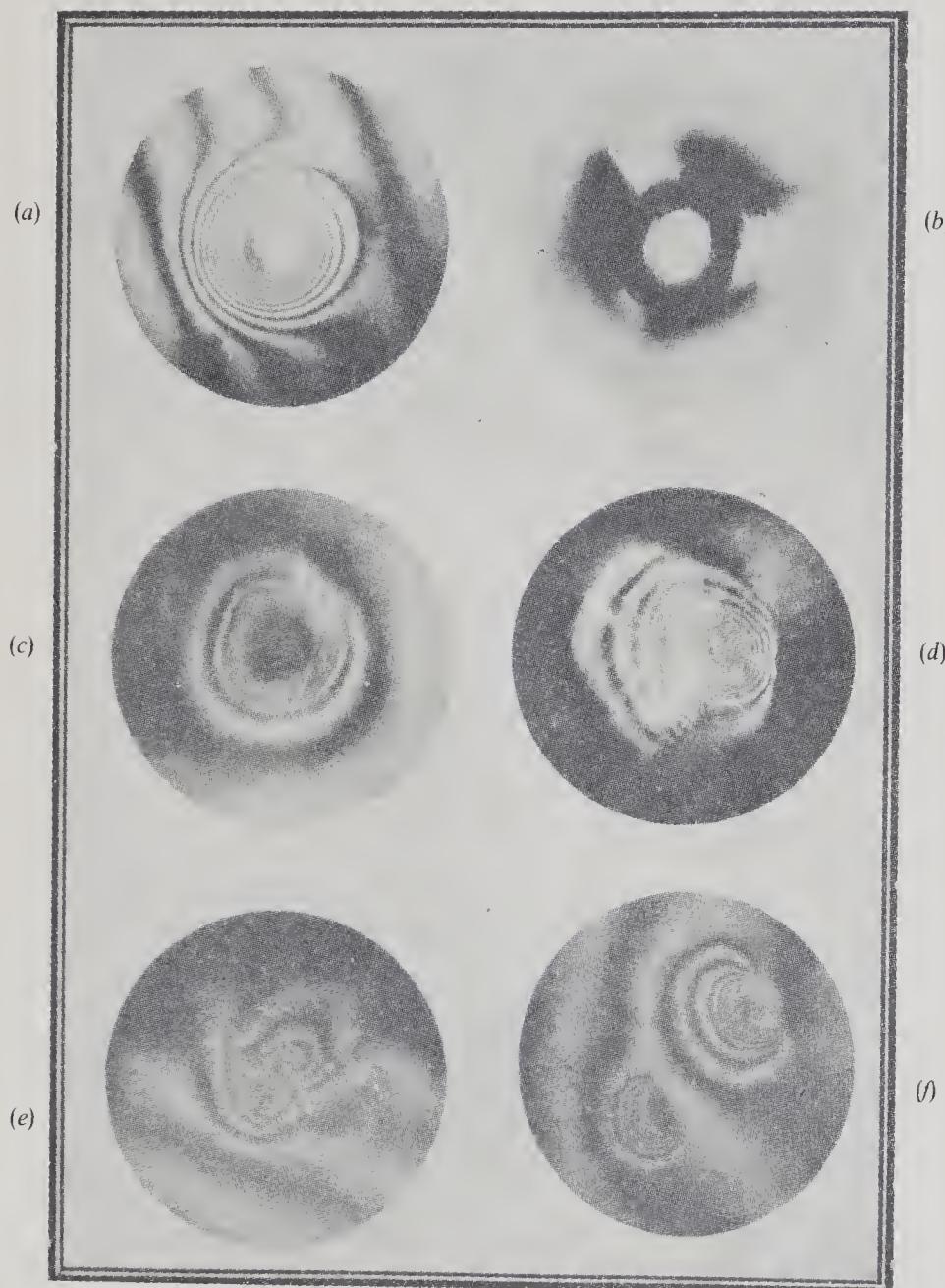


Figure 1. Percussion figures.

#### 4. Percussion figures in calcite

Figure 1(d) illustrates the effect of dropping a small steel sphere on the rhombohedral face of a crystal of calcite which had been smoothed and polished to optical perfection. The photograph was taken with a test flat laid on the surface and allowed to settle down. Much the same features are also exhibited by the percussion figure itself without a test plate. An examination of the percussion figure reveals that the characteristic cleavages of calcite play an important role in determining the results of the impact. Indeed, it is observed that on either side of the area of contact between the impinging sphere and the crystal, two cleavages making an acute angle with each other develop and extend outwards from the edges of that area. These cleavages are clearly visible on the face of the crystal and they sharply limit the area within which the fracture develops and spreads inwards. Another interesting feature is the appearance of a whole series of parallel lines outside the region of contact and only on one side of it. These lines are equally inclined to the two sets of cleavages and may be explained as due to glides occurring within the crystal along the direction of a rhombohedral edge.

#### 5. Percussion figures in other crystals

Quartz and calcite are specially suited for studies of the kind described, since it is possible to obtain fairly large specimens which are clear enough to enable the results of the impact within the crystal to be satisfactorily observed. In other cases, it is not so easy to find material of this quality which could be used for such studies. There is usually no difficulty, however, in obtaining single crystals of the desired size on which surfaces of the desired orientation can be cut, ground and polished to optical perfection. The results of the impact on the *external* surface can then be readily studied by placing a test plate on it and observing the configuration of the interference patterns seen in monochromatic light. These patterns are found to be highly characteristic of the material studied as well as of the chosen orientation of the surface. Figure 1(e) in the plate shows the pattern observed with barytes and figure 1(f) with felspar.

## India's debt to Faraday

SIR C V RAMAN, F.R.S.  
University of Calcutta

The idea of a life dedicated and consecrated to the service of humanity and involving the renunciation of personal advantages makes a powerful appeal to the mind of India. It is doubtful if, amongst men of science, a finer example of such a life could be discovered than that of Michael Faraday. His ideas and discoveries have benefited all mankind, and, in common with the rest of the world, India owes him a debt which can never be repaid. I consider it a great privilege to be allowed, on behalf of India, to offer my humble tribute of homage to the immortal soul of Faraday.

So long as seventy years ago the career and achievements of Faraday had made a profound impression in India. It is sufficient to mention the fact that, when the late Dr Mahendra Lal Sircar in the sixties of the last century laboured to promote science in India, he adopted the Royal Institution of Great Britain as the model to follow in establishing a centre for scientific research. The Association for the Cultivation of Science, which he founded at Calcutta in 1876, is thus itself an Indian memorial in honour of Faraday. It has been the great privilege of the present writer and of his numerous collaborators from all over India to have enjoyed the unique facilities for research provided by this institution during the last quarter of a century.

Amongst Faraday's discoveries, the most significant in its theoretical implications was the magneto-optic effect known by his name. It established an experimental connexion between light and electromagnetism, and thus paved the way for the demonstration by Maxwell and Hertz that light is itself an electromagnetic influence propagated through space. But a further implication of the discovery was that the particles of matter which are disturbed during the propagation of light are capable of being influenced by a magnetic field and are therefore themselves electromagnetic in their nature. It required the labours of Larmor, Lorentz, and many others to elucidate and develop this implication of the Faraday effect. But let it be emphasised that the discovery of magneto-optic rotation by Faraday was the seed from which grew the mighty tree of the electron theory of the dispersion and scattering of light.

It was the hope that fundamental advances in knowledge would result from a study of the relation between dispersion and scattering of light that induced me to make it the principal subject of my activities during the last ten years. The hopes

which inspired the work have not been unfulfilled. Incidentally, the researches it involved have had the result of taking the workers in Calcutta into other fields of work in which Faraday was also the pioneer. Amongst these may be mentioned diamagnetism, magne-crystallic action, and magneto-chemistry. The scattering of light by molecules stands in close relation not only with their optical dispersion but also with their magneto-optic behaviour, and especially the magnetic birefringence exhibited by fluids. The result of computations, based on the theory of magnetic birefringence, is to indicate that the molecule of benzene, the aromatic hydrocarbon discovered by Faraday, and even more so, the molecules of naphthalene, anthracene, and so on, possess an astonishing degree of magnetic anisotropy. Experiments undertaken at Calcutta led to the discovery that the aliphatic hydrocarbons also exhibit magnetic birefringence, but this is extraordinarily *feeble*, and *negative* in sign, while the magnetic birefringence of the aromatic hydrocarbons is known to be *strong* and *positive*. The significance of this discovery is, in the first place, that the magnetic anisotropy of the aliphatic molecules is very small. In other words, the chemical difference between the two classes of organic compounds corresponds to a striking magnetic difference. In the second place, the relations between the optic and magnetic axes of the two kinds of molecules are curiously different, and this gives rise to the difference in the sign of the magnetic birefringence. Experimental studies by Mr S Bhagavantam of the magne-crystallic behaviour of organic solids, especially of naphthalene, anthracene, and hexamethylbenzene, gave results in striking agreement with those inferred from magneto-optical experiments with solutions of these substances.

The importance of studying magne-crystallic behaviour, both of diamagnetic and of paramagnetic substances, cannot be over emphasised. Mr K S Krishnan has taken up this subject enthusiastically at the University of Dacca, and has developed very precise methods of measurement, and examined a large number of compounds both inorganic and organic. He has further attempted to correlate the magnetic results with the crystal structure of the substance wherever this is known from X-ray investigations. In the case of diamagnetic crystals, and especially of non-polar substances, we are probably justified in assuming the molecular susceptibility to be a constant characteristic of the substance. On the basis of this assumption, which admits of ready experimental test, it is possible to discuss the question whether the crystal structure assigned by X-ray workers is in accordance with the observed magnetic character of the crystal and the magnetic anisotropy of the molecule ascertained from magneto-optic experiments. It is possible, in fact, to determine what orientations of the molecules are possible within the crystal lattice which are consistent with its observed magnetic properties. This new method of crystal analysis developed by Krishnan appears to be full of promise.

The interpretation of the Faraday effect is itself at the present time not completely free from obscurity. Recent work by J Becquerel, Ladenburg, and

others indicates that we have to distinguish between two kinds of magneto-optic rotation, one associated with paramagnetic substances and the other with diamagnetic bodies. For the latter class, the theory originally suggested by Larmor indicates that the frequency of the 'Larmor precession' in the magnetic field, taken in conjunction with the known optical dispersion, determines the coefficient of magneto-optic rotation. Unfortunately for the theory, however, the observed rotation in many cases falls much short of the calculated value. It seems likely that this anomaly is connected with the known optical and magnetic anisotropy of the molecules, which is not taken into account in the Larmor theory of the Faraday effect. The consideration further suggests itself that, just as we have two kinds of Faraday effect, we should also have two kinds of magnetic birefringence in fluids. In addition to the diamagnetic type of birefringence which is already known, there should be a paramagnetic type of birefringence. Experiments made at my suggestion by Mr S W Chinchalkar indicate that solutions of salts of the rare earths, such as cerium chloride, actually exhibit such an effect. How this special type of birefringence actually arises is not clear. But it seems possible that the cerium ion is optically anisotropic, and that in consequence of the magnetic moment it possesses tends to orientate in the field.

The study of the magnetic behaviour of gases and vapours is a special field of great interest in which Faraday was a pioneer. The experimental technique is very difficult, especially in the case of diamagnetic bodies where slight traces of oxygen as impurity would wholly vitiate the result. Recently the subject has attracted much interest owing to the reported discovery by Dr Glaser of a curious anomaly at low pressures. The subject was taken up by Dr V I Vaidyanathan, who showed that in all probability the Glaser effect was spurious. Further, he found that ozone and ethylene are diamagnetic gases and not paramagnetic ones as had previously been reported by other workers. Measurements were also made and reported by him for a number of other gases and organic vapours.

The question arises whether diamagnetism is purely a molecular property or whether it is also influenced by the state of aggregation of the substance. The accuracy of measurement in the case of vapours is not sufficient to enable this question to be decided for the transition from the gaseous to the liquid condition. *Prima facie* we should not expect any appreciable changes in passing from the liquid to the solid state except in the case of metallic bodies and electrically polar substances where questions of molecular association enter into consideration. In certain well known cases, for example, those of metallic bismuth and graphite, large changes with temperature have been reported, and the susceptibility of bismuth is reduced to a very small fraction of itself on fusion. In such cases, the interesting question arises whether mechanical subdivision of the substance into a fine colloidal state would influence susceptibility. From experiments reported from Chidambaram, by Dr V I Vaidyanathan, and more recently by Dr S Ramachandra Rao, it would seem that this is actually the case.

Closely related to the general question of dependence of diamagnetism on the

state of aggregation is the problem whether the susceptibility of a liquid mixture strictly obeys the additive law in respect of the mass proportions of its constituents. In those cases where anomalies in density and other properties are known, we should expect small deviations from additivity of molecular susceptibilities. A high degree of precision in measurement is necessary to decide this question, and this has been attained by a special optical method developed at Calcutta by Mr S P Ranganadham. It would seem that in certain cases, for example, water and alcohol mixtures, distinct deviations from a straight-line graph are actually obtained.

Before leaving the subject of magneto-chemistry, reference should be made to the work of two notable Indian exponents of the subject, Prof D M Bose of Calcutta and Prof. S S Bhatnagar of Lahore respectively. The former has done extensive and valuable experimental work in tracing the relation between paramagnetic susceptibility and chemical constitution and correlating it with atomic and molecular structure. The theoretical considerations advanced by him in regard to the paramagnetism of the compounds of the transition group of elements lay emphasis on the magnetic moment derived from electron spin and yield results different from those indicated by the well known theory of Hund. They appear to agree better with the experimental facts than the results of Hund's theory. Prof. Bhatnagar is the author of a systematic treatise on magneto-chemistry. He has devised a sensitive interference apparatus for measuring the susceptibilities of small quantities of substances, and discussed very fully the relation between chemical constitution and diamagnetic susceptibility in organic compounds.

Limitations of space do not permit detailed mention of the work of Dr J C Ghosh and others in the field of electrochemistry, in which Faraday was a great pioneer. Reference may, however, be made to the subject of dielectric behaviour, which has received much attention from Indian workers. The study of light-scattering leads one very naturally to consider the question of dielectric behaviour. The birefringence shown by a gas or liquid in an electric field may be connected quantitatively with the electric polarity and anisotropy of its molecules. As was shown by the present writer with Mr Krishnan, it is actually possible to compute the electric moment of the molecule, and even to indicate its geometric position in the molecule from such considerations. Further, the connexion between dielectric behaviour and electric birefringence indicates that in the case of viscous liquids we should expect at low temperatures or in rapidly oscillating fields a disappearance, or even reversal, in the sign of their electric double refraction. Experiments by Mr S C Sircar and the present writer appear to indicate that the suggested phenomenon is actually observed. The interest of this observation lies in its furnishing a demonstration that the electric polarisation of a polar molecule is of two kinds, one arising from its deformation and the other from its orientation under the action of the field.

## Newton and the history of optics

The 25th of December 1942 is the three-hundredth anniversary of the birth of Isaac Newton, discoverer of the law of universal gravitation and one of the greatest figures in the history of science. Newton's fame rests most securely on his great work "*Principia Mathematica Philosophiae Naturalis*". In this work Newton developed a system of mechanics on broad foundations and opened up many new fields of knowledge. In particular, he laid the basis of dynamical astronomy including especially planetary and lunar theory, the theory of the figure of the earth and the theory of the tides, as also of hydrodynamics and the theory of sound. The magnitude of the scientific achievements embodied in the *Principia* of Newton has been described by Lenard in the following words:

"If we open the book in order to examine it in detail, we are astonished, quite apart from the main discovery, by every part of it, and overwhelmed with admiration for the greatness, the extent, the power, as well as the fineness of structure of what he erects upon the foundations given by Pythagoras, Archimedes, Leonardo, Stevin, and in particular Galileo and Huygens using the material afforded by Copernicus, Tycho and Kepler, and the tools provided by mathematicians from Euclid to Descartes, with very essential additions of his own. We are not less astonished and almost overwhelmed, by the countless number of single achievements, which, from whatever side the work is regarded and studied, are revealed to any one capable of comprehending them. The whole, when we consider the richness of its contents, the general and detailed form, and the impression it makes of towering greatness, can only be compared to a grand old Gothic cathedral: one stands in front of it filled with astonishment, absorbed in gazing at it, and without words to express one's impressions. Great cathedrals were built in numbers by the masters of Gothic, but among the works of men of science, Newton's *Principia* is unique of its kind."

The two years 1665 and 1666 which Newton spent at his country home of Woolsthorpe after taking his Bachelor's degree at Cambridge appear to have been the formative period of his youthful genius. To these two years have been traced back his fundamental discovery of the spectral character of white light, his invention of the fluxional calculus, and his first conception of the universal law of gravitation. The recognition of Newton's transcendent abilities fortunately also came quickly, for in 1669 when he was only twenty-seven years of age, he was called to the Lucasian Professorship of Mathematics at Cambridge. In the years that followed and which were passed quietly at Cambridge, Newton published much of his work on optics and developed his thoughts on gravitation. The writing of the *Principia* was completed in 1684 and the work appeared in print in

1686. Newton's major scientific activities practically terminated in 1692. The later years of his life were spent in London in the discharge of his official duties as Warden and later as Master of the Mint. He was President of the Royal Society of London from 1703 till his death on the 20th of March 1727. Newton was buried in Westminster Abbey.

While Newton appears as a mathematical philosopher in his *Principia*, he is essentially the practical experimentalist and observer in his optical investigations which had as their starting point his desire to construct improved forms of astronomical telescope. Newton's approach to the subject is clearly stated in the opening words of the first book of his *Optics* which disclaim any desire to explain the properties of light by the aid of hypotheses. The reprint of the fourth and final edition of the book issued in 1931 makes Newton's work on the subject conveniently accessible to readers of the present day. The first book in the treatise sets out in full detail his observations on the spectral composition of white light and its consequences. The second book deals with the colours of thin and thick plates and their interpretation. The third book contains some evidently incomplete observations on what we would today call the diffraction of light by obstacles and narrow slits. The work terminates with the famous queries, thirty-one in all, in which Newton wrote down his thoughts on a wide range of topics.

As is well known, Newton favoured a corpuscular view of the nature of light. Indeed, he made it quite clear in his treatise that he rejected the wave-concepts of light advanced by Robert Hooke in his *Micrographia* (1665–67) and by Christian Huygens in his celebrated *Traite de la Lumiere* (1690). As is also well known, this had unfortunate consequences for the progress of optical science, Newton's great authority having kept back the inevitable triumph of the wave-theory of light by well over a century. The specific objection raised by Newton to the wave-theory of light in his query 28, namely that light does not bend into the region of shadow of an obstacle, was clearly based on an incomplete knowledge of the facts. This would, no doubt, have become evident to Newton himself if he had continued the experiments described in the third part of his book and approached the subject with an open mind. There has been a tendency in recent times to find some support for Newton's attitude towards the wave-theory of light in the recent revival of corpuscular idea and even to find in his hypothesis of "fits" of easy reflection and transmission, a resemblance to the ideas of the quantum mechanics. It is sufficient to remark that it is precisely the phenomena of the kind described in the second and third books of Newton's optics that form the strongest bulwarks of the wave-theory of light, and that the corpuscular aspects of the behaviour of light do not enter in the interpretation of these phenomena. Indeed, it does not seem easy to discover any real justification for Newton's rejection of the ideas advanced by his contemporaries Hooke and Huygens in explanation of the facts of optics known in their day.

## Astronomical research in India: I

Astronomy is the oldest of the natural sciences, its beginnings being traceable to the remotest periods of recorded human history. There is ample indication in ancient Sanskrit literature of the interest with which the subject was studied in India from the earliest times, while the later writings of Aryabhatta, Varahamihira, Brahmagupta and of Bhaskaracharya, which have come down to us, show that astronomy was actively studied in India at a time when the lamp of learning lighted by the ancient Greeks had burnt out, and Europe was passing through the dark ages. The vicissitudes of Indian history in the later centuries of the present millennium were not favourable to the development and expansion of cultural interests. Some indication that active interest in astronomy nevertheless did not altogether disappear in India is furnished by the astronomical instruments of an earlier era which have been preserved to us, and by the curious structures known as Jaisingh's observatories which are still to be seen at Delhi, Benares and Jaipur.

During the three hundred and odd years which have elapsed since Galileo first directed his little telescope towards the heavens, the progress of astronomical science has been of the most spectacular character. This progress has largely been the result of the success achieved in making bigger and better telescopes. A study of the fascinating autobiography of John A Brashear—the American who loved the stars and made great telescopes for observing them—may be warmly recommended to anyone who is interested in the development of astronomical research in India. It brings home to the reader the extent to which the progress of astronomical science in a country depends on the existence in it of skilled opticians who can grind, polish and figure great lenses and mirrors up to the most exacting requirements. Without telescopes, interest in astronomy must languish, and without an active interest in astronomy, there obviously can be no telescopes in a country. That was the vicious circle which Brashear sought to break in a spirit of genuine altruism. The immense interest in astronomical science and the generous support accorded to it by wealthy men in the United States of America must, to no small extent, be credited to the influence of Brashear's life and work. The making of great lenses and mirrors is practical in optics on an engineering scale, and it is no accident that Brashear was a mechanical engineer before he became a maker of telescopes. The mounting and driving of telescopes is also mechanical engineering of a very exacting nature. In a modern observatory, the ton-loads of material making the telescope and its accessories move with the same accuracy and smoothness as the hands of a wrist-watch go round its dial. Optics and engineering are the handmaids of observational astronomy without whose services she cannot live and flourish.

It may be asked, why trouble about astronomy? Why spend money on making great telescopes and building great observatories? These are pertinent questions to which it is the purpose of this article to return an answer. My reply would be that an interest in astronomy is a part of the cultural heritage of India, and that we would be unworthy recipients of that heritage if we did not cherish that interest and do our utmost to promote the science. As has been truly said, man does not live by bread alone. Astronomy is not only the oldest but the grandest of the sciences. The interest which it evokes in all thinking and cultured minds is instinctive—an expression of man's desire to understand and comprehend the universe he lives in. Modern science is accused—perhaps not unjustly—of allying herself with powers of destruction and helping to make death-dealing weapons of all kinds. I do not know, however, of anyone who has had the hardihood of including the science of astronomy in such an indictment. Like all other sciences, astronomy is not without some practical applications—such as time-keeping and aid to navigation at sea—which have given it claims to support from public funds. But the real purpose of astronomy is very remote from such applications. Broadly, it may be described as the investigation of the nature of the physical universe. Defined in that way, we begin to realize that astronomy occupies the premier position amongst the sciences. Indeed, it may be described as a heaven-born river of knowledge which flows to the earth and fertilizes the fields of learning and culture. That this view of astronomy is fully justified will be evident to anyone who makes a comprehensive survey of the history of modern science during the past three hundred years.

As some of the outstanding results of astronomical research which have influenced the orientation of scientific thought, we may mention the discovery of the finite velocity of light by Romer, of aberration by Bradley, of the laws of planetary motion by Kepler, of the dark lines in stellar spectra by Fraunhofer, of helium in the sun by Lockyer, of the magnetic field in sunspots by Hale, and of the recession of the nebulae by Hubble. When we examine the structures of modern physical and chemical thought, we find that they are laid on foundations built out of the results of observational astronomy. *Vice versa*, observational astronomy calls to its aid all the resources of the experimental physicist, while astronomical thought and speculation have as their basis the well-established laws of experimental physics and chemistry.

It will be evident from what has been said that the organization of scientific research in India must be considered radically defective unless and until adequate provision is made for astronomical study and research of the highest grade in the country.

C V RAMAN

## Astronomical research in India: II

In *Current Science* for July 1943, a plea was entered for the promotion of astronomical study and research of the highest grade in our country. We require, in the first place, the establishment of observatories in different parts of India staffed by competent and enthusiastic astronomers and equipped with instruments capable of yielding results of real interest and importance. From Kashmir in the north to Trivandrum in the south, from Shillong in the east to Karachi in the west, the territories of the Indian Empire include a variety of latitudes, elevations, climates and observing conditions. A selection could be made of possible locations for a group of observatories which between them could cover the heavens in systematic programmes of exploration and study, all the year round. Then again, the Universities in India should take steps to give astronomical studies and research a proper place in their activities, instead of relegating them, as at present, to an unimportant and practically negligible status\*. Astronomy can have no future in India, unless opportunities are given to talented young men to interest themselves in the subject at the Universities. It is necessary also to take steps to encourage and develop public interest in astronomy. Every city of any importance in India should maintain at public expense an observatory of reasonable dimensions which would be open to the public free of charge. Such an institution would be a cultural centre where even the humblest individual who desires to do so could acquaint himself at first hand with the facts of astronomy. There should also be societies and groups of amateur astronomers in every province to maintain and develop an active interest in the progress of astronomical science, by regular meetings, discussions and public lectures.

The programme outlined above presupposes many things—an enthusiasm for astronomy, a willingness to work for its progress, the desire and ability to find the money needed for its active promotion, and above all an atmosphere in which the pursuit of the science could flourish and not be regarded as a useless luxury. It might be urged that a poor country in which the vast majority of the people live at or below the marginal level of human existence, should not trouble itself about astronomy—a non-utilitarian pursuit, as some might be disposed to regard it. To convert those who hold this view to a different state of mind, it might be useful to point out clearly the enormously important part that astronomical studies have

---

\*The Osmania University at Hyderabad is an honourable exception in this respect—C V R.

played and are playing in the development of both scientific knowledge and general culture. That astronomy occupies the premier position amongst the sciences will be evident if we recall its organic relationships with the other sciences. The basic idea of all science is the concept of law in Nature—the view which regards natural phenomena as an ordered sequence of events linked together by a chain of causation. This concept is an intellectual conviction which established itself in the first instance from the observational facts of astronomy, including especially the most familiar of them all, such as the daily rising and setting of the sun and the moon, the variation of the seasons, the predictability of eclipses and the like. The fundamental ideas which lie at the basis of all the sciences, viz., the notions of time and space, matter and gravitation, light and darkness, heat and cold, all come to us as part of the astronomical environment in which we live. The deeper we delve into the various branches of natural knowledge, the more clearly do we perceive that everything on this earth and inside it, both in the remote past and in the immediate present, has been determined by the astronomical history of our planet. The structure and functions of every living object on the face of the earth and the rhythm of its daily life bear the imprint of our astronomical environment and history in language which can be read very plainly.

The pursuit of astronomical studies in any country has an enormously stimulating influence on other branches of scientific investigation. Consider, for instance, that most abstract of all sciences, mathematics. A long roll of illustrious names in the history of science could be cited to indicate how the facts of astronomy and the attempt to interpret them furnish the motive power for the development of new kinds of mathematical thought. Just to mention, Archimedes, Bhaskaracharya, Kepler and Newton should be a sufficient lesson to us from the history of the past. The contents of Newton's immortal work, the *Principia*, opened up a new world of thought alike in the regions of mathematics, astronomy and physics. Laplace and Einstein may be mentioned amongst the intellectual giants to whom the facts of astronomy were at once a challenge and an inspiration to develop new ways of mathematical thinking. An astronomical theorist has, of necessity, to be a first-rate mathematician, but his work benefits not only astronomy but all fields of science in which analogous methods could be applied. A striking illustration of this is the recent work of Chandrasekhar on the dynamical theory of stellar systems. As a published report by him reveals, the mathematical developments he has initiated are applicable also in the realms of molecular physics and of colloid chemistry!

As every physicist knows, the study of the stars and the study of the atoms are only two different phases of the attack on the fundamental problems of his subject. In the July article, mention was made of the discovery of the finite velocity of light by Romer, of aberration by Bradley, of laws of planetary motion by Kepler, of the dark lines in stellar spectra by Fraunhofer, of helium in the sun by Lockyer, of the magnetic field in sunspots by Hale, and of the recession of the

nebulae by Hubble. These are typical examples of what might be called the purely observational discoveries of astronomy, which have exercised a profound influence on the orientation of physical thought. Such a list could be extended almost indefinitely. We may put the situation briefly by saying that the Universe is a physico-chemical laboratory of cosmic dimensions and that we are privileged to watch through our giant telescopes a never-ending succession of experiments made on a scale and under conditions which we could never hope to reproduce with our comparatively Lilliputian resources. What we see has much to teach us. It forces us to think deeply. With minds strengthened and refreshed by new ideas, we look again through the telescopes and understand better what we see. But that is not all. The facts of astronomy suggest new modes of attack on the problems of experimental and theoretical physics. When, for example, Niels Bohr set out in 1913 to solve the problem of atomic structure, he found his inspiration in the work of Copernicus, Kepler and Newton. His astronomical model of the hydrogen atom with the electron going round the nucleus in an elliptic orbit as the earth goes round the sun was a magnificent success. As every student of physics and chemistry knows, it opened up great new vistas of physical and chemical thought. Today, the physicists are watching the skies to discover, if possible, the origin of the mysterious cosmic rays which have meant so much to them in every possible way!

Chemistry is a subject of vast practical importance, and to the uninitiated, it might seem that it could have nothing in common with the science of astronomy which lives with its head up amongst the stars! It is useful to dispel such an illusion if it exists in the minds of any. The vital link between chemistry and astronomy is to be found in the problems of the origin of the elements, of their abundance, and of their associations and segregations, all of which are of the utmost importance not only to the chemist, but also to the geologist, the mining engineer and the metallurgist. The spectroscope reveals that all or nearly all the elements present in the earth are also present in the stars. Even the mysterious nebulium proved to be nothing more mysterious than oxygen and nitrogen under somewhat unfamiliar conditions. The problem of the origin of the elements is, therefore, not so much a terrestrial problem as an astronomical one. The transmutations of the chemical elements successfully effected, though on a very minute scale, in the atom-smashing laboratories of the world suggest that such or other analogous transmutations are in progress in the cosmic crucibles which we call the stars. Indeed, the suggestion has been made (and is probably well-founded) that such transmutations are the origin of the tremendous outpouring of energy continually going on from the sun and the stars. Such extra-terrestrial knowledge cannot but prove ultimately of the highest value and importance to terrestrially-minded capitalists and *entrepreneurs* of industry!

The tremendous interest aroused at the time by the observations of Lowell at the Flagstaff observatory on the planet Mars may be cited as an indication of the possible or probable relations between astronomy and the as-yet-unsolved

problems of the origin and distribution of organised life. There can be little doubt that the history of life on the earth as illustrated in the record of the rocks was to a great extent determined by the astronomical history of our planet. There is striking evidence in the record of notable climatic changes and associated with them also of the disappearance of some of the older forms and the appearance of newer forms of life from age to age. It cannot be assumed that the evolution of life on the earth has come to an end. Far from this being the case, man is now keenly interested in the process and is taking an active part in the creation or development of new plants and even new animals, which could be of service to him. Can it be assumed that the radiations of various kinds received by the earth from space play no part in biological evolution? Probably not. Be this as it may, no geologist or biologist afford to ignore what astronomy can tell him about the past, present and future of the earth.

Let us leave science now and consider for a moment the cultural aspects of astronomical study. Can it be denied that astronomy is the noblest and the grandest of the sciences, that it takes us away, if only for a while, from the noise and the dust of terrestrial conflicts and leads us to a better comprehension of the universe we live in and its eternal verities? Our politicians and philosophers are constantly reminding us of India's great spiritual heritage. Should they not raise their voice also to remind us of India's intellectual heritage as reflected in our age-old interest in astronomy, and help to build up a renewed and active interest in its study?

C V RAMAN

## Astronomical research in India: III

Astronomy makes an instinctive appeal to all cultured persons. Of a different nature is the interest it has for the physicist. As indicated in an earlier article, the observational discoveries of astronomy have had a profound influence on physical thought. *Vice versa*, the speculatively-minded physicist turns naturally to the facts of astronomy to find in them a confirmation of his ideas or at least some support for them. This interplay between astronomy and physics has been vastly more active during the last thirty years, since Niels Bohr put forward his Keplerian model of the hydrogen atom and offered an intelligible explanation of the observed spectra of both terrestrial and astronomical sources of light. The influence of Bohr's theory of atomic structure on astronomical and astrophysical research has indeed been no less remarkable than its influence on the sciences of physics and chemistry. The interpretation of the spectra of the sun, the stars, of the nebulae, of inter-stellar clouds, and nearer to us, the spectra of the major planets and of the comets has been notably advanced and aided by the simultaneous advance in our knowledge of the structure of atoms and molecules and by laboratory investigations on the light emitted or absorbed by them under various conditions. The more recent advances in our knowledge of the structure of atomic nuclei and of their transmutations has similarly exercised a profound influence on speculative astronomy, and stimulated discussion on the internal constitution of the stars and the origin of the vast outpouring of energy from them which we witness daily. The work of the astronomical theorist on these problems has necessarily to be based on the results of terrestrial experimentation and on such inferences from them as are justified by established physical principles having the widest generality. Such work has a claim to acceptance which would not be extended to *ad hoc* hypotheses and speculations having no solid basis of experience behind them.

It is not surprising that the general advance of scientific activity in India during the past thirty years has been accompanied by an increased interest on the part of Indian physicists and mathematicians in the problems of astronomy, astrophysics and cosmology. The contributions by them to these sciences have not passed unheeded by the professional astronomers in other countries. Indeed, it may be claimed without exaggeration that the influence of Indian work in this field has been surprisingly great in proportion either to its volume or the actual effort put into it.

Astronomy, however, like all other sciences, depends for her progress mainly on the work of those who have devoted their lives exclusively to her service.

Surveying the contribution of India to astronomy during recent years, one of its most heartening features is the work done by the Nizamiah Observatory at Hyderabad (Dn.) under its present Director, Rao Saheb T P Bhaskara Sastri. The equipment of this Observatory is comparatively modest and consists principally of an eight-inch photographic telescope and a fifteen-inch visual instrument. This equipment has been used mainly for co-operating in the great international undertaking known as the "Carte du Ceil" which consists in making a detailed photographic survey and chart of the stellar universe. Regular observations of the variable stars is also part of the programme of the Nizamiah Observatory. The reports of the International Astronomical Union bear testimony to the speed and thoroughness with which the undertaking has been carried forward. The twelve volumes of the *Hyderabad Astrographic Catalogue* published by the Observatory form an impressive record of its work. Numerous short papers arising out of the variable star observations have also appeared in the scientific periodicals.

Though not actually "made in India", the work of S Chandrasekhar, now Professor of Astrophysics at Chicago University, has a claim to notice in an article on astronomical research in India, if only as an indication of what could be accomplished in this country under favourable conditions. It would require an entire number of *Current Science* and not a paragraph or two to sketch the many fields of astronomical and astrophysical research traversed by Chandrasekhar and the results obtained by him during the last fifteen years. The *Monthly Notices* of the Royal Astronomical Society during the years Chandrasekhar was at Cambridge, and the last ten volumes of the *Astrophysical Journal* since he went to the United States bear witness to his energy, the strength and range of his scientific interests and his powers of investigation and exposition. His two treatises, "Stellar Structure" and "Dynamics of Stellar Systems", published by the Chicago University Press, make his work in the respective fields conveniently accessible to specialist and non-specialist alike. A memoir on "Stochastic problems in physics and astronomy" which appeared as the January 1943 issue of the *Reviews of Modern Physics* establishes links between the problems of stellar astronomy and those arising in colloid chemistry, and is a very remarkable effort in scientific synthesis.

In concluding this series of articles, the writer ventures to express the hope that they will not altogether fail to accomplish their purpose, namely that of impressing on all those interested in the scientific and cultural progress of India, the need for making generous provision for the promotion of astronomical study and research in our country, of encouraging those who are interested in the subject, and of making it possible for Indians working in their own country to contribute to its progress.

C V RAMAN

## Centenary of the Faraday effect

Exactly a century ago, in November 1845, Faraday announced to the Royal Society the discovery of the phenomenon now known as the Faraday effect in his honour. The discovery was not made by accident but was the result of systematic experiments undertaken by Faraday in the hope of establishing a connexion between the phenomena of light and those of electromagnetism. His first attempts were to find whether an electrostatic field influenced the propagation of light through a material medium. As these experiments failed to yield an observable result, he was led to try the effect of a magnetic field. It was known at the time that a plate of glass under mechanical strain placed between crossed nicols gives a visible restoration of light. Hence, probably, Faraday was led to try a somewhat similar experimental arrangement in which an unstrained block of glass was placed between the poles of the electromagnet. A beam of light polarised by a nicol traverses the glass along the lines of magnetic force and then enters a second nicol which is set in the crossed position with respect to the first. In the absence of a magnetic field, the light transmitted in succession by the first nicol and by the block of glass is blocked by the second nicol. Faraday observed that when the electromagnet was excited, there was a visible restoration of light. That this was due to a rotation of the plane of polarisation of the light was shown by the fact that the light could again be quenched by a suitable rotation of the second nicol, the rotation necessary for this purpose increasing with the strength of the field and changing sign when the direction of the magnetic field was reversed. The magnitude of the effect depends greatly on the substance placed in the field. That Faraday succeeded in observing the phenomenon with the electromagnet of modest dimensions available to him was due to the fortunate circumstance that he used a block of special glass of high refractive index which he had himself manufactured in some earlier researches.

Faraday's discovery must have seemed strange and almost incomprehensible at the time to his contemporaries. In the fullness of time, however, it exercised a profound influence on the progress of physics. The phenomenon showed clearly enough that Faraday was right in thinking of electrical and magnetic actions as field phenomena and not as actions at a distance, as was then generally believed. Faraday's ideas, as is well-known, inspired Maxwell to develop his well-known theory of the electromagnetic field which indicated that light itself is an electromagnetic wave-motion in space. Hertz's successful experiments of 1888 on the artificial production of electromagnetic waves were inspired in their turn by Maxwell's theory of which they were a confirmation. The identity of all forms of

radiation in respect of their nature is now a common place of physics, but its recognition is nevertheless one of the greatest achievements of modern science, and it is well to emphasise that Faraday's discovery of his magneto-optic effect pointed the way to its establishment. Incidentally, it may be remarked that the Faraday effect has itself since been observed with electromagnetic radiations over a wide range of frequency. The rotation of the plane of polarisation of radio-waves in the upper layers of the earth's atmosphere by the action of the earth's magnetic field is now a well-established result. A similar phenomenon has also been demonstrated in the laboratory with short electric waves and a strong magnetic field, the necessary density of free electrons in the path of the waves being obtained by sending an electric discharge through a gas such as neon, argon or nitrogen at low pressure. The Faraday effect in the region of infra-red frequencies was observed very early in the history of the subject. Curiously enough, its observation with ultra-violet radiation had to wait nearly half a century. More recently also, reports have appeared which indicate that the plane of polarisation of Röntgen rays is rotated in their passage through a thin sheet of iron placed in a magnetic field.

It is obvious that the presence of a magnetic field would have no effect on the passage of light through a transparent substance, unless the latter is itself capable of being magnetised by the field. This train of thought naturally induced Faraday to examine the question whether the block of glass used in his magneto-optic experiment was capable of magnetisation. Accordingly, he suspended the rod freely by means of a thread between the poles of the electromagnet and found to his astonishment that it set itself at right angles to the lines of magnetic force and not parallel to them as in the familiar case of an iron rod. This discovery naturally interested Faraday immensely, and he was so fully engaged in following it up that, as the story goes, he could not attend the meeting of the Royal Society at which his paper on the discovery of the magneto-optic effect was taken up for reading.

Most ordinary substances, both solid and liquid, which transmit light are diamagnetic like Faraday's block of glass. It is not surprising, therefore, that in practically all cases, the sense of the rotation of the plane of polarisation is the same, though the magnitude may be different in different substances. Even the so-called paramagnetic substances, which are attracted and not repelled by a magnetic field, show, in most cases, rotation in the same sense as diamagnetic bodies. This is not surprising when we recall that diamagnetism is a universal property which must be assumed to exist, though in a suppressed form, even in paramagnetic substances. That the Faraday effect arises from the magnetisation of the medium is strikingly shown by the phenomenon (discovered by Kundt in 1884) of the rotation of the plane of polarisation of light in its passage through thin films of iron when placed in a magnetic field. The rotation in this case depends directly on the magnetisation of the film, reaching a saturation value at high field strengths, and altering with temperature in the same way as the magnetisation itself.

The observation of a special form of the Faraday effect characteristic of paramagnetic bodies was first made by J Becquerel in 1906 and has recently received a great deal of attention. The distinction between the diamagnetic and the paramagnetic rotations arises in respect of the dependence of their magnitude on the temperature of the substance, the strength of the magnetic field and also its variation with the wavelength of the light. The most obvious difference between the two types of rotation is that the dispersion curve of the rotation is symmetric about a characteristic absorption frequency in the diamagnetic case and unsymmetric in the paramagnetic one.

The further question arises as to why, even granting the magnetisability of the medium, the propagation of light through it should be influenced by such magnetisation. It is clear enough that the answer to this question must be in the identity of the structures in the medium which are responsible alike for its magnetisability and for its influence on the propagation of light. Further, since the refractivity of a substance is connected with the possession by the substance of characteristic absorption and emission frequencies, it follows that the same structures must also be responsible for these latter properties. Thus, the successful observation of the Faraday effect involves as a necessary consequence that the characteristic emissions and absorptions of light by a substance would be influenced when the latter is placed in a magnetic field. It is on record that Faraday looked for such an effect but failed to find it. We may take it that the discovery of this phenomenon made by Zeeman in 1896 was prompted by the same train of ideas as that indicated above. Indeed, the magnetic behaviour of substances, the Faraday effect and the Zeeman effect are all intimately related to each other.

H Becquerel in 1897 derived, from very simple considerations, a formula connecting the magnitude of the Faraday rotation with the field strength and the refractive dispersion of the medium for light of the particular frequency under consideration. Even according to the most recent theories, the diamagnetic part of the Faraday rotation in a medium composed of atoms is given exactly by Becquerel's formula. This is understood easily enough if we recall that a rotation of the plane of polarisation may be regarded as the result of a difference in the refractive index for left- and right-handed circularly polarised beams of light. In the absence of a magnetic field, the two indices would be identical. In the presence of the field, they would be different and the difference would be the same as that produced by a change of frequency of the light equal to twice the precession frequency of the electrons in the magnetic field given by the famous theorem of Larmor.

It is an interesting fact that the magnitude of the Faraday rotation in many ordinary substances (gas, liquid or solid) is given fairly accurately over the whole range of frequency of the visible spectrum and of the ultra-violet by the Becquerel formula. The observed rotation is, however, smaller than the calculated one by a constant numerical factor (less than unity) which may be called the magneto-

optic anomaly of the substance. When we consider the complexity of the molecular structure of most ordinary substances, as also the complexity of their state of molecular aggregation, the appearance of such a simple numerical connection between the refractive dispersion and the Faraday rotation over a wide range of the spectrum must be considered very remarkable. Darwin and Watson, who in 1927 drew attention to the general validity of the Becquerel formula subject to this correction, remarked that while no anomaly greater than unity has been found and that while it is usually between 40 and 60 per cent, there did not appear to be any general principle governing the magnitude of the anomaly.

It is obvious that for real progress in the study of the Faraday effect, a satisfactory explanation of the magneto-optic anomaly referred to above is essential. We may regard the anomaly as a characteristic constant for the molecule, analogous to its optical anisotropy determined from studies on light scattering. A careful study of the figures given by Darwin and Watson shows that there is no direct or simple relationship between the magneto-optic anomaly and the optical anisotropy of a molecule. It is true that there are indications of such a connection, as for instance, in the fact that the constant is somewhat smaller for aromatic compounds than for aliphatic ones and is particularly small for substances such as carbon disulphide, nitrous oxide and nitrobenzene which show large depolarisations in light-scattering. On the other hand, we have to consider the fact that the factor for carbon tetrachloride which is optically isotropic is 0.51, whereas for benzene which is highly anisotropic, it is 0.56. While, therefore, there is obviously no direct connection between the optical anisotropy and the magneto-optic anomaly of molecules, the facts do not rule out a deeper connection in which the specific properties of the individual chemical bonds are involved. Long ago, in a remarkable series of investigations, W H Perkin showed that the magnetic rotatory power of organic compounds can be used as a powerful instrument for the study of their constitution. On the other hand, we also know that the optical anisotropy of a molecule is related both to its chemical constitution, and to its geometric configuration. The fuller elucidation of the relationship between these properties would obviously be a matter of great interest.

It is also now fairly certain that the Faraday effect can also be used with great success in the elucidation of the states of molecular aggregation. Here again, the problem centres round the explanation of the magneto-optic anomaly. Some progress has been made towards the solution of this problem in investigations undertaken recently at Bangalore. A fuller report of these investigations will appear in due course.

C V RAMAN

## Science in Eastern Europe: I

SIR C V RAMAN

Lady Raman and myself left for Europe by the s.s. "ASIA" which sailed from Bombay on the 9th of May this year and docked at Genoa in Italy on the morning of the 23rd of the same month. We were in Europe for nine weeks and took the same steamer back to India, leaving Genoa on the 30th of July and reaching Bombay early morning on the 13th of August. We travelled by rail, stopping off at various places for a shorter or longer period as we thought fit. The tour gave us a wonderful opportunity of seeing the countries through which we passed and of obtaining some knowledge of their condition and activities at the present time. This article records some of my personal impressions and it is hoped that it may be of interest to readers of *Current Science*.

The countries we had arranged to visit were in Eastern Europe, but our journey to them took us through Italy and Austria. Proceeding from Genoa to Milan, a brief stop was made at the latter city where we visited the Science Museum recently set up by the civic authorities, in which a remarkable exposition of the pioneer investigations of Leonardo Da Vinci is a noteworthy feature. Travelling from Milan through Verona and the Brenner pass, we reached Innsbruck in Austria where we made an overnight stop. We found Innsbruck to be a town of great charm set in Alpine surroundings of impressive grandeur, and we were thereby confirmed in our resolution to return to it for a longer stop during our return journey. The railway took us across Austria from Innsbruck to Linz via Salzburg, through a region of mountains, lakes and valleys of entrancing beauty. At Linz we made an overnight stop, and left next morning for Prague which we reached on the afternoon of the 27th of May.

### 2. Prague

A feature that impressed us during the journey through Czechoslovakia was the meticulous attention given to agriculture, not an acre of land, so far as we could see, escaping the attention of the cultivator. It was also obvious that we were passing through a highly industrialised country. It did not therefore surprise us to discover when we arrived at Prague that Czechoslovakia pays much attention to advanced studies in science and technology and that research is assiduously pursued.

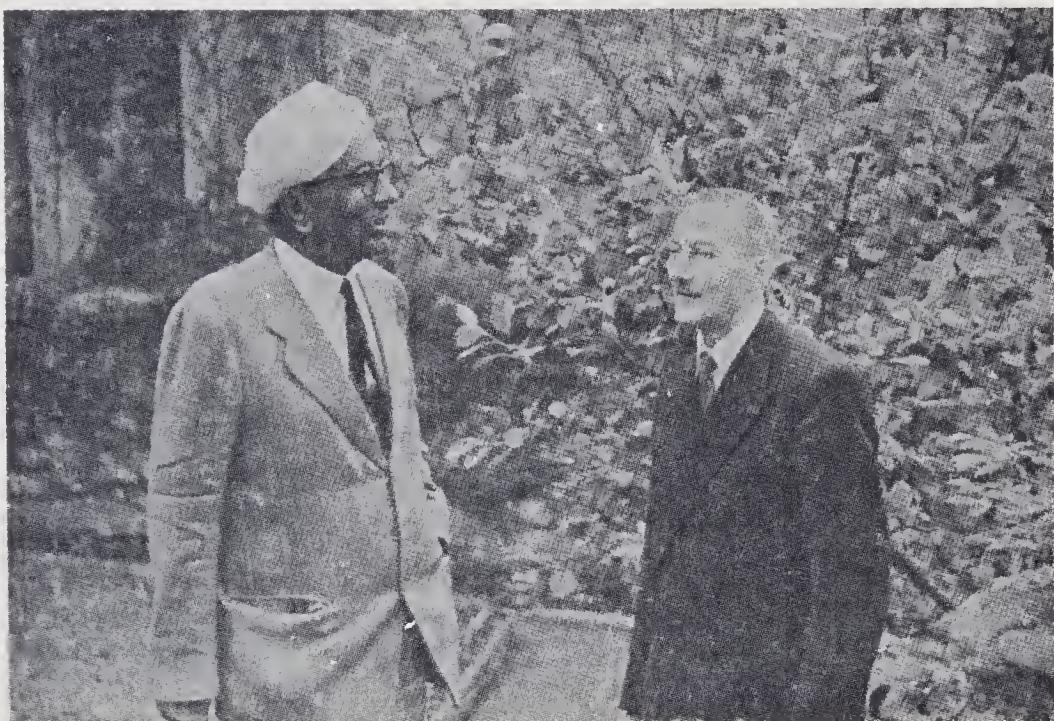


Figure 1. Prof. Heyrovsky in the garden of the Polarographic Institute.

The Czechoslovakian Academy of Sciences played host to us at Prague. The Academy had placed a young spectroscopist—Dr Josef Pliva—on special duty to take me around and he carried out the assignment with energy and enthusiasm. Indeed, the five days of our stay at Prague were crowded with activity. Formal receptions, social engagements, visits to the Research Institutes of the Academy and to the Laboratories of the Technical University and excursions to places of interest around Prague filled up most of the time. I also delivered two lectures at the Physical Institute of the Charles University, the first on "The specific heats of crystals", and the second on "The physics of the diamond".

It is not possible here to summarise all that I saw of the scientific life of Czechoslovakia or even to mention the many distinguished men of science with whom I conversed and discussed scientific problems during my stay at Prague. The barest reference to a few items must suffice. I was highly impressed by my visit to the unpretentious laboratory of Professor Jaroslav Heyrovsky, famous as the founder of the polarographic method in physical chemistry. He received me most cordially and expounded for my benefit the basic principles of the subject.

At the Institute of Technical Physics of the Academy, I saw much of interest, a notable item being the preparation of a rod of pure silicon which was in progress. During my visit to the Technical University, I was much struck by the excellence of the mineralogical museum which I saw on one of its floors. The museum was a wonderful collection of beautiful specimens from all parts of the world arranged

and exhibited in a remarkably perfect fashion. Finally, I should mention my visit to the Institute for Research in Minerals situated in Tournov about seventy kilometres from Prague. The journey was made by motor through a beautiful landscape known locally as the Czech Paradise. I found that an important section of the Institute was devoted to the synthetic production on a large scale of crystals required for the electrical and other industries. There was also a section devoted to the cutting of quartz and the fabrication of optical instruments made from quartz. A demonstration was given to me of the performance of the so-called birefringent filter made of quartz plates which finds application in astronomy.

### 3. Moscow and Leningrad

We were at Moscow from the 4th to the 7th of June, and again from the 11th to the 14th of the month, the interval of three days from the 8th to the 10th being taken up by a brief visit to Leningrad. The time thus devoted to these two great centres of scientific activity was, of course, much too short to enable them to be adequately explored. Even what I saw was sufficient, however, to impress upon me the vast scale on which scientific advance is encouraged and supported by the USSR.

The Institute for Physical Problems directed by Academician Peter Kapitza was the very first to be visited by me. That Institute specializes in the production of low temperatures and the study of the physical properties of matter at such temperatures. I utilized the facilities available in it for making some preliminary studies on the luminescence spectrum of diamond held at liquid helium temperature. A highly interesting forenoon was spent at the Institute of Crystallography where I was welcomed with special enthusiasm by Academician Belov and his collaborators. A striking exhibit had been there arranged for my benefit of moving films exhibiting the growth of crystals as well as the order-disorder phenomena observed in them. During my return visit to Moscow, I delivered a lecture at the Institute of Prof. Kapitza on "The thermal energy of crystals". On the 12th of June, I was officially received by President Nesmeyanov and his staff at the administrative offices of the USSR Academy of Sciences. The next evening, at his invitation, I delivered in the conference room of the Academy a lecture on "The dextro and laevo forms of the carbon atom", standing beside a gigantic portrait in oils of the great Russian chemist, Mendeljeff. The Lebedev Institute of Physics directed by Professor Skobelcyn and the grandiose building of the University of Moscow and its Institute of Physics were also visited.

One day of my brief visit to Leningrad was utilized for a call at the Institute of Semiconductors directed by the celebrated Russian physicist, Academician Joffe. I was there shown the thermoelectric batteries and the thermoelectric refrigerators which had been developed in the Institute as practical applications of thermoelectricity. On another day the well known observatory at Pulkovo near

Leningrad directed by Academician Mikhailov was visited. The observatory which had almost been completely destroyed during the war had been reconstructed and is functioning once again. During my tour of the observatory buildings, I was shown a new type of coronograph which had been developed at the observatory. It was evident from what I saw at Pulkovo and elsewhere that great advances in optical technology had been made in the USSR and that in the production of optical instruments such as spectrographs, gratings, large mirrors and lenses, the USSR is now completely self-sufficient.

#### 4. Kiev

We were at Kiev from the 15th to the 18th of June. This city, the capital of the Ukraine, is beautifully situated on an elevation overlooking the river Dneiper. It has been almost completely reconstructed after the war and but little evidence remains of the destruction caused by the latter. Civic pride is manifest in the tidiness of the roads and the beautifully kept boulevards and gardens.

Though our visit to Kiev was very brief, it was full of interest. The Ukraine has its own Academy of Sciences. At some little distance from the city a new Institute of Physics has been built and equipped which is devoted for the most part to nuclear studies. I was very warmly received by its Director, Academician Pasechnik and his colleagues and went round the laboratories. In the auditorium of the Institute which was filled to capacity, I gave a lecture on the theory of the atomic vibrations in crystals. On the afternoon of the same day, I delivered a semi-popular address in the hall of the University of Kiev describing the results of the Bangalore investigations on iridescent minerals. The various departments of the University were visited later the same evening. The next morning, I went round the Institute of Metals conducted by the Academy and was greatly impressed by the wide range of the problems being investigated by its staff. Here, again, I gave a lecture on "The diffraction of X-rays by diamond". In the afternoon, I visited the Institute of Physical Chemistry of the Ukrainian Academy of Sciences and had a long conference with Academician Brodsky and his colleagues in which problems of common interest to us were discussed.

#### 5. Budapest

Many years ago, before the war, I had been at Budapest for a fortnight. Seeing it again, it was evident that the scars left by war had not all been effaced. Nevertheless, Budapest was beautiful as ever, standing as it does astride the Danube and with the hills overlooking it. We were very happy to be able to devote ten days for our visit to Hungary. The Magyars—as they call

themselves—are a gifted people fully capable of rising to great heights of achievement in all the realms of knowledge.

The Hungarian Academy of Sciences played the host to us and we had a wonderfully interesting time. A young spectroscopist, Dr Laszlo Szalay, Lecturer in Physics in the University of Szeged, was on special duty to look after us and make all the necessary arrangements. Dr Szalay had prepared for my perusal a highly informative account giving us a complete picture of the state of physics in Hungary and a brief outline of the activities currently in progress under the auspices of the Academy and at the different universities in Hungary. An outstanding recent development has been the establishment of a Central Physical Research Institute—with ten departments—under the auspices of the Academy with Prof. L Janossy as Director. Prof. Janossy was away in China on a lecturing tour when I arrived at Budapest. Fortunately, however, he returned in time to be able to take an active part in a meeting of the Hungarian Physical Society held on the 27th June. One of the items on the programme of this meeting was a lecture by me on “Physical research in India”. I spoke in English and Prof. Janossy gave a fluent running translation of my speech into Hungarian. Besides this lecture, I gave a systematic course of three lectures on “The physics of crystals” under the auspices of the Hungarian Physical Society. These lectures were attended by a large and distinguished audience and every lecture was followed by a vigorous discussion. The rest of my time was fruitfully spent in visits to the Central Physical



Figure 2. Tihany and Lake Balaton.

Research Institute referred to above and to the various other laboratories in Budapest including especially that directed by Prof. Z Gyulai—the doyen of Hungarian physicists—which concerned itself with crystal physics and the Research Laboratory of the Tungsten Lamp Industry directed by Dr G Szigeti. I witnessed fascinating demonstrations of the work in progress in both of these Institutes.

Limitations of space prevent my giving a fuller account of the scientific activities in Hungary which I witnessed and referring to the other distinguished men of science whom I was privileged to meet and discuss scientific problems with. This account of my sojourn in Hungary would however be incomplete if I do not at least mention the Lake of Balaton and Tihany where we stayed on Sunday, the 21st of June—a lovely beauty spot as can be seen from the picture reproduced. The day before we left for Rumania, Dr Szalay took us on a motor ride across Hungary to visit his own University of Szeged. The physicists of the University were mostly away attending the meetings at Budapest. But we had the pleasure of visiting Dr Szalay's own home and of a short conference with the theoretical physicist, Dr János Horváth on subjects of common interest to us.

## Science in Eastern Europe: II

SIR C V RAMAN

### 6. Bucharest

Leaving Budapest in the forenoon of the 28th of June, we arrived at Bucharest early next morning and remained there till late at night on the 7th of July. During our stay we were the guests of the Rumanian Academy of Sciences and the Rumanian Institute for Cultural Relations with Foreign Lands. These two organisations took it upon themselves to make our sojourn in Rumania a most interesting experience. The enthusiasm and cordiality with which we were received and entertained cannot easily be described.

Three days, namely, the 2nd, 3rd and 4th of July were devoted to the preparation and delivery of a course of three lectures on the "Physics of the diamond". The hall of the Academy where the lectures were delivered was filled to capacity on all the three evenings. In giving these lectures, I had the assistance of Dr Gavrilă, a young theoretical physicist who spoke and understood English very well. The main points of each lecture were discussed with him and written out in advance and he could therefore translate my lecture as delivered orally in a perfect manner. The results were satisfactory both to myself and to the audience.

A notable recent development in Rumania is an Institute of Atomic Physics which has been built a few miles away from Bucharest and is accommodated in a group of buildings, the two largest of which contain respectively an atomic reactor and a cyclotron with their controls and accessories. As the Director of the Institute, Academician Hulubei, was away in Geneva at the time of my visit, I was shown round the Institute by the members of the staff. The latter includes Academician Titeica who is the leader of an active school of theoretical physics. I also paid a visit to the Institute of General Physics at Bucharest of which Academician Bădărău is the Director. I was shown round the various laboratories in which I found much valuable work in progress in diverse fields and had the pleasure of learning about the details of that work individually from Prof. Bădărău's colleagues. I was also much interested in the arrangements made to give a preparatory course of experimental work in nuclear physics to the University students.

During our stay at Bucharest I had the pleasure of meeting the Prime Minister of Rumania at his office and had a long and interesting conversation with him. The Prime Minister gave me a detailed account of the progress being made by

Rumania in the economic, educational and scientific spheres and expressed with sincerity and emphasis his desire that Rumania should come into much closer relationships with India in various fields of activity for their mutual benefit.

Two days were devoted to a tour by motor from Bucharest to Ploesti up the valley of the river Prahova to the mountains and back. On our way we passed through the region where the famous Rumanian oil wells and the oil refineries are located. The terminus of our tour was at Sinaia, a well known hill resort at which we made a short stay. From the verandahs of our lodge we could see the mountains encompassing Sinaia. We motored to a hotel perched up on the heights and on our way back visited the Peles Castle, formerly a royal residence and now a public museum which has lovely gardens and terraces with beautiful views on every side.

That Rumania has an active scientific life and an intellectual climate favourable to achievement was very evident. A extensive scientific literature exists in the language of the country, merely as a sample of which I may mention a book on the physics of the solid state written by the young physicist Sergescu and a book on the acoustics of the violin by Professor Bianu, copies of which the authors were good enough to present to me.

We had a wonderful send-off from Bucharest. At the station we were handed two beautifully bound albums containing photographs of our visits respectively to the Institute of Atomic Physics and the Institute of General Physics.

## 7. Belgrade

Yugoslavia lies on the railway route between Rumania and Italy, and in our travel programme which had been arranged in advance, two weeks had been set apart for a journey through that country with a stop-off at each of its three chief cities, viz., Belgrade, Zagreb and Ljubljana. The holiday season had however already begun and I was under the impression that the time chosen for the visit of Yugoslavia was not a suitable one for making any useful contacts with its scientific men. This anticipation, however, turned out to be false. Nawab Ali Yavar Jung who is the Ambassador of India at Belgrade is an old friend of mine. He welcomed us on arrival and told us that he had taken the initiative in arranging a programme for our stay at Belgrade. This, in the event, proved to be highly interesting and fruitful.

Belgrade is the capital of Serbia and has been the scene of many conflicts in its past history. It is now also the capital of the Federal Republic of Yugoslavia. The city is situated near the confluence of the Sava and the Danube which join here to form a single mighty stream. Standing on the ramparts of the ancient fortress of Belgrade, one sees an impressive panorama over the rivers and the neighbouring city of Zemun. Very appropriately also, in the Citadel of Belgrade have been set up the memorials of the recent conflict in which the partisans under the leadership

of Marshal Tito successfully defended their country against the armies of Hitler.

Professor Milojević of the Physical Institute of the University of Belgrade had arranged for a lecture by me on the 9th of July following the day of our arrival. Professor Savić took the Chair and I expounded as briefly and as clearly as possible the ideas regarding crystal physics which had emerged from the Bangalore investigations. On each of the three following days (10th, 11th and 12th of July) I visited the Institute of Nuclear Sciences which had been set up by the Federal Government. The Institute is located at Vinča about fifteen kilometres away from Belgrade and the motor road leading to it took us through some lovely countryside, and Vinča itself is most picturesquely situated. I was warmly welcomed at the Institute by Director Popović who is in charge of the administration and by Professor Savić who is in charge of the scientific activities. Great progress had been made in building up and equipping the Institute and further developments were in full swing. I found many young scientists at work and much activity in the laboratories.

On the 11th of July, I gave a lecture at the Vinča Institute in which I expounded my ideas regarding the structure of diamond and the explanation of its properties. Prof. Savić presided at the lecture and led the discussion which followed it. The rest of my time at the Institute was taken up in visiting its various departments, viewing the equipment which had been set up or was being set up and discussing the investigations in progress with the workers in its laboratories. In the evening of the 12th of July, I visited the Serbian Academy at Belgrade of which Professor Belić and Professor Kasanin are respectively the President and Vice-President. The Mathematical Institute of the Academy which I inspected is an active organisation and has a fine library. The publications of the Institute are regarded with respect in mathematical circles everywhere.

Our hosts of the Institute and the Academy did their very best to give us a happy time. On the afternoon of the 11th of July, there was an excursion to the hill-top of Avala, a few miles out of Belgrade, on which a highly impressive monument to the Unknown Warrior stands. Extensive views are to be seen on all sides from the monument. On Sunday the 13th of July, we were taken on an all-day motor tour through the Serbian landscape. We visited the valley of the Danube and saw several of its beauty-spots.

## 8. Zagreb

As had been planned earlier, we were at Zagreb for three full days, arriving on Monday evening, the 14th of July, and leaving for Ljubljana on the forenoon of Friday the 18th. The holiday season was in full swing and we travelled in a train which was very crowded, but the special consideration which was given to us by the railway staff saved us from discomfort. We were met at the station by Dr S Asperger and taken to our hotel.

Croatia is one of the several Republics which have federated to form Yugoslavia. It includes a great part of the coast-line of that country from Fiume in the north to Kotor in the south, as also an immense number of islands, great and small, in the Adriatic Sea. Zagreb is the capital of Croatia, and is a large city. The river Sava runs a few miles south of it while immediately to the north of the city are some high hills which help to make Zagreb and its surroundings very picturesque.

Local patriotism runs strong in Yugoslavia, and since a great new Institute of Nuclear Physics is going up at Belgrade, it was only to be expected that Zagreb would not lag behind. Indeed, our visit to Zagreb, brief though it was, owed its great interest to us by reason of that very circumstance. On the rising ground between the city and the mountains a great new Institute had been set up named quite appropriately as the Boscovitch Institute after the great pioneer of an earlier age in the field of atomic physics. The Institute is by no means a duplication of the effort which is building the organization at Belgrade. The scientific ideology animating the Boscovitch Institute is indeed different, embracing a wider range of scientific topics. Nuclear physics was of course represented and indeed showed every sign of being an active field of interest at Zagreb. The fitting up of a laboratory containing a large cyclotron was in an advanced state of progress. Prof. Paić also showed me the equipment that he had set up for investigating the behaviour of atomic nuclei under neutron bombardment. During my visit to the chemical laboratory of the Institute, I was much impressed by the work being done by Dr Asperger on the detection of traces of mercury in the atmosphere by its effect upon the rate of chemical reactions. This is a subject of practical importance, since Yugoslavia is an important producer of mercury from its naturally occurring minerals.

An interesting function at which I was present was the final examination for the Doctor's Degree in Physics of two young aspirants for that distinction. I sat alongside of the Board of three Examiners which consisted of three professors of the Zagreb University. In view of my presence at the examination, the candidates were asked to give the oral presentation of their theses in the English language. That they could do so and very well indeed was not surprising, since the experimental work of one candidate was done at Cambridge in England and by the other at Rochester in USA. The *viva voce* examination which followed the oral presentation of the theses was very searching but the candidates showed up very well. I felt that the system followed at Zagreb of having only internal examiners for the doctorate was an admirable one which was worthy of being followed elsewhere.

Apart from the activities referred to above, our three days at Zagreb were fully occupied. On Tuesday the 15th of July, I spoke on the problems of crystal physics at a colloquium at which Dr Supek and his colleagues in theoretical physics were present. The discussions with him on this and other topics were continued later in the day when he drove us up to a mountain lodge some miles behind Zagreb



Figure 3. The Plitvice lakes, Yugoslavia.

where we spent a few happy hours wandering through the woods. The next day, Prof. Paić and Mrs Paić took us out on an all-day motor excursion in the course of which we visited the medieval town of Karlovie and thence proceeded to the famous national park containing the Plitvice lakes. Here we spent the rest of the day exploring the lakes, returning to Zagreb late in the evening, tired but happy.

To describe the Plitvice lakes adequately and convey an impression of their transcendental beauty would need a whole article to itself. We can only reproduce here a photograph of a very small part of the region including the waterfalls characteristic of the area.

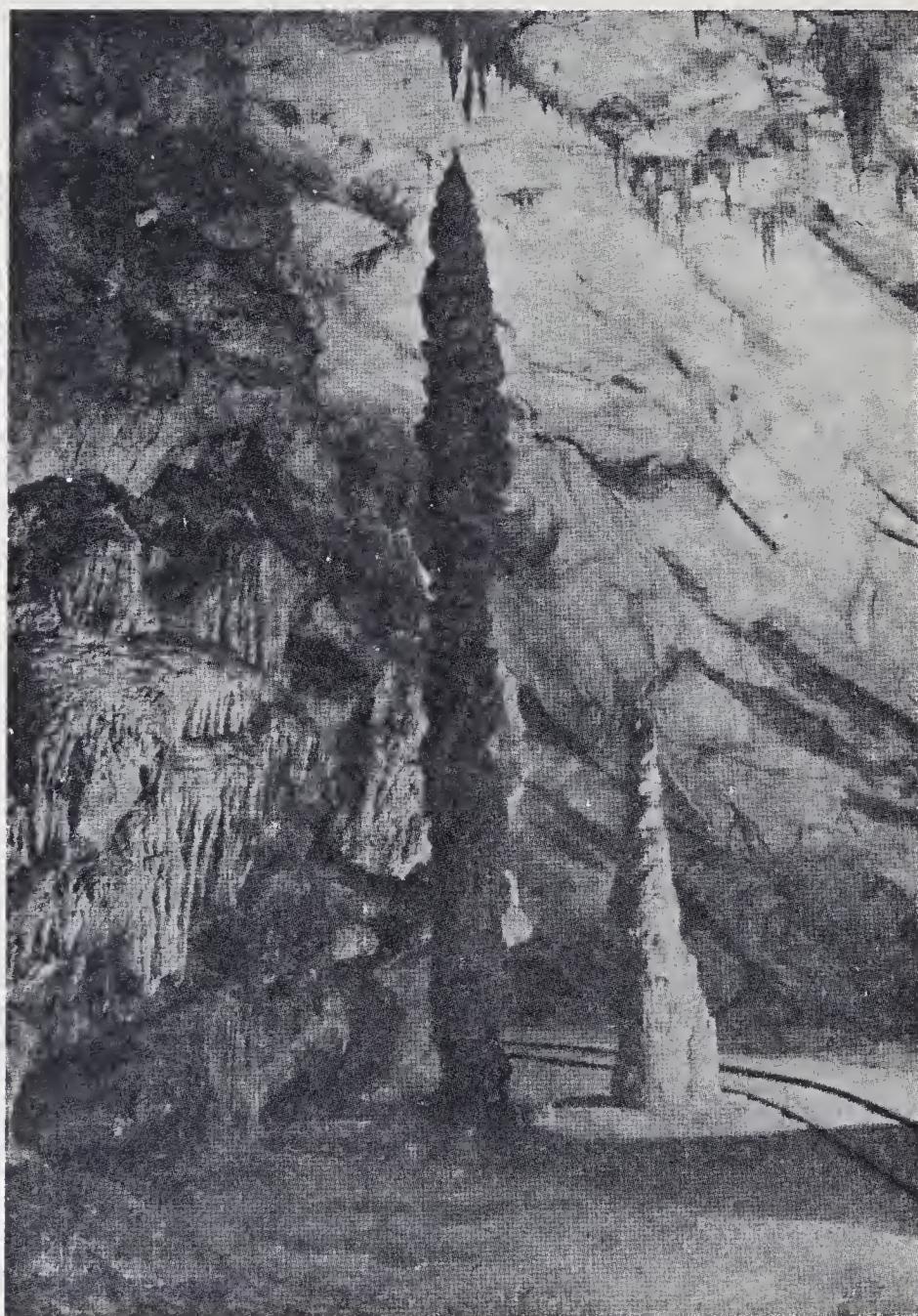


Figure 4. Near the entrance to Posthumia caves.

On the third day, the 17th of July, we were entertained by Prof. Paić and Mrs Paić at their home. They bid us an affectionate farewell next morning at the station when we left for Ljubljana.

## 9. The rest of the tour

My scientific activities ceased when we left Zagreb. But a brief reference to the later parts of the tour may be of some interest to the readers of *Current Science*. The railway journey from Zagreb to Ljubljana is not a long one. It took us through the beautiful valleys and gorges which the river Sava has made for itself in flowing through Slovenia. Ljubljana itself is a charming town with a medieval castle on a hill right at its centre and a great city park extending into the hills. The day after our arrival, we drove up to the celebrated limestone caves at Postumia which lies halfway between Ljubljana and Trieste. These caves run for several miles underground, and indeed one has to make a good part of the journey within them by electric trolley. The rest of the journey on foot through the cavernous interior takes us through a region of which the magnificence and fantastic



Figure 5. Lake Bled and its island.

character beggars all description. The photograph reproduced shows a region near the entrance to the caves. On Sunday, we undertook a motor tour to the region of the Julian Alps including the two lakes, Bled and Bohini which lie in that area. Lake Bled and its environs appear comparatively sophisticated. The picture reproduced shows the church on an island in the lake and the Julian Alps beyond. Lake Bohini which is much further west is not far from Triklav, the highest peak of the Julian Alps. It lies right at the foot of the mountains and has a sombre beauty of its own.

Leaving Ljubljana on the morning of the 21st, we travelled via Trieste and the coast of the Adriatic to Italy and Venice reaching the latter city the same afternoon. We spent the next day at Venice visiting its palaces, the Lido and the lagoons. The next day, again, we toured through Venetia by motor, viewing its many beautiful villas with their Palladian architecture. Crossing the river Brenta by its celebrated wooden bridge, we went as far as Asolo before finding our way back to the Grand Canal of Venice and our hotel.

The evening of the 24th of July found us back again at Innsbruck where we remained three days. Innsbruck is a convenient centre for visiting the surrounding regions in Austria, Italy and Germany. The opportunities thus open to us were fully utilised before we left finally to catch our steamer at Genoa.

## Zonal winds and jet-streams in the atmosphere

SIR C V RAMAN

The atmosphere of the earth is a gaseous mantle which completely surrounds the globe and is held down to the surface by its own weight. Being a compressible gas, its density is determined by the pressure of its own weight and is accordingly a maximum at the surface of the earth and rapidly diminishes as we proceed upwards, becoming very low at great heights. The atmosphere is carried round by the earth in its annual motion around the sun, and it is therefore appropriate to regard it as an integral part of the earth in much the same way as the land masses or the oceanic waters. But a difficulty arises when we seek to extend the same idea to the behaviour of the atmosphere in relation to the rotation of the earth about its polar axis. The atmosphere enjoys a freedom of lateral movement in all directions transverse to the surface of the earth. It also possesses no fixed external boundary. It follows that the atmosphere is not rigidly coupled in its rotation about the polar axis. The question thus arises to what extent does the atmosphere actually follow the rotation of the earth about the polar axis, and what are the observable consequences of any differences between the atmosphere and the earth in regard to this rotatory movement.

The issues stated above are obviously of fundamental importance. Unless the questions which have been asked are squarely faced and satisfactorily answered, it seems scarcely possible to discuss the problems of atmospheric behaviour meaningfully and to reach a clear understanding of the same. Strangely enough, the meteorologists who are professionally interested in the dynamic behaviour of the atmosphere and are perfectly well aware of the basic role played by the rotation of the earth in their subject, have apparently been content to assume that the atmosphere goes round with the earth unless specially disturbed from that condition. Why it should so behave and whether it actually follows the earth in its rotation at all levels and in all latitudes is the problem which we shall proceed to discuss.

The surface of the globe presents a wide diversity in its appearance at various places. In particular, the areas of land and water are distributed in a very unequal manner in the northern and southern hemispheres. We shall, however, here ignore these differences and proceed to regard the surface of the earth as consisting of three distinct belts on each side of the equator, comprised respectively in the ranges of latitude from  $0^{\circ}$  to  $30^{\circ}$ ,  $30^{\circ}$  to  $60^{\circ}$  and from  $60^{\circ}$  to  $90^{\circ}$ . The superficial areas of these three belts diminish quickly as we proceed from

each to the next. Of particular importance also in relation to our present topic is the actual speed of motion at the surface of the rotating globe. This falls off as we proceed polewards from each belt to the next. It is 465 metres per second at the equator, 450 metres per second at  $15^\circ$  latitude and 403 metres per second at  $30^\circ$  latitude. In the second belt, the diminution of speed is much more rapid, being 329 metres per second at  $45^\circ$  and 232 metres per second at  $60^\circ$ . In the third belt it is still smaller, being 110 metres per second at  $75^\circ$  and zero at  $90^\circ$ . A further and highly noteworthy difference between the three belts is in respect of the heating of the surface of the earth by solar radiation and the turbulent movements in the atmosphere which arise by reason of its contact with the heated earth. These effects are highly pronounced in the first belt, moderate by comparison in the second belt, and relatively small in the third belt.

The coupling of the atmosphere to the earth in its rotation about the poles is attributable entirely to the forces acting at the surface of the globe when there is any movement of the air relative to the solid or liquid material with which it is in contact. We shall here ignore the part played by molecular viscosity. The interactions with which we are concerned express themselves by producing eddies or turbulence in the vicinity of the interface. The question arises, how far would the effect of such eddies or turbulence extend and what would be their ultimate effect on the movement of the air at considerable heights above the surface or in regions remote from the areas where there is relative movement.

Considerations of a very general nature suggest that the further away we move from the actual surface of the earth, the less and less would be the controlling influence of any particular area of the surface on the movement of the parcel of air immediately above it. *Per contra*, we are justified in assuming that the air at any given height would be influenced in its movements by the movement of areas on the surface of larger and larger extent as we proceed upwards. At sufficiently high levels, the effective areas on the surface may be expected to be of very considerable dimensions.

The approach indicated above leads us to certain inferences. As has been remarked above, the three parts of the surface of the globe between  $0^\circ$  and  $30^\circ$ , between  $30^\circ$  and  $60^\circ$  and between  $60^\circ$  and  $90^\circ$ , differ widely in those characteristics which may be expected to determine or influence the rotation of the atmosphere above the surface in those belts. We may therefore feel justified in drawing the inference that the atmosphere of the earth would exhibit these differences very noticeably in its rotational behaviour. In other words, we may expect to find three distinct belts of atmospheric rotation in each hemisphere, a broad belt extending on either side of the equator from  $30^\circ$  north to  $30^\circ$  south, a belt in the middle latitudes between  $30^\circ$  and  $60^\circ$  and the third belt between  $60^\circ$  and  $90^\circ$ . In the equatorial belt, the speed of atmospheric rotation would be a maximum, being everywhere nearly the same as the speed of movement of the surface at the equator itself. When we pass to the adjoining belt in the latitudes between  $30^\circ$  and  $60^\circ$ , the speed of rotation may be expected to exhibit a large and

sudden drop to a smaller value, since the speed of atmospheric rotation would be determined by the much lower speeds of the surface of the earth in these latitudes. Finally, when we pass to the third belt in the latitudes between  $60^{\circ}$  and  $90^{\circ}$ , we may expect a further and fairly sudden slowing down of the rotational movement, by reason of the large fall in the speed of movement of the surface as we move to the highest latitudes.

The existence of these belts in which the movement of the atmosphere parallel to the circles of latitude differs in speed from the surface of the earth below would reveal itself to an observer located in those areas as a zonal wind, blowing from the east or the west as the case may be, the speed of the zonal wind being the difference between the speeds of the atmosphere and of the earth. In the broad belt which extends from  $30^{\circ}$  north to  $30^{\circ}$  south of the equator where the surface speed is a maximum, we may expect the atmospheric speed to be also a maximum at the equator and to differ but little from the speed of the surface below. Accordingly, at the equator itself, there would be no zonal wind. But, as we move north or south of the equator, the atmospheric speed would be greater than the speed of the surface. Accordingly, we would have in these regions an easterly wind which gains strength as we proceed north or south and which may be expected to reach its maximum speed at or about a latitude of  $15^{\circ}$  north or south. Beyond this, the easterly wind would diminish in strength and vanish when we reach the limit of the equatorial belt of easterly zonal winds at  $30^{\circ}$  latitude.

In the latitude belts between  $30^{\circ}$  and  $60^{\circ}$ , north or south of the equator, considerations of the same nature as those stated above for the equatorial belt indicate that an observer would find them to be regions in which there are zonal winds which appear to blow from the west. These winds would naturally be weak at the surface and might be expected to be absent at the boundary between the zones of easterly and westerly winds. The westerlies would become stronger as we proceed polewards from this boundary. The considerations already set out indicate that the westerlies would gain notably in strength as we proceed to higher levels above the surface. For, the influence of the slowly-moving surface areas on the air-speeds aloft would then progressively become greater.

We may also expect to meet with zonal winds in the latitude range between  $60^{\circ}$  and  $90^{\circ}$ . The speed of movement of the surface goes down to zero at the poles, but elsewhere would be finite. Hence, if we assume the atmospheric speed to be determined by some sort of averaging over the surface speed, the air-speed everywhere in this belt would be greater than the surface-speed. Accordingly, in this region we would meet with easterly zonal winds.

We now proceed to consider the question of the elevation up to which the atmospheric layers which rotate faster or slower than the surface of the earth below may be expected to extend. The transference of momentum from the surface upwards into the atmosphere is made possible by the process of eddy diffusion. Where this process comes to a stop, the transference of momentum will also cease.

As is well known, the atmosphere of the earth falls roughly into two divisions referred to respectively as the lower and the upper atmospheres. The dividing surface between them is called the tropopause; the region below is the troposphere and the region above is the stratosphere. The troposphere is characterised by its exhibition of a steady fall of the atmospheric temperature as we proceed upwards, while in the stratosphere the temperature does not exhibit this feature, but remains approximately constant. The most recent studies indicate that the tropopause has a multiple structure, there being three distinct parts of it, one at low latitudes, one in the middle latitudes, and the third in high latitudes. The first is at the highest level, 16 kilometres or more. The second is between 10 and 12 kilometres above the surface and the third between 6 and 8 kilometres.

The tropopause is usually identified as the boundary between the regions in which heat transfer is principally by convection and turbulence, and those in which heat transfer is predominantly by radiation. On this basis, we can also identify the tropopause as the upper limit of the belts of air of which the speed of rotational movement differs from that of the surface below. It is readily understood on this basis why the tropopause exhibits a multiple structure as remarked above.

The recognition that there exist three wind-belts in the atmosphere with the characteristics already stated above enables a simple explanation to be given of the origin of the jet-streams which manifest themselves at fairly high levels in the atmosphere. There are two of these, viz., one known as the polar-front jet and the other as the sub-tropical jet. The locations where these appear are the regions in the atmosphere where there is a steep fall in the atmospheric speed as we pass from one wind belt to the next. This steep fall manifests itself as a large increase in the zonal wind-speed.

# The atmosphere of the earth\*

SIR C V RAMAN

## Abstract

The processes by which the movements at the surface of the earth due to its rotation around the polar axis can influence the atmosphere above are considered in detail. It emerges that the fast-moving areas in the equatorial belt off the surface of the earth play a highly important role in determining the behaviour of the atmosphere. The jet-stream in the sub-tropical regions, the westerly zonal winds in the region of middle latitudes and the easterly surface-winds in the equatorial belt are explained on this basis and shown to stand in close relationship with each other. The winds observed in the polar belt are also discussed and explained.

## 1. Introduction

It is proposed in this address to consider the following questions and endeavour to find answers to them. The earth revolves around its polar axis once in every twenty-four hours; does the atmosphere which is a gaseous mantle enveloping the globe rotate with it and in the same manner at all elevations and in all latitudes? What are the considerations which determine the behaviour of the atmosphere in this respect? What are the observable consequences of any differences between the globe and the atmosphere in the speed of their movements around the polar axis? In dealing with these questions we have necessarily to leave out of consideration, the complexities in the behaviour of the atmosphere at various times and at various places which manifest themselves as the phenomena of the weather. It is these latter phenomena and the interpretations of their origin which are the preoccupations of the meteorologist who watches the weather and seeks to forecast the changes in it. But it is not impracticable to regard the manifestations of weather as variations from a standard state of the atmosphere which may be defined as its average taken over a sufficient range of time and over a sufficiently extended area of the surface of the earth. In other words, we consider the behaviour of the earth's atmosphere in its broadest aspects, taking a global and long-term view of the subject.

\*Presidential address to the Indian Academy of Sciences at its thirty-third annual meeting in Madras, 19th December 1967, as subsequently revised and rewritten.

## 2. The atmospheric rotation belts

In dealing with the problems set forth above, it is necessary at the very outset to recognize that the atmosphere which envelops the globe cannot be considered for the present purposes as a single entity. The reason for this is that all the factors which influence or can influence the atmospheric movements vary enormously over the surface of the earth. Among them we may mention particularly the actual speed of movement of the surface arising out of the rotation around the polar axis, as well as the rate at which this speed alters as we move longitudinally along the surface. The insolation by solar radiation and the magnitude of its variation during the year with the seasons are also very different in various regions. The speed of movement as well as the magnitude of the insolation are both functions of the latitude. Hence, and to avoid any suggestion of arbitrariness, we partition the surface by drawing circles of latitude which are equally spaced. We thus obtain the following areas on the surface exhibiting distinctive features.

*Firstly*, we have the region which we designate as the equatorial belt and which includes the entire area comprised between the circles of latitude  $30^{\circ}$  north and south of the equator. This forms a single continuous surface which occupies one-half of the entire superficial area of the globe. The speed of movement is a maximum, viz, 465 metres per second at the centre of the belt which is the equator. The speed falls off quite slowly at first, to 457 metres per second at  $10^{\circ}$  latitude and to 437 metres per second at  $20^{\circ}$ . The drop in speed then becomes rather more rapid. It is 403 metres per second at the circles of  $30^{\circ}$  latitude which are the extremities of the belt on either side of the equator. The equatorial belt is also distinguished by its being the recipient of the maximum amount of solar radiation at all seasons of the year.

*Secondly*, we have the belts of middle latitude comprised between the latitudes of  $30^{\circ}$  and  $60^{\circ}$  on either side of the equator. Each of these belts covers an area which is roughly one-sixth of the total area of the globe. The speed of movement is substantially less than in the equatorial belt, and also falls off steeply from 403 metres per second at  $30^{\circ}$  to 233 metres per second at  $60^{\circ}$ . The insolation of the belts of middle latitude is also notably less than that of the equatorial belt and progressively diminishes as we move polewards. It also shows large differences between the summer and winter months.

*Thirdly*, we have the polar belts, by which term we refer to the parts comprised between the latitudes of  $60^{\circ}$  and  $90^{\circ}$ . These are of relatively small area, each being about one-fifteenth of the earth's surface. The speed of movement of the ground falls off from 233 metres per second at  $60^{\circ}$  to 120 metres per second at  $75^{\circ}$  and becomes zero at the poles. The insolation of this belt when summed up for the whole year is much less than that of other areas on the surface of the earth. The insolation also shows large variations with the season of the year and actually vanishes during the long polar nights.

### 3. Rotational coupling of earth and atmosphere

A clear understanding of the manner in which the rotation of the globe influences its gaseous envelope is of the utmost importance in the present context. The forces in the nature of a frictional resistance which operate at and near the surface of contact when there is a relative motion between ground and air obviously play an important role. But this role is purely a negative one. In other words, the frictional forces act merely as a check on the relative motion, their direction being reversed when the sign of the relative motion alters. The frictional forces cannot set up or maintain a steady state of relative motion, and when such a state exists, we have to look elsewhere for an explanation of its cause or origin. It is also necessary to remark that the range of action of the frictional forces on the atmosphere is strictly limited. Some idea of this range can be obtained from observations on the manner in which the strength of a wind alters as we approach nearer the ground or move away from it. This effect is found to depend on the actual strength of the wind, on the roughness of the ground and on other factors. It may be inferred from the observations that the frictional resistance is effectively restricted to comparatively low levels in the atmosphere. A hundred metres above ground is a fair estimate of the height up to which the frictional forces dominate the behaviour of the wind, while a kilometre may be put as the upper limit of the height beyond which their effect may be considered as negligible.

But we shall be wholly in error if we were to assume that the atmosphere at all levels above one kilometre from the ground can be regarded as a completely free medium on which the rotation of the ground below is without influence. In reality, the state of the atmosphere in its higher levels is influenced and indeed fully determined with reference to the rotation of the ground below by processes of a quasi-permanent nature which we shall now proceed to describe and discuss.

### 4. The vertical transport of momentum

The atmosphere when in contact with land or water heated by solar radiation takes up both moisture and thermal energy. When the temperature of the air is thereby raised sufficiently with respect to that of the superincumbent layers, its equilibrium becomes unstable, and masses of air break off and move upwards, expanding as they go, thereby maintaining an equality of pressure with their surroundings. The expansion results in an adiabatic cooling and this suffices to check the upward movement beyond a certain height. But if the initial moisture content of the heated air is sufficient, part of it condenses out to form fine droplets of water which remain in suspension. The heat of condensation of this water is released, thereby warming the air and enabling it to mount up to still higher levels. This upward movement of heated air accompanied by the formation of clouds is a familiar phenomenon and may reach up to great heights. The important aspect

of it from our present point of view is that it involves a vertical transport of momentum from the rotating earth to the upper levels of the atmosphere by a process which is both quick and efficient. The actual momentum transported by an individual parcel of air may be small. But a great many parcels keep going up, and their total effect would evidently be cumulative when summed up over a long period of time. The final result would be to bring the air at all levels up to which these processes operate into a definite relationship with the ground below in its rotatory movement about the polar axis of the earth.

### 5. The origin of the jet-stream

The equatorial belt on the surface of the earth plays a highly important role in terrestrial meteorology. This is a consequence of several factors, viz., the large area and central position of the belt, the high speed of its surface movement, and, above all, the fact that its insolation is more intense and much more constant through the year than that of other areas on the globe. Of particular importance in the present context is that the insolation is a maximum at the equator itself and changes but slowly within the range of ten degrees of latitude on either side of the equator. But the insolation falls off rapidly as we proceed to higher latitudes.

In the circumstance stated above, it is fully to be expected that a powerful updraft of heated air from the area in the equatorial belt comprised between the latitudes of  $10^{\circ}$  north and  $10^{\circ}$  south of the equator would be a constant feature throughout the year. The association of such heated air with water vapour would enable this updraft which carries with it the momentum of a surface-speed of 465 metres per second to reach great heights. This would also result in heavy precipitation, an inference which is strikingly confirmed on an inspection of a map showing the distribution of rainfall over the surface of the earth. The regions of heavy rainfall with a precipitation exceeding two metres of water per annum are all found in the belt of latitudes between  $10^{\circ}$  north and  $10^{\circ}$  south of the equator. The northern parts of South America, the equatorial regions in Africa, Ceylon, Malaya, Sumatra, Java, Borneo, Celebes and New Guinea, are all regions of such heavy rainfall and lie within this range of latitudes. Indeed, outside this range, there are few areas in which there is such heavy rainfall ascribable to convectional precipitation.

It is evident that when an updraft of air from the latitude belt between  $10^{\circ}$  north and  $10^{\circ}$  south of the equator reaches the higher levels of the atmosphere, there would arise a drift of air outwards from these regions towards latitudes north and south of the equator. Two questions then arise. At what level would this outward flow commence, and how far outwards would it extend? To the first question, the answer evidently is that the outward flow would commence at the level at which

the updraft has lost its driving force. The atmospheric temperature at the equator falls to the freezing point of water at a level of some five kilometres above ground. It falls further to  $-20^{\circ}\text{C}$  at 8 kilometres, to  $-30^{\circ}\text{C}$  at 9 kilometres and to  $-40^{\circ}\text{C}$  at 11 kilometres. It is evident that at a height of about 10 kilometers above ground level at the equator and in all neighbouring regions, the entire content of moisture in the air would have been frozen out. The motive power for any further upward movement would then have practically disappeared. It may therefore be justifiably assumed that the horizontal drift would manifest itself principally at a height of some 10 kilometres from the ground but might extend a little both above and below that height. It is also evident that the air thus moving north and south at high levels cannot subside or sink to lower levels in latitudes where there is even a moderate updrift of heated air. We may therefore normally expect the movement to extend over the whole of the equatorial belt, viz., upto  $30^{\circ}$  of latitude or even beyond.

As the cumulative effect of the mixing with high-speed air from the equator, the air between  $0^{\circ}$  and  $30^{\circ}$  latitude at and near the 10 kilometre level would acquire a speed of approximately 465 metres per second or close to it. The difference between this speed and that of the ground below would appear as a circumpolar or zonal wind in these latitudes. The difference would be small in regions quite close to the equator. But as we proceed further north or south of the equator, the ground speed falls off rapidly, and the difference would be perceived as a circumpolar westerly wind of considerable force. If the speed of 465 metres per second is maintained upto the limits of the equatorial belt, viz.,  $30^{\circ}$  north or south, the circumpolar or zonal wind would have a speed in those latitudes of  $(465 - 403) = 62$  metres per second or 140 miles per hour.

## 6. The westerly winds in middle latitudes

When the flow of air at high levels near the equator towards the north or south reaches latitudes where it does not meet with any updraft from below, the air-stream would subside to lower levels and at the same time become more diffuse. The belts of middle latitudes would thereby become the recipients of fast-moving air from the equatorial belt. The admixture of such air with the more slowly moving air in those latitudes would result in the atmosphere in these areas moving faster than the ground below. As a consequence, these regions would exhibit westerly zonal winds which may be considered to be downward and poleward extensions of the high-level stream in the equatorial belt. The westerly zonal winds would extend down to ground level but their speeds would diminish in the lower levels. The winds would evidently be strongest in latitudes between  $30^{\circ}$  and  $45^{\circ}$  (north or south) and become weaker as we proceed further polewards.

## 7. The easterly surface-winds

The void in the atmosphere left by the streaming upwards of heated air from near the equator has, of necessity, to be filled up by air moving in towards the equator at various levels. Some of this replacement may be effected in the equatorial belt by an inflow in the marginal regions at various levels. But a substantial part of the air needed must come in at and near the ground level. Admixture of air from the higher latitudes with the atmosphere nearer the equator would reduce the speed of rotation of the atmosphere in the lower levels. Hence, at these levels, zonal easterly winds would be perceived.

## 8. Winds in the polar belt

The difference between the heating effect of solar radiation in the belt of mid-latitudes and in the polar belt is sufficiently great to allow of a circuit of convection being established in these areas. Warm air goes up into the troposphere from the belt of middle latitudes. Its replacement has to be effected by colder air moving in from the polar regions. Since the surface speeds of movement are very low near the poles, the air drifting away from the poles would result in reducing the surface-speeds of the atmosphere with which it mixes. Hence, we would have a regime of easterly surface-winds in the polar belt. The warm air going up from mid-latitudes has necessarily to find its way back into polar belts. This can be achieved by its going to the tropopause level and then drifting polewards and then slowly subsiding into the polar area. As the air thus going up is derived from the mid-latitudes where the surface speeds are much higher than in the polar belt, it follows that westerly winds with considerable speeds would be perceived as blowing over the polar areas at high levels.

# The origin of the colours in the plumage of birds

SIR C V RAMAN, Kt., F.R.S., N.L.  
(Indian Institute of Science, Bangalore)

Received May 28, 1934

## 1. Introduction

Great interest naturally attaches to the investigation of the colours that form a striking feature of the plumage of numerous species of birds. Even a cursory examination, as for instance the observation of the feathers under a microscope, shows that the distribution of colour in the material and its optical characters are very different in different cases, indicating that no single explanation will suffice to cover the variety of phenomena met with in practice. It is usual to distinguish between those cases in which the colour is chemical in origin and those in which it is physical or structural. It must not be overlooked, however, that in any particular instance both physical and chemical colouration may be jointly operative. Then again, it is usual to divide the structural colours of feathers into two classes: those of the *iridescent* type in which the colour changes very obviously with the angles of incidence and observation, and the *non-iridescent* class in which such change, if any, is not very patent. In the feathers of the tail of the peacock and in the gorgeous plumage which covers the head and neck of the Himalayan pheasant we have striking examples of iridescent colours. The non-iridescent type of colouration is also common and is shown by the feathers of certain birds, such as the jay, the kingfisher, the parrot and so on. It is proposed to describe in the present paper the results of a detailed study of the coloured plumage of the bird *Coracias Indica*. This is a species of jay, very common in Southern India, which furnishes readily accessible material for the investigation of this type of colouration of birds.

## 2. Some preliminary observations

Seen sitting with its wings folded up, *Coracias Indica* is not a particularly striking bird, though even in this posture its head, sides and tail show vivid colouration. It is when in flight that the gorgeous plumage of this bird is most strikingly seen, and museum specimens of the bird are therefore best mounted with the wings

outstretched. The wings then exhibit a succession of bands of colours alternately a deep indigo-blue and a light greenish-blue; the tips of the wings show a delicate mixture of both colours. A remarkable feature is the striking variation in the appearance of the wings with their position relatively to the source of light and the observer. Held between the observer and the source of light, such as an open door or window, the wings appear dark and dull, while when observed with the light behind the observer, they have a brilliant sheen, and at some angles an enamel-like lustre. There is also a distinct difference in the colours exhibited in the two positions. With the light behind the observer, the predominant colours are deep blue and a light greenish-blue, while with the light facing the observer, the same regions exhibit respectively a dark indigo colour and a light blue tint.

Very noticeable changes in colour take place when the feathers are immersed in water and after some soaking the superfluous water is shaken off. The indigo-blue portions of the feather then appear green in colour, while the greenish-blue portions appear pinkish red. At the same time, the variation of colour with the position of the feathers relatively to the source of light and the observer becomes very conspicuous. The portions originally indigo-blue appear green in the damp feather only when the light is behind the observer. They change over to a dark blue and even a deep violet (depending on the angle of observation) when the feathers are held between the observer and the source of light. In the same way, the lighter regions appear pinkish red with the light behind the observer, but a light blue when viewed with the light facing the observer.

The foregoing observations indicate very clearly that the cause of the colouration is mainly physical. It should be remarked, however, that when the feathers are held against a bright source of light and viewed by transmitted light, the dark blue portions appear a deep brown, while the light blue portions are translucent and almost perfectly white. The presence of a dark pigment (melanin) is thus suggested in the darker portions of the feather and to a much less extent, if at all, in the lighter portions. It would not, however, be justifiable to infer from this that a difference in the amount of the melanin is *directly* responsible for the difference in colour between the dark blue and the light blue portions of the feather when viewed by reflected light.

### 3. Observations with the "Ultra-opak" microscope

Further insight into the nature of the colours is obtained when the feathers are examined microscopically. It is noticed at once that the characteristic colouration is confined entirely to the barbs of the feather. The usual method of microscopic lighting from below the stage is obviously unsuitable in the present case, and it is necessary to illuminate the barbs from above the stage. For a critical examination, a strong beam of light, as for instance from a pointolite lamp, may be projected on to the feather at a suitable angle. Some useful observations may be

made in this way with an ordinary microscope or better still, with a binocular microscope. It has, however, been found that a much more interesting way of examining the feathers is to use the "Ultra-opak" microscope recently introduced by the firm of Leitz. In this microscope, the illumination of the object is secured by an incandescent lamp placed in a side tube attached to the microscope, the light from which is reflected down towards the object under study by suitable optical arrangements. The special feature of the instrument is that light does not pass down directly through the objective as in an ordinary metallographic microscope. Instead, it is reflected down through a ring-shaped aperture surrounding the objective and then through a cone of glass, polished flat at the lower end, which intervenes between the objective and the stage. In this way, an illumination of the objective itself is avoided, while the illuminated field can be made as bright as desired by controlling the lamp with a rheostat. The microscope itself is mounted on a cross slide fitted with ball bearings, so that it can be readily moved about and fixed in any position. The stage of the instrument is of considerable size, so that large objects such as the entire wing of a bird can be placed on it and any desired part may be conveniently examined under the very powerful illumination provided by the instrument.

The observations made with the "Ultra-opak" microscope are very significant. It is found that the colour of the barbs is by no means uniform even in the portions which appear ordinarily as dark blue or light blue respectively. The layer of colour in the barb appears divided up into a series of cells, polygonal in shape, and the colour varies individually from cell to cell. The appearances are particularly striking when the microscope is directed to a portion of the feather on the boundary between the dark blue and the light blue regions or, to a portion near the tips of the wings where the two colours intermix. The individual cells may then be seen showing a surprising range of colours. Some cells are violet in colour, some a deep blue or indigo, some lighter blue, some a bright green, some yellowish green, and here and there cells may be observed which are yellow or even orange in colour. Under the highest powers with which the "Ultra-opak" microscope is provided, it can be seen that the individual cell has a granular structure and that the different granules in a cell are usually of the same colour, though, occasionally, distinct differences in colour between the different granules in a cell may also be noticed.

The study of the wetted barbs under the "Ultra-opak" microscope is exceedingly interesting. When the barb is fully damp, the portions originally dark blue now show up as a bright green, while the portions originally light blue now become a light red. The variations in the colour of the individual cells are then much more striking, particularly so as the drying of the barb proceeds. In an individual barb, it is then possible to observe cells with colours ranging over practically the whole spectrum from a deep violet to a bright red, and the cellular structure of the barb is much more conspicuous than ordinarily. As each cell dries up, its colour changes and ultimately goes back to the original. During the

process of drying, the cell boundaries may momentarily possess a different colour from the interior; for instance they may be picked out in red while the interior of the cell is a greenish yellow. The whole appearance is then very picturesque.

#### 4. Is the blue of feathers a Tyndall effect?

Bancroft and others, including especially C W Mason<sup>1</sup>, have put forward the theory that the non-iridescent blue colour exhibited by the feathers of numerous birds is a Tyndall effect due to the scattering of light by very fine air-bubbles or cavities contained in the substance of the barbs. Mason includes *Coracias Indica* in the list of birds examined by him in the investigations which are claimed to support the theory. The observations described in the preceding paragraphs, however, throw doubt on the correctness of this theory, at least so far as this particular bird is concerned. The surprising variety of colours exhibited by the individual cells which under suitable conditions cover the whole range of the spectrum cannot be reconciled with the idea of a simple scattering in accordance with the Rayleigh law ( $\lambda^{-4}$ ) for small particles. We may of course attempt to evade the difficulty by postulating that we have to deal with scattering particles which are not sufficiently small for the Rayleigh law to be valid, or by assuming that the Tyndall blue is modified by the absorbing action of melanin or other pigment. The latter suggestion is negatived in the present case by the evident absence of pigment in the lighter parts of the feather which nevertheless show green, yellow or orange tints by reflected light and also red when wetted. As regards the former possibility, it may be mentioned that numerous experimental and theoretical investigations have been made on the subject of light-scattering by particles which are not small enough for the Rayleigh inverse fourth-power law of wavelength to be operative. We may for instance cite the experimental observations and the calculations based on the electromagnetic theory of light made by B B Ray for the case of small droplets of water suspended in air,<sup>2</sup> and small spheres of sulphur suspended in water.<sup>3</sup> These observations and calculations cannot be regarded as applicable without modification to the present case in which we are dealing with cavities having a *lower* refractive index than the surrounding medium. In the cases of particles having a higher refractive index than the surrounding medium, the most striking results of an increase of size which accompany a break-down of the inverse fourth-power law are: (a) a large increase in the forward scattering relatively to that in a backward direction, (b) disappearance of colour in the forward scattering, (c) the appearance of colour

<sup>1</sup>C W Mason, *J. Phys. Chem.*, **27**, 201, 1923.

<sup>2</sup>*Proc. Indian Assoc. Sci.*, **8**, 23, 1923.

<sup>3</sup>*Proc. Indian Assoc. Sci.*, **7**, 1, 1921.

varying with the angle of observation in other directions, these being most pronounced in the backward scattering, and (d) a large dependence of the intensity of the scattered light on the plane of polarisation except in the forward and adjacent directions. In the case of the colours exhibited by *Coracias Indica*, none of these features is observed. Actually, the layer of colour in the feathers appears much less luminous when viewed with the light facing the observer than in the opposite direction; immersing the feathers in a cell of benzene abolishes the surface reflexion at the exterior of the barbs without altering this particular feature of the internal colour.

Then again the colour in the forward direction though of low intensity is saturated in hue. Polarisation effects are hardly noticeable with *Coracias Indica*. Thus the observations seem unfavourable to the general idea that the colours are due to diffraction by spherical cavities, though in view of the strict inapplicability of the theoretical investigations to the present case, some reservation of opinion would be justifiable. It is not improbable, for example, that theoretical investigations for the case of a hollow cavity in a medium of much higher refractive index may actually indicate the backward scattering to be more intense than the forward one, as actually observed with *Coracias Indica*.

## 5. A possible alternative theory

The highly saturated nature of the colours, the fact that they change, though only slowly, with the angle of observation and the change of colour produced by the penetration of water into the barbs, all conspire to indicate that the phenomena, while undoubtedly due to the presence of cavities in the material of the barb, should be classed as interference rather than as diffraction effects. The succession of colours observed correspond to the colours of Newton's Rings in the second or third order and not to those of the first order. This may perhaps be regarded as a difficulty, since if very thin films are present, one would expect that colours of the first order should also be capable of being observed in individual cases. It is clear that further investigation of the problem of light-scattering by a spherical hollow cavity in a medium of higher refractive index is necessary, before we can definitely decide between the scattering and the interference theories of the colours of *Coracias Indica*. That these colours are not a simple Tyndall blue is evident enough. The difference between the diffraction and interference theories resolves itself into a question of knowing the exact form of the cavities responsible for the return of the light from within the barb. Only in the case of simple spherical cavities would we be justified in regarding the colours as a diffraction effect. With elongated or flattened cavities, the phenomena should be assimilated with those of interference.

It is obvious that elongated or highly flattened cavities would scatter light very differently indeed from simple spherical cavities. A cylindrical cavity, for example,

would concentrate most of the light scattered by it along with the surface of a cone co-axial with itself and having its generating lines inclined to the axis at the same angle as the incident ray, but on the opposite of the normal. Then again, a flattened cavity would concentrate most of the scattered light in a single direction, namely, that of regular reflection. A simple spherical cavity, on the other hand, would distribute the scattered light impartially in all directions if it were sufficiently small.

Some insight into the form of the cavities responsible for the colours in *Coracias Indica* may be obtained by placing a feather on the rotating stage of an ordinary microscope and illuminating the same by a strong beam of light at a suitable angle. As the feather is rotated, positions are obtained in which the exterior surface of the barbs reflects light strongly and shows a brilliant white line superposed on the interior coloured background. The brightness of the colours is found to vary very strikingly at the same time, as the stage is rotated. This effect cannot be explained as due to a screening of the surface of the barbs by the barbules, inasmuch as the light is incident at a suitable angle to the surface of the barb and the latter is fully illuminated. Nor can it be ascribed to surface reflection depleting the intensity of the light entering the barb. The latter effect can completely be avoided by immersing the feather in a cell containing a suitable liquid placed on the stage of the microscope. It seems unlikely that such immersion would make any difference to the observed effects. We are thus forced to the conclusion that the cavities responsible for the colour reflection are extended structures capable of giving rise to interference effects rather than simple spherical cavities scattering equally in all directions.

## 6. Effect of penetration by liquids

In the preceding paragraphs we have already described the changes of colour produced by damping the feathers with water. Apart from the change of colour, such damping undoubtedly reduces the intensity of the colours. This is readily explained by the weakened reflections at the surface of the cavities when filled with water. If, instead of water, we use a liquid such as benzene of higher refractive index, the penetration is much slower but is ultimately more or less complete. On a rough inspection, it then appears as if the colours have disappeared. Placing the feathers under the "Ultra-opak" microscope, however, it is seen that the layer responsible for the colours, though only feebly luminous, can still be seen, the dark blue portions now appearing green and the light blue, dark red. In the absence of knowledge as to the exact extent to which the absorption of fluid might result in an enlargement of the cavities, it is not possible to definitely correlate the change of colour with the refractive index of the penetrating liquid. In a general way, however, it can be seen that the displacement of the colours towards the red end of the spectrum is what we should expect theoretically.

## 7. Summary

Observations are described with the feathers of *Coracias Indica* which throw doubt on the correctness of the theory that the blue of these feathers is a simple Tyndall effect due to the scattering of light by minute air cavities within the substance of the barb. Observations with the "Ultra-opak" microscope show that the coloured layers may exhibit tints ranging over the whole spectrum. A simple Tyndall effect is thus definitely insufficient to explain the observed phenomena. Further studies indicate that the cavities responsible for the colours are extended structures. The two alternative possibilities, namely, diffraction by cavities not small compared with the wavelength and interferences from the surfaces of minute films are considered and discussed, without a final decision being reached.

## On iridescent shells—Part I. Introductory

C V RAMAN

(Department of Physics, Indian Institute of Science, Bangalore)

Received February 15, 1935

### 1. Introduction

The study of the iridescence of nacreous shells is of importance from various points of view. The employment of the material in decorative art and for other useful purposes gives the subject some practical interest and invests it with an appeal even for the layman. Students of physical optics had long been familiar with Sir David Brewster's pioneer investigations on the origin of the colours of mother-of-pearl, references to which were to be found in most treatises on light, and were apt to imagine that the subject had been fully elucidated. This impression was dispelled by the more recent studies of A H Pfund<sup>1</sup> and of Lord Rayleigh<sup>2</sup> which served to draw attention to the subject and revealed some features overlooked by Brewster. The present investigation indicates that the subject has so far been only very imperfectly explored and offers much scope for further research.

To the chemist and the crystallographer, the structure of the nacreous substance offers problems of peculiar interest. The periodic stratifications which are characteristic of the material depend on the presence, distributed through the volume of the substance, of a small proportion of an organic compound—conchyolin—which serves to hold the particles of calcium carbonate together and gives strength and elasticity to the structure. These facts have led colloid chemists to postulate that mother-of-pearl is essentially analogous to the periodic precipitates in gels studied by Leduc,<sup>3</sup> Liesegang and others. It has even been claimed that by slow precipitation of calcium carbonate by diffusion in a gelatinous medium, structures resembling mother-of-pearl in their structure and optical properties have been synthesised.<sup>4</sup> One of the remarkable features of

<sup>1</sup>A H Pfund, *Franklin Inst. J.*, 1917, **183**, 453.

<sup>2</sup>Lord Rayleigh, *Proc. R. Soc. (A)*, 1923, **102**, 674.

<sup>3</sup>Leduc, *Alexander's Colloid Chemistry*, New York, 1928, **2**, 72.

<sup>4</sup>Clement and Riviere, *Alexander's Colloid Chemistry*, New York, 1932, **4**, 503.

mother-of-pearl is that the calcium carbonate is present in the form of aragonite instead of the commoner crystalline variety calcite. Optical and X-ray examination indicates that in many cases the crystals of aragonite are laid down with considerable regularity so as to build up the laminated structure of nacre. It may be remarked that the foliated structures containing calcite present in certain shells, e.g., the *Anomiidae*, though sometimes faintly iridescent, do not show the characteristic properties of nacre. Why the aragonitic form of calcium carbonate is preferred and what determines the size and orientation of the crystals in nacre are problems still awaiting solution.

To the zoologist, the nature of the nacreous substance in molluscan shells is part of the general problem of the structure of calcareous shells and the manner of their formation and growth from the secretions of the animal which they enclose, on which subjects there has been a great output of literature. Owing to the kindness of the present Director of the Zoological Survey of India who is himself a specialist in this field of research, I have obtained access to the most recent zoological publications on the structure of calcareous shells. Detailed references to the literature will be found later in the course of this paper. It will be sufficient here to mention the name of W J Schmidt who is very generally regarded as the principal authority in this field and whose book is an invaluable work of reference.<sup>5</sup> A very complete account of Schmidt's latest work is contained in a monograph on bivalves by F Haas.<sup>6</sup>

If anything were needed to add to the fascination attaching to the subject of the iridescence of mother-of-pearl, it is the connection between it and the study of the pearls (natural or cultured) found in association with it in molluscan shells.<sup>7</sup> It is known that the structure of pearls presents many points of analogy with that of mother-of-pearl<sup>8</sup> and the optical characters of the two substances are therefore very intimately related.

## 2. Material for the study

According to Boggild,<sup>9</sup> the nacreous substance is rather common among the three main groups of the molluscs, the Pelecypoda, the Gastropoda and the Cephalopoda, while it is never found outside the molluscs. The shell structure of the molluscs is elaborately described in Boggild's memoir and the families in which a nacreous layer is to be found are enumerated. It will be sufficient for our

---

<sup>5</sup>W J Schmidt, *Die Bausteine Des Tierkörpers in Polarisertem Lichte*, F Cohen, Bonn. 1924.

<sup>6</sup>F Haas, *Bronn's Klassen und Ordnungen Des Tierreichs*, 3, iii, 3, Akad. Verlag. Leipzig, 1931.

<sup>7</sup>L Boutan, *La Perle*. Gaston Doin, Paris, 1925.

<sup>8</sup>F Haas, *Bau und Bildung Der Perlen*, Akad. Verlag. Leipzig, 1931.

<sup>9</sup>O B Boggild, *Mem. R. Acad. Copenhagen*, 1930, 2, 235.

purpose to mention some of the material available which is specially suitable for the purpose of optical study.

The bivalves include the following families in which a nacreous layer is present: *Aviculidae*, *Pinnidae*, *Pernidae*, *Vulsellidae*, *Mytilidae*, *Nuculidae*, *Nayadidae*, *Trigonidae*, *Anatinidae*.

The large family of the *Aviculidae* is of great interest to Indian students, for in the waters of the Indian Ocean<sup>10</sup> are found some of the best known representatives; they include the Pearl-Oyster (*Margaritifera*), the Wing-shells (Aviculids proper) and the Hammer-Oyster (*Malleus*). The Indian and Ceylon Pearl-Oyster (*Margaritifera vulgaris*) is amongst the smallest of its kind and compares unfavourably in size with the huge Gold-lip Pearl-Oyster from Mergui and the South seas, a species with shell large enough for a dinner-plate. The larger Black-lip Oyster (*M. Margaritifera*) is also occasionally found in the Indian seas, and is a handsome stoutly-built shell with a thick layer of nacre. Figure 8 in the plate represents a carved shell of pearl-oyster exhibiting a beautiful lustre and iridescence. The Aviculids proper, the true Wing-shells, have often very curious shapes (e.g., *Pteria castanea*, *Pteria semisagitta*), and include some larger forms (*Pteria macroptera*) displaying plenty of iridescent nacre. The *Pinnidae* are represented in Indian waters by several species of which the commonest is *Pinna bicolor*, a big wedge-shaped shell often a full foot in length, and *Pinna fumata* which is shorter and stouter. *Vulsella rugosa*, a deep oblong shell without ears is the chief Indian representative of the *Vulsellidae*. The *Mytilidae* form a large family, the three common genera in Indian seas being *Mytilus*, *Modiola* and *Lithodomus*. Deserving of special mention is the very handsome green mussel (*Mytilus viridis*) widely distributed round the South Indian Coast and readily recognised because of the striking green colouration of the horny membrane or periostracum investing the exterior surface of its valves. This shell can be found in fairly large sizes and displays a beautiful and characteristic iridescence in its nacreous layer. Amongst the numerous fresh-water bivalves of 'India,'<sup>11</sup> the mussel *Lamellidens marginalis* is a conspicuous species. It has a thick layer of nacre which, however, exhibits little colour.

The gastropods, according to Boggild, include the following families in which a nacreous layer is present:

*Pleurotomariidae*, *Haliotidae*, *Stomatidae*, *Turbinidae*, *Delphinulidae*, *Trochidae*, *Umboniidae*.

This group of molluscs includes some of the most gorgeously iridescent shells known, amongst which should be mentioned particularly the *Haliotidae*, the

<sup>10</sup> J Hornell, *The Common Molluscs of South India*, Govt. Press, Madras, 1924.

<sup>11</sup> H B Preston, *Fauna of British India: Freshwater Molluscs*, London, 1915.

*Turbinidae* and the *Trochidae*. A common Indian species among the Ear-shells is *Haliotis varia*, which, however, is quite a small one, seldom exceeding  $1\frac{1}{2}$  inch in length—a poor representative of the family. Much larger specimens of the *Haliotidae* are to be found in the waters around France, Japan, New Zealand and California, attaining lengths from 4 to 6 inches and displaying a vivid colouration of the mother-of-pearl lining of the shell. The Californian specimens of the *Haliotidae*, known locally as the abalone, are the most remarkable in this respect. At least three distinct species of abalone are known which differ greatly in their optical characters, as will be described more fully later. The polished convex surfaces of the shells of two species of abalone are illustrated in figures 1 and 2. Other species of *Haliotidae* of large size are known which differ from the abalone in being far more translucent to light. The *Turbinidae* and the *Trochidae* include numerous species and are some of the commonest shells to be met with on the South Indian littoral, but usually only in relatively small sizes. Very large specimens of *Turbo* and *Trochus* are, however, available from the vicinity of the Andaman and Laccadive islands, and when cleaned and polished externally make a remarkable display of lustre and iridescence. One such shell of *Turbo* (not of specially large size) is illustrated in figure 3. *Trochus* shells in large sizes also make beautiful and lustrous objects when the nacreous layer is exposed, though the colours are less vivid than with *Turbo* shells. One such shell of *Trochus* from which the periostracum and prismatic layer had been brushed out with dilute hydrochloric acid is illustrated in four different positions in figures 4, 5, 6 and 7. The conical form, the spiral structure, the sculpturing on the ridges and the lines of growth on the nacre are all beautifully seen.

Unique amongst the Cephalopods is the well known *Nautilus pompilius*, shells of which are a familiar sight on tropic beaches. Many text-books on Zoology contain figures of the remarkable internal architecture of this shell containing a series of septa with a perforation running through them. In the natural state, the shell is covered externally with a thin white enamel-like layer ornamented with brown stripes. When this is brushed off with dilute acid, the beautiful nacreous substance is exposed which exhibits bands of colour following the visible lines of growth on the shell. One such specimen, unfortunately incomplete, is illustrated in figure 9. The septa which may be exposed by sawing the shell in two also consist wholly of nacre. It may be mentioned that the septa of the beautiful little *Spirulidae* are nacreous but are not iridescent.

### 3. Structure of iridescent shells

The shell structures of molluscs generally, and in particular, the structures of the various layers in iridescent shells have been the subject of elaborate investigation by zoologists. Accounts of the subject are given by W J Schmidt in his book, by Boggild in the memoir already quoted, and a detailed review with numerous

illustrations in F Haas's monograph on the bivalves. The subject has been studied mainly by the examination under the polarisation microscope of thin sections of the shell cut in one or another of three perpendicular directions, namely parallel to the surface of the shell, transverse to the surface and either parallel or perpendicular to the lines of growth on it. Many photographs under low magnifications of such sections illustrate Boggild's monograph. It appears that the nacreous structure is only one of the numerous forms which the calcareous substance in shells can assume. Boggild describes no fewer than eight different modes of aggregation, the four commonest according to him being "the homogeneous", "the prismatic", "the crossed lamellar" and "the nacreous" structures. A fifth kind namely "the foliated structure" is of special interest as it also exhibits a pearly lustre and appears in certain families, namely in the *Ostreidae*, *Pectinidae*, *Spondylidae* and the *Anomiidae*; it differs however from the nacreous structure in being less regular and in being composed of calcite instead of aragonite.

In all iridescent shells, we have at least three layers, the first and outermost being the periostracum which is a thin layer of organic material known as conchin or conchyolin. This is followed by a second layer which in most bivalve shells is prismatic in structure, but in certain others, e.g., the *Mytilidae*, the *Stomatidae*, the *Turbinidae* and the *Trochidae*, is "homogeneously prismatic" and in the *Haliotidae* "homogeneously grained". This second layer is followed by the nacreous substance which save in a very few cases is the innermost or final layer.<sup>12</sup> The outer layers namely, the periostracum and the prismatic layer, may be removed mechanically, or alternatively by brushing with dilute hydrochloric acid which acts upon them more readily than upon the nacreous substance. The latter which is thus exposed may then be ground and polished in order the more effectively to display its optical properties.

The chemical and physical nature of the nacreous substance has been elaborately investigated and described by W J Schmidt and illustrated by numerous diagrams and photographs. We may here quote Schmidt's definition of the nacreous substance. "Mother-of-pearl consists of microscopically small, tablet-shaped crystals of aragonite formed along the basis, the so-called platelets of mother-of-pearl,—which are regularly arranged in positions parallel to the surface of the shell and are cemented together by an organic substance, the so-called conchin or conchyolin." The platelets so held together form elementary laminae and these are in their turn superposed on one another in great numbers and cemented together by immeasurably thin layers of the same organic substance. The individual platelets of aragonite are about  $10\mu$  in diameter; they are sometimes rounded in form (for instance in *Meleagrina* and *Pinna*), sometimes

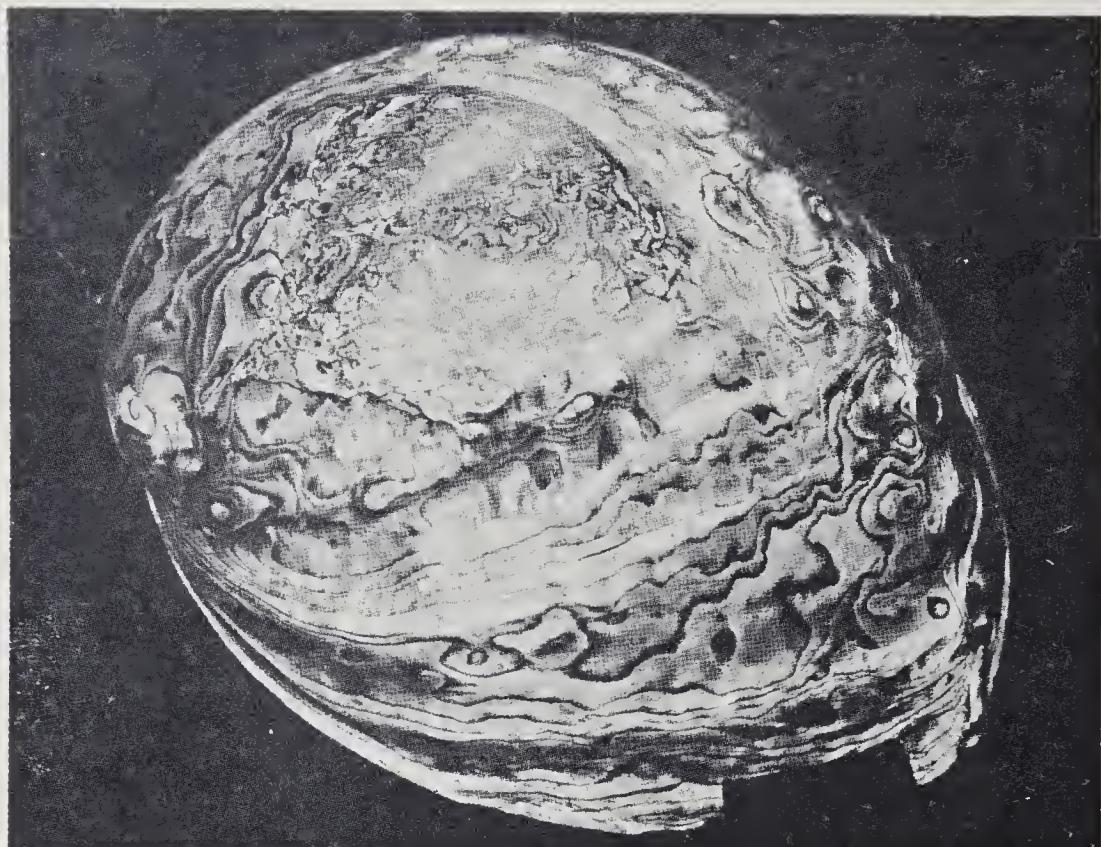
---

<sup>12</sup>"The Helle Schicht" or "Hypostrakum" which appears on the shell at the regions of attachment to it of the muscles of the animal is regarded by Schmidt as merely a modification of the nacreous layer, but this is a disputed point.

bounded by straight edges (e.g., in *Mytilus*) and may also assume other shapes. The thickness of the elementary laminae corresponds to that of the platelets of which they are composed, and is of the order of magnitude  $1\mu$  but may vary between the extreme limits  $0.5$  and  $2\mu$  in different species. According to Schmidt, the statement often found in the older text-books that mother-of-pearl consists of alternate and equally thick layers of calcareous and organic material is definitely erroneous. (This erroneous statement is, strangely enough, repeated by Boggild in his memoir quoting Schmidt as his authority.) That the actual thickness of the organic layers is immeasurably small compared with that of the aragonite layers has been inferred by Schmidt from his observations of the cross-sections of mother-of-pearl under the highest available magnifications.

From his studies of cross-sections of mother-of-pearl under the polarisation microscope, as also of the tiny crystalline platelets separated by digesting the material with alkali, Schmidt drew important conclusions regarding the optical characters of the substance. According to him, mother-of-pearl is an aggregate of crystals, which both in the individual elementary laminae and also in neighbouring ones are arranged essentially parallel to one another. This regular arrangement of innumerable single crystals explains the more or less complete optical homogeneity of the substance, as shown by the more or less uniform extinction and axial picture which is determined by the aggregate effect of the regularly-arranged ultimate units. The transverse cross-sections have their extinction parallel to the laminae and always behave as optically negative with reference to the normal to the laminae. The parallel sections have their extinction parallel to the lines of growth on the shell and generally behave as positive (rarely as negative) with reference to this direction. The normal to the laminae is the first middle line of the axial picture seen in the parallel section. The *c*-axis is therefore normal to the elementary laminae, and the lines of growth lie in the axial plane and are parallel to the macro-axis. (In rare cases, the axial plane and the lines of growth cross each other, and the latter then correspond to the brachy-axis.) The form and arrangement of the platelets determine the structure of the substance, and the intimate connection between the morphological structure and the optical properties is thus explained. Smaller and larger disturbances of the regularity of the structure show themselves in the incompleteness and irregularity of the extinctions and the varying values of the axial angles.

*Note*—The photographs illustrating this paper were taken by Mr C S Venkateswaran to whom my best thanks are due. To Dr Baini Prashad, Director of the Zoological Survey of India who furnished me with valuable specimens and loaned a collection of zoological literature I am greatly indebted. Dr H Srinivasa Rao, of the Zoological Survey, has also very kindly presented to me a collection of *Trochus* and *Turbo* shells from the Andamans. The scientific results of the study of the material placed at my disposal by these and other friends will be reported upon in the subsequent instalments of the paper.

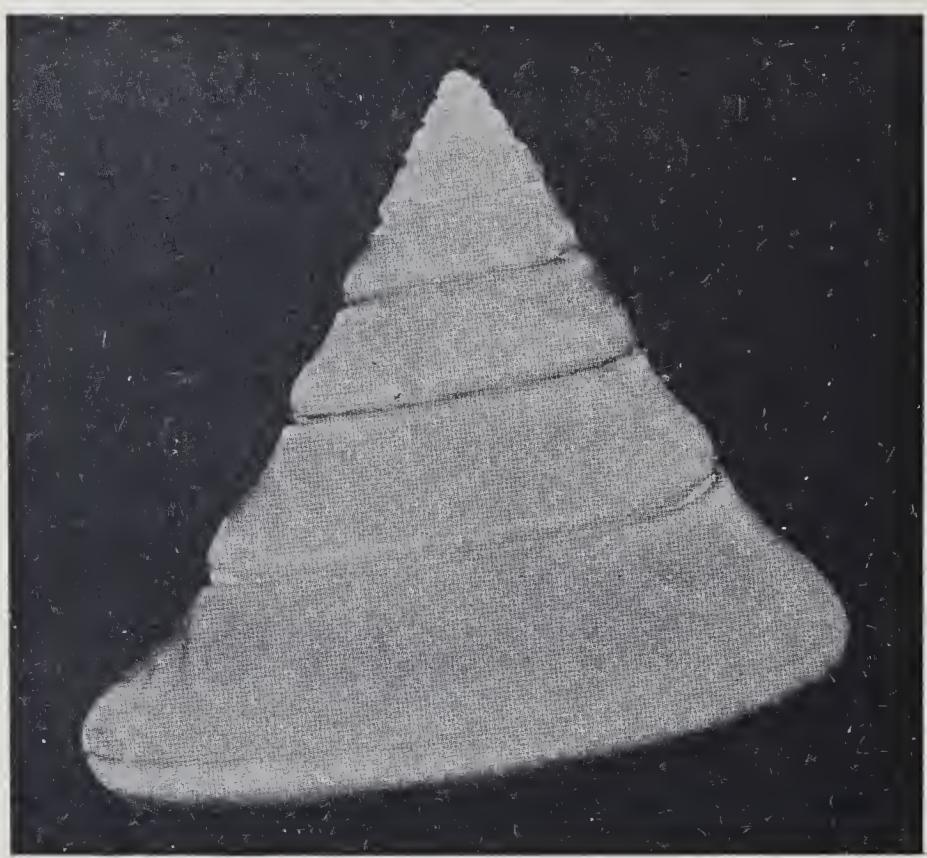


**Figures 1 and 2.** Abalone shell (*Haliotis* Sp.).  
Plate I



Figure 3. Shell of *Turbo* Sp.

Plate II



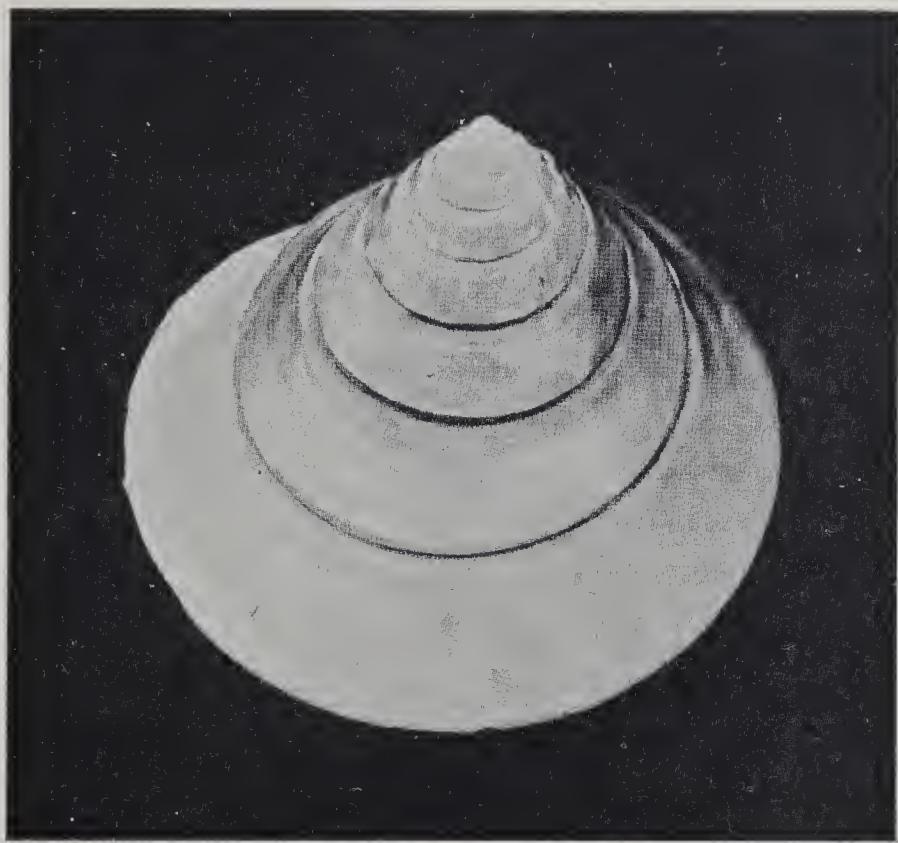
(4)



(5)

Figures 4 and 5. Shell of *Trochus* Sp.

Plate III

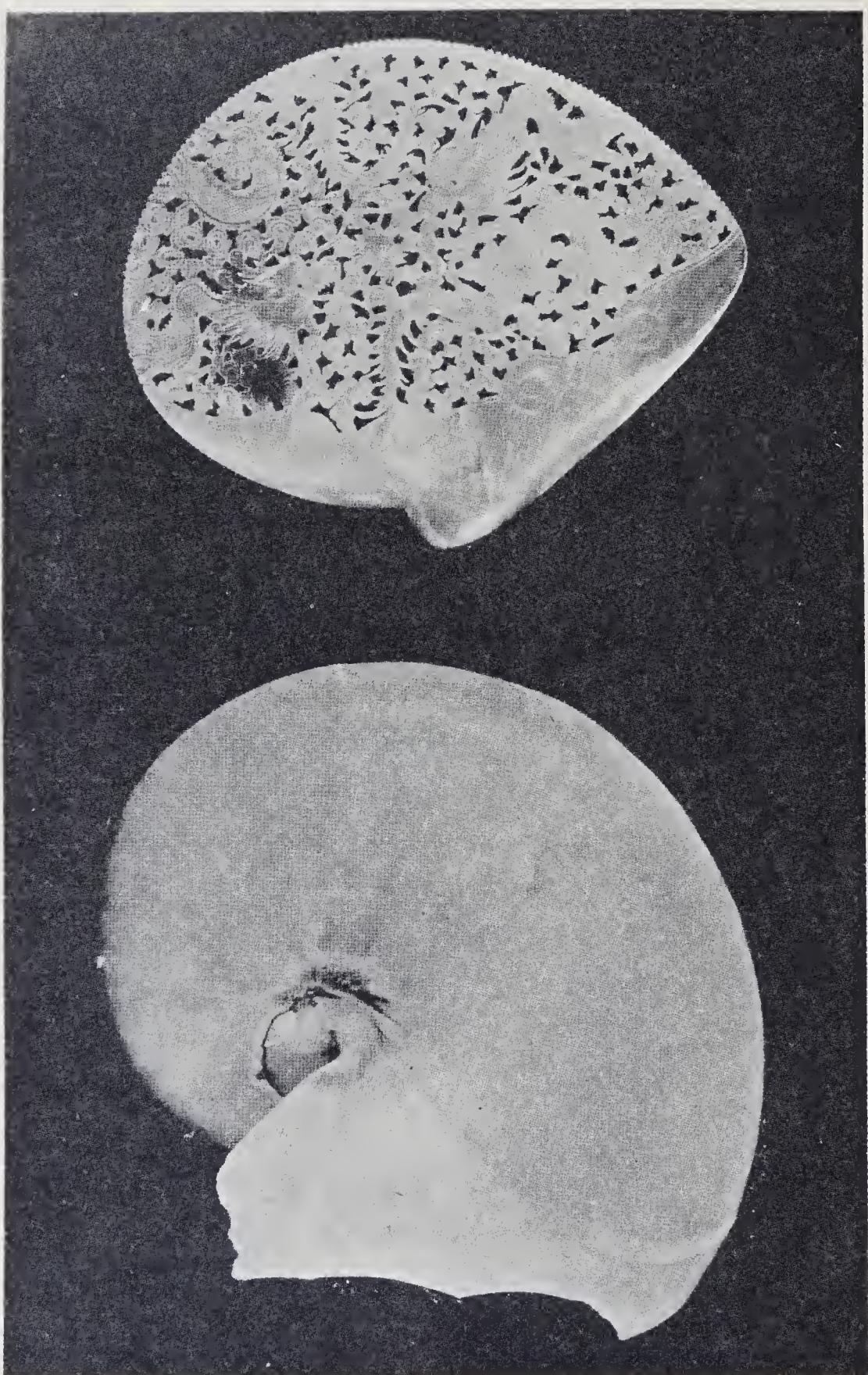


(6)



(7)

**Figures 6 and 7.** Shell of *Trochus* Sp.  
**Plate IV**



Figures 8 and 9. 8. Shell of *Margaritifera*. 9. Shell of *Nautilus pompilius*.

Plate V

## On iridescent shells—Part II. Colours of laminar diffraction

C V RAMAN

(Department of Physics, Indian Institute of Science, Bangalore)

Received February 15, 1935

### 1. Colours of stratified films

The late Lord Rayleigh<sup>1</sup> was the first to draw attention to the special character of the iridescence exhibited by regularly stratified films, namely that a narrow region of the spectrum is strongly and selectively reflected. Several examples of such iridescence are known, e.g., Lippmann's spectrum photographs in natural colours, twinned crystals of potassium chlorate, fiery opals and the metallically coloured wing-cases of certain beetles.<sup>2</sup> In the case of iridescent shells, we have three special features which distinguish it from the examples cited: (1) the internal laminations are nearly always inclined to the external surface instead of being parallel to it; (2) the laminae are granular and not homogeneous in structure; (3) considerable thicknesses of the material have usually to be considered and not thin films. Before we consider the special effects arising from these causes, it is useful to recall the features exhibited by the simpler cases mentioned above.

The theory of the reflection of light by a stratified film has been discussed by Rayleigh.<sup>3</sup> His investigation indicates that the permissible cases fall into one or another of two classes, the first in which the reflection tends to become complete as the number of laminae becomes large, and the second in which the reflection and transmission remain fluctuating however great this number may be. Whether the one or the other state obtains is determined by the relation between the reflecting power of the individual laminae and the phase relation between the reflections occurring at the successive laminae. If the reflecting power of each lamina be small, many laminae are required even with the most favourable phase-relations to give a tolerably complete reflection and a nearly complete cut-off in transmission. The reflection is at the same time highly selective in respect of its

<sup>1</sup> Rayleigh (I), *Scientific Papers*, 3, 1, 190, 204, 264.

<sup>2</sup> Old decomposed glass also shows a marked iridescence due to a stratified film covering it.

<sup>3</sup> Rayleigh (I), *Proc. R. Soc. London*, A93, 565 (1917), also *Scientific Papers*, 6, 492.

spectral character. On the other hand, if the individual reflections be strong, fewer laminae suffice to give a strong reflection, and a correspondingly broader spectral range of reflection is obtained. The effects of varying the factors involved, namely the spacing of the laminae, their reflecting power and their number, may be studied with the examples of stratified films already mentioned. The spectrum of the reflected light frequently includes not one, but several bands, these representing successive orders of interference. The light reflected at nearly normal incidence exhibits comparatively narrow bands in its spectrum; as the angle of incidence is increased, these bands move towards shorter wavelengths and increase rapidly in width. Very interesting effects are noticed when the number of laminae operative is limited; in such cases, the bands of maximum reflection in the spectrum of the reflected light are accompanied by subsidiary bands of smaller intensity on either side of them. The appearance of these secondary maxima is readily understood by analogy with the secondary maxima observed in diffraction spectra with gratings having a finite number of rulings.

## 2. Laminar diffraction spectra

As is well known, Sir David Brewster who investigated the colours of mother-of-pearl classified them under two heads, what he called transferable and non-transferable colours. The former could be transferred to gelatine or other soft substances employed to take an impression of the surface of the material, and hence it was inferred that they were due to diffraction by grooves on the exterior of the nacreous substance. The non-transferable colours on the other hand were regarded as interference or thin film colours due to the internal reflecting layers. The grooves on the surface capable of diffracting light were interpreted as the outcrops of these internal stratifications. Later writers have accepted Brewster's classification without comment. A little consideration will show, however, that this separation of the optical effects into two independent and superposable phenomena is not justifiable. Assuming that the laminae meet the surface at an angle and that in consequence the surface is grooved, diffraction effects must arise not only when the light is incident externally on the surface, but also when it emerges at the surface after suffering reflection at the internal laminations. The non-transferable diffraction effects arising in this way should be quite as important as the transferable effects associated with the comparatively weak reflection at the external surface. Further, as both the externally and internally reflected wave-trains are derived from the same original beam, the effects arising from them would be coherent and capable of interfering with each other and not simply superposable. These considerations indicate that the phenomena observed should be considered as a whole, and that the optical effects exhibited by a cast of the surface would be very different from those actually observed at the surface of the shell. Even if the latter were perfectly plane, the laminations meeting

the surface obliquely would in effect form a grating giving rise to diffraction effects of a non-transferable character.

The full significance of the foregoing remarks is best indicated by the results of a simple experiment. A narrow pencil of light is allowed to fall on the polished surface of an iridescent shell. A polished piece of *Turbo* shell serves admirably for this purpose, and in fact *Turbo* was the species of shell with which the observations to be described were first made, though other species may also be successfully employed. The pencil of light after falling on the surface and being reflected by it is received on a white screen. It is then found that the reflected pencil is accompanied by diffraction spectra. With the particular specimen of *Turbo* shell, three spectra were conspicuously observed on one side of the reflected light, and only one on the other (figure 1). The first-order spectra on both sides showed the complete set of colours present in white light. But the second-order and third-order spectra which were present only on one side did not show all the colours of the spectrum, and the third-order spectrum in particular, though very intense, exhibited only one pronounced colour, namely that of the characteristic green iridescence of the shell for the particular angle of incidence. In other words, *the characteristic iridescence of the shell appeared as the third-order diffraction spectrum due to the laminar grating formed by the surface of the shell.*

An interesting variation on the experiment is made by cementing a thin microscope cover-slip of glass with a little Canada-balsam on the surface of the shell and reflecting a pencil of light from it at the same angle of incidence as previously (figure 2). It will be noticed that all the diffraction spectra disappear except the third-order spectrum on one side which remains in identically the same position. The effect of the Canada-balsam is virtually to suppress the grooves present externally on the surface of the shell. But the periodic internal structure persists and gives rise to the characteristic reflection at the same angle of diffraction as previously. Examination of the third-order spectrum with a pocket spectroscope shows that only a comparatively narrow region of the spectrum has an appreciable intensity in it. Experimenting with different shells and even with different areas on the same shell, it is found that *the characteristic iridescence may sometimes appear as the diffraction spectrum of the second order instead of as the third. A superposition of the second and third orders for wavelengths near the two ends of the visible spectrum may also be observed in certain cases. The iridescence then appears as a mixed colour instead of being monochromatic.*

That the direction in which the light of appropriate wavelength reflected by the internal laminations emerges should be identical with that of one of the diffraction-spectra produced by the surface of the shell is intuitively evident and may be readily proved theoretically. In figure 3(a) and (b) we have the internal laminations meeting the surface at an angle  $\alpha$ . If  $d$  is the thickness of the laminations, the grating space on the surface is  $d \operatorname{cosec} \alpha$ . We denote by  $\theta$  and  $\phi$  the angles of incidence and refraction of the in-falling light, and by  $\psi$  and  $\chi$  the

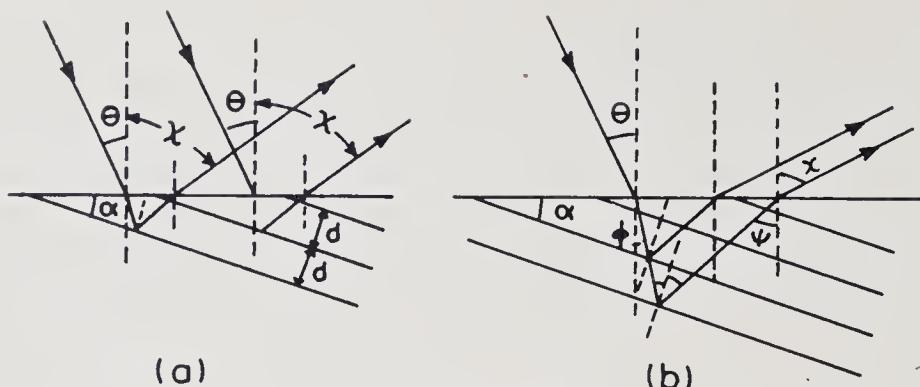


Figure 3. Identity of direction of iridescent reflection with diffraction spectrum.

angles of incidence and refraction of the beams emerging from the surface of the shell.

For the diffraction at the surface of the shell, we have the usual grating formula (figure 3a)

$$d \operatorname{cosec} \alpha (\sin \chi - \sin \theta) = \pm n\lambda. \quad (1)$$

The beam of light entering the substance of the shell is incident on the internal laminations at the angle  $(\phi + \alpha)$ , and the wavelength of the characteristic reflection is given by the usual formula (figure 3b)

$$2\mu d \cos(\phi + \alpha) = n\lambda. \quad (2)$$

But

$$\sin \theta = \mu \sin \phi, \quad \text{and} \quad \sin \chi = \mu \sin \psi, \quad \text{where } \psi = \phi + 2\alpha. \quad (3)$$

Substituting these in formula (1), the latter assumes the form

$$2\mu d \cos(\phi + \alpha) = \pm n\lambda, \quad (4)$$

which is identical with (2) except for the presence of the alternative signs  $\pm$ . In other words, *the internal reflection emerges from the surface of the shell in a direction coinciding with one of the orders of diffraction spectra produced by the surface of the shell*, on the side corresponding to a positive value of  $n(\chi > \theta)$ . The order of the spectrum which exhibits the characteristic colour is also the order of interference of the light reflected from the successive internal laminae.

The foregoing formulae admit of ready experimental check. The grating space  $d \operatorname{cosec} \alpha$  may be directly measured on the surface of the shell by observation under the microscope. The angles of incidence and emergence  $\theta$  and  $\chi$  at the surface of the shell can be measured on a divided circle. The order of interference  $n$  is directly accessible to observation, and the wavelength of the iridescent reflection can be read off with a pocket spectroscope having a scale in the eye-piece. The quantities appearing on both sides of formula (1) are thus completely accessible to observation and should check each other. The three equations (3) contain four

unknowns,  $\phi$ ,  $\psi$ ,  $\alpha$  and  $\mu$ , and one additional observation should therefore enable all the quantities to be determined. For instance, if  $\mu$  were determined by some independent method, the formula would enable us to evaluate  $\phi$  and  $\alpha$ , and therefore also from (2) the value of  $d$ . What the measurements would enable us to do in effect is to check the assumption that the spacing of the laminae visible on the surface should agree with that calculated from the internal spacing of the laminae meeting the surface obliquely at a known angle. That such a check would not be superfluous is indicated by a discrepancy encountered by Lord Rayleigh (II) who found that he had to multiply by two the optically determined spacing in order to obtain a value for the spacing of the laminations agreeing with that observed microscopically in a cross-section of mother-of-pearl. Rayleigh endeavoured to explain this on the assumption that the alternate layers of aragonite and of organic material have equal thickness and the same refractive index, and that the optical spacing should therefore be half that observed under the polarisation microscope.<sup>4</sup> According to Schmidt, however, whose conclusions are supported by strong evidence, the organic layers are excessively thin in comparison with the aragonite layers and the spacing observed under the microscope and deduced optically should be identical. It appears likely that the discrepancy encountered by Rayleigh is not real but is due to the difficulty of interpreting the microscopic appearances.

As an illustration of the foregoing theory and of its agreement with the facts may be mentioned some observations made with a piece of *Turbo* shell which gave a greenish-blue iridescence appearing in the third-order diffraction spectrum. The following were the observational data:

$$\theta = 0^\circ, \quad \chi = 24^\circ 8', \quad n = 3, \quad \lambda = 5000 \text{ A.U.}$$

From these data, the grating space on the surface was calculated. The refractive index of the material was determined by observing the Brewsterian angle of complete polarisation of the reflection from the polished surface of the shell and was found to be 1.66. Using this value of  $\mu$ ,  $\alpha$  is calculated from equation (3), and hence from equation (4)  $d$  can be calculated. It is thus found

$$d = 0.456 \times 10^{-3} \text{ mm.}, \quad \alpha = 7^\circ 9', \quad d \operatorname{cosec} \alpha = 3.66 \times 10^{-3} \text{ mm.}$$

The grating space on the surface directly observed under the microscope was  $3.69 \times 10^{-3}$  mm showing satisfactory agreement with the optically determined value.

<sup>4</sup>Rayleigh's argument (*Proc. R. Soc. London*, **102**, 677, 1923) appears a little difficult to follow. The refractive indices of the aragonite and conchyolin layers must differ at least slightly for any reflection to be possible. Phase changes must, therefore, occur in reflection which are different at the alternate boundaries. The optical spacing would, therefore, in any case be determined by the thickness of both layers considered together and not that of either layer separately. As will be remarked later, the effects observed when the surface of iridescent shell is examined under the "ultra-opak" microscope support Schmidt's view of the structure of nacre.

### 3. Effect of grinding and polishing on surface structure

Nearly all nacreous shells which exhibit iridescence do so in their natural state on their inner concave surfaces. In some cases it may be possible to expose the other (convex) surface of the nacreous layer by simple mechanical removal of the super-incident layers. It is thus possible, at least in many cases, to study the iridescence of the material in its natural state. This procedure is, however, not very convenient. Owing to the curvature of the surfaces and their inevitable optical imperfections, the shells in their natural state do not lend themselves to optical investigation so well as material prepared therefrom by cutting, grinding and polishing. As is well known, mother-of-pearl lends itself readily to mechanical working and takes a good polish, and indeed its practical utility as a decorative material depends to a great extent on these valuable properties. So far as the optical effects arising from the internal structure of the material are concerned, it is obvious that optical preparation of the external surfaces would facilitate rather than interfere with their study. It is very remarkable that even the surface or diffraction effects are more conveniently studied with artificially prepared material. Why this is so will presently be explained. It may be remarked that the general appearance of an iridescent shell as well as the more recondite phenomena observed on detailed examination are largely determined by the inclination of the internal laminations to the external surface of the shell. The form of these laminations depends on the shape and structure of the shell and is of course fixed, while the exterior surface of the shell (and, therefore, also the angle at which it meets the laminations) can be artificially determined by grinding and polishing the material. How greatly the form of the internal laminations may vary in different species of shell is evident on a comparison of figures 1 and 2 in paper I of this series which represent the ground and polished convex surface of two abalone shells. The ripplings which form so conspicuous a feature in figure 2 are due entirely to light reflected by the internal laminations and do not exist on the external surface.

The nature of the structure existing at the surface of the shell and the effects produced on it by grinding or polishing the material are obviously very relevant to our investigation. That all the diffraction spectra other than that corresponding to the characteristic iridescence disappear on covering the surface with a layer of Canada-balsam and a glass cover-slip indicates that the surface even after grinding and polishing is not optically plane, but is of grooved form. The explanation of this is to be found in the fact that the material is not very hard and is readily abraded even by the mildest agents. Examination under the microscope indicates a strongly pronounced tendency for the material to break off under the action of an abrasive, leaving the surface in the form of terraces or steps with sharp edges. Polishing tends to round off the edges of these terraces but only very slowly. Very prolonged polishing is required before all trace of periodicity on the external surface is lost.

Very interesting changes are observed in the relative intensity of the diffraction spectra produced by the surface of the shell during the process of polishing. When the surface is still rough with pronounced terraces, the ordinary white light reflection is very weak, and most of the light is thrown into the first-order diffraction spectrum on one side which is intermediate in direction between the ordinary (white) reflection and the characteristic (iridescent) reflection from the surface of the shell. The iridescent reflection is also rather weak and diffuse. In a general way, these facts are readily understood, if we recollect that the appearance of terraces with sharp edges on the surface *ipso facto* involves an inclination of the level of the surface to the surface of the individual terraces. The diffraction effects produced by the rugosities on the surface must, in these circumstances, be very pronounced and at the same time very unsymmetrical. As the polishing proceeds, the ordinary reflection brightens up, the first-order spectrum on the one side falls off in intensity and the first-order spectrum on the other side begins to appear. The iridescent reflection also brightens up and becomes better defined in direction. The asymmetry of the diffraction pattern, however, persists even after prolonged polishing, being evidently the result of the inclination of the internal laminations to the external surface.

An interesting example of material prepared by grinding and polishing for the investigation of iridescence is the box covered by pieces of abalone shell (ground, flat and polished from the natural material) a photograph of which is reproduced as figure 4 of the present paper. The photograph was taken under the oblique illumination from a mercury lamp, and a patchiness due to the internal reflections being at various angles is very noticeable, the brighter areas representing places where the iridescent reflections occurred in such directions that they reached the lens of the camera. Figure 17 represents one end of the same box photographed under the 4358 A.U. radiation of the mercury lamp. The illumination in this case was approximately normal but indirect being due to a large sheet of Bristol board with an aperture in it encircling the lens of the camera. The appearance of the surface as seen by reflected light is made more uniform by this arrangement, but even so, it will be noticed that considerable areas of the mosaic are quite dark, and these represent areas where the coloured internal reflections were quite strong but so oblique that they could not be caught by the camera. Very interesting and conspicuous features are the ring-shaped structures seen in many pieces of the mosaic. These consist of lustrous areas of nacre separated by dark regions which do not exhibit any iridescence. In each case, the centre of the ring system represents an area where the coloured reflections are normal to the surface, while in the surrounding rings, they occur at greater obliquities. Each ring-system, in fact, presents by reflected light, the illusion of a hollow cup viewed from the concave side. Actually, the illusion has some correspondence with reality, as it indicates that the laminations responsible for the iridescence take the form of concave surfaces which meet the polished exterior of the plate at various angles. Most of the pieces of shell in the mosaic which showed ring-systems presented the

illusion of a hollow cup while only three presented the illusion of a *convex* surface. It is evident that these three pieces unlike the others, had been polished flat from the convex side of the natural curvature of the shell.

#### 4. Observations with the ultra-opak microscope

Very remarkable effects are observed when the abalone box illustrated in figure 4 is examined on the stage of the Leitz ultra-opak microscope. The latter instrument has already been referred to in a paper in these *Proceedings*<sup>5</sup> on the colours of birds' feathers. It is essentially an opaque illuminator of the kind used for metallurgical work, the source of light being an 8-volt lamp in a side tube attached to the microscope. The beam of light consists of a hollow cylindrical pencil of rays which is reflected downwards and instead of, as in metallurgical microscopes, passing through the objective, envelopes the latter and is focussed as a hollow cone of rays having its vertex on the surface under examination. The instrument thus combines the principles of opaque lighting and of dark-ground illumination, and is exceptionally suitable for examining optical surfaces that reflect and diffract light. A very useful device supplied with the instrument is a diaphragm with a variable sector opening which can be inserted in the path of the cylindrical beam of light before it goes down the microscope tube. By narrowing the sector, and turning it round, we can arrange that instead of a complete hollow cone of rays being focussed on the surface, only a sheaf of rays of any desired angular opening adjacent to a particular generator of the cone is used to illuminate the surface. A sector of 90° opening is convenient and gives four distinct positions of the illuminating beam as it is turned round to successive quadrants. The unsymmetrical illumination of the surface obtained in this way is very useful. The microscope has a series of objectives and eye-pieces. The angle of the cone of the illuminating beam increases with the power of the objective, and the luminous effects observed with the lower-power objectives therefore differ greatly from those seen with the higher powers. In what follows will be described the effects observed with one of the objectives of higher powers ( $\times 11$ ). (The effects observed with lower powers will be dealt with in later papers of the series).

*Effects observed with hollow cone illumination:* On examining the pieces of abalone shell forming the mosaic on the box, it is noticed immediately that the surface exhibits a large number of sharp luminous lines on a relatively dark field, the lines in many cases exhibiting vivid colours. Photographs of the phenomenon (without the beautiful colour effects) are reproduced in figures 5 to 13. It will be

---

<sup>5</sup>C V Raman, *Proc. Indian Acad. Sci.*, 1934, 1, 1.

noticed that while the lines are equally sharp in all these figures, the configuration and distance of the successive lines vary greatly. Very simple and general rules connect the form and spacing of these lines with the optical behaviour of the particular part of the shell under examination. (a) If the laminations responsible for the iridescence are nearly plane and parallel to the external surface, the luminous lines seen on the latter are relatively few and far apart; they are then either irregular in shape or else form closed curves, and their colours are less prominent. (See figures 5, 6, 7, 9, 10, 11 and 12 for example). (b) If, however, the laminations are rather oblique to the surface, the lines seen on the latter are much more numerous, close together, run approximately parallel to each other in any limited field of view and also exhibit more striking colours. (See figures 8 and 13 as examples). (c) If the inclination of the laminae to the surface is very considerable, the lines are very close and may cease to be resolved by the microscope with the powers used. (d) If the inclination of the laminations to the surface is so considerable that the iridescent reflections enter the objective of the microscope, the lines appear superposed on a bright field and may even become invisible. (e) Irregularities in the laminations result in corresponding irregularities in the lines seen on the surface, and also in patches of light seen here and there in the field of view. (See figures 12, 13 and 16 as examples.)

The features described above indicate that the luminous lines seen on the surface represent the edges of the terraces on the exterior surface of the shell. This is definitely proved by the fact that the luminous lines weaken or disappear when the surface is covered over with a layer of Canada-balsam and a slip of glass, or if the polishing of the surface be sufficiently prolonged. There seems little doubt also that the edges of the terraces coincide with the curves along which the internal laminations meet the surface of the shell. This point is particularly convincingly shown by examining a ring structure of the kind seen in figure 17 under the microscope. It will then be seen that the luminous lines are themselves rings running round the system in approximately the same way as the visible areas of colour. The spacing of the lines is extremely large in the centre of the ring-system and gets closer and closer together in the outer rings, as is to be expected from the increasing obliquity of the laminations to the surface. The sharpness of the edges which is unaffected by their spacing on the surface is most easily understood if we assume that they coincide with the intersections of the surface with the excessively thin organic layers separating the layers of aragonite postulated by Schmidt.

*Effects observed with sector illumination:* Some very interesting modifications of the effects described above are observed, if instead of using the complete cone of  $360^\circ$  illumination, we use only a sector of small opening, say,  $45^\circ$  in the microscope and place it successively in four positions  $90^\circ$  apart. If a field such as that shown in figure 8 or figure 13 composed of lines running approximately parallel and close together is observed in this way, we see the following sequence

of effects in four positions of the sector  $90^\circ$  apart:

- (a) Lines bright and strongly coloured.
- (b) Lines invisible.
- (c) Lines weak and yellowish white.
- (d) Lines invisible.

These changes clearly indicate that the luminosity of the edges is due to diffracted light radiating from them in the form of cylindrical waves, and further that the diffraction is strongly asymmetrical with reference to the normal to the surface of the shell and the diffracting edges.

The same effects can be shown in a different way by observing a field consisting of lines forming closed curves; firstly with the complete cone illumination (see figure 10), and then with a sector of  $90^\circ$  opening in two positions  $180^\circ$  apart. The very great difference in the intensity of the lines running parallel to each other but in opposite directions in the two positions of the sector, can be seen on comparing figures 9 and 11 which represent identically the same field illuminated by a  $90^\circ$  sector in two positions  $180^\circ$  apart.

## 5. Interpretation of the effects

There can be no doubt that the phenomena described in the preceding section are essentially diffraction effects due to the sharply-defined laminar edges producing an abrupt difference of phase in the optical wave-front on either side of them. Such laminar boundaries can easily be obtained by splitting a piece of mica not quite evenly with the result that the thickness of the split mica is not absolutely identical throughout, but differs very slightly in different parts. On examining such a piece of mica under the ultra-opak microscope, the lines separating the parts of the mica with slightly different thicknesses are seen as bright lines in a dark field. On putting in a  $45^\circ$  sector in the illuminating tube and rotating it, a sequence of effects somewhat similar to those described in the preceding paragraphs is observed. The colours of laminar diffraction exhibited by the striae in mica<sup>6</sup> were observed many years ago and were subsequently investigated by P N Ghosh, N K Sur and I R Rao and described in a series of papers from Calcutta. The effects noticed in the present case, while essentially analogous to those observed with mica exhibit important differences in detail due to the altered circumstances of the case. Instead of a discontinuity of thickness in the surface of a plane-parallel plate, we have in the present case, a series of edges forming a diffraction-grating which terminate sloping terraces on the surface of the material. Further, we are concerned simultaneously with the light incident externally on the surface and with light emerging after reflection at the internal laminations.

---

<sup>6</sup>C V Raman and P N Ghosh, *Nature*, 1918, **102**, 205.

The most obvious way of interpreting the effects observed in the ultra-opak microscope and described in section 4 is to connect them with the laminar diffraction spectra described in section 2 and illustrated in figure 1 of the present paper. The laminar edges are in fact responsible for the diffraction spectra, and all that the microscope does is to collect the diffracted rays and focus them as images of the edges themselves. The colours exhibited by the edges as seen in the microscope are, therefore, determined by the predominant wavelengths in the bundle of diffracted rays entering the objective of the microscope and focussed by it. The unsymmetrical distribution of intensity of the diffracted rays, and especially the changes of colour and intensity observed as the illuminating sector in the microscope is rotated are naturally interpreted as consequences of the unsymmetrical distribution of intensity in the diffraction spectra. The edges exhibit the most striking colours when observed by the rays diffracted by them in directions not too far removed from that of the characteristic iridescent reflection. In directions lying on the remote side of the normal to the plate where the higher order spectra are absent, the diffracted rays are weak and do not show any pronounced colour.

There is an alternative and perhaps preferable way of viewing the subject. It is known that a thick laminar edge shows a striking asymmetry<sup>7</sup> in the distribution of the radiations diffracted by it, and the asymmetry of the whole diffraction pattern produced by the sequence of edges may be regarded as a consequence of

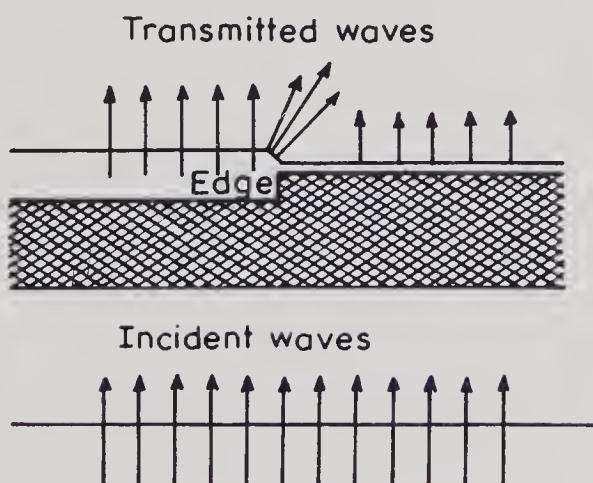


Figure 18. Asymmetrical diffraction by laminar edge.

<sup>7</sup>I R Rao, *Indian J. Phys.*, 1928, 2, 381.

This asymmetry of diffraction by a laminar edge is closely connected with the well known "Becke phenomenon" which is noticed when such an edge is examined under the microscope.

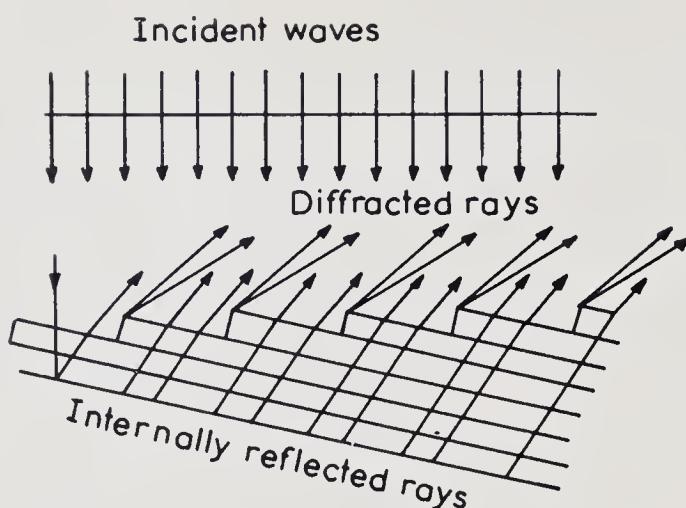


Figure 19. Asymmetrical diffraction of internally reflected rays on emergence.

the behaviour of the individual edges. The reason for the asymmetry will be evident from figure 18 which is a diagrammatic representation of the form of a plane-wave before and after passage through a plate containing a laminar edge. Owing to the inflection in the wave-front after passage through the plate, the rays diffracted by the edge towards the *retarded* side of the wave-front would obviously be more intense than those diffracted towards the other side. In our present case we are concerned chiefly with the light emerging from *within* the material after reflection at the internal laminations. Comparing figures 18 and 19, it will be seen that the tendency would be for the edges to diffract light unsymmetrically away from the normal and towards the surface of the plate on the side on which the iridescent reflection is observed. It may be remarked in this connection that by holding a piece of abalone shell in a dark room in the path of a strong beam of light and viewing its surface from various directions, the distribution of the diffracted light may be ascertained qualitatively without any instrumental aid whatsoever. Visual observations made in this way with the abalone box indicate that the laminar edges on the surface of the shell diffract light unsymmetrically through large angles in the manner indicated in figure 19.

The effects described and discussed above refer explicitly to the case of abalone shells, which, as mentioned in Part I, exhibit a remarkably pronounced iridescence. Similar, though perhaps less striking, effects are also exhibited by other iridescent shells, particularly those belonging to the *Haliotidae* and *Turbinidae* families. It should be mentioned that all iridescent shells whose surfaces have been prepared by grinding and polishing but on which the process of polishing has not been carried too far exhibit luminous lines on their surface when examined on the stage of the ultra-opak microscope, as also the

characteristic asymmetry effects with the method of sector illumination (see figure 15 for example); the colour phenomena are usually not so striking as with the *Haliotidae*.

## 6. Other laminar diffraction effects

Before leaving the subject of laminar diffraction phenomena exhibited by iridescent shells to consider other aspects of the subject, it would be desirable to mention some features of minor importance connected with those already described. If instead of using the principle of dark-ground illumination, the laminar edges on the surface of iridescent shells are examined by the usual methods of microscopic examination, the optical effects are reversed. Instead of the laminar edges appearing as brightly coloured lines on a dark field, they appear as dark lines on a bright field. This reversal may be observed either when the surface of the shell in its normal state is viewed by reflected light under the microscope using any form of opaque illuminator, or when examining a thin section by transmitted light in the usual way. The edges appear as narrow black lines when examined in sharp focus (see figure 14), and when put out of focus show the Becke phenomenon of bright line detaching itself unsymmetrically from the boundary. *It is readily verified that the successive edges seen under the microscope behave in a similar way, supporting Schmidt's view of the structure of mother-of-pearl, namely that the material consists of layers of aragonite separated by immeasurably thin strata of organic matter.*

A few remarks may also be made regarding the laminar diffraction effects observed when a thin plate (not too highly polished) is held up against the eye and a distant source of light viewed through it. It has already been remarked (section 3 above) that the surface of the shell gives by reflection in similar circumstances a strong first-order diffraction spectrum on one side only of the ordinary white reflection. This is due to the sloping terraces on the surface of the shell which reflect the bulk of the light into a direction different from that of the ordinary reflection. When examining the spectrum given by a thin plate *by transmission*, it must be remembered that there are *two* surfaces to be considered giving rise to diffraction effects. The effect produced by each surface can be examined separately by covering the other with a layer of Canada-balsam and a cover-slip of glass. It will then be found that each surface gives strongly unsymmetrical diffraction spectra in which the first-order spectrum on one side is much stronger than all the others. The two surfaces of the plate give intense spectra on opposite sides of the direct image, and each surface gives a strong spectrum by transmission on the side opposite to that in which it gives a spectrum by reflection. These effects are very readily explicable from optical principles, when we take into account the slope of the terraces on the two sides of the plate, and the opposite deviations produced by reflection and refraction respectively.

A passing reference may also be made to a curious luminous effect which accompanies the diffraction spectra mentioned above and is seen in the immediate neighbourhood of the image of a source of light viewed through a thin piece of mother-of-pearl with imperfectly polished surfaces. A brush of bluish-violet light, with the violet end nearest the source appears to stretch out unsymmetrically from it. This appears to be a secondary diffraction spectrum due to the sloping terraces on the surface of the shell influencing the transmission of light through the plate.

### 7. Acknowledgements

I have to express my appreciation of the valuable assistance rendered by Mr C S Venkateswaran who prepared the photographs illustrating the paper and Mr P Pattabhiramayya who prepared numerous specimens and made interesting observations on the behaviour of a nacreous surface during the process of grinding and polishing. I have also to thank Dr Baini Prashad and Dr H Srinivasa Rao of the Zoological Survey of India, Dr R P Paranjpye, Vice-Chancellor, Lucknow University, the Director of Fisheries, Madras and his Research Assistant at Ennur for their kind assistance in obtaining suitable material for the investigation.

### 8. Summary of parts I and II

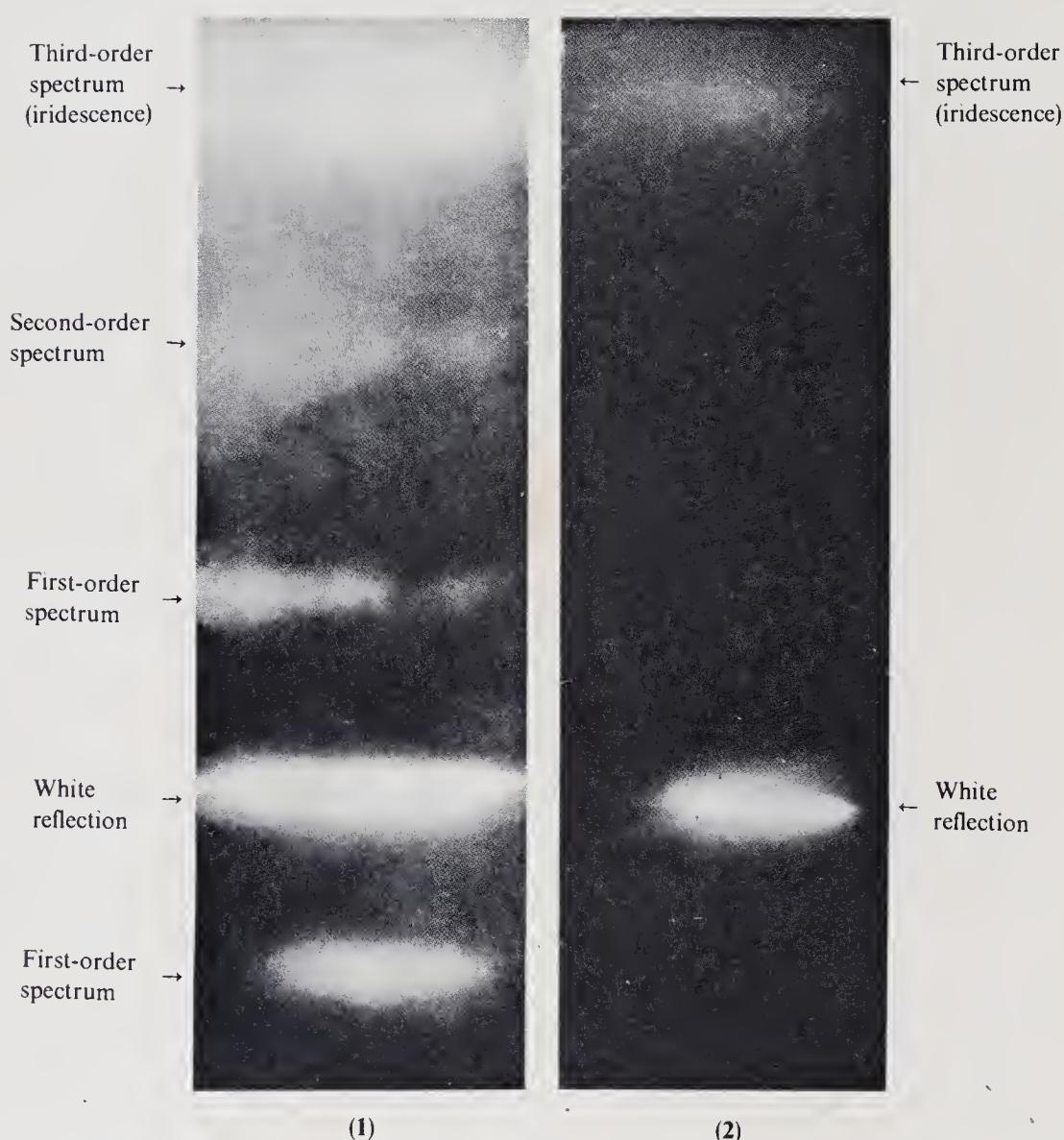
The two communications appearing in the present issue are the first two of a series of papers (of which several more are to follow) describing the results of a study of the iridescence of calcareous shells in relation to their structure. The following is a summary of the material so far published:

**Part I. *Introductory:*** Section 1 is mainly historical and indicates the various points of view (optical, crystallographic, colloid-chemical, zoological) from which the study of iridescent shells is of interest. Section 2 surveys the zoological material available for the study. Section 3 summarises the literature on the structure of calcareous shells generally and the work of W J Schmidt on the structure of the nacreous substance in particular.

**Part II. *Colours of laminar diffraction:*** Section 1 summarises the known optical effects observed with stratified films. The difference between these and the phenomena of iridescent shells arises from three factors: (a) the inclination of the laminae to the external surface, (b) the granular structure of the laminae, and (c) the considerable thickness of the material. Section 2 considers Brewster's classification of mother-of-pearl colours and shows it to have no theoretical justification.

Experiment and theory alike prove the characteristic iridescence of shells to be a diffraction effect which appears as one of the orders of spectra produced by the periodic structure at the surface of the shell. Section 3 considers the distribution of intensity in the laminar diffraction spectra and describes the effect of grinding and polishing the surface on the same. Section 4 describes the phenomena exhibited by the surface of iridescent shells when examined under the hollow cone illumination provided by the ultra-opak microscope. Remarkable colour effects are exhibited by the laminar edges which appear as bright lines of light on a dark field. Section 5 interprets these effects and correlates them with the intensity distribution in the laminar diffraction spectra, and with the asymmetrical diffraction by laminar edges. Section 6 considers other laminar diffraction phenomena and shows that the observations generally support Schmidt's view of the structure of nacre, namely that it consists of layers of aragonite crystals separated by immeasurably thin layers of organic matter.

Numerous photographs illustrate the paper.



**Figures 1 and 2.** Diffraction spectra given by iridescent *Turbo* shell. 1. Without cover-slip.  
2. With cover-slip.

Plate I

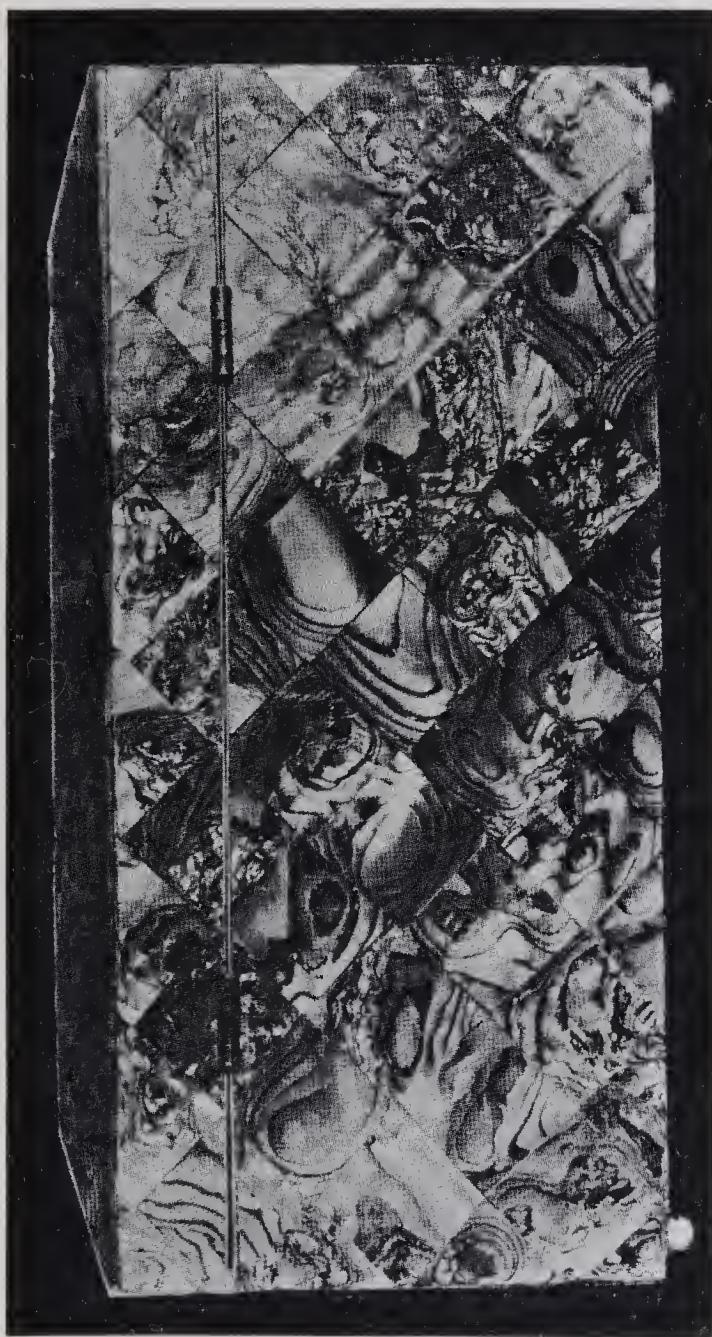


Figure 4. Box of polished abalone shell.  
Plate II



(5)



(6)



(7)



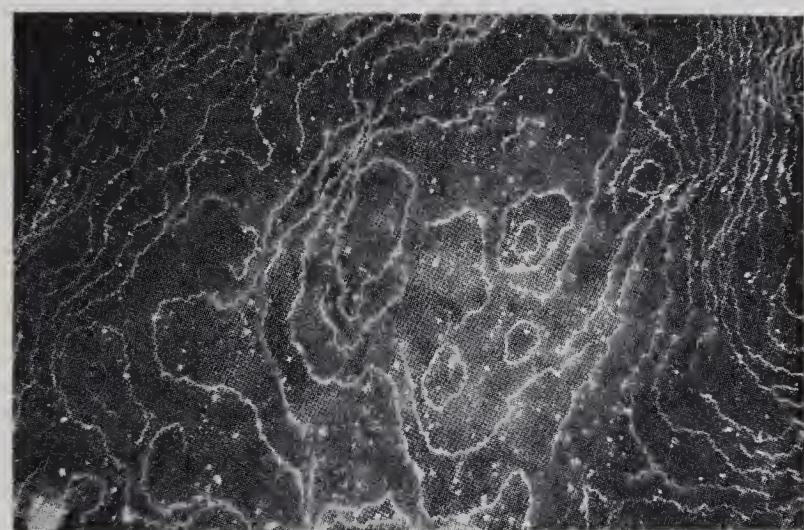
(8)

Figures 5–8. Abalone shell under hollow cone illumination.

Plate III



(9)



(10)

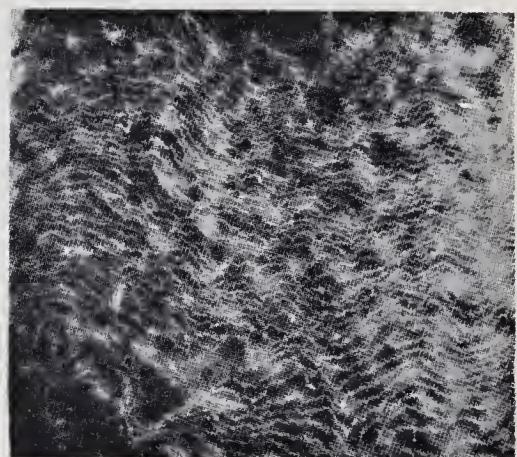


(11)

**Figures 9–11.** Abalone box under ultra-opak microscope. **9.** Sector illumination (from right). **10.** Hollow cone illumination. **11.** Sector illumination (from left).

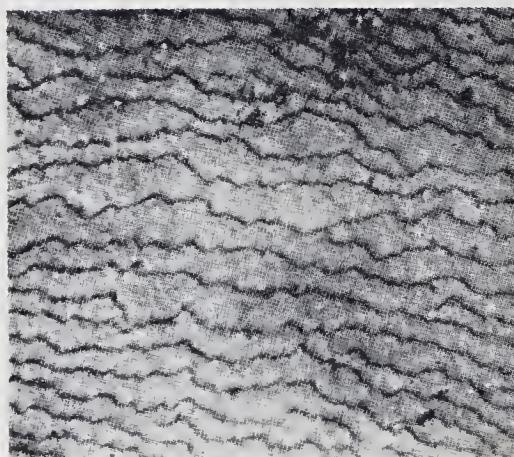


(12)

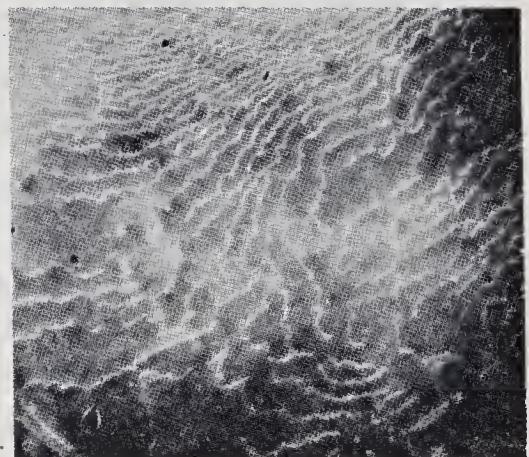


(13)

**Figures 12 and 13.** Abalone under hollow cone illumination.



(14)



(15)

**Figures 14 and 15.** Shell of *M. margaritifera*. **14.** Transmitted light. **15.** Hollow cone illumination.



(16)



(17)

**Figures 16 and 17.** 16. Abalone under hollow cone illumination. 17. Abalone box in 4358 A.U. illumination.

## On iridescent shells—Part III. Body-colours and diffusion-haloës

C V RAMAN

(Department of Physics, Indian Institute of Science, Bangalore)

Received May 9, 1935

### 1. Introduction

Paper II of this series<sup>1</sup> which appeared under the sub-title “Colours of laminar diffraction” dealt with various optical effects exhibited by nacre which owed their origin primarily to the laminated structure of this substance. Owing to the circumstance that the laminations are, in practice, not quite parallel to the external surface of the substance but intersect it, the phenomena cease to be identical with the simple interference effects exhibited by stratified films in which the laminations are parallel to the external surfaces. Instead of the familiar coloured reflections exhibited by films of the latter description, we obtain a series of diffraction-spectra produced by the grating-like structure of the external surface due to the laminations meeting it obliquely. The characteristic iridescence of the shell manifests itself in one or other of these diffraction spectra being specially intense and approximately monochromatic in character, besides also influencing neighbouring orders of spectra in their intensity and colour distribution. The distribution of intensity in the spectra is found to depend greatly on the condition of the external surface and especially the degree of its optical polish.

In the present paper, we shall concern ourselves with a group of optical effects exhibited by nacre which have till now received little or no attention in the literature of the subject and which are nevertheless of interest and importance as they play an essential part in the appearance and colours of nacreous shells as ordinarily observed. These effects have no analogue in the optics of transparent stratified films and owe their origin to the granular and colloidal structure of the nacreous substance. As was remarked in paper I of the series,<sup>2</sup> the laminae of which the nacreous substance is composed are not continuous but consist of a great many individual crystalline particles arranged in some kind of order and cemented together by the organic substance conchyolin. These individual

<sup>1</sup>C V Raman, *Proc. Indian Acad. Sci.*, 1935, **1**, 574.

<sup>2</sup>C V Raman, *Proc. Indian Acad. Sci.*, 1935, **1**, 567.

particles in their environment should obviously be capable of diffracting or diffusing light in a manner determined by their size, shape, orientation and grouping relatively to each other in the laminae. Direct evidence that such diffraction effects occur is furnished by the "diffusion-haloës" exhibited by thin plates of nacre which we shall describe in the course of the paper and which will be found illustrated in figures 1 to 10 in the accompanying plates. These diffusion-haloës form a unique method of revealing the structure of the nacreous substance, and indicate that this structure is entirely different in the three great divisions of the mollusca, namely, the Bivalves, the Gastropods and the Cephalopods, and that it also exhibits notable variations as between individual families and species. The recognition of the great differences in the structure of nacre in different kinds of shell and a consideration of the important part played by the structure in determining the optical properties of nacre are fundamental to our subject. It will be seen in the sequel that the phenomena considered in this paper all arise, in one way or other, as consequences of the diffusion of light within the substance of nacre.

## 2. Translucency of nacreous shells

One of the most beautiful properties of the nacreous substance is its "translucency" to light, a property which, it may be added, is also exhibited by shells which do not contain nacre but are porcelain-like in appearance, e.g., the Indian Chank (*Turbinella pirum*). The translucency of nacre is however specially remarkable in consequence of the fact that the light which diffuses through the substance exhibits colours which in many cases, e.g., with shells of *Turbo*, *Haliotis* or *Nautilus*, rival in richness the colours observed in reflection. To observe these diffusion colours, it is necessary to expose the nacre by removing the superincumbent concholin and prismatic layers and desirable also to polish the external surface formed by such removal. The shell should be viewed interposed between the eye and the source of illumination. The effects are most striking when the observations are made in a dark room and the shell is held up against an aperture illuminated by a powerful source, e.g., sunlight. *The penetration of light through the substance of the shell accompanied by diffusion which is observed in these circumstances should not be confused with the phenomenon of transparency or regular transmission.* When a beam of light enters the substance of the shell, the extinction of its energy due to diffusion is so rapid that its path as a coherent pencil of radiation travelling in a specific direction is practically very limited, and the light that penetrates the shell, except in the case of relatively thin layers, consists almost entirely of diffuse radiation. Light which diffuses through and exhibits colours may readily be observed with shells which are much too thick to transmit any light in the regular way.

Large shells of *Nautilus pompilius* and of *Turbo* form most beautiful objects

when examined in the manner described in the preceding paragraph. Figure 11 reproduces a photograph of the shell of *Nautilus pompilius* seen in a dark room when held against an aperture illuminated by sunlight. The photograph, of course, does not reproduce the beautiful colours actually seen. The internal septa characteristic of the *Nautilus* shell and the thickening of the walls of the shell at the regions of attachment of the septa are however strikingly visible in the photograph. It must not be imagined from this photograph that the shell of the *Nautilus* is transparent to light; on the contrary it is remarkably opaque even compared with other nacreous shells, and does not allow any light to be transmitted through it in the regular optical way except in the thinnest layers. Figure 12 reproduces a photograph of a *Turbo* shell taken in similar circumstances. The most noticeable feature in this photograph is the progressive weakening due to the spiral structure of the shell, of the light that diffuses through as we approach the vertex of the shell.

Gorgeous colours are exhibited by the nacreous shells of many species of *Haliotis* when held up against a window and viewed as "translucencies". The Californian species of the Haliotidae (known as abalone) which exhibit remarkably rich colours by reflected light form however a noteworthy exception. A shell of abalone when held up against a window illumined by sunlight is observed to allow very little light to diffuse through. Of three different species of shell which have been examined, the one which exhibits the most striking colours of all by reflection on both sides of the nacreous layer (figure 1 in plate I accompanying paper I of the series) is completely opaque in some areas and only allows a little deep red light to filter through in other areas. A second species exhibiting rippled markings on the convex side, and richer colours on the concave than on the convex side (figure 2 in plate I of paper I) behaves very similarly, but is somewhat less opaque, and in some relatively more translucent areas gives hints of diffusion colours other than a deep red. A third species which is the least striking in respect of the colours shown by reflection (weak and almost silvery-white on the convex side, stronger on the concave side) is the least opaque of all, and allows some smoky-red light to filter through almost everywhere. Thin sections cut transversely through the nacre of the three species of abalone and examined under the microscope disclose the existence of dark layers traversing the nacre which appear to be responsible for the exceptional optical behaviour of these shells.

*The diffusion colours of translucent nacreous shells are found to depend both on the angle at which the incident light falls on the first surface and on the angle at which the second surface is viewed.* The simplest case is that in which the light is incident normally on the first surface and is observed in a direction nearly normal to the second. The colours are best seen under these conditions, and if the plate is of moderate thickness, are roughly complementary to the colour of the iridescence at the first surface. This is readily understood, if we assume that the part of the spectrum which is strongest in the iridescent reflection is missing in the

light which diffuses through the shell. This does not, however, account for the richness of colour of the light that diffuses through, nor for the change of this colour with the direction of observation when the angle of incidence remains constant. It is evident that for a full understanding of the phenomena, we have to consider the changes in spectral character which occur in the process of diffusion through the substance of the shell, especially those which occur in the layers adjacent to the second surface prior to emergence of the light from it. A fuller consideration of these matters may conveniently be deferred to a later paper describing spectroscopic observations on the colours of nacreous shells. Meanwhile, it will be sufficient to draw attention to two important features. Firstly, the colours of diffusion, besides shifting their position in the spectrum when the directions of incidence or of observation are altered, tend to weaken and disappear as these directions are made more oblique. Secondly, when the thickness of the shell is very considerable, the light that diffuses through it tends to assume a pronounced reddish hue, submerging the characteristic colours arising from the laminated structure of the shell.

### 3. Body-colours

The diffusion of light by the granular structure of the shell naturally occurs in all directions with reference to the incident beam, namely, *forwards*, *backwards* and *laterally*. The preceding section dealt with the colours in the light diffused *forwards* and observed after it has penetrated through the thickness of the shell. We may reserve the designation of "diffusion colours" for the phenomena arising from such forward diffusion, and indicate by the term "body-colours," the very significant effects due to *backward* diffusion of the light which are observable on the same side of the shell as the iridescent reflection. The phenomenon of body-colour is shown by all varieties of iridescent nacre, including *Margaritifera*, *Turbo*, *Trochus*, *Haliotis* and *Nautilus pompilius*, and its recognition is essential to an understanding of the colour-effects exhibited by nacre. The body-colours are, in fact, quite striking when observed in directions adjacent to that of the iridescent reflection and are then complementary to it in hue. They determine to a surprising extent the appearance of mother-of-pearl as seen in ordinary circumstances. Either the iridescence or the complementary body-colour may reach the eye from any given part of the surface of a mother-of-pearl object depending on the optical conditions, namely, the relative positions of the source of the light, the object, and the eye, as well as the inclination of the internal laminations responsible for the iridescence and the degree of polish of the external surface. If the conditions are favourable, the iridescent reflection reaches the eye, while if they are unfavourable, it is the complementary body-colour that is perceived. When a mother-of-pearl object, e.g., a polished *Turbo* shell, is viewed inside a room, the reflections of the window or of the lamps in the room by the

internal laminations exhibit the iridescence, while the shell as a whole exhibits the complementary body-colours. The complementarity of the colours is readily observed and appreciated in such circumstances.

Figure 13 illustrates a polished bowl made of *Turbo* shell when viewed with the light behind the observer. The upper portion of the bowl exhibits a brilliant arch of light (just over the fret-work) due to a fold in the internal laminations which reflects the light in the direction of observation and shows the characteristic iridescence. The rest of the surface of the bowl is so greatly inclined to the direction of observation that the coloured reflections cannot reach the observer's eye. The bands so strikingly visible on the lower part of the shell are, in fact, bands of body-colour. Bands having the same configuration but of complementary colours and exhibiting the brilliant iridescent reflections are seen when the bowl is moved to a position between the eye and the source of light.

Figure 14(a) and (b) are intended to illustrate the complementarity of the iridescence and the body-colours exhibited by a shell of *Margaritifera*. Seen from inside the room, the light from a door or a window reflected by the shell exhibits brilliant bands of colour, while if the shell be slightly tilted so that the reflection does not reach the eye, the complementary body-colours are observed over the whole surface of the shell. An attempt has been made to exhibit this complementarity by photographing the shell in the two positions with a panchromatic plate and a red filter covering the lens of the camera. The exposure given in taking picture (b) was considerably greater than that required for picture (a). On carefully comparing the two pictures, especially the bands of light and darkness seen to the left of the central elliptic area, it will be noticed that the areas which appear dark in (a) are bright in (b) and *vice versa*. Some complications however arise from the irregularity of the internal structure of the shell which is very evident in the photograph, especially in picture (a), and which does not exist in the smoothly worked exterior surface of the shell.

When, as is generally the case, an extended source of light is employed and its reflection at the surface of a shell is observed, the iridescence and the body-colour would in general be seen superposed, and since they are complementary in hue, they tend to neutralise each other's colours. The striking extent to which the iridescence and body-colour dilute one another is most clearly realised when a fairly flat plate of nacre such as that illustrated in figure 14(a) and (b) is viewed, first inside a room and then is taken outside and viewed under the open sky. *An astonishing change is observed; the gorgeous colours observed within the room disappear, and the plate appears dead white and flat under the open sky.* The explanation of this result is that the iridescent reflection of a particular part of the sky, and the body-colour due to the illumination of the plate by the whole hemisphere of the sky are seen superposed. Since, in these circumstances, no colour is observed, we may draw the inference that the two phenomena are essentially complementary to each other, in other words, *that a plate of nacre returns as a body-colour diffused in various directions the whole of the light that falls upon it and is not specularly reflected as the characteristic iridescence.*

We must here recognise two limitations to the correctness of the foregoing statement. It is obviously necessary that a plate of nacre should be of sufficient thickness if the whole of the light that falls upon it is to be returned either as iridescence or as body-colour. Secondly, we must assume that no material absorbing light *per se* is present in the nacre, as otherwise the light that penetrates would disappear by absorption before it can be returned by diffusion. The thickness necessary for the full development of the body-colour would be considerable for relatively clear varieties of nacre, e.g., *Mytilus viridis* and may not actually be available, while small thicknesses may be quite sufficient in the case of strongly diffusing varieties of nacre, e.g., *Nautilus pompilius*. It is significant in this connection that the shell of *Nautilus pompilius*, though comparatively thin, exhibits on its surface the stripes of body-colour complementary to the iridescent reflections in a most conspicuous manner. For the same reason, it follows that if we wish to observe the iridescence of any variety of nacre with the maximum of spectral purity, we should work with comparatively thin plates of the material so as to reduce to a minimum the intensity of the complementary body-colour which appears superposed on it.

It has already been remarked that the shells of the Californian abalone contain layers of some darker material traversing their nacreous substance and that these layers appear to be responsible for the remarkable opacity of these shells. The presence of absorbing layers within the nacre must, as remarked above, greatly diminish the intensity of the body-colour. This appears to be actually the case, as is indicated for instance by the fact that the abalone box illustrated in Paper II (unlike the shell of *Margaritifera*) exhibits under the open sky, an iridescence which is perceptibly but not greatly inferior to that visible under less extended illumination. These remarks and observations suggest that the richness of the reflection colours shown by the abalone shells is at least partially to be ascribed to the presence in their nacre of absorbing layers and the consequent weakening of the complementary body-colours.

A detailed study of the spectral characters of the body-colours is reserved for a future paper. It may be remarked that the colours naturally vary with the angle of incidence of the light on the surface of shell, and also it may be noted, to an appreciable extent with the angle of observation. The complementarity with the iridescence-colours for directions adjacent to that in which the latter colours are observed appears however to be maintained in all cases. The body-colours of nacre may be exhibited in an objective manner on a screen by allowing a narrow beam of sunlight to fall on the surface of the shell and receiving the reflected and diffused light on a white bristol board. The effects observed naturally depend on a variety of circumstances including especially the variety of nacre employed, the degree of its optical polish and the angle of incidence of light. With shells of *Turbo*, a disk of diffuse light having a well-defined outer margin and exhibiting a colour complementary to that of the iridescent spectrum appears surrounding it. That this disk of diffuse radiation is due to the internal structure of the nacre and

not to external surface irregularities is indicated by the fact that it does not disappear when the surface is covered with a layer of Canada-balsam and a cover-slip of glass. Other varieties of nacre also exhibit similar phenomena but differing in detail and not always so well-defined.

An alternative method of studying the body-colours and their angular distribution is to observe the surface of the shell under the hollow-cone illumination provided by the Leitz ultra-opak microscope as described in Paper II, using for this purpose, one or the other of the series of objectives with varying angles of illumination and, if desired, also the sector diaphragm provided with this instrument. The change from iridescence to body-colour is readily demonstrated by slightly tilting the specimen under the microscope so as to bring one or the other into view. Effects of surprising brilliance may be observed in this way with suitable specimens.

#### 4. Diffusion-haloes

We now pass on to consider the diffusion-haloes already mentioned in the introductory section of the paper and illustrated in figures 1 to 10. To observe them, all that is necessary is to rub down a piece of nacre to a sufficient degree of thinness, polish both its faces with the finest rouge on chamois leather, and then to mount the piece in Canada-balsam between cover-slips of glass, and thus minimise the disturbances due to the imperfections of the external surfaces. The diffusion-haloes may then be studied either subjectively or objectively. For subjective observation, all that is necessary is to hold the mounted specimen in front of the eye and view a bright source of light, e.g., a filament lamp from a distance in a dark room. For objective demonstration of the diffusion-haloes, a thin pencil of sunlight is allowed to pass through the specimen and is received on a white piece of bristol board held at a suitable distance from the specimen. The haloes may also be readily photographed using a small aperture illuminated by an electric arc as the source and placing the specimen close to the lens of the camera.

The photographs reproduced in figures 1 to 10 disclose a remarkable variety in the configuration of the diffusion-haloes. It will be noticed that the Gastropod shells, *Turbo*, *Trochus* and *Haliotis* give haloes that form more or less complete circles. The halo of the Cephalopod *Nautilus pompilius* is of very peculiar form, consisting of two roughly circular but incomplete arcs of about  $60^\circ$  angle on either side of the direct beam. The bivalve shells, of which five different species have been studied, give again quite a different type of halo, namely, two spots or rather diffraction-spectra, one on either side of the central diffraction disk and distinctly separated from it. It will thus be seen that the three great groups of molluscan shells are strikingly differentiated by the general type of diffusion-haloes exhibited by their nacreous layers.

Closer study reveals further and very interesting differences in the character of the haloes obtained with the nacre of individual families and species of molluscs. Perhaps the most striking type of halo is that given by the nacre of the species of *Turbo* examined (figure 1). This consists of a well-defined circular halo which with white light exhibits the regular colour-sequence corresponding to a proportionality of the size of the halo to the wavelength employed. The halo is separated from the image of the source of light by a dark region, and there is hardly any corona seen surrounding the source. It should be mentioned that to obtain a symmetric circular halo with the nacre of *Turbo*, it is necessary to carefully orientate the specimen in front of the eye till the complete circle is obtained. With an incorrect orientation, only parts of the circle are observed. It is to be inferred from the effects noticed that the complete circular halo is obtained when the plane of the internal laminations containing the diffracting particles is exactly normal to the line joining the source of light and the eye.

The diffusion-halo given by the nacre of *Trochus* and of *Haliotis*, though resembling that of *Turbo* in having circular symmetry, differ strikingly in detail. With *Trochus*, the central corona surrounding the image of the source is much more marked, and the outer ring is therefore much less clearly separated from the latter. The halo of *Haliotis* is intermediate in type between those of *Turbo* and *Trochus*. (The transverse bar of light seen running across the halo in figure 3 is due to scratches on the surface of the specimen not having been removed during polishing). The halo of the species of Californian abalone examined is of very curious form, being of distinctly elliptic shape, with a dark bar running along the major axis. This type of halo evidently deserves further examination with more specimens and other species of abalone.

Though the five different species of bivalves examined show the same general type of diffusion-halo, they differ considerably in such details as the angular separation of the two spectra and their brightness, both absolutely and relatively to the central corona surrounding the image of the source. In some bivalves, e.g., the species of *Parreysia* examined (figure 7), the two spectra are very bright and clear, and rather close together. In others, e.g., *Pinctada lentiginosa* (figure 8), they are weak and rather further apart, while with the nacre of *Mytilus viridis*, the spectra are so weak and so widely separated that it is not easy to observe or photograph them.

It is not difficult to infer in a general way, the size and arrangement of the crystalline particles in the laminae which give rise to the diffusion phenomena, from the observed angular size of the haloes as well as their general character. For instance, in the case of *Turbo*, we may infer that the crystal particles are about  $4\mu$  in diameter and are arranged with a considerable approach to regularity and circular symmetry. On the other hand, in the bivalves, the particles are distinctly smaller in size and are evidently arranged in a manner which simulates the lines of a coarsely ruled grating. Since the crystalline particles in nacre are accessible to microscopic observation, it should be possible to check the foregoing inferences

directly and to closely correlate the observed form of the diffusion-haloës with the microscopically determined orientation and arrangement of the particles. Meanwhile, it is gratifying to note that an X-ray examination of different species of nacre, carried out by Dr Rama Swamy and published in the same issue of these *Proceedings* (see following paper) indicates differences of the crystal orientation in the nacre of Gastropods, Cephalopods and Bivalves, closely analogous to and evidently connected with the differences in the spatial arrangement of the particles deduced from the foregoing observations of the optical haloës. A fuller discussion of the optical and X-ray results may advantageously be reserved for a future occasion.

### 5. Transmission colours

In the second section of the paper, we have already had occasion to remark on the rapid extinction of the primary beam of light which occurs as the result of diffusion in its passage through the substance of nacre, and also on the great difference between different species as regards the transparency of their nacre. How small is the actual transparency of shells will be readily appreciated on attempting to view through them a bright source of light, e.g., the sun or the electric arc. It will be found that except when relatively thin layers of the order of a few tenths of a millimeter are employed, the image of the source is either invisible or else is seen very feebly with a deep red colour. The observations clearly indicate that the colours of the transmitted light are a composite phenomenon and are a function of the thickness of the shell. *Firstly*, owing to the iridescent reflection at the surface of the shell, certain well-defined regions of the spectrum are removed and are consequently missing in the transmitted light. *Secondly*, there is a rapid attenuation of the beam in passing through the substance of the shell as the result of scattering or diffusion of light. Observations with thin sections of nacre suggest that such scattering or diffusion is only in part due to the relatively coarse crystalline particles present in the laminae of the nacre, and that a much finer colloidal structure is also present in the nacre which is responsible for a selective scattering through large angles of the shorter waves in the spectrum. On this view, we should expect a rapid extinction of the blue end of the spectrum in the transmitted light in its progress through the specimen. *Thirdly*, we must also consider the possibility of a genuine absorption of light in the substance of the nacre, particularly in the case of those species where a marked colour, independent of the angles of incidence and observation is exhibited by the nacre.

It is clear from what has been said above that the colour of the transmitted light must progressively alter with increasing thickness of the specimen, and that only with comparatively thin pieces can we expect it to be roughly complementary to the colour of the reflected light. Such a progressive change of colour in the transmission is actually observed with all varieties of nacre; as already remarked, the colour of the transmitted light tends to a deep red with increasing thickness of

the nacre, irrespective of what the colour is for relatively thin pieces of the same nacre. One curious consequence of this is that pieces of nacre which have their characteristic reflection in the red region of the spectrum transmit much less light for the same thickness than pieces which exhibit a blue or green reflection; the reason obviously is that in the former case, two causes of extinction operate simultaneously in the same region of the spectrum.

Further details regarding the spectral character of the transmitted light and the relative importance of the three causes of extinction specified above in different species of nacre are reserved for future consideration.

## 6. Lateral or transverse diffusion of light

We may conclude this paper by a brief discussion of some remarkable effects which are observed in a very simple experiment with a plate of nacreous shell. A small aperture, say 5 millimeters in diameter, is illuminated with sunlight, and the plate of nacre is pressed closely against it. The observations are conveniently made in a dark room. When the plate employed is a millimeter or two thick, the incident beam of light is unable to penetrate the shell. The light is however observed to diffuse laterally in the plate through surprisingly large distances. For instance, with a shell of *Margaritifera* two or three millimeters thick, the light penetrates laterally to distance of twenty or more millimeters in all directions. The phenomenon is illustrated\* in figures 15 (a) and (b). The latter, in particular, shows clearly the central spot which is the portion of the plate in contact with the illuminated aperture as also an extended area of fainter luminosity surrounding it. The central spot corresponds to the area of nacre illuminated by the incident beam and by the forward diffusion, while the outer luminosity represents the regions illuminated by lateral diffusion. As already remarked, the ordinary transmission of light through nacre is limited to a few tenths of a millimeter, while its penetration by forward diffusion is limited to a few millimeters. The lateral diffusion to distances up to twenty millimeters or more must therefore be regarded as a very remarkable phenomenon.

The natural interpretation of the effects described above is that nacre considered as a diffusing medium is very anisotropic in its properties, and that light can penetrate by diffusion to far greater distances parallel to the laminations than perpendicular to them. Why this should be so is a question, the answer to which may be reserved for a future occasion. We may however point out that the interpretation given above is favoured by several of the observed details regarding the phenomenon. We have already remarked (sections 2 and 5) that the colour of the transmitted light tends to a deep red with increasing thickness of the nacre, and the same feature is also shown by the forward diffusion. In the

\*Figure 15(a) reproduces a photograph taken in a lighted room, and the whole of the shell is visible. The central spot is submerged in the lateral diffusion.

experiment described in the present section, the same feature is noticed as regards the colour of the central spot which tends to a deep red with increasing thicknesses of the nacre employed. The laterally diffused light shows however quite a different colour, except in its outermost edges where it tends again to a deep red. This observation indicates that the lateral diffusion is quite a distinct phenomenon and possesses characters different from that of the forward or backward diffusion. It may be remarked that different types of nacre differ greatly in this as in other properties. The phenomenon of lateral diffusion is, for example, hardly to be observed with the shell of *Nautilus pompilius*.

## 7. Summary

The paper describes a group of interesting optical phenomena which have their origin in the granular and colloidal structure of nacre and have no analogue in the optics of transparent stratified films. Section 1 points out that the crystalline particles present in nacre diffract or diffuse light in a manner determined by their size, shape and arrangement and in consequence give rise to various optical effects. Section 2 describes the forward diffusion of light through nacre and the colours arising therefrom exhibited by iridescent shells observed as "translucencies". These colours depend both on the angles of incidence and of observation. Section 3 describes the phenomena of backward diffusion of light or body-colours which are complementary to the iridescent reflections and tend to dilute the latter to an extent determined by the circumstances of observation. Section 4 describes the diffusion-haloës observed when a source of light is viewed through a thin polished plate of nacre. These haloës assume very different forms for the three great groups of molluscs, namely, the Gastropods, the Bivalves and the Cephalopods, and indicate that the arrangements of the crystalline particles in nacre are very different in these three groups and also show distinct differences as between individual families and species. Section 5 deals with the colours of the transmitted light which are a function of the thickness of the nacre and indicates the existence of three distinct factors which determine the extinction coefficient. Section 6 deals with the phenomena of lateral or transverse diffusion of light which occurs through surprisingly great thickness in several kinds of nacre and which indicates that nacre is a highly anisotropic medium in this respect.

Numerous photographs of the diffusion-haloës and other phenomena illustrate the paper.

In conclusion, I have to express my thanks to Mr C S Venkateswaran who assisted me in these studies and obtained the photographs illustrating the paper, as also to Mr P Pattabhiramayya who prepared numerous thin sections of nacre for optical and microscopic observation. The Research Assistant of the Fisheries Department at Ennur has been very helpful in the supply of suitable specimens for the work.



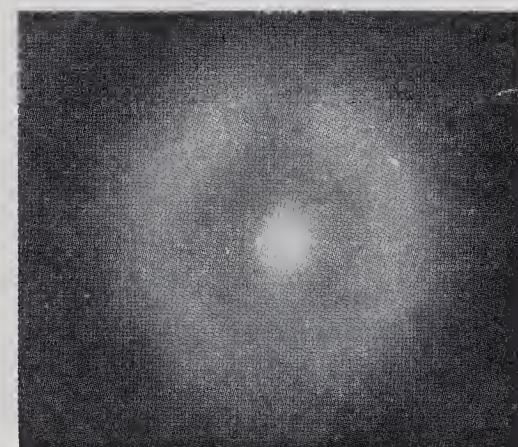
(1)



(2)



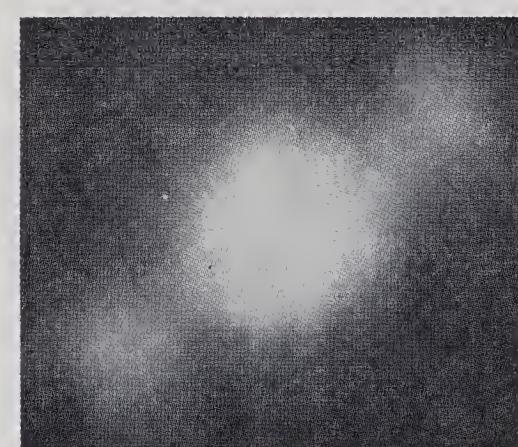
(3)



(4)



(5)



(6)

**Figures 1–6.** Diffusion haloes of iridescent shells. 1. *Turbo* Sp. 2. *Haliotis* Sp. 3. *Trochus* Sp.  
4. *Abalone* Sp. 5. *Nautilus pomilius*. 6. *M. margaritifera*.



(7)



(8)

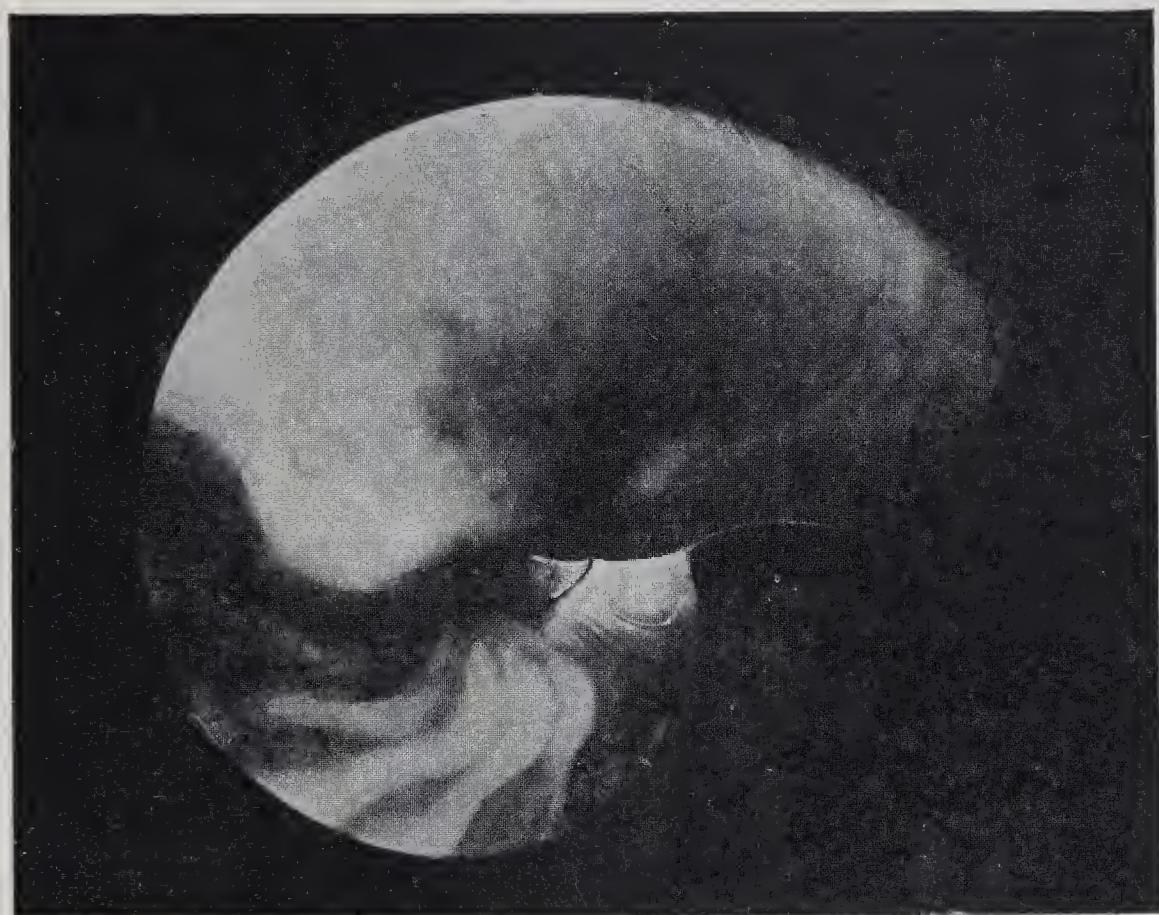


(9)



(10)

Figures 7–10. Diffusion-haloes of iridescent shells. 7. *Parreysia* Sp. 8. *Pinctada lentiginosa*.  
9. *Lamellidens marginalis*. 10. *Pinctada vulgaris*.



**Figure 11.** Shell of *Nautilus pompilius* photographed as a translucency.

**Plate III**



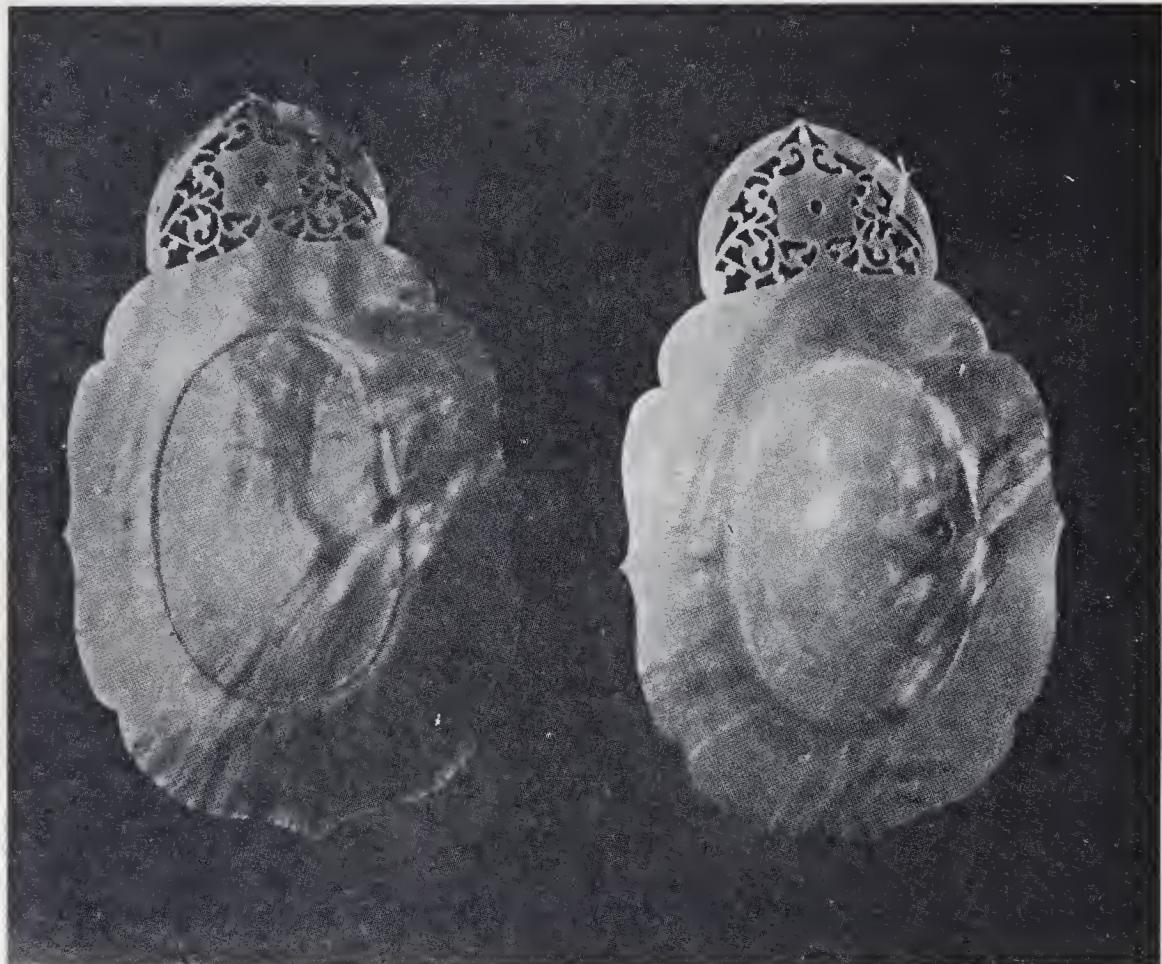
Figure 12. Shell of *Turbo* Sp. photographed as a *translucency*.

Plate IV



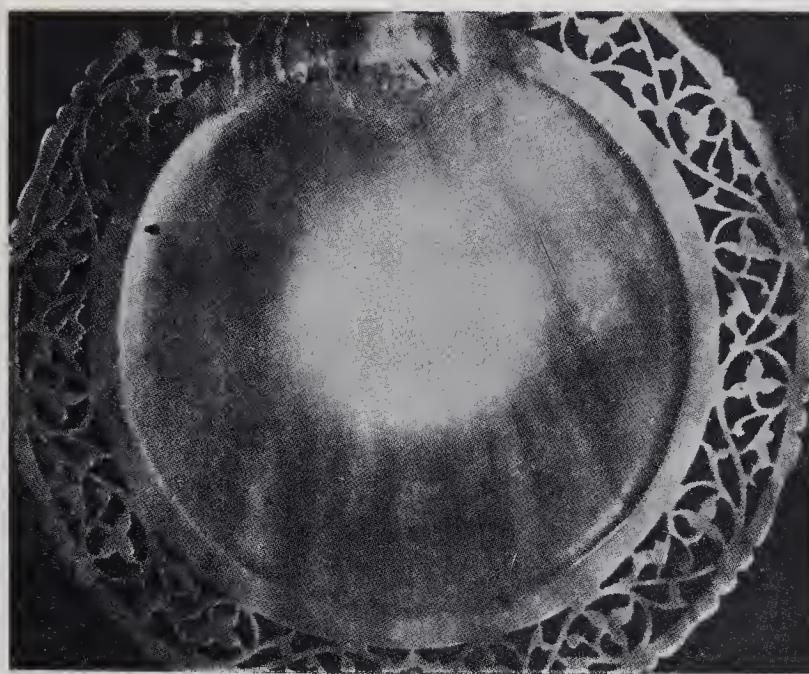
Figure 13. Bowl of *Turbo* shell: Upper surface showing bright arc of iridescent reflection and lower surface, bands of body-colour.

Plate V



**Figure 14.** Plate of iridescent shell of *M. margaritifera* photographed with panchromatic plate and red filter. (a) Iridescence. (b) Body-colour.

**Plate VI**



(a)



(b)

Figure 15. Shell of *M. margaritifera* showing lateral diffusion of light.

# The structure and optical behaviour of iridescent shells

SIR C V RAMAN and D KRISHNAMURTI  
(Memoir No. 45 of the Raman Research Institute, Bangalore)

Received December 23, 1953

## 1. Introduction

As is well known, the innermost layer of the shells of numerous molluscan species consists of a material known as nacre or more familiarly as mother-of-pearl. The outer opaque layers covering the nacreous substance may usually be removed without difficulty and its surface thus exposed may be smoothed and polished, thereby enabling its characteristic lustre and iridescence to be fully displayed. Large shells of the molluscan species *Margaratifera*, *Turbo*, *Haliotis* and *Nautilus* thus prepared are magnificent objects. Some twenty years ago, one of us became interested in the optical phenomena exhibited by these shells. An extensive collection of material was got together, and the studies made with the same, revealed many facts of interest.<sup>1,2,3</sup> It was shown that the colours of internal reflection and of exterior diffraction at the surface of the shells are so related that the monochromatic light-beam arising from the mutual interference of the reflections from the successive layers of the nacre has the same direction as the diffracted beam of that wavelength in the spectrum of the same order. A notable part was also found to be played by the diffusion of light in the nacreous material arising by reason of its structure which consists of discrete crystallites of aragonite imbedded in a cementing network of conchyolin and arranged in a series of equidistant layers. The size, orientation and ordering of the crystallites in the layers is altogether different in the different classes of mollusca, viz., *Bivalvia*, *Gastropoda* and *Cephalopoda* and differs in detail even as between the different species within the same class. These structural differences are made evident in a very striking way by the variation in the nature of the diffusion halo observed in the different cases when a bright source of light, preferably a sodium vapour lamp, is viewed through a thin plate of nacre. The actual appearance of an iridescent shell in any given set of circumstances was found to be profoundly influenced by the diffusion and absorption of light within its material, apart from the internal reflections at the successive layers of the structure.

Recent issues of these *Proceedings* have contained papers describing the results of investigations on the structure and optical behaviour of various solids exhibiting structural colours. The phenomena encountered in those investiga-

tions suggested that further studies on the same lines with iridescent shells might prove fruitful, and this has actually been found to be the case. Some noteworthy results have emerged which are reported in the present paper. Of special interest is the discovery that the monochromatic reflections and extinctions bifurcate at oblique incidences and appear in the spectrum as separate components which are polarised differently. This result could have been anticipated as a consequence of the strong birefringence of aragonite. Secondary maxima of reflection and extinction accompanying the principal components have also been observed and recorded. The diffusion haloes referred to in the foregoing paragraph have also been found to exhibit remarkable changes in their geometric form and their state of polarisation when a source of light is viewed obliquely through the plate of the material. Closely connected with these diffusion phenomena is the polarisation of the transmitted light which is observed and which is of the opposite character to that ordinarily exhibited by a pile of plates at oblique incidences. In these and various other effects that have been noticed, the individual features in the structure of the nacre in the different species of mollusca come very prominently into evidence.

## 2. The structure of the nacreous material

The lamellar structure which is responsible for the iridescence of nacre is on a very fine scale. Nevertheless, it is often possible to observe and enumerate the individual layers, because in their natural form the shells are curved and hence when a plate is cut and polished *flat*, the successive layers meet the surface obliquely and exhibit the contours of the form on which the material of the nacre was originally laid down. These contours can be readily observed through a magnifying lens or a low-power microscope. They appear as a series of circles, ellipses, hyperbolae or other curves following each other in great number. From the inclination of the lamellae to the surface and their observed separation, the spacing of the stratifications can be determined.

That the nacre consists of discrete crystallites becomes evident when a small bright source of light is viewed normally through a thin polished plate of the material. Overlying the original source of light we observe a diffusion halo which, as mentioned above, exhibits totally different characters in the different orders of mollusca. In the *Gastropoda* which include such well known shells as *Turbo*, *Trochus* and *Haliotis*, we observe a circular halo with faint extensions outside and a dark area inside surrounding the source. The halo of *Turbo* is reproduced as figure 1 of plate I. In the *Bivalvia* on the other hand, the halo consists of two diffuse spots, one on either side of the image of the source, with a distinct bright corona overlying the latter. This is illustrated in figure 5 of plate II. The most interesting halo of all is that given by *Nautilus*. This shell is remarkably opaque and has to be thinned down very considerably to enable the halo to be seen. It is of

peculiar form, consisting of two circular but incomplete arcs of about  $60^{\circ}$  angle, one on either side of the direct beam. In the outer regions we observe faint extensions, including especially a pair of brushes extending out obliquely from the terminations of each of the circular arcs mentioned above. A picture of the halo of *Nautilus* as observed in the normal setting of the shell is reproduced as figure 8 in plate III.

In all cases, if the source of light is monochromatic, the haloes exhibit a finely mottled structure as can be seen in plates I, II and III. On the other hand, if the source of light is white, we notice long coloured streaks radiating out from the centre, the most intense portions of these forming the observed halo. From these facts it is clear that the haloes arise from the interference of the light diffracted by the individual crystallites of aragonite in their setting of conchyolin. From their configuration one can deduce the size, shape and ordering of the crystallites in the individual layers of the nacreous material.

Useful information regarding the structure of nacre is also forthcoming from a variety of other sources. In particular, should be mentioned the appearance of thin sections of nacre under the microscope. Studies of this kind accompanied by numerous microphotographs are described in a paper by V S Rajagopalan.<sup>4</sup> As has been shown by him, the results are in full accord with the inferences derived from a study of the diffusion haloes. Of particular interest are the photographs of the conoscopic figures of different specimens of nacre also recorded and reproduced in the same paper. The figures exhibit the birefringence of the material very clearly and represent the integrated effect of the crystallites. For the *Gastropoda*, the figures observed in convergent polarised light are indistinguishable from that of a uniaxial crystal cut normal to the optic axis. On the other hand, the *Bivalvia* show figures resembling that of a biaxial crystal but with varying optic axial angles. *Nautilus* gives a biaxial figure with a very small axial angle.

These observations indicate that in the *Gastropoda*, the crystallites are orientated at random in the plane of the stratifications, while on the average, their *c*-axes are normal to that plane. On the other hand, in the *Bivalvia*, it is evident that the crystallites are set in more or less precisely defined orientations in the plane of the stratifications, while their *c*-axes lie normal to that plane on the average. The case of *Nautilus* is of a more complex character. Observations under the microscope with high powers exhibit a twinning of the crystallites which appear ordered in the layers in a fairly regular manner. However, fairly large errors in orientation are indicated by the fact that no complete extinctions are observed under crossed nicols.

The foregoing inferences regarding the orientation of the crystallites in the nacreous shells receive support from X-ray diffraction studies. Numerous examples have been investigated by S Rama Swamy<sup>5,6</sup> in different settings of the specimens using monochromatic X-radiations. The patterns recorded are found to be totally different for the *Bivalvia*, *Gastropoda* and for *Nautilus* respectively.

They also show that the orientation of the individual crystallites fluctuates observably about the average in all cases.

### 3. The reflection-diffraction spectra

As remarked earlier, the laminations of nacre, in general, meet its external boundary obliquely. As a consequence, the surface of the material is usually corrugated and gives rise to diffraction spectra accompanying the reflected light. Simultaneously also, the incident beam penetrating into the nacre is reflected backwards by the stratifications, and since the latter are regularly spaced, there is a selective monochromatic reflection, the direction of emergence of which is determined by the inclination of the stratifications to the surface and the refractive index of the material. Since both effects have their origin in the same incident beam, they are necessarily coherent, and it is easily shown<sup>2</sup> that the internal reflection emerges in a direction coinciding with one of the orders of the diffraction spectra of the same wavelength produced by the surface of the shell. Further, the order of the diffraction spectrum in which it appears is also the order of the interferences giving the characteristic internal reflections. All that is necessary to determine the latter is to allow a thin pencil of white light to fall on the surface of the shell and to receive it after reflection on a white card. The iridescent reflection then appears in its proper place in the sequence of diffraction spectra produced by the corrugated surface.

The coherence of the internally reflected and externally diffracted radiations also exhibits itself in other ways. A faint diffraction spectrum of a higher order than the characteristic iridescence is frequently observed and this is usually monochromatic. Further, the distribution of intensity in the spectra of the lower orders is modified and may be very different from that observed in a normal spectrum. Such an effect is clearly seen in figures 14, 15 and 17 in plate IV.

Four reflection-diffraction spectra obtained with *Margaritifera*, *Turbo*, *Nutilus* and *Haliothis* are shown as figures 14, 15, 16 and 17 respectively in plate IV. In each figure the diffraction spectrum of zero order appears as the most intense and best defined spot. Owing to the asymmetric configuration of the surface, the diffraction spectra are far more intense on the one side than on the other. In each figure the last bright spot to the right is the characteristic reflection. In figure 14 it appears in the diffraction spectrum of the fourth order, in figure 15 in the third, and in figures 16 and 17 in the second order.

Some special points of interest may be mentioned in this connection. The iridescent reflection usually appears surrounded by a halo of scattered light. The angular diameter of this halo is large and its intensity is low for *Margaritifera*. Indeed it is hardly visible in figure 14. On the other hand, it is of smaller dimensions and more intense in the case of *Turbo* (see figure 15). These differences are explicable in terms of the size of the crystallites which are much smaller in

*Margaratifera* than in *Turbo*. The diffusion halo overlying the iridescence in the case of *Nautilus* is very intense as can be seen from figure 16. This is evidently a consequence of the special structure of the nacre in this mollusc and is closely connected with the extreme opacity of its shell referred to earlier.

It is evident that the reflection colours exhibited by nacre would be more lively if they arise from interferences of a lower order than in the case of higher orders. There are however also other factors which require to be considered in this connection. One of them is the intensity and colour of the overlying diffusion of light already referred to. Another factor is the specific absorption of light by the organic matter present in the nacre. The effect of such absorption would be to diminish the intensity of the diffuse light emerging from within the shell and hence would help to make the coloured reflections more vividly observable. *Per contra*, the absence of such material or a specially strong diffusion would reduce the vividness of the iridescence. As examples of the working of these factors, we may mention a few cases. The iridescence of *Turbo* is more vivid than that of *Margaratifera* evidently as a consequence of the interferences being of a lower order. The brilliant colours often seen with the shells of the Californian abalone may likewise be ascribed to the interferences being of a still lower order, namely the second. They are further enriched when absorbing material is present in the shell. *Nautilus*, on the other hand, presents a silvery appearance and a generally inconspicuous iridescence, clearly because of the intense diffusion of light by the material.

#### 4. Spectral character of the reflections and extinctions

In plates V and VI are reproduced the reflection and extinction spectra respectively of iridescent shells in typical cases. They exhibit several features of interest which will now be described.

Figure 18(a) in plate V is a record of the spectrum of the light reflected at nearly normal incidence from the outer convex surface of a large well-polished shell of *Margaratifera*. The reflecting area chosen was located on a part of the shell in which some absorbing material was present which in consequence was quite dark when viewed by diffuse light and *per contra* exhibited vivid colours by reflection. Other areas where there was no such absorption appeared silvery white by reflected light with scarcely any visible colour. Figure 18(a) shows the third and the fourth order reflections in this case. The latter is highly monochromatic and is accompanied by secondary maxima. Figures 18(b) and (c) recorded with a polaroid before the slit of the spectrograph in two perpendicular settings give no indication of any polarisation of the spectrum at the incidence employed. On the other hand, the spectra recorded with the same shell and with the light incident at an angle of about  $50^\circ$  and reproduced in figure 19 show such an effect in a striking manner. Figure 19(a) gives the whole of the reflected

light, while figures 19(b) and (c) were recorded with a polaroid in front of the slit with its vibration directions respectively perpendicular and parallel to the plane of incidence. The splitting of the spectral reflection into two polarised components, each accompanied by its own secondaries, is thus clearly demonstrated. A similar effect is shown by figures 20(a), (b) and (c) recorded in a similar manner, of the reflection from a piece of *Turbo* at oblique incidence. Figures 21 and 22 in plate VI are similar records of the transmission spectra of a thin polished plate of *Turbo* at normal and at oblique incidence respectively. The former exhibits the high monochromatism of the extinctions, the secondaries accompanying them, as also the absence of any polarisation. But in figure 22(a) which was recorded in oblique transmission through the plate, the splitting of the extinctions into two components appearing at  $\lambda$  4380 and  $\lambda$  4520 respectively is very clearly seen. It is also apparent from figures 22(b) and (c) that the two components are polarised differently; the extinction at  $\lambda$  4520 is very prominent in figure 22(b), while that at  $\lambda$  4380 is hardly visible; in figure 22(c), on the other hand, the extinction at  $\lambda$  4520 is not perceptible while that at  $\lambda$  4380 is distinctly visible.

The splitting of the reflections and extinctions into polarised components in oblique reflection and transmission is readily understood when the birefringence of the nacre is taken into consideration. The refractive index of aragonite for vibrations parallel to the *c*-axis is 1.530 while for vibrations parallel to the *a*- and *b*-axes are respectively 1.681 and 1.685. The values for nacre would, of course, be modified by reason of the presence of conchyolin. We may, as a first approximation, ignore the difference in the refractive indices for vibrations along the *a*- and *b*-axes and treat the nacre as equivalent to a negative uniaxial crystal. Such an assumption would be strictly correct for the *Gastropoda* and approximately so for the *Bivalvia* and for *Nautilus*. The monochromatism of the reflections and extinctions at normal incidence and their splitting into two components at oblique incidences with the component of shorter wavelength vibrating in the plane of incidence follow as consequences of this situation.

It may be mentioned that the splitting and polarisation of the spectral components can be observed visually with a pocket spectroscope. It can also be demonstrated in an objective manner with the aid of the reflection-diffraction spectra illustrated in plate IV, when these are observed at oblique incidences with a polaroid placed in the path of the reflected light.

The high degree of monochromatism of the reflections exhibited in figure 18(a) calls for remark. The theory of the reflection of light by a periodically stratified medium was discussed by G N Ramachandran in these *Proceedings*<sup>7</sup> some years ago. His paper considers the influence of the several factors which influence the observed results, viz., the reflecting power of the stratifications, the relative thicknesses of the alternate layers, the total number of strata and so forth. As was shown by him, the sharpness of the spectral maxima cannot be indefinitely increased by increasing the number of the stratifications but is limited by their reflecting power. In the present case, the difference in the refractive indices of

aragonite and conchyolin at normal incidences is very large. In these circumstances, the observed spectral sharpness of the reflection maxima is, at first sight, a very surprising fact. An explanation of this is to be found in the circumstance that the layers of conchyolin separating those of aragonite are very thin in comparison with the latter. Thus, in spite of the large difference in the refractive indices of the two materials, the reflecting power of an individual stratification is small. The light can therefore penetrate to considerable depths and bring effectively into operation a large number of strata and thereby sharpen the spectral bands of reflection.

### 5. The diffusion haloes and their polarisation

As remarked in the introduction, the diffusion haloes observed when a source of light is viewed through a plate of nacre undergo most remarkable changes in respect of their geometric form and state of polarisation when the plate is tilted from the normal position to one in which the light traverses it obliquely. These changes are illustrated by a series of photographs in plate I for the case of *Turbo*, in plate II for the case of *Margaratifera* and plate III for the case of *Nautilus*. Certain features common to all the three cases may first be mentioned. When the light traverses the plate normally, neither the source of light itself nor the halo seen around it exhibit any polarisation. In other words, if a polaroid covers the source of light and is turned round in its own plane, no change is observable in the field. However, when the plate is tilted, polarisation effects immediately become visible. The source itself as seen by the transmitted light is weakened in intensity, the component of vibration lying in the plane of incidence much more so than the other: indeed, the former component is nearly extinguished when the plate is held sufficiently obliquely. This effect is exactly the opposite to that exhibited by a pile of plates and also appears at much smaller angles of incidence than in the latter case. The explanation of the phenomenon is evidently to be found in another effect which is noticed at the same time, viz., the appearance of an increasingly intense diffusion halo seen covering the source of light and which is strongly polarised in the opposite sense, that is, with its light vibrations predominantly in the plane of incidence. The extinction of the same component in the transmitted light is thus revealed to be a direct consequence of the strong diffusion of the same component at oblique incidences. In all three cases, however, part of the diffusion halo as seen at oblique incidence is found to be polarised with the vibrations perpendicular to the plane of incidence. Both the configuration of the halo and the state of polarisation in the different parts of the field alter progressively with the increasing obliquity of the plate.

The case of *Turbo* illustrated in plate I shows the most rapid changes of the diffusion halo as the incidence is made oblique. To observe the circular halo represented in figure 1, the orientation of the plate has to be precisely normal to

the light-beam from the source. A slight tilt of the plate causes the disappearance of a part of the circular halo and the simultaneous appearance of a corona of light surrounding the source with the consequence that the picture is strongly asymmetric (figure 2 in plate I). With a further tilt, the surviving part of the circular halo divides into two spots which shift towards a diametral setting with reference to the central corona which then appears with greatly enhanced intensity. The picture is then rather reminiscent of the planet Saturn with its rings protruding on either side. Seen through a polaroid, the two outer spots are strongly polarised, being visible in one setting and completely absent in a perpendicular setting; the central corona is also partially polarised but in the opposite sense. These two cases are represented respectively in figures 3 and 4 of plate I. It will be noticed from the latter figure that the central corona has a distinctly elliptic shape with its major axis in the plane of incidence.

In the case of *Margaratifera*, a tilt of the specimen away from the normal results principally in an enlargement and intensification of the central corona covering the source of light. There is however an important difference in its shape and extension according as the tilt of the specimen is about the line joining the two outer spots of the halo or about a perpendicular line. In either case, the extension of the corona is greater in a plane perpendicular to the axis about which the plate is tilted. If the corona extends more along the line of the spots, it tends to overlap and cover them up. Figure 6 corresponds to this case and figure 7 to the other case.

The most remarkable changes are those observed with *Nautilus* and illustrated in figures 8 to 13 of plate III. Some of the features noticed in this case resemble those noted above in the case of *Turbo*, while others resemble the effects observed with *Margaratifera*. The phenomena are totally different in the two cases in which the axis about which the plate is tilted is respectively parallel or perpendicular to the line joining the centres of the two short circular arcs seen in the normal setting. Taking first the parallel case, we find as with *Turbo* a shortening of the circular arcs; they appear to drift to one side or the other according as the tilt is in one sense or the opposite. The pattern thus becomes distinctly unsymmetrical with reference to the image of the source of light. This asymmetry becomes most clearly evident when the pattern is seen through a polaroid. The two outer arcs alone and the source of light are seen in one setting of the polaroid, while in the other perpendicular setting a bright central corona with a diffuse outlying patch is seen. The extraordinary perfection of the polarisation of this corona will be realised on a comparison of figures 10 and 11 in plate III which represent the diffusion halo as seen through the polaroid respectively in two mutually perpendicular settings. Figure 9 is the diffusion halo in the same situation but photographed without a polariser. It will be noticed that the outer arcs have shifted distinctly downwards with respect to the centre of the corona; on the other hand, when the tilt of the plate is in the opposite sense, they drift upwards with respect to it. The latter case is represented by figure 12. When the axis about

which the plate is tilted is perpendicular to the line joining the centres of the circular arcs seen in the normal setting, we observe the strikingly asymmetric pattern reproduced in figure 13, one of the arcs being then much more intense and elongated than the other.

## 6. The origin of the diffusion haloes

Two distinct types of diffusion arise when a beam of light traverses the nacreous substance even in the relatively simple case of normal incidence on the stratifications. We have firstly, the diffusion backwards towards the source referred to in section 3, which is due to the fact that the reflecting layers are not continuous and that when considered on a microscopic scale they are not perfectly plane. The second type of diffusion appears in directions adjacent to that of forward travel of the light. This is a consequence of the different retardations of the advancing wavefront produced respectively by aragonite and by conchyolin in each layer of the stratification. As this difference is not negligible, a powerful diffusion would result. Indeed nacre would be completely opaque to light but for the fact that the largest proportion of the area in each layer is occupied by the aragonite crystallites, the conchyolin only filling the narrow gaps between them. It is scarcely to be doubted that the high opacity of the shell of *Nautilus* is to be ascribed to this condition being less perfectly fulfilled than in the other cases, as is indeed evident from the microphotographs of thin sections of the material.<sup>4</sup>

The linear fibrous grouping of the crystallites in *Margaritifera* results in the diffusion appearing principally in a plane perpendicular to the fibre direction. As a consequence of the approximate uniformity of the size of the crystallites, the nacre behaves somewhat in the manner of a diffraction grating: a central corona appears surrounding the source of light and is accompanied by two bright spots on either side. On the other hand, the central corona is very weak in the normal patterns of *Turbo* and almost completely absent in that of *Nautilus*. The pattern for *Turbo* resembles pretty closely the diffraction pattern due to a large number of circular discs arranged in a plane with a high degree of regularity which is reproduced as figure 3(a) in plate XVI in a paper by Y V Kathavate<sup>8</sup> in these *Proceedings*. We may therefore infer a remarkable combination of random orientation with regularity of spacing of the crystallites of aragonite in *Turbo*. The special form of the diffusion halo in *Nautilus* is likewise to be ascribed to the peculiar shape and very characteristic arrangement of the crystallites in its structure revealed by microscopic and X-ray studies.

When the characteristic monochromatically reflected beam travels backwards towards the source of light, it would necessarily suffer a diffusion of the second type. This would be characterised by its being also monochromatic and would thus be different from the backward diffusion of the first type which would be white in colour. The overlapping of the two effects would determine the colour of the backward diffusion actually observed.

## 7. The case of oblique incidences

We now have to consider the explanation of the remarkable changes in the general configuration of the diffusion pattern, as also the striking polarisation effects exhibited by it in different areas, consequent on a tilting of the plate with respect to the light beam. There could scarcely be any doubt that the latter feature arises from the birefringence of the crystallites of aragonite. When the light traverses them normally, the refractive index is effectively the same or nearly the same for all directions of vibration in the wave front. Hence, the diffusion haloes cannot be expected to exhibit any polarisation, and indeed no such effect is observed. On the other hand, when the light traverses the plate obliquely, the refractive indices of the aragonite differ notably for the two components. There is therefore no reason to anticipate that either the transmission or the diffusion of the light through nacre would exhibit identical features in respect of both components. What is remarkable, however, is that in certain parts of the field the diffused radiation is predominantly polarised in one way and in the rest of the field predominantly in the opposite sense. We have now to ask ourselves why this is the case.

In order that there should be either a high concentration of intensity or a nearly vanishing intensity of the diffracted light in any particular part of the field, it is clearly necessary that the scattered radiations from the crystallites should be in regular phase relationships with each other in the corresponding directions, mutually reinforcing or mutually cancelling out each other's effects by interference, as the case may be. The retardation of phase of the light-waves in passage through a crystallite would be different for the two components of vibration, and it is readily seen that the fluctuations in such retardation due to the varying orientation of the crystallites would be much larger for the vibration component in the plane of incidence than for the other component. It follows that the features in the pattern arising from the coherence-in-phase of the effects of the individual crystallites would be most clearly evident for the component perpendicular to the plane of incidence; *per contra*, the results of their incoherence would be most marked in the parallel component. Pursuing this line of thought, one can readily understand in a general way the phenomena described above for the different species of nacre. A preferential extinction of the parallel component in the transmitted light follows as a consequence of the same train of ideas. This effect is very evident on a comparison of figures 22(b) and (c) in plate VI, which represent the spectra of the transmitted light for the two components respectively and which were recorded with identical exposures.

## 8. Optical behaviour of transverse sections

So far, we have been concerned with the passage of light through nacre in directions either normal or moderately inclined to the stratifications. Very

beautiful effects which appear worthy of record are also noticed when a pencil of light passes through a thin plate of nacre cut transversely. Such a section, in effect, constitutes a diffraction grating. As a consequence, when a narrow pencil of light passes through it and is received on a screen, diffraction spectra are observed, one on either side of the transmitted beam, in directions making fairly large angles with it. The transmitted beam also shows a distinct measure of polarisation, but the sense of this differs in the two cases of light traversing the section normally and in very oblique directions. Within a certain range of these directions, a bright cross exhibiting brilliant colours with complementary tints in the two arms appears, having the transmitted pencil at the point of intersection of the two arms. The colours change in a remarkable manner with the inclination of the section to the pencil of light. The two arms are also polarised but with their vibration directions perpendicular to each other.

In seeking an explanation for the effects briefly mentioned above, one takes into account the fact that the refractive indices of aragonite and of conchyolin are different, such difference varying both with the direction of travel of the light beam and with the direction of vibration in it. Laminar diffraction effects varying with these factors would arise in consequence. The phenomenon of the cross with coloured arms may be ascribed to the discrete structure of the layers of aragonite. It may be mentioned that the phenomenon is best shown by transverse sections of *Turbo*.

## 9. Summary

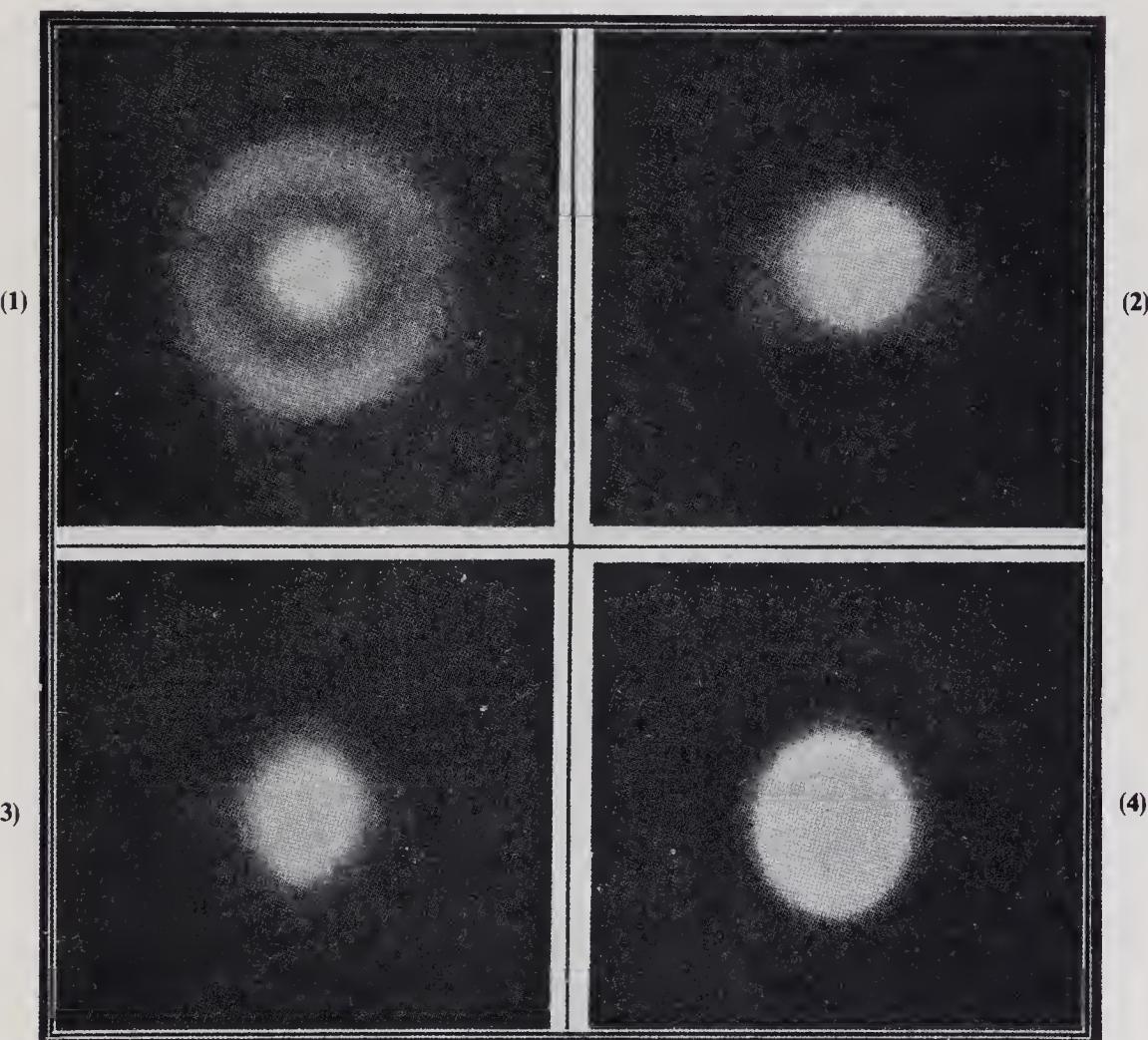
Some remarkable optical effects exhibited by nacreous shells have been observed and reported, the following amongst others: The monochromatic reflections and extinctions split into two polarised components at oblique incidences as a result of the birefringence of the material. Light traversing the stratifications obliquely suffers extinction by reason of diffusion by the crystallites of aragonite, this being most rapid for the component of vibration in the plane of incidence. Striking changes are also observed in the character of the diffusion haloes with increasing obliquity of observation, a particularly noteworthy feature being that the different parts of the diffusion field are differently polarised.

## Bibliography

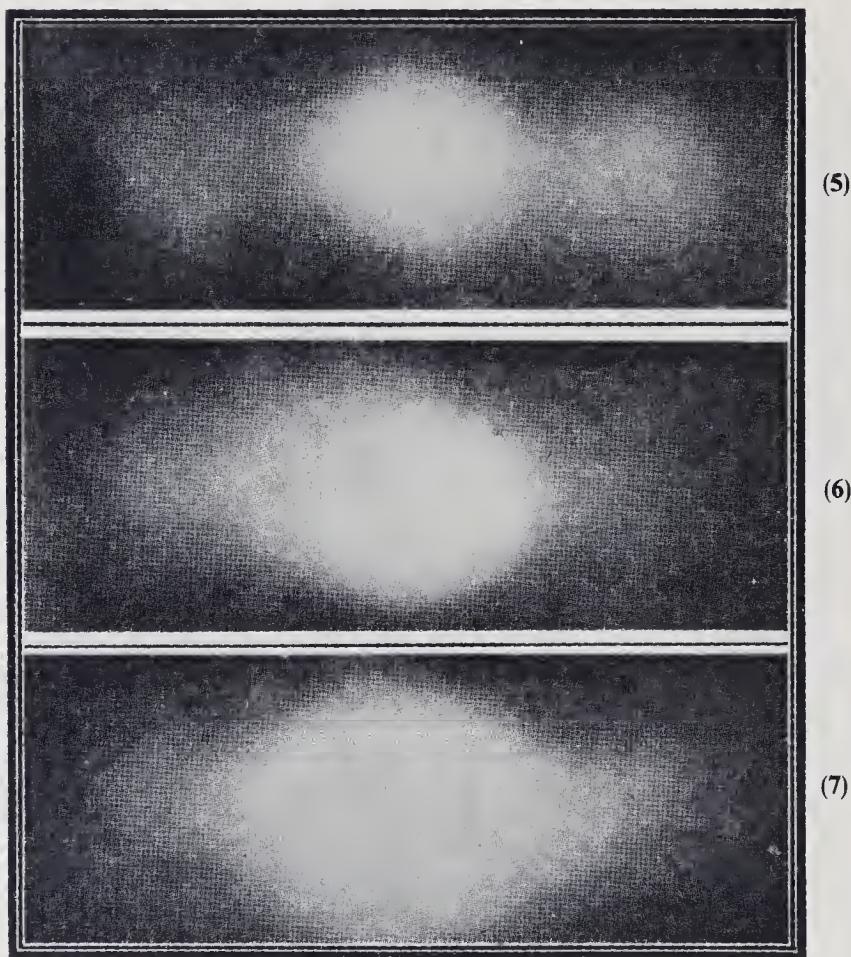
Important studies on the structure of mother-of-pearl were made by W J Schmidt, a summary of whose findings is given in pages 155 to 165 of his book *Die Bausteine Des Tierkorpers in Polarisiertem Lichte*, 1924. The following papers are those referred to in the text.

1. Raman C V, *Proc. Indian Acad. Sci.*, 1935, 1A, 567.
2. Raman C V *Ibid.*, 1935, 1A, 574.

3. Raman C V, *Ibid.*, 1935, **1A**, 859.
4. Rajagopalan V S, *Ibid.*, 1936, **3A**, 572.
5. Rama Swamy S, *Ibid.*, 1935, **1A**, 871.
6. Rama Swamy S, *Ibid.*, 1935, **2A**, 345
7. Ramachandran G N, *Ibid.*, 1942, **16A**, 336.
8. Kathavate Y V, *Ibid.*, 1945, **21A**, 233.

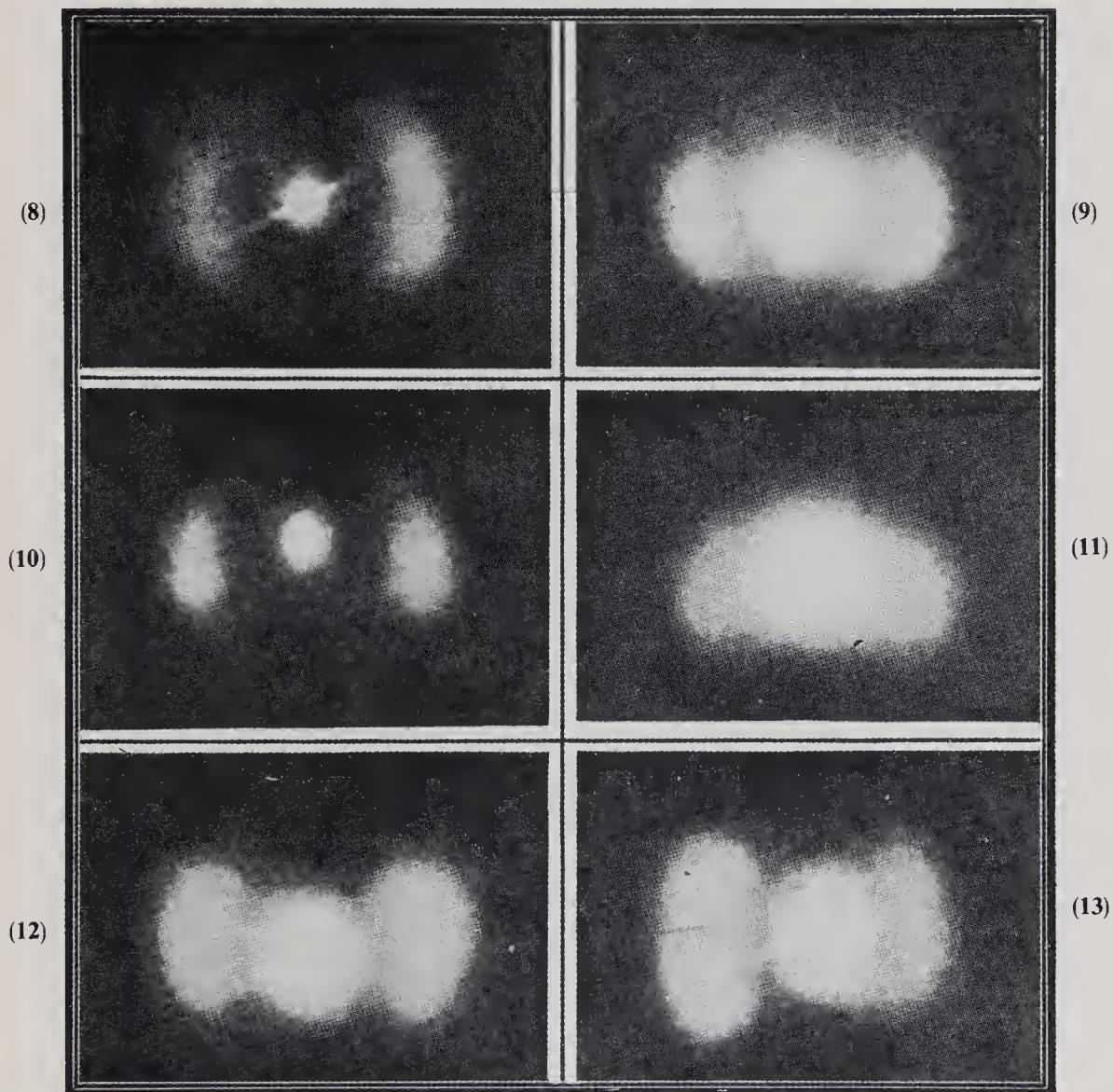


Figures 1-4. Polarised diffusion haloes of *Turbo*.



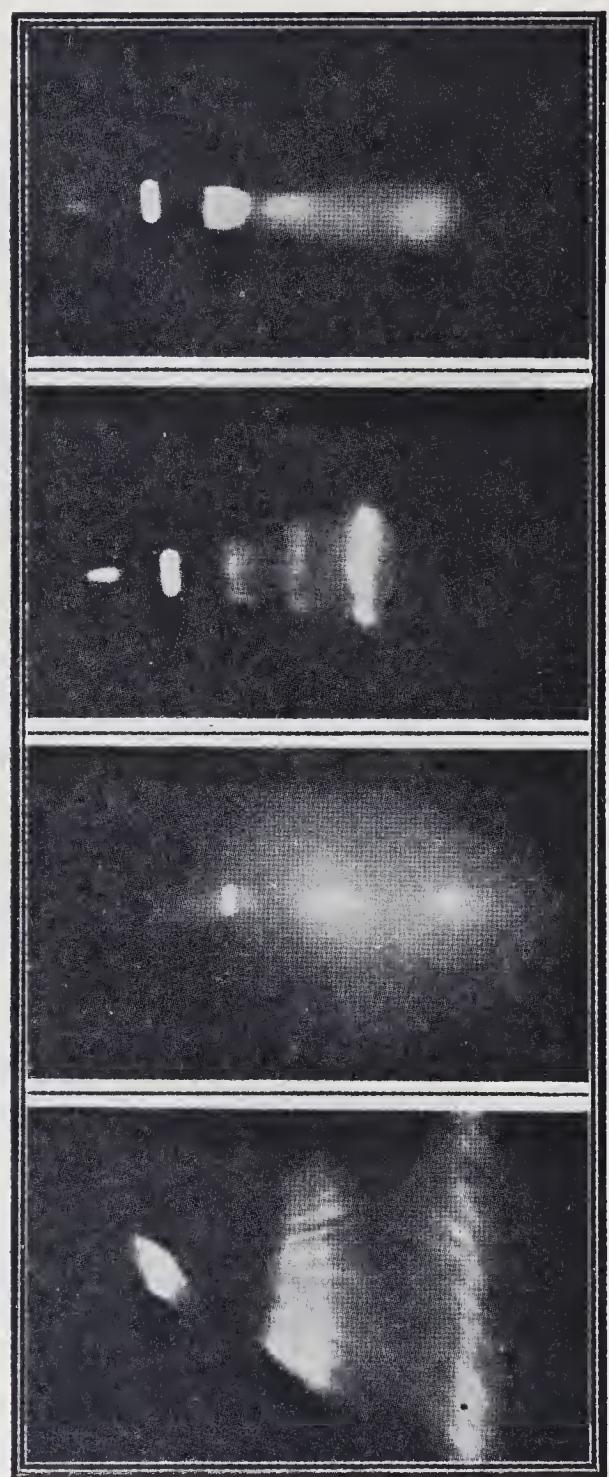
**Figures 5–7.** Polarised diffusion haloes of *Margaratifera*.

**Plate II**

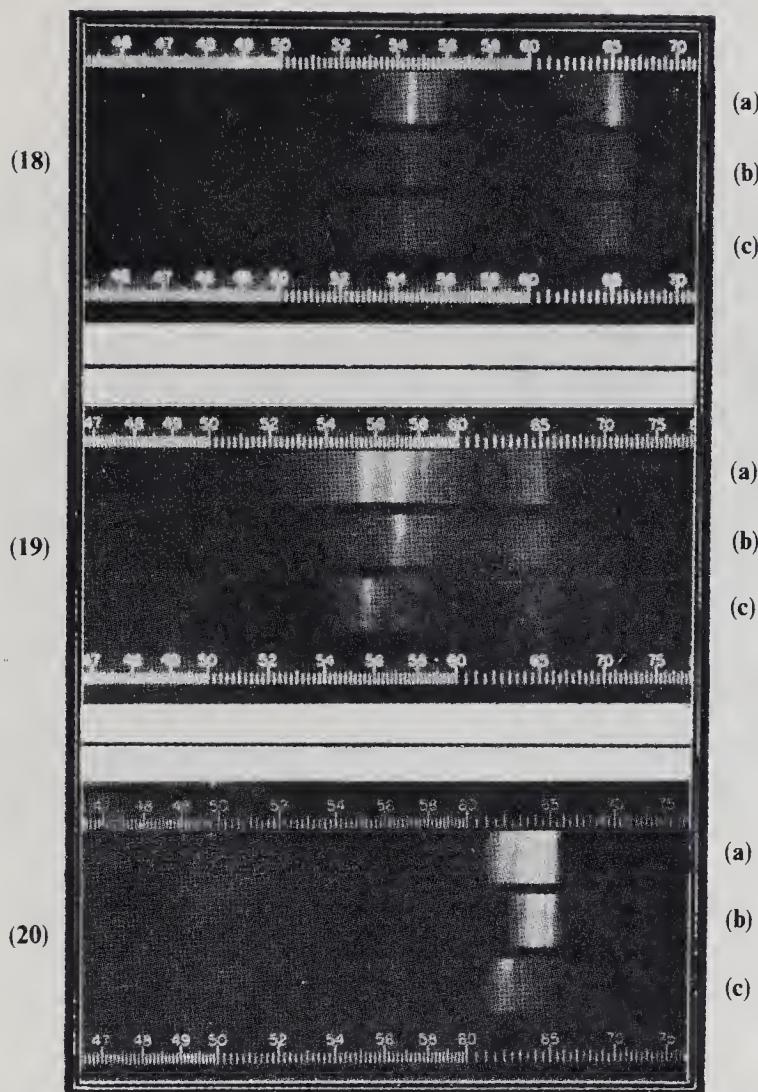


Figures 8–13. Polarised diffusion haloes of *Nautilus*.

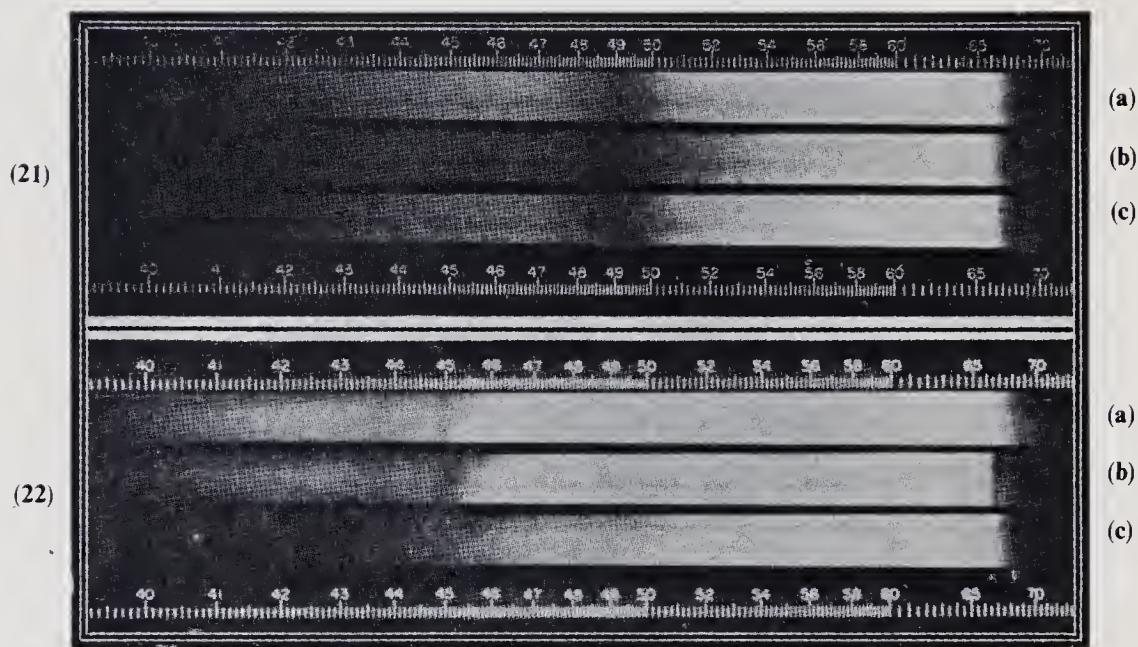
Plate III



**Figures 14–17.** Reflection diffraction spectra. **14.** *Margaritifera*, **15.** *Turbo*, **16.** *Nautilus*, **17.** *Haliotis*.



Figures 18–20. Reflection spectra. 18 and 19. *Margaritifera*, 20. *Turbo*.



Figures 21 and 22. Transmission spectra of *Turbo*.

Plate VI

# The structure and optical characters of iridescent glass

SIR C V RAMAN and V S RAJAGOPALAN

Received April 29, 1939

## 1. Introduction

In the museums of Europe will be found exhibited specimens of ancient glassware excavated from archaeological sites and distinguished by a very beautiful iridescence. Nearly a century ago, Sir David Brewster (1840, 1859, 1860, 1864) examined and described specimens of such glass. According to him, the iridescence of glass which has suffered decomposition is due to its lamellar structure; in other words, the material is an ensemble of thin films optically distinct from each other. In consequence of this structure, it exhibits a large reflecting power, presenting vivid colours both by reflection and by transmission, these being complementary. Brewster noticed that only rarely do the laminae possess specularly reflecting surfaces; in many cases their surfaces are rough due to the presence of a large number of small cavities which may lie separate or run into each other; in other cases again, according to him, the films are covered with concentric stratified structures presenting between crossed nicols the phenomenon of a black cross.

Brewster's explanation of the iridescence of ancient glass appears to have been accepted without question by all subsequent observers. Considerable interest naturally attaches to the question why the glass acquires with time a laminar structure which in its normal state it does not possess. It is a matter of common knowledge that glass under prolonged exposure to wind and weather or to the action of suitable chemical reagents often acquires a superficial iridescence, and attempts have not been lacking to accelerate this process of attack and thus to reproduce experimentally some of the structures observed and described by Brewster in ancient glass. Some remarks on earlier attempts in this connection will be found in an interesting note by M Marcel Guillot (1934) who has shown that when a saturated solution of sodium bicarbonate is kept in contact with a surface of alkaline glass for some weeks or months, marked iridescence results; he suggests that such iridescence is due to the formation of stratified films by a chemical process analogous to the Leisegang phenomenon.

It should be remarked that Brewster's views regarding the structure and optical characters of iridescent glass are not altogether free from obscurity. The refractive

index of the decomposed material presumably differs little from that of the original glass. Assuming this to be the case, it is not easy to understand how the coloured reflections arise. If in order to explain the optical effects, we postulate the existence of thin films of air separating the decomposed layers of glass from each other, it is not understood why the films are actually adherent to each other and to the glass, and why they exhibit in many cases a remarkable uniformity of colour and brightness over considerable areas. If, on the other hand, we assume that the cementing material is some solid substance, it would be necessary that its refractive index should be considerably higher or lower than that of glass, in order that sensible reflections should result; moreover, such an assumption would be difficult to reconcile with the astonishing rapidity of penetration of a liquid such as water or alcohol into the decomposed glass, and the equal facility with which it can evaporate and leave the iridescence unaffected.

For the reasons remarked above, it appeared to us worth while to re-examine the subject with a view to clarifying the position. The investigation was taken up in spite of the fact that we had at first no archaeological material available; the impulse to study the subject arose from the observation that specimens of decomposed glass of no great age picked up from the ground often showed beautiful effects when examined under the Leitz ultra-opak microscope. In this instrument, the illuminating beam has the form of a hollow cone which is reflected downwards and converges on the surface of the object. If the axis of the cone is normal to the surface, we have "dark field" illumination, the surface becoming visible by reason of the light scattered or diffracted by it. On the other hand, by suitably tilting the plate of glass, it is possible to arrange that the light "regularly reflected" by its surface enters the microscope, in which case, we have the ordinary or "bright field" observing conditions. These arrangements are specially suitable for the study of the structures produced in glass by its decomposition. The photomicrographs illustrating the paper (figures 1 to 30) were taken with the Leitz ultra-opak microscope and exhibit various types of structure observed in the course of this study. It should be mentioned that examination by transmitted light in the ordinary form of microscope is also useful in many cases, particularly if high powers are to be employed or when it is desired to work with polarised light.

## 2. Structures in iridescent glass

As was remarked by Brewster, the structures observed in decomposed glass are of rather varied type. In the present investigation, several distinct forms have been observed which give characteristic optical effects. These may be listed as follows: (a) cavities; (b) films without boundaries; (c) films with sharply defined boundaries; (d) films scattering light; (e) films with cavities, and (f) dark areas.

**Cavities:** Small cavities with a circular outline are very common in decomposed glass. When seen by diffracted light, these appear as luminous circles surrounding a dark area. The manner in which such cavities are formed in decomposed glass is made beautifully clear by a study of some plates of dark-blue glass which were picked up at the site of an extinct glass factory at Ennur near Madras. The plates exhibit by reflected light a large number of white circular spots of varying size on a dark ground; the spots in some areas are so close together as to form a continuous white film covering the blue glass. The individual white spots on careful examination are seen to consist of a number of concentric rings, the central region where the material is thickest being white, and the margins which are thinner showing traces of colour in the rings. The white material, though strongly adherent to the plate, can be removed by applying sufficient force; when it comes off, it leaves behind a hollow cavity exhibiting a number of concentric circular rings within its area, *these being in many cases vividly coloured*. The depth of the cavity formed by the removal of the white material is indicated by the difference in microscopic focus between top and centre which becomes evident after such removal. The circular rings are the step-like walls of the cavity which correspond to the diminishing diameter of the successive laminae in the decomposed material, the number of such laminae being greatest at the centre and least at the margins of the cavity. These laminae in the material removed appear to run more or less parallel to the surface of the glass plate.

Figures 1 and 2 in plate I and figures 3 and 4 in plate II illustrate the foregoing remarks, the white patches with indistinct rings being the material produced by the decomposition of the glass, and the concentric rings with dark centres being the cavities formed by its removal. Figures 3 and 4 are photographs of multiple cavities, the latter being on an enlarged scale; it will be noticed how the rings surrounding neighbouring cavities join up sharply at their points of intersection. Figures 5 and 6 in plate III show cavities with comparatively few rings. Figure 7 in plate IV exhibits numerous cavities, while figure 8 in the same plate shows a large number of such cavities forming a continuous area.

Examination of the cavities and of the material removed therefrom by transmitted light under a high power microscope confirms the structure and the manner of formation described above. The high powers of the microscope reveal a large number of fine edges running round the walls of the cavities, and it is seen that these walls are laid out in step-like terraces. Seen by transmitted light between crossed nicols, the walls of a cavity appear as an array of concentric dark and bright circles traversed by a black cross. These effects arise from the fact that a laminar diffracting edge which is not parallel or perpendicular to the electric vector in the light incident on it gives rise to elliptic polarisation (Raman and Rao, 1927). Brewster described certain structures in decomposed glass which he considered as similar to the concentric spherical laminations of a pearl or an onion and which he found to exhibit a black cross in polarised light between crossed nicols; this phenomenon he ascribed to the results of oblique trans-

mission of light through a pile of plates. This, however, is a different phenomenon; on the other hand, Brewster's descriptions of some of the structures exhibiting a black cross between crossed nicols agree so closely with those illustrated in figures 1 to 4 of the present paper that we are obliged to assume that he was really observing the same phenomena as that described above.

*Films without boundaries:* The general appearance of iridescent glass and in particular, the intensity and hue of the colours exhibited by it and the distribution of the same on the surface depend greatly on the particular sample under study and the treatment it has undergone. We must in this connection distinguish between the effects noticed in the earlier stages of decomposition and in the later stages where the decomposition is far advanced; the difference has also to be remembered between the cases in which the surface is untouched and those in which the underlying iridescent films have been exposed by removal of the upper layers containing the decomposed material. The type of iridescence referred to under the present sub-heading appears to belong to the earlier stages of decomposition; its distinguishing feature is that there are no sharp boundaries dividing the differently coloured regions. This type of film is illustrated in figure 9 in plate V, figure 11 in plate VI and figure 16 in plate VIII. It will be seen that, except for a few detached patches, the variations of intensity over the surface of the plate are more or less gradual.

*Films with sharply defined boundaries:* In sharp contrast with the foregoing type of iridescence, we have the discontinuous distributions of colour in map-like patterns illustrated in figure 10 in plate V and figures 13 and 14 in plate VII. This is a common type of structure and is to be found sometimes even in the earlier stages of decomposition. Its characteristic features are a strict uniformity of colour and brightness over each "area" in the "map" and a sharply defined boundary limiting each such area. Further, the brightness and colour of the different areas is very varied, ranging from the darkest tones to the brightest and from the most saturated hues to the palest. There can be no doubt that this type of iridescence is due to a laminated structure bounded by sharp edges; the uniformity of colour and brightness over each "area" in the "map" indicates that the laminae are of uniform thickness and solidly adherent, and not loose formations separated by air films. Indeed, any tendency to separation of the laminae by air films is revealed by a variation of colour over each "area" and in some cases even by a succession of colours of the Newton's rings type appearing within it. For instance, we notice that figure 12 in plate VI clearly reveals the presence of a film of air of variable thickness between the laminae. Figure 15 in plate VIII is specially interesting as it shows the extreme sharpness of the boundaries of colour, which in the photograph are recorded as laminar edges on a dark field by reason of the light diffracted by them. Figure 13 in plate VII is also of interest, as it exhibits detached areas of iridescence showing the luminosity at the

edges due to diffraction, as also the reflection and scattering of light by the film itself against a background of undecomposed glass.

*Films scattering light:* The fact that in figure 15, the edges of the iridescent area are seen as luminous lines diffracting light while the film itself is invisible, shows that it is possible to obtain films which reflect without appreciably scattering light. In general, however, the surface of decomposed glass scatters light rather strongly; the intensity of such scattering varies greatly and depends both on the nature and extent of the decomposition of the surface and the treatment it has undergone. With certain exceptions, the films which scatter most light usually reflect the least light and display the feeblest iridescence; *per contra*, the films which reflect the most light and display the most vivid iridescence generally scatter the least amount of light. As a consequence of this, it will be noticed that when the surface is held at the proper angle to reflect the light, the iridescent areas are the brightest and the scattering areas are the darkest; when the plate is turned away from the correct angle, the iridescent areas are dark and the scattering areas are bright. It is also noticed that the parts of the films which are seen to scatter most light by this rough test are those in which the decomposed material which is usually white remains still adherent to the glass; when this is removed, the iridescent reflections become more prominent. It may be presumed that the scattering of light by the films is due to the optical heterogeneity of the material formed by the decomposition of the glass. It is however not easy to distinguish such scattering microscopically from that due to cavities present in the film which are too small or too close together to be resolved completely.

The scattering of light by unresolved or imperfectly resolved structures in decomposed glass is evident in many of the figures reproduced with the paper, as for instance, the right half of figure 8 in plate IV, the central bright area in figure 9 in plate V, figure 12 in plate VI, figure 13 in plate VII and the bright areas in figures 17 and 18 in plate IX.

*Films with cavities:* Examined with the Leitz ultra-opak microscope under "dark field" conditions, decomposed areas in glass usually exhibit illumination, the intensity of this varying enormously with the conditions. In many cases, the luminosity is due for the greater part to the presence of hollow cavities of lesser or greater size, which are either discrete or which run into each other to form patterns or networks of the most varied forms. Under the conical illumination of the microscope, the cavities appear as small luminous circles, vividly coloured, and in most cases, a great many circles lying in a well-defined "area" have the same colour and thus remind one of flowers laid out in a bed. Illustrations of such patterns appear in figures 19 and 20 in plate X (the latter being a part of the field appearing in figure 19 magnified threefold), figures 21 and 22 in plate XI, figures 23 and 24 in plate XII and figure 26 in plate XIII. In many cases numerous small cavities appear superposed on single large ones, giving rise to beautiful patterns in

colour. By suitable illumination, the cavities may be caused to appear reversed and stand out in relief in the field of the microscope. Illustrations of the effects then observed are reproduced in figure 25 in plate XIII and in figures 27 and 28 in plate XIV.

*Dark areas:* On examination of the photographs reproduced in figures 1 to 28, plates I to XIV, it will be seen that in numerous cases extensive "dark areas" are to be observed. These may, in some cases, merely represent areas of undecomposed glass which do not scatter light and therefore fail to appear on the photographic plate under "dark field" conditions. Such cases may be readily identified by tilting the specimen so that the reflected light enters the microscope, as the dark areas then turn bright. On making this simple test, it is found that decomposed glass does exhibit in many cases extensive areas which are dark both under "bright field" and under "dark field" observing conditions, in other words, do not either reflect, or scatter light appreciably. This result is theoretically intelligible, for reflection can be abolished without involving scattering of light, if the change of refractive index at the surface takes place in a continuous manner instead of being discontinuous, in other words, if it is spread over a depth which is not small compared with the wavelength of light. The superficial decomposition of glass may lead to such a result if it extends over a sufficient depth, and if the gradient of refractive index produced thereby is continuous instead of being oscillatory. The latter condition would give rise to an iridescent reflection, while the former would abolish reflection altogether.

### 3. Effect of immersion in liquids

If a piece of iridescent glass is breathed upon when cold, moisture condenses on it and the colour of the film apparently vanishes immediately; it however reappears when the plate is warmed up. Brewster noticed the apparent suppression of colour produced by placing a drop of water or alcohol on the film, as also its restoration when the fluid has evaporated. He noticed further that oil or balsam penetrates the film slowly and unequally, producing a succession of tints on the plate during its advance. A careful study of these and other effects produced by contact with liquids is evidently of importance in order to elucidate the problem of the structure of these films and their optical characters.

It should be remarked in the first place that the observations made in the rather crude way mentioned above are deceptive. *In reality, the iridescence of decomposed glass does not disappear on immersion in a liquid; on the other hand, the colours actually become more vivid, though their intensity is considerably diminished.* This is readily shown, for instance, by dipping the plate in a cell containing water and observing it within the liquid by reflected light. The

iridescence can then be readily seen through the sides of the cell, and may conveniently be examined with the aid of a hand-lens. Its general appearance is made more striking on submergence by reason of the diminished reflection of light from the front of the film and the back of the plate, as well as by the reduction in the amount of scattered light. This improvement is particularly marked for oblique incidences. *When the plate is in air, the colours of decomposed glass disappear when the light falls sufficiently obliquely; but with the plate submerged in water, the colours may be observed right up to grazing incidence.* It is thus clear that the range of study is considerably extended by the use of the technique of immersion of the film in a liquid cell.

A special feature of the Leitz ultra-opak microscope is that its stage is of ample size and can accommodate a container for liquid in which the objective as well as the material under study can be immersed. The instrument can therefore be very conveniently used for studying the iridescence of submerged films. The disturbance due to the reflection of light from the free surface of the liquid is avoided completely, and the iridescence can be seen under either "bright field" or "dark field" conditions as desired; the effects following immersion can also be watched from instant to instant. Using this procedure and examining a variety of examples, the results already stated are readily verified. In seeking to explain the effects observed, we have to remember that the liquid has a twofold influence; firstly, the reflection at the external surface of the film is greatly diminished; secondly, the liquid enters the cavities of the film—those visible in the microscope as well as the invisible cavities forming part of its structure; as a result of this penetration, the optical properties of the film are altered in a manner depending upon the quantity of liquid which penetrates, its distribution within the thickness of the film and the refractive indices of the film and of the liquid.

A little consideration indicates that the effects referred to above would be most pronounced when the refractive index of the liquid approximates most closely to the refractive index of the film. When this is the case, the surface reflection would be negligible and the variations of index within the film would be greatly reduced; we should accordingly expect the iridescence to become enfeebled in intensity. *Per contra*, we should expect the iridescence to be less enfeebled when the refractive index of the liquid deviates considerably from that of the film. These anticipations from theory are found to be fulfilled in observation. A variety of liquids can be used e.g., water, glycerine, carbon tetrachloride, benzene, carbon disulphide and monobrom-naphthalene and suitable admixtures thereof, so that the immersion liquid can have any desired refractive index from 1·33 to 1·66. In every case, it is found that immersion produces a marked change of colour. The diminution of its intensity is most striking when the immersion liquid has a refractive index about the same as that of the glass used and is less marked when the refractive index of the liquid is either greater or less. Judging from the observations, it would appear possible to determine the index for minimum iridescence fairly accurately. The fact that the colours do not vanish for any index is significant but is not

surprising when we recollect that the penetration of liquid can scarcely be expected to produce a complete uniformity of refractive index within the film.

#### 4. Effect of absorption of liquids

When the plate is completely immersed in a liquid, the latter can penetrate the film to the maximum extent provided sufficient time is allowed. It is however of interest to be able to study the effect of absorption of liquid on the iridescence of the film when the latter is not actually submerged. Further, it is desirable also to be able to study the cases in which the absorption is incomplete and takes place to an extent which can be controlled, and when it is variable with time. For this purpose, again, the Leitz ultra-opak microscope is very suitable. A convenient technique is to place a drop of the chosen liquid on the film while it is under observation in the field of the microscope. The properties of the liquid which should be capable of influencing the results under these conditions are its refractive index, its speed of spreading over the surface and of penetration into the film, as well as its rate of evaporation. Benzene, for instance, penetrates quickly and also evaporates quickly. Water also enters the films quickly but is slower to evaporate, while monobrom-naphthalene is slow in both respects. An interesting variation of the technique is to use a mixture of liquids, e.g., benzene and monobrom-naphthalene which can penetrate quickly but which on evaporation leaves the less volatile component behind in the film, thus altering its optical characters.

In making the observations mentioned, it is convenient to work with a film which initially shows a uniform colour so that the variations of the same with the quantity of liquid absorbed can be more readily recognised. Films with a uniform colour over a considerable area may be obtained by chemically iridising glass. (A reagent bottle which had developed a strikingly uniform internal iridescence was broken up and furnished suitable material for these investigations.) Figure 29 in plate XV is a photomicrograph of such a plate with a drop of monobrom-naphthalene placed on it. The sharply bounded black central area (with a bright overlying ring due to reflected light) is the portion of the film actually covered by the liquid. The moderately dark circle surrounding the drop is the area of the film internally saturated with liquid, while beyond the same is seen a succession of dark and bright rings which indicate a variation in the quantity and distribution of the liquid absorbed by the film. In the actual experiments, these rings exhibit varied colours which are even more striking than the colour of the part of the film free from liquid.

When a comparatively non-volatile liquid such as monobrom-naphthalene is used, the pattern surrounding the drop when fully developed remains practically static and can therefore be photographed easily. The case is entirely different when a quickly spreading and volatile liquid such as benzene is used. The colour

patterns due to its absorption and subsequent evaporation change with extraordinary rapidity, so much so that they can only be observed visually. The essential point is that the colour of the film is greatly altered by the presence within it of even small quantities of fluid and is fully restored only when the same has completely evaporated or has been otherwise removed. Using the technique of a non-volatile substance dissolved in a volatile fluid, it should be possible to introduce definite quantities of a substance of known refractive index into a measured area of the film and to correlate the same with the changes of colour produced thereby.

### 5. Effect of mechanical pressure

The penetration of liquid into the iridescent film which is shown by the change in colour resulting therefrom indicates that the material of the film, at least in some cases, has an "open structure" which permits of entry of fluid. Such partial emptiness may be ascribed to the loose packing of the material in a manner which may be either continuous or periodic. If this view be correct, it should be possible by mechanical compression to increase the density of the film and at the same make it more uniform. The experiment is readily tried, and in the particular case of the chemically iridised glass used in obtaining figure 29, it is strikingly successful. Figure 30, plate XV, shows a uniform film which had been subjected to the rolling pressure of the rounded end of an ivory rod. It will be noticed that the whole of the compressed area appears dark in the picture, the greenish-blue iridescence having turned dark-red as the result of pressure. The margin of the compressed area shows a bright belt, indicating that the first effect of the pressure is actually to increase the intensity of the iridescence. Spectroscopic examination showed that the bands in the spectrum of the reflected light brighten and then shift as the result by the application of pressure: with greatly increased pressure, their intensity falls off to a small value.

It must be remarked, however, that the effect of mechanical pressure on the iridescence is by no means equally striking in respect of all films. It must be presumed that in those cases where the pressure produces a relatively small effect, the structure is more compact and the film should then have a smaller capacity for absorbing liquid. This is a matter however to be tested by more detailed investigation.

### 6. Polarisation phenomena

A careful study of the state of polarisation of the light reflected at various angles of incidence should evidently be capable of furnishing useful information regarding the optical properties of the film responsible for the iridescence. Preliminary

observations indicate that the coloured reflections exhibit the maximum polarisation at an angle of incidence which does not differ much from the Brewsterian angle for the undecomposed glass. At this angle and for incidences somewhat more oblique, a distinct change in the colour of the film to the complementary tint is noticed, at least in some cases, when the observing nicol is turned to the position which transmits the minimum of reflected light. Such an effect is to be expected if the film has a refractive index less than that of the undecomposed glass. On the other hand, when the film is submerged in a liquid, the effect mentioned above is not noticeable, and the polarisation of the reflected light is found to be sensibly complete at or about the Brewsterian angle of incidence for the liquid-glass boundary. This is to be expected if the colours are then due to relatively small fluctuations of refractive index within a stratified film having nearly the same refractive index as glass. Precise measurements would however be necessary to distinguish between the different possibilities regarding the manner in which the refractive index fluctuates within the film and to determine its average value in relation to that of the glass.

## 7. Summary

A study of numerous specimens and of 30 photomicrographs of the same shows that the structures in decomposed glass may be divided into six categories exhibiting distinct optical phenomena: (1) Cavities with terraced walls; (2) films exhibiting iridescence of varying colour without defined boundaries; (3) films exhibiting map-like patterns of colour with sharply defined laminar boundaries; (4) films containing unresolved or imperfectly resolved structures scattering light; (5) films containing hollow cavities, and (6) dark areas which neither reflect nor scatter light. Contrary to Brewster's observation, the colours of decomposed glass actually become more striking when the material is covered by liquid; the intensity diminishes but does not disappear even when the index of the surrounding fluid is identical with that of the film. The films are capable of absorbing liquid in variable amount, their colours being altered thereby. The openness of internal structure indicated by this fact is confirmed by observations on the effect of mechanical pressure on the iridescence, and on the polarisation of the reflected light at various incidences both in air and when submerged in liquids.

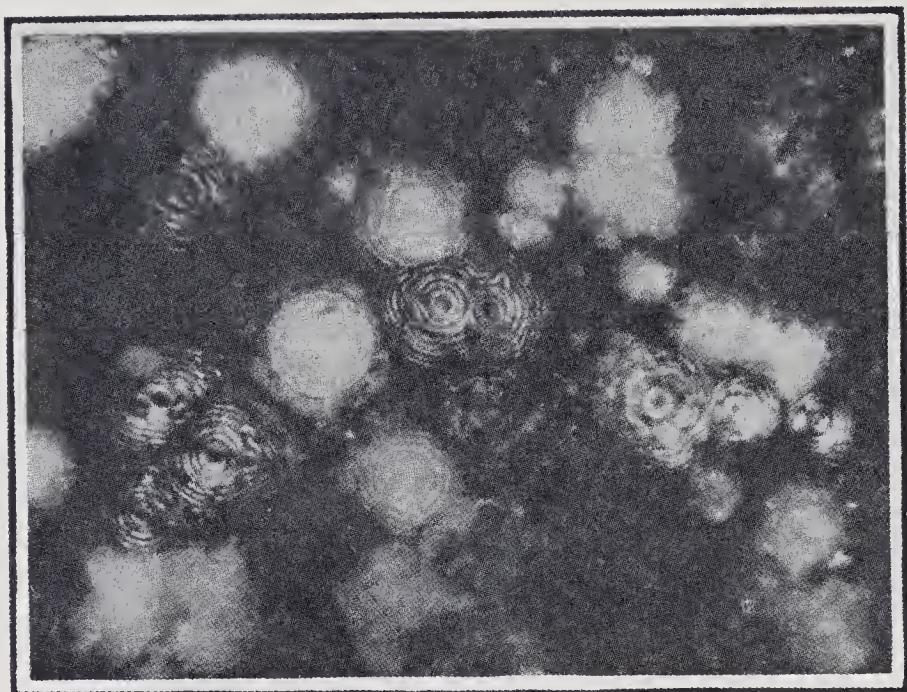
## Literature and references

Berl F and Bender F, *Chem. Ztg.*, 1930, **54**, 913–14.

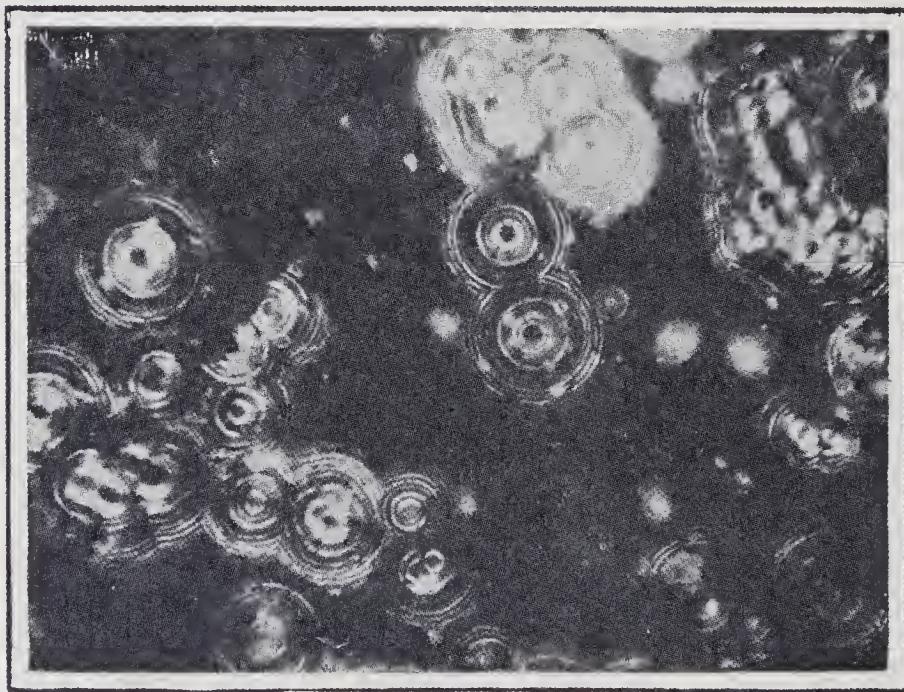
Sir David Brewster, *Br. Assoc. Rep.*, 1840, **2**, 5–6; 1859, **2**, 11; 1860, **2**, 9–12; *Edinburgh R. Soc. Trans.*, 1864, **23**, 193.

Ford K L, *J. Am. Ceram Soc.*, 1922, **5**, 837.

- Guillot M, *Comp. Rend.*, 1934, **198**, 2093–2095.  
Noel Heaton, *J. Soc. Arts.*, 1907, **55**, 468–484.  
Hugel G and Voltz T H, *Bull. Soc. und Mulhouse*, 1932, **88**, 27–30.  
Laubengayer A W, *J. Am. Ceram. Soc.*, 1931, **14**, 833–36.  
Mylius F, *Berichte*, 1910, **43**, 2130–2137; *Z. Anorg. Chem.*, 1910, **67**, 200–224.  
Raman C V and Rao I R, *Proc. Phys. Soc. London*, 1937, **39**, 453–57.  
Tabata K, *J. Am. Ceram. Soc.*, 1927, **10**, 6–22.  
Tabata K, Yegami K and Moriyasu S, *Res. Elec. Tech. Lab. Jpn.* 1926, **179**, 1–11.



**Figure 1** ( $\times 150$ )



**Figure 2** ( $\times 150$ )

## Plate I



Figure 3

(x 180)

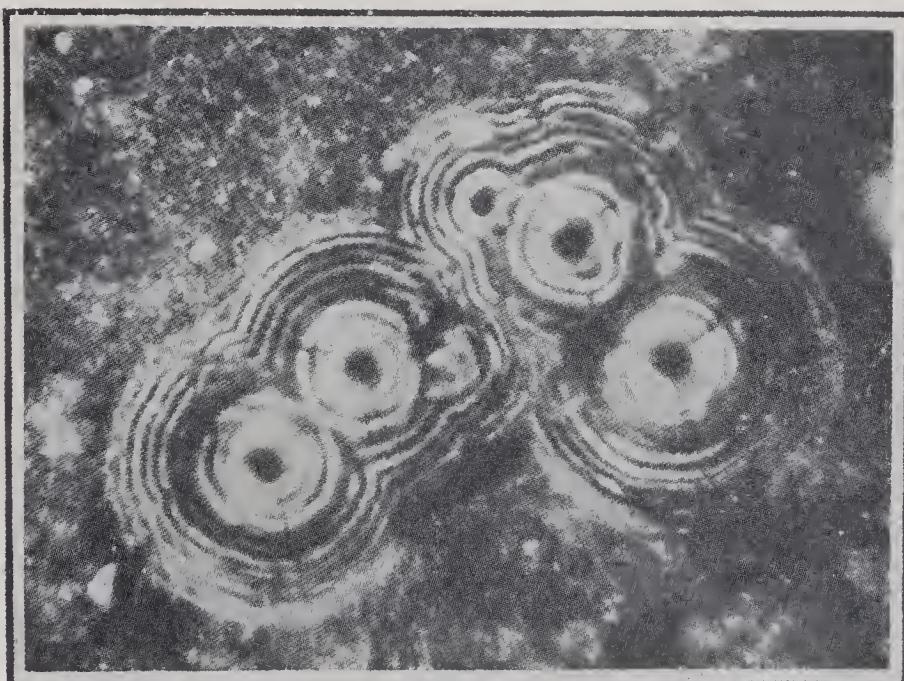


Figure 4

(x 350)

Plate II

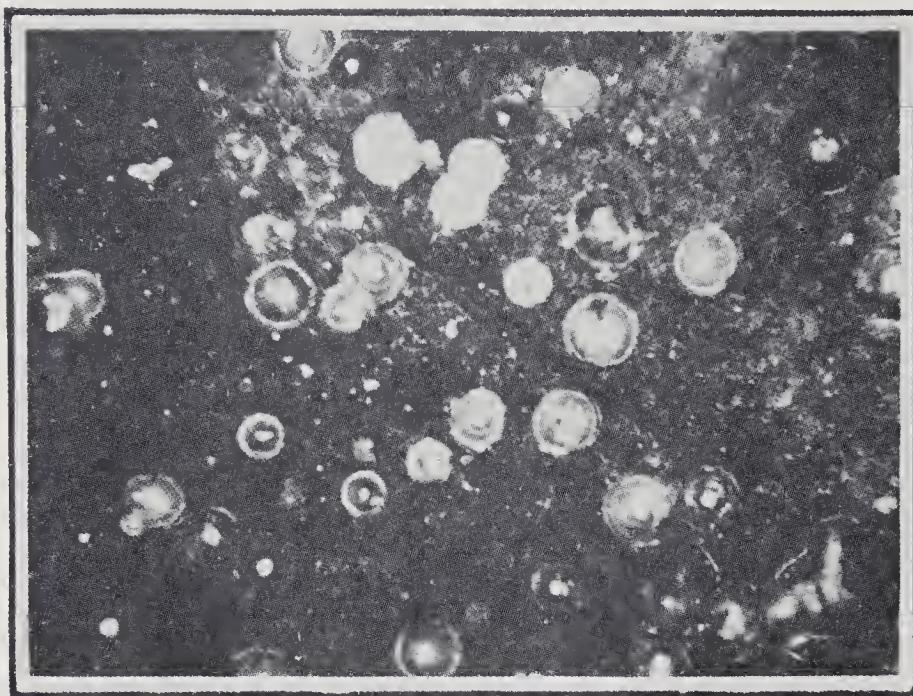


Figure 5

(x 120)



Figure 6

(x 180)

Plate III

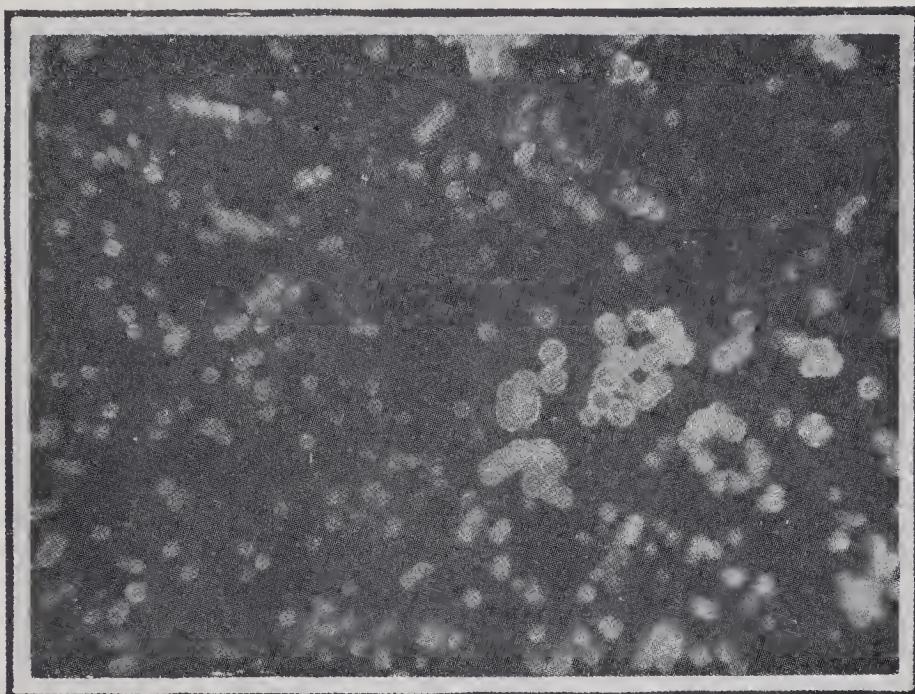


Figure 7

 $(\times 300)$ 

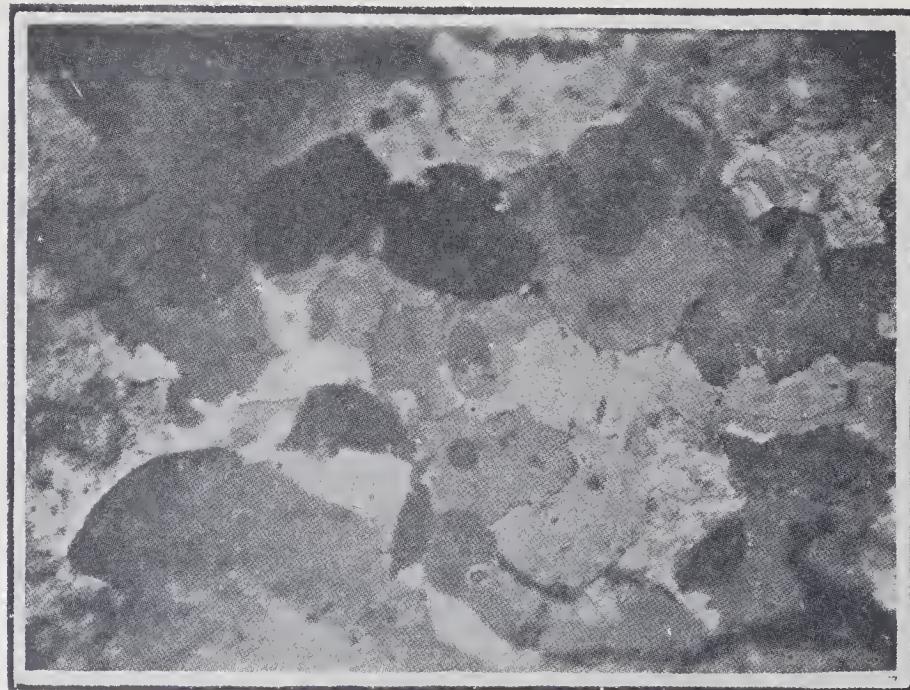
Figure 8

 $(\times 180)$ 

Plate IV



**Figure 9** (x 65)



**Figure 10** ( $\times 65$ )

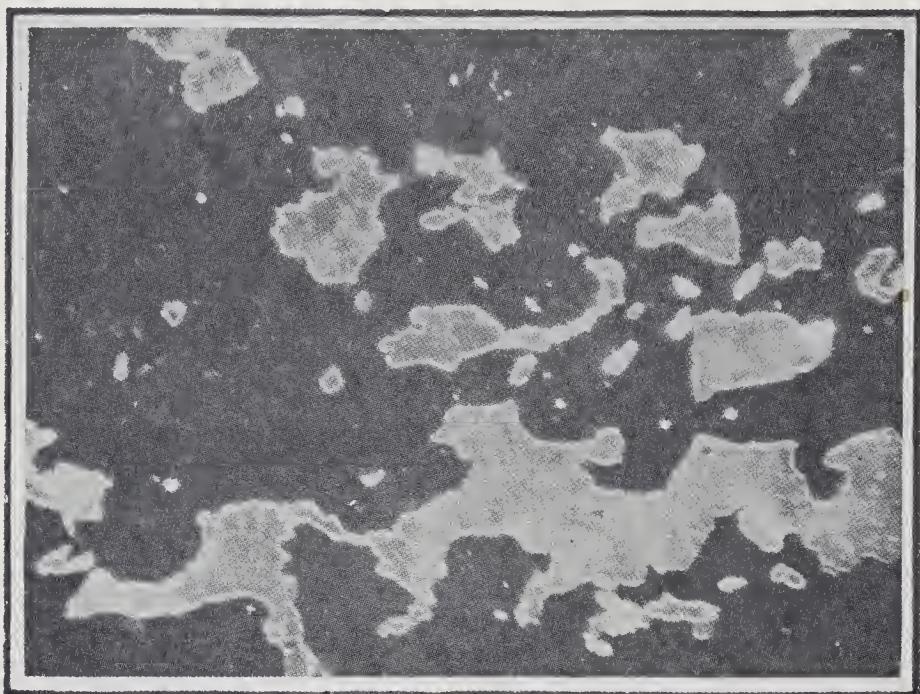
## Plate V



Figure 11 ( $\times 100$ )



Figure 12 ( $\times 180$ )



**Figure 13** ( $\times 180$ )



**Figure 14** ( $\times 100$ )

## Plate VII



Figure 15                                   ( $\times 90$ )

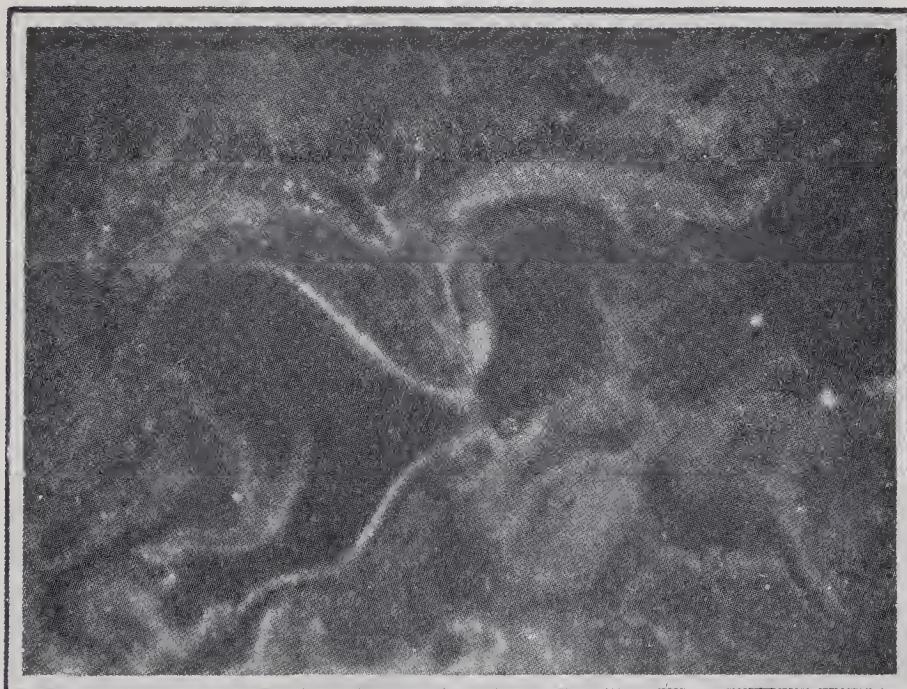


Figure 16                                   ( $\times 65$ )

Plate VIII



Figure 17

 $(\times 90)$ 

Figure 18

 $(\times 90)$ 

Plate IX

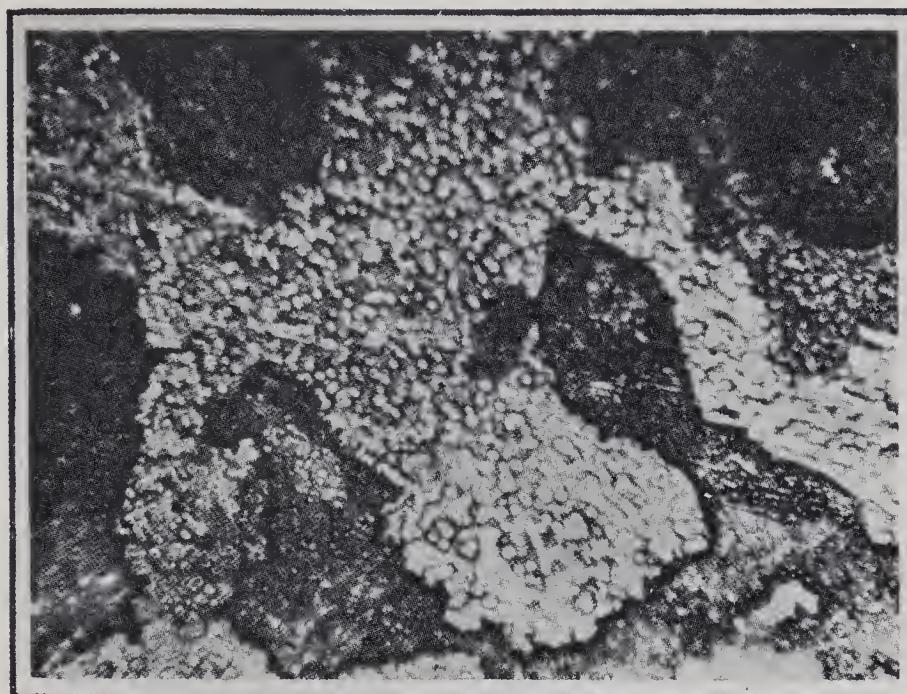


Figure 19 (x 65)

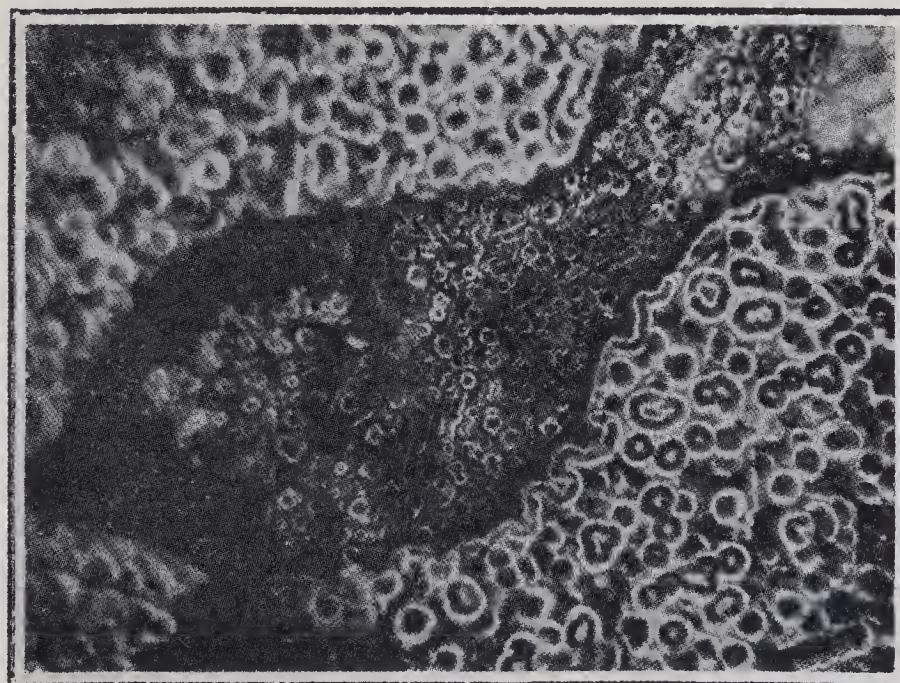


Figure 20 (x 180)

Plate X



Figure 21 (× 120)

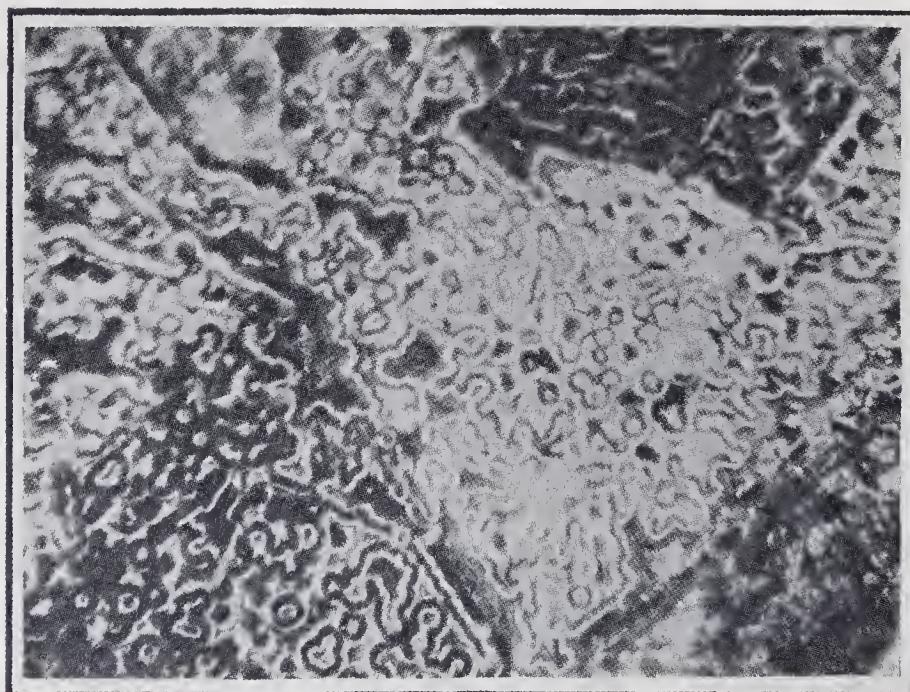


Figure 22 (× 250)

Plate XI

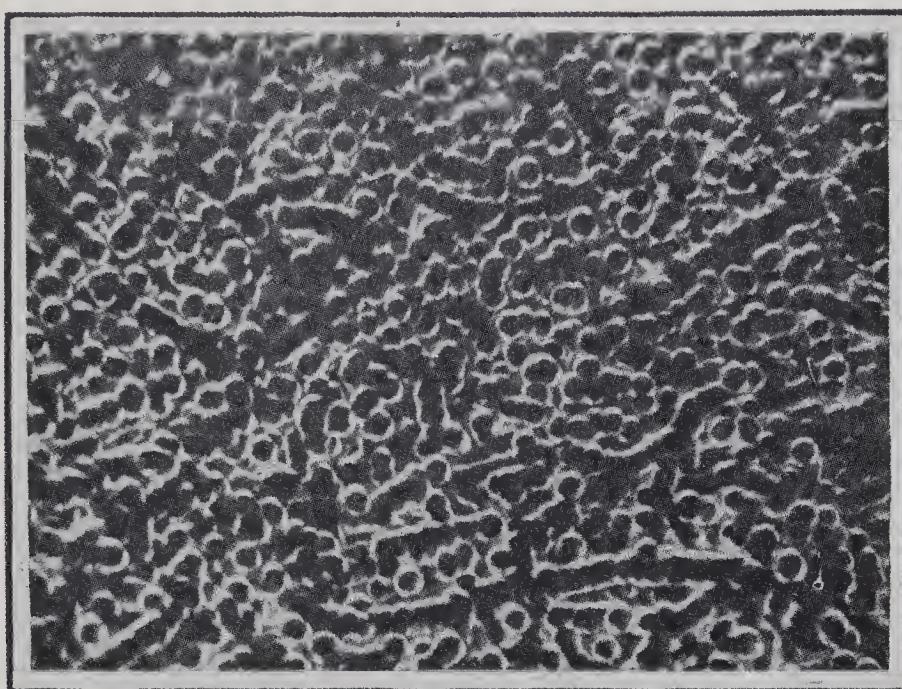


Figure 23

( $\times 200$ )

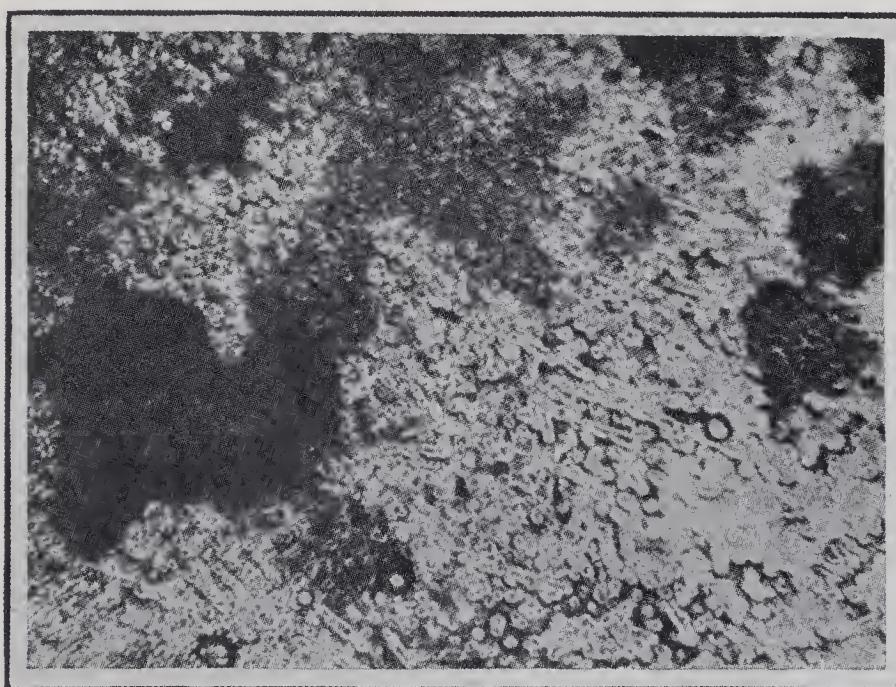


Figure 24

( $\times 180$ )

Plate XII

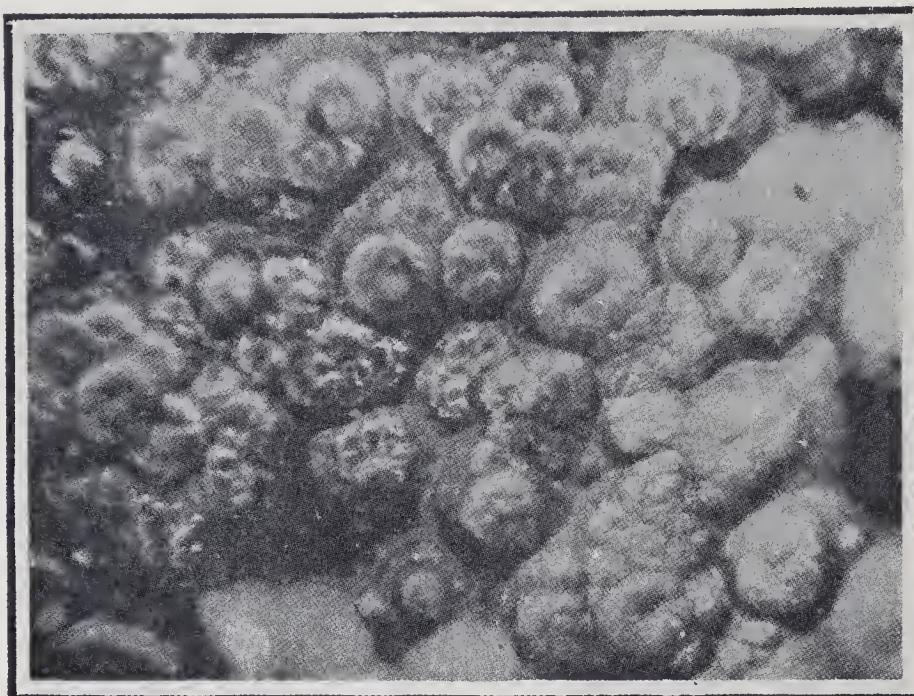


Figure 25

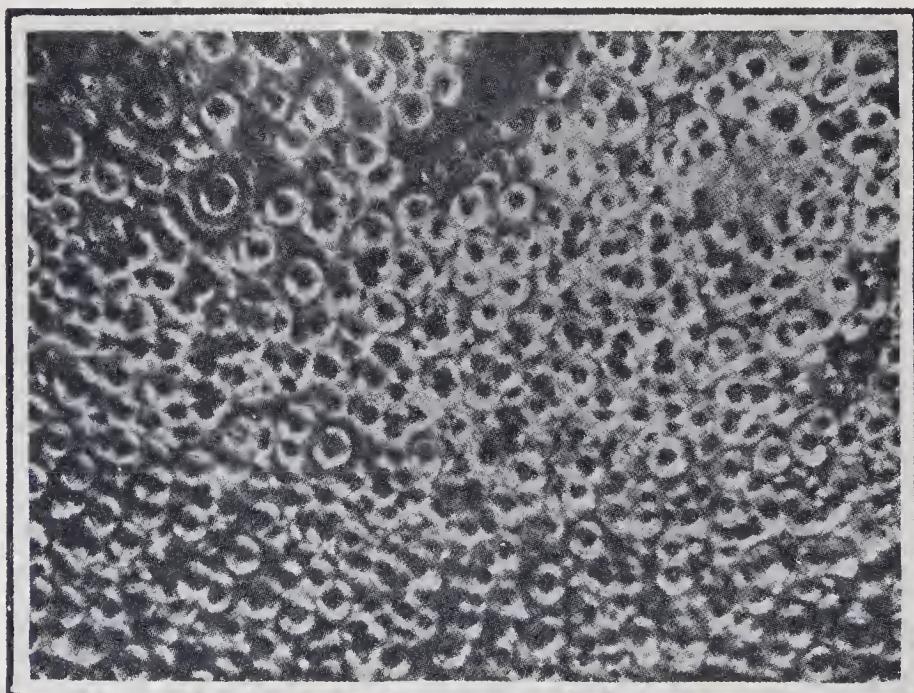
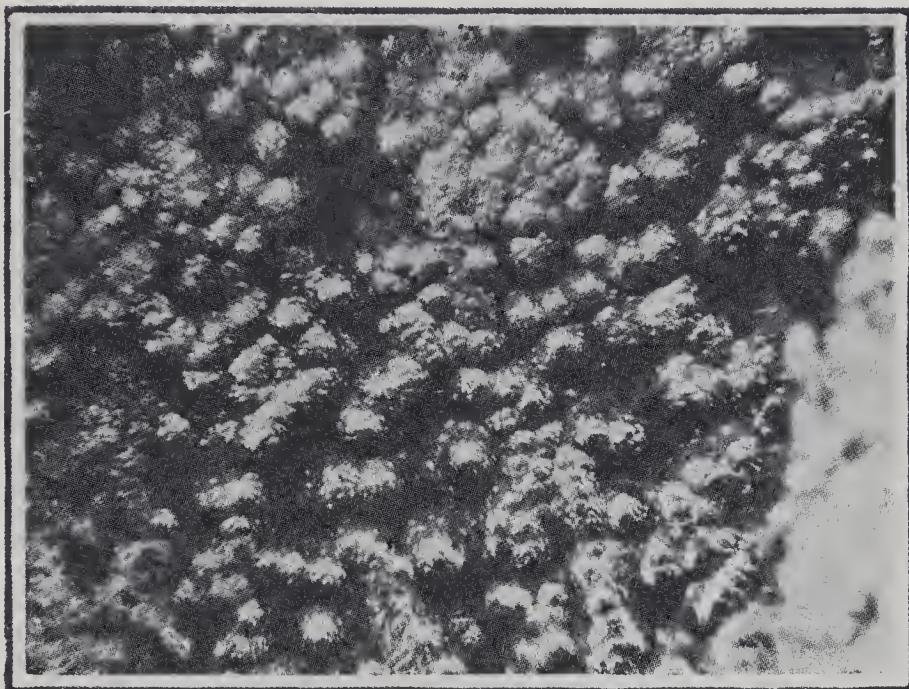
(  $\times 120$  )

Figure 26

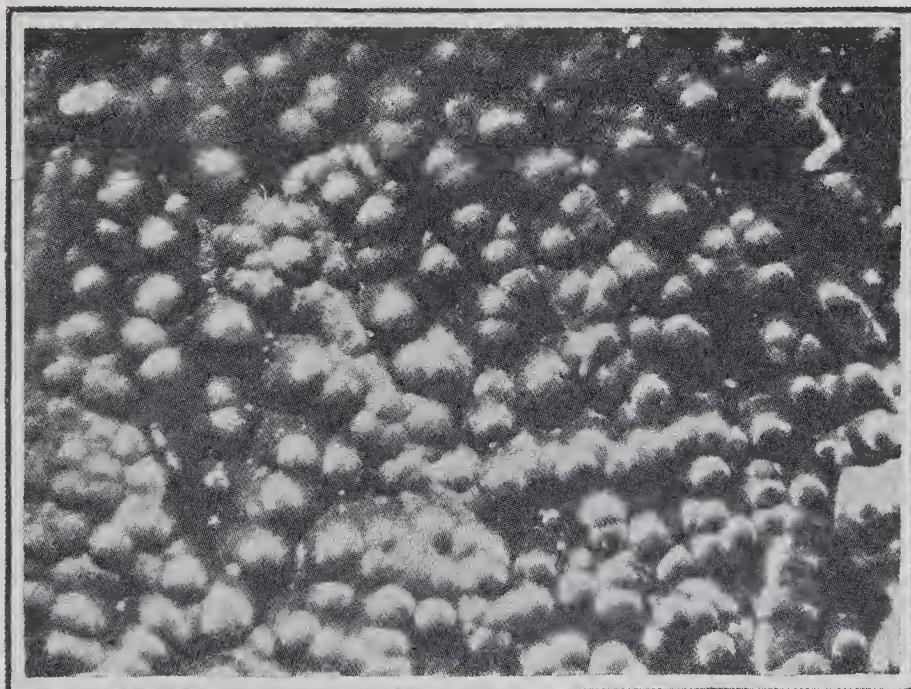
(  $\times 300$  )

Plate XIII



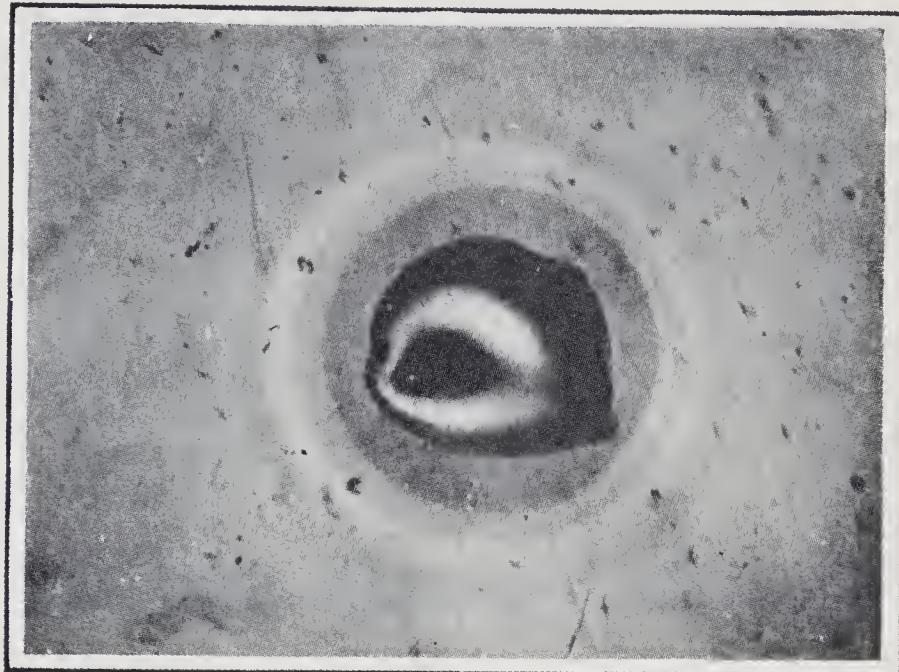
**Figure 27**

( $\times 120$ )



**Figure 28**

( $\times 120$ )



**Figure 29** ( $\times 100$ )



**Figure 30** ( $\times 100$ )

## Plate XV

## Colours of stratified media—I. Ancient decomposed glass

SIR C V RAMAN and V S RAJAGOPALAN

(Department of Physics, Indian Institute of Science, Bangalore)

Received June 5, 1940

### 1. Introduction

In a memoir published many years ago, Sir David Brewster (1863) described the structures found in ancient decomposed glass as well as the optical phenomena which they exhibit and illustrated them by reproductions of coloured drawings. The effects are most beautifully shown by specimens of antique glass-ware discovered in archaeological excavations, but as these usually find their way into museums, few physicists have the opportunity of examining them and acquainting themselves with the facts by personal observation. At the Palais de la Découverte in the Paris Exposition of 1937, one of us saw in the section of Optics a very striking exhibit of an ancient vase of glass which had been excavated in Syria by the French archaeologist M Pupil. The remains of the vase together with numerous iridescent flakes resulting from its disintegration were placed in a plate-glass cabinet which was provided with viewing mirrors inclined at  $45^\circ$  to the vertical, and illuminated both from above and below, so that they could be seen simultaneously by transmitted and reflected light. The brilliance of the colours and the complementarity of the same as seen in transmission and by reflection were thus beautifully made evident. Through the kind offices of Prof. A Cotton, a few flakes of glass from this exhibit were presented to us by M Pupil. This gift enabled us to undertake the present investigation, which indeed we were desirous of doing, to supplement and complete our earlier work on the optical behaviour of decomposed glass of modern origin described recently in these *Proceedings* (1939). The important researches of M Marcel Guillot (1934) on the production of iridescent laminae on glass by chemical action should also be mentioned in this connection. His work indeed suggests the possibility that the processes which take place in glass very slowly under natural conditions may be reproduced in a more rapid and controllable manner by laboratory methods. Reference may also be made to the very interesting thesis by Dr Coeling (1939) in which she has studied the absorption of water-vapour by films of decomposed glass and the resulting changes of colour.

The flakes derived from the Syrian vase reflect light strongly, exhibiting an almost metallic lustre, the colour of which varies greatly. The thicker flakes amongst those given to us exhibit a bluish-white silvery lustre, while the thinner ones exhibit other tints in which greens and oranges are the most striking colours observed at normal incidence. The flakes also exhibit vivid colours by transmitted light, being in this respect much superior to the specimens of decomposed glass of modern origin considered in our recent paper. The latter show scarcely any perceptible tints when observed in transmission, while on the other hand, the flakes from the Syrian vase show colours in transmitted light which in many cases are more striking than those seen by reflected light. The transmission colours for the thicker specimens tend towards a rich red, while the thinner flakes showed colours ranging over the whole spectrum from violet to red. It is thus evident that the development of colour occurs in antique glasses to a greater depth and in a more uniform manner than in the modern specimens. This makes it all the more desirable that they should be thoroughly studied.

Figures 1 to 9 in plates I-VII accompanying this paper are photomicrographs of selected areas on the iridescent flakes of Syrian glass. Figures 1, 2, 3, 4, 5 and 9 are pictures taken by monochromatic light in transmission with a petrographic microscope, a mercury arc lamp with a green ray filter being used as the source. Amongst these figures 2 and 9 were taken with the specimens placed between crossed nicols, while in taking the other photographs the polariser and analyser were removed. The fact that these photographs have been taken with monochromatic illumination has enabled us to notice and record certain characteristic features which would not otherwise have been evident. Figures 6, 7 and 8 are pictures taken by reflection using the Leitz ultra-opak microscope and white light. We have also obtained spectrograms (with incident white light) of the transmission and reflection by several of the flakes. These are reproduced as figures 10(a) to (f) in plate VIII. The present paper deals with the question of the structure of the decomposed glass and the origin of the colours which it exhibits as indicated by the microscopic examination and by the spectroscopic studies.

## 2. The lamellar structure

That decomposed glass is composed of thin laminae adherent to each other is readily noticeable, even without the use of a microscope. The details of its structure however become more evident on microscopic examination and are quite remarkable and interesting. Figure 1 (plate I) illustrates a common but by no means universal feature, namely that the laminae, instead of being perfectly plane, consist of shallow cups shaped like watch-glasses fitting together and dividing the surface of the flake into a large number of irregular polygons bounded by straight lines. The uniformity of curvature of the surface of the cups and the perfect sharpness of the lines in which they intersect are noticeable

features. The former feature is shown in figure 1 by the perfectly concentric arrangement of the interference rings between the upper surface of the lamina and a plane sheet of mica which was laid over it when the photomicrograph was taken. It will be noticed that each of the polygons shows a ring system and that all of them are very much alike, in other words, that the curvatures of the cups are nearly the same, though their areas vary greatly. It will be noticed also that the dividing lines or sides of the polygons present a very similar appearance everywhere. These dividing lines are actually seen, however, as sets of diffraction bands running parallel to the boundaries: these have a bright centre when the microscope is focussed slightly above the plane of the lamina and a dark centre when the focus is below the plane. At critical focus the diffraction bands tend to become rather inconspicuous. From these observations it may be inferred that the dividing lines between the cup-shaped areas are extremely fine, indeed of razor-edge sharpness.

The hollow cup-like forms are naturally convex on one side of the lamina and concave on the other. This is noticeable on turning the lamina over on the stage of the microscope. The curvature of the surfaces may be made conspicuously evident by illuminating the lamina rather obliquely and observing it by reflected light. Figure 6 shows this effect when the cavities are shallow and figure 8 when they are rather deep. The smoothness and uniformity of curvature of the cavities is indicated by the fact that they are capable of forming sharply defined images by reflection. This can be demonstrated with the reflecting microscope by pushing up or pushing down the objective as the case may be. Each cup-shaped area then shows an image of the illuminating annulus of the microscope, the surfaces themselves appearing dark except at the polygonal boundaries which continue to be seen faintly by reason of diffracted light (figure 7).

It is possible to find laminae which do not exhibit the cup-like cavities referred to above, but have a smooth surface either wholly or except for discrete single or multiple cavities which they may exhibit. Examination of such a lamina under the polarising microscope between crossed nicols shows the surface as quite dark when there are no cavities, but as faintly illuminated when there are shallow cavities present. The deeper cavities appear strongly luminous round their inner margins and also exhibit the phenomenon of the black cross observed by Brewster (figure 9), which is due to the rotation of the plane of polarisation of the light in its passage through the oblique surfaces of the lamina. Particularly beautiful are those cases in which there are numerous deep cavities which are discrete and do not meet to form polygonal figures. One such lamina as seen between crossed nicols is shown in figure 2 which exhibits quite a number of ellipsoidal cavities. Further, it will be seen that the luminosity is not confined to the edge of each cavity, but also extends within in the form of rings running parallel to its margin. In most cases, this appears to be a diffraction effect, but there is no doubt that occasionally also we may have multiple cavities forming concentric rings.

### 3. Colour effects

The laminar structure of the decomposed glass is shown very prettily by the colours seen in transmission through the microscope. As was remarked by Brewster, areas of different colours will be noticed around the edges where the flakes have broken off unevenly. These correspond to the different thicknesses through which the light has to pass before reaching the eye. The boundaries of these areas act as diffracting edges and appear as sharp lines in the field of the microscope. Except when the laminae have thus split off unevenly or when they have actually parted off from each other so as to admit a film of air between, the colours seen are very uniform over the surface of the flake, thereby showing that the glass, though laminar in structure, nevertheless consists of coherent layers in optical contact. Brewster's view that the colours are due to thin plates of air separating the laminae thus appears to be incorrect. Indeed, the fact to which Brewster himself drew attention, namely that the elementary films of glass adhere with such force that it is difficult to separate them, is very strong evidence that they are in optical contact and not separated by continuous films of air.

The colour effects observed with those laminae which exhibit cup-like depressions over their area are very pretty and significant. If the cups are very shallow, the colour of the laminae is nearly uniform in tint over the area of the cup, though just at and near the boundary lines the colour is slightly different. When the cups are deep, the colour near their margins differs strikingly from that near the centre. This is due to the lamina being inclined to the line of vision round the periphery of a cup, whereas at its centre it is seen normally. To show that this is the correct explanation, we have merely to tilt the lamina on the stage of the microscope. The colours then change unsymmetrically, the part of the periphery of the cup which is now seen nearly normally has the colour which was originally observed at the centre, while the part at the periphery which is now still more inclined to the line of vision changes its colour still further in the sequence of increasing obliquity. It is equally easy to follow the change of colour with increase of obliquity in these areas where there is no curvature, by merely tilting the lamina on the stage of the microscope. It is then seen that the sequence of colour is the same as over the areas which exhibit curvature. This demonstrates that the lamina is uniform in its structure and thickness in spite of the curvature and consequent apparent difference in colour over certain of its areas.

When optical contact between the layers of a lamina is actually broken, and a thin film of air enters, this makes itself evident by continuous variations of colour over the area of the flake as seen under the microscope. If the air film is sufficiently thick and, as must generally be the case, variable in thickness, regular bands of colour appear over such area. If more than one such film of air has found entry into a given flake, each film gives its own sequence of colour running along its direction of most rapid variation of thickness. We would then see two or more sequences of colour running across the film in different directions and intersecting

each other. In view of the fact that the light transmitted by the flake as a whole is itself only a part of the spectrum, the colour sequences are quite different from the usual Newtonian scale. Even apart from this, they present peculiar features which become more intelligible when the incident light is monochromatic and the transmission through such film is examined under the microscope. Figures 3, 4 and 5 reproduce three photomicrographs obtained in this way which will repay careful examination. It will be seen that each of them is traversed by a series of sharply defined bright lines running more or less parallel to each other in a relatively dark field and that in some cases, (particularly figure 3) two or more such series of lines running in different directions and intersecting each other are seen. That these effects are due to air films having entered the flake and broken optical contact between the laminae is shown by gently pressing the flakes on the stage of the microscope. The bright bands are then seen to curve and move about in the field, but they recover their position when the pressure is removed. The fact that the band systems are more frequently seen near the edges of a flake where it is obviously easier for the laminae to part company and admit a continuous film of air (see for instance the left-hand side of figure 3) is another indication that they do, in fact, arise in this way.

A remarkable feature noticed in figures 3, 4 and 5 is that in the interference bands which are so prominent, the maxima of illumination are sharp lines separated by broad dark bands. This feature suggests an analogy with the sharp interferences seen in a Fabry-Perot etalon and indeed is very similar to that seen under the microscope when a wedge-shaped film of air between the silvered faces of two plates of glass is examined by transmitted monochromatic light. The two parts of the flake separated by an air-film behave therefore much as if they were heavily silvered surfaces in passing through which the light also undergoes multiple reflection, thereby sharpening the maxima. That this is the correct explanation of the sharpness of the maxima of illumination in these interference bands is indicated by the fact that the maxima are not so sharp when they are seen in air-films separated by very thin laminae (see for instance, the bands towards the thin edge of the flake in figure 3). The laminae chosen for obtaining figures 3, 4 and 5 were as nearly as possible uniform. They however exhibit a number of circular curved depressions which will be seen in the figures. When the interference bands due to the film of air are seen through such a depression, they appear wider apart or reduced in width, according as the curvature faces one way or the other. A fine example of a deep cavity is seen at the lower right-hand corner of figure 3, while several relatively shallow ones will be seen in figures 4 and 5. Three very curious examples of sharply-defined and concentric bright ring-systems will be noticed in figure 4; these however evidently arise in a different way, presumably as the result of the local separation of the laminae by a film of air over these areas. The fact that a small dark and rather elongated nucleus can be seen at the centre of each of these ring-systems is probably a connected circumstance.

#### 4. Effect of immersion in liquids

It has been remarked above that the laminae in the flake are adherent to each other and form a continuous structure. The colours seen in reflection and in transmission must therefore be ascribed to this structure being stratified in such a manner that the refractive index of the medium varies quasi-periodically. An insight into the nature of the stratifications and of the resulting variations of refractive index is obtained by studying the effect of immersing the iridescent flakes in various liquids. Putting a small flake in the cavity on a microscope slide and allowing a little liquid to flow in, it will be noticed that the colours usually observed in transmission generally disappear or become inconspicuous, and that this is the case, whatever may be the refractive index of the liquid ranging from water ( $\mu = 1.33$ ) to methylene iodide ( $\mu = 1.74$ ). The colours of reflection however continue to be observable, but they are altered and enfeebled to an extent depending on the refractive index of the liquid used. To enable this effect to be studied critically, it is convenient to immerse the flake diagonally inside a small glass cell of square cross-section containing the chosen liquid which is then held facing the light. The reflection by the flake at an angle of  $45^\circ$  deviates the light incident on it by a right angle and may be viewed through the cell against a dark background. Even a feeble reflection may then be readily recognised. Actually the iridescence is seen quite brightly if the flake is immersed in water ( $\mu = 1.33$ ), ether ( $\mu = 1.35$ ) or acetone ( $\mu = 1.36$ ) though a progressive diminution in intensity with increasing refractive index may be noticed. In hexane ( $\mu = 1.38$ ) and in paraldehyde ( $\mu = 1.40$ ) the iridescence is still conspicuous, though weaker. In chloroform ( $\mu = 1.44$ ) the coloured reflection is very weak but may still be seen. In carbon tetrachloride ( $\mu = 1.463$ ) it is practically unobservable. In benzene which has a higher refractive index ( $\mu = 1.50$ ) it is once again visible, while in chlorobenzene ( $\mu = 1.530$ ) and in bromobenzene ( $\mu = 1.56$ ) it is conspicuous. In carbon disulphide ( $\mu = 1.63$ ), it is quite bright, in fact, many times more intense than the reflection from the surface of a single plate of glass immersed in the liquid.

Placing the flake in a cell containing carbon tetrachloride, we may add a little chloroform and depress the index of the liquid, or add a little benzene, and raise its index until the reflection becomes observable. It is found in this way that an elevation of the refractive index to 1.470 or a depression to 1.460 is sufficient to make the reflection visible. The disappearance of the reflection may be explained by assuming that the decomposed glass has an open or "frame-work" structure into which the liquid, allowed sufficient time, can penetrate, and that when such liquid has a refractive index 1.465 the stratifications of optical density within the substance of the flake vanish and that it therefore ceases to reflect light. At the same time, according to this view, the refractive index of the saturated substance should itself be the same as that of the surrounding fluid, and its edges should therefore cease to be observable. This is actually found to be the case, and an

application of the Becke immersion test under the microscope shows that the difference of refractive index between the flake and the surrounding fluid changes sign when the latter is altered from 1·460 to 1·470.

There is a definite change in the colour of the reflected light when the flake is immersed in the cell of liquid. This change is most readily seen in the colour of the normally reflected light, and is more conspicuous, the greater the refractive index of the immersion liquid. In general, it is found possible to compensate the change of colour produced by such immersion by viewing the flake obliquely. In other words, we can set off the effect of the increased index on the optical paths within the flake by the diminution in such paths due to a greater obliquity of incidence of the light on it. That an obliquity of the order of 45° or less is sufficient to achieve this indicates that the optical paths within the flake which are altered by the entry of liquid are not a very large part of the whole. It should be remarked also that though the effect of immersion is to diminish the intensity of the coloured reflections and, as stated above, also to alter them appreciably, nevertheless the liveliness of the colours is actually improved instead of being impaired by such immersion. Further, the coloured reflections by the immersed films continue to be visible at greater obliquities instead of changing rapidly to white light as is the case when the flakes are observed in air. When the refractive index of the immersion liquid approaches that of the decomposed glass, the colours may be seen by reflection even at nearly grazing incidences.

The very low index (1·465) of the decomposed glass indicated by these observations is a noteworthy feature. It must be assumed that as the result of the decomposition and of the leaching out of some of the material in the course of long years, the average index, even of the more relatively compact parts of the glass has been reduced below that of normal glass. If the openings into which liquid can penetrate are taken into account, the effective reduction of the refractive index of the substance would of course be still greater.

## 5. Spectroscopic examination

Each of the figures 10(a), (b), (c), (d), (e) and (f) in plate VIII relates to a distinct specimen of iridescent glass and contains a group of four spectra. The first and fourth of these are the spectra of the light source employed, namely, a filament lamp, and have been included for comparison with the second and third spectra in the same group which refer respectively to the light transmitted and reflected normally by the particular flake of glass.

It will be noticed that figures 10(a) and (d) present a remarkable contrast, indeed being almost exactly the opposites of each other. In the former, the entire spectrum is cut off in transmission except for a band at the red end which comes through, while in the latter, the whole spectrum is transmitted except a band at the red end which is cut off. *Per contra* again, in figure 10(a) practically the whole

spectrum appears in the reflected light except the red end which is greatly weakened, while in figure 10(d), only the red end of the spectrum appears in the reflected light and the rest is cut off. Figures 10(b) and (e) also present contrasting features of the same general description, though not of so marked a character. The principal feature in figure 10(c) is the cut-off in the transmitted light of a portion of the spectrum in the yellow region and the appearance of the same region in the reflected light. Figure 10(f) shows no special feature except a large number of bands in the spectra of both the reflected and the transmitted light. The following table shows the colours of the normally transmitted and reflected light with the different specimens:

Table of colours

Figure	Transmission colour	Reflection colour
10(a)	Orange red	Blue
10(b)	Brick red	Bluish white
10(c)	Purple	Yellowish white
10(d)	Blue-green	Red
10(e)	Blue-green	Red
10(f)	Neutral	Neutral

The vividness of the colours exhibited will be readily understood from the character of the observed spectra.

It is very remarkable that, as mentioned above, specimens of iridescent glass should exhibit two entirely different types of spectra, the first in which a limited region of the spectrum is strongly reflected while the rest of the spectrum is transmitted, and the second in which a limited region of the spectrum is transmitted while the rest is reflected. The first type of spectrum is characteristic of regularly stratified media with a large number of layers when the reflecting power of an individual layer is small. In such a case, the incident light is transmitted freely except in respect of the narrow band of wavelengths for which the successive *reflections* reinforce each other by agreement in phase. This band of wavelengths is selectively reflected and disappears from the transmitted light. If, however, the number of layers is small, the reflected spectrum contains a wider band of wavelengths with subsidiary maxima on either side. There is little doubt that the transmission and reflection spectra illustrated in figures 10(d) and (e) are to be explained in this general way, though it is clear that the regularity of the actual stratifications is far from being perfect. The spectra of the second type illustrated in figures 10(a) and (b) resemble those observed when a beam of white light passes through a thin film of air between two heavily-silvered plates. In this case, as is well known, the effect of the large reflecting power of the surfaces is to reduce the transmitted light to a negligible intensity except in respect of those

wavelengths for which there is an agreement in phase of the successive *transmitted* pencils. Only the narrow bands of such wavelengths appear in the spectrum of the transmitted light and the rest are cut off. The spectra reproduced in figures 10(a), (b) and (c) have evidently to be explained in this way. The difference in optical behaviour between the two classes of cases may be the result of either the spacings or their reflecting power or both being widely different. In this connection, reference may be made to a mathematical investigation by the late Lord Rayleigh (1917) in which he has shown that the passage of light through a regularly stratified medium may result in effects which are the opposites of each other, depending on the circumstances. In one set of cases, the effect of increasing the number of the stratifications is to make the reflection approach totality. In the second set of cases, the intensity of the reflected beam continues to fluctuate however large the number of stratifications might be, and might even vanish, in which case the light is completely transmitted. Rayleigh has discussed the criterion which distinguishes the two sets of cases and shown that the results are determined by the relation between the reflecting power of an individual stratification and the phase differences arising in passage through it.

The effect of tilting an iridescent lamina on the spectra of the transmitted and of the reflected light may be readily studied. In either case, the bands observed in the spectrum shift towards the violet and broaden with increasing obliquity. The actual effect of this on the observed colours is rather different in the two types of cases considered above. If, for instance, the transmission shows a dark band in the red region at normal incidence, the displacement of this towards the violet with increasing obliquity results in the colour seen changing from blue-green to blue, then to purple and yellow, while the reflected colours march from red to violet through all the rich tints of the spectrum. If, on the other hand, the transmission is initially limited to a band at the red end, the effect of increasing obliquity is to cause more and more of the spectrum from the red towards the violet to be freely transmitted. As the result of this, the transmission colour fades out rapidly, changing from red to a pale orange or yellow. The reflected colour which is initially a bluish white however becomes a richer and darker blue and finally tends towards indigo or violet.

As is to be expected, both the reflection and the transmission are strongly polarised and in opposite ways at the Brewsterian angle of incidence. Here again, there are remarkable differences between the character of the effects observed in the two sets of cases. When the transmitted light includes the whole spectrum except a limited band of wavelengths, striking changes are observed when the obliquely transmitted light is viewed through a polarising Nicol. With the light vector in the plane of incidence, the film appears practically colourless, but with the light vector perpendicular to its plane, it appears richly coloured. On the other hand, the films showing only a narrow transmission band at normal incidence are practically colourless at the polarising angle, the effect of rotating the observing Nicol being merely to alter the intensity of the transmitted light.

These same films however, show a remarkable increase in the richness of the colour of the *reflected* light at the polarising angle. The explanation of these facts will be clear in the light of the preceding discussion, when we remember that the reflecting power of an individual stratification is diminished for one of the components of the light vector and increased for the other by oblique incidence.

On immersing the iridescent flake in a cylindrical vessel of liquid of refractive index greater or less than that of glass, it is readily possible to observe the spectral character of the light reflected by it at various obliquities up to grazing incidence and to determine its state of polarisation. As remarked earlier in the paper, the transmission colours disappear on immersion in the liquid, but the reflected colours continue to be visible with great liveliness up to grazing incidence. They are also completely polarised at the Brewsterian angle of incidence on the liquid-glass boundary. These facts will be readily understood in the light of the preceding discussion, when it is recollected that the reflecting power of an individual stratification is greatly reduced when the lamina is immersed in a liquid. In the spectrum of the normally reflected light, narrow bands are observed which broaden out at oblique incidences, thus indicating that the iridescence is the cooperative effect of several laminations.

## 6. Effect of absorption of liquid

Very interesting phenomena are exhibited by an iridescent flake of glass when it is immersed in a liquid and then taken out and allowed to dry. As has already been mentioned, the flake appears nearly or quite colourless by transmitted light when wet, and it might be thought that the colour would reappear progressively as the drying proceeds. Actually, the colour reappears with remarkable suddenness and with extreme saturation. The phenomenon may readily be observed by holding up the film against the light from a window and watching it as it dries. Almost immediately the drying commences, the film turns black as viewed by transmitted light and silvery white as seen by reflected light. The film then gradually clears up, showing rich colours which fade away until finally the usual colours are restored. The phenomenon may be watched by transmitted light under the microscope, and this is specially advantageous when it is desired to scrutinise it in detail. A boundary of intense colour or opacity appears near the edge of the colourless film and moves inwards as the drying progresses, finally covering the whole film. It then gradually weakens and disappears.

It is not necessary for observing these effects that the refractive index of the liquid should be different from that of glass. Indeed, carbon tetrachloride which, as we have seen, causes the reflection colours to disappear, shows the effects described above just as effectively as any other liquid. If it is desired to prolong the duration of the stage of opacity, the flake may be kept under a microscope cover-slip, thus delaying the evaporation. Alternatively, a less volatile liquid may be

used to wet the film. On the other hand, its drying may be speeded up by holding it in a current of hot air. This is a useful procedure when the liquid has been wetted by water or by a liquid of high boiling point.

These effects throw light on the structure of the iridescent films and show clearly that Brewster's explanation of the colours as due to thin films of air separating the layers of glass is untenable. The observations indicate that the glass has a continuous frame-work structure which is quasi-periodic or stratified. When the flake is completely wetted, the liquid penetrates into the minutest cavities and tends to render the glass optically homogeneous, though if its refractive index differs from that of glass, the stratifications persist and give observable colours by reflection. As the film dries, the liquid naturally withdraws first from the largest cavities but remains in the smaller pores and the minutest cavities. At the earliest stages of drying, therefore, the layers containing the minutest pores which continue to hold liquid have a higher refractive index and are optically more uniform than when the film is completely dry; on the other hand, the layers containing the larger cavities are empty of liquid and have the usual low refractive index. At this stage, therefore, the stratifications of refractive index are actually more pronounced than with the dry film and their reflecting power is accordingly greater. The reflection of light by the film therefore approaches totality.

The liquid held by a wetted film may be divided into at least three categories, (a) that held by the largest cavities, (b) that held by the finest pores, and (c) that molecularly adsorbed on the capillary surfaces. The rate at which the liquid evaporates and its temperature equilibrium with the vapour would naturally be different for the three categories. The colour of the film would depend on the nature and quantity of the liquid held and the manner in which it is distributed in the film. The detailed study of these effects for the iridescent films of ancient decomposed glass would obviously be of considerable interest and should enable the capillary structure of the glass to be investigated in detail. In this connection, it is important to remember that the entry or withdrawal of liquid is far from being instantaneous. The flow of liquid through very minute capillaries is a slow phenomenon especially if it be viscous, and the capillary forces which cause the flow may sometimes vanish, e.g., when the pore has a bottle-neck shape such as has been postulated to explain hysteresis phenomena in the adsorption of liquids. These considerations help us to understand the remarkable tenacity with which liquid is sometimes held by a flake of decomposed glass as is demonstrated by its influence on the observed colour.

## 7. Effect of mechanical pressure

That the decomposed glass has an open structure and that the colours arise from this structure being stratified or quasi-periodic is very clearly indicated by the

observations already set out. It is a reasonable presumption that the structure is the result of the decomposition of the glass and the leaching out of the more soluble layers formed during its progress, the periodicity of the decomposition being probably analogous to the Leisegang effect as has been suggested by M Guillot. On the assumption that the colours of the ancient glass are due to a periodic distribution of cavities or pores in its structure, we must expect that mechanical pressure should destroy or reduce the colours of the glass. The equipment may readily be tried by placing a small flake covered with a piece of cellophane on the stage of the microscope, and then pressing or rolling a blunt steel point firmly on its surface. The colour is then observed practically to disappear from the area of pressure and does not recover on its removal. The success of the experiment indicates that the colours in the Syrian vase do not arise from an alternation of solid layers of different refractive index in the material of the glass. The latter supposition would also be inconsistent with the observed easy penetration of liquid into the substance of the films.

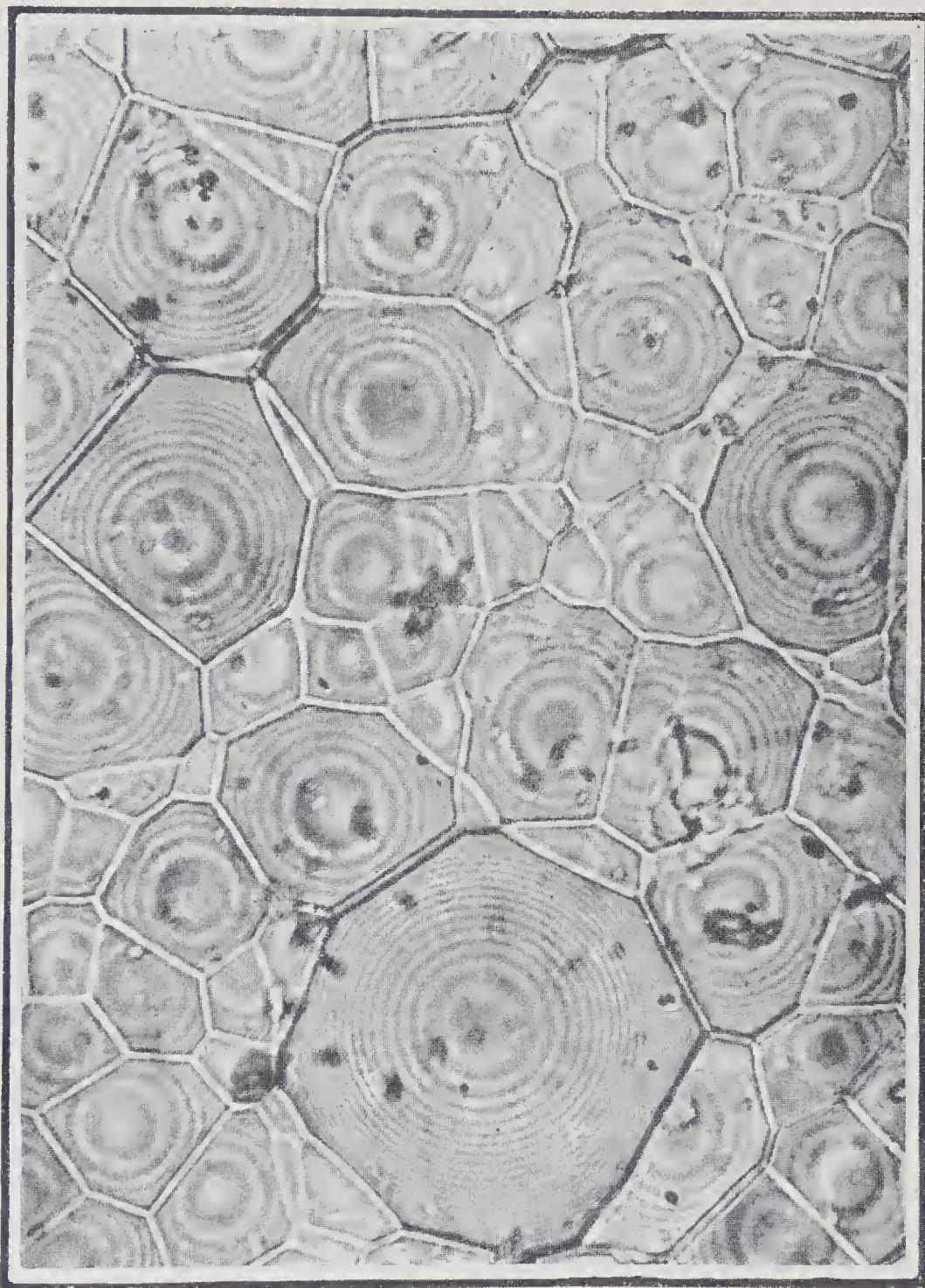
### 8. Summary

The paper describes a detailed microscopic study of the structure of the films of decomposed glass derived from an ancient Syrian vase excavated by M Pupil, and a spectroscopic examination of their iridescence. The investigation makes it clear that Brewster's explanation of the iridescence as due to films of air separating thin layers of glass is definitely erroneous. The material is optically and mechanically continuous, but has an open framework structure which is quasi-periodic or stratified. The stratifications are moderately regular with the result that in certain specimens, a limited region of the spectrum is totally reflected and the rest is freely transmitted, while in other specimens we have the opposite effect, namely that the whole of the incident light is reflected except for a limited region of the spectrum which is transmitted. At oblique incidences and especially near the polarising angle, the colours seen vary with the azimuth of the vibration and in different ways in these two cases. Mechanical pressure destroys the structure and with it also the iridescence. Liquids can penetrate into the structure of the film, but the latter becomes optically homogeneous and ceases to reflect light only when the refractive index of the liquid is equal to that of the glass (1.465). When the wetted film commences to dry, the liquid withdraws first from the larger cavities while it is retained in the smaller pores. This results in the optical stratifications being actually more pronounced than in the dry film, with the consequence that the flake appears black by transmission and silvery white by reflection.

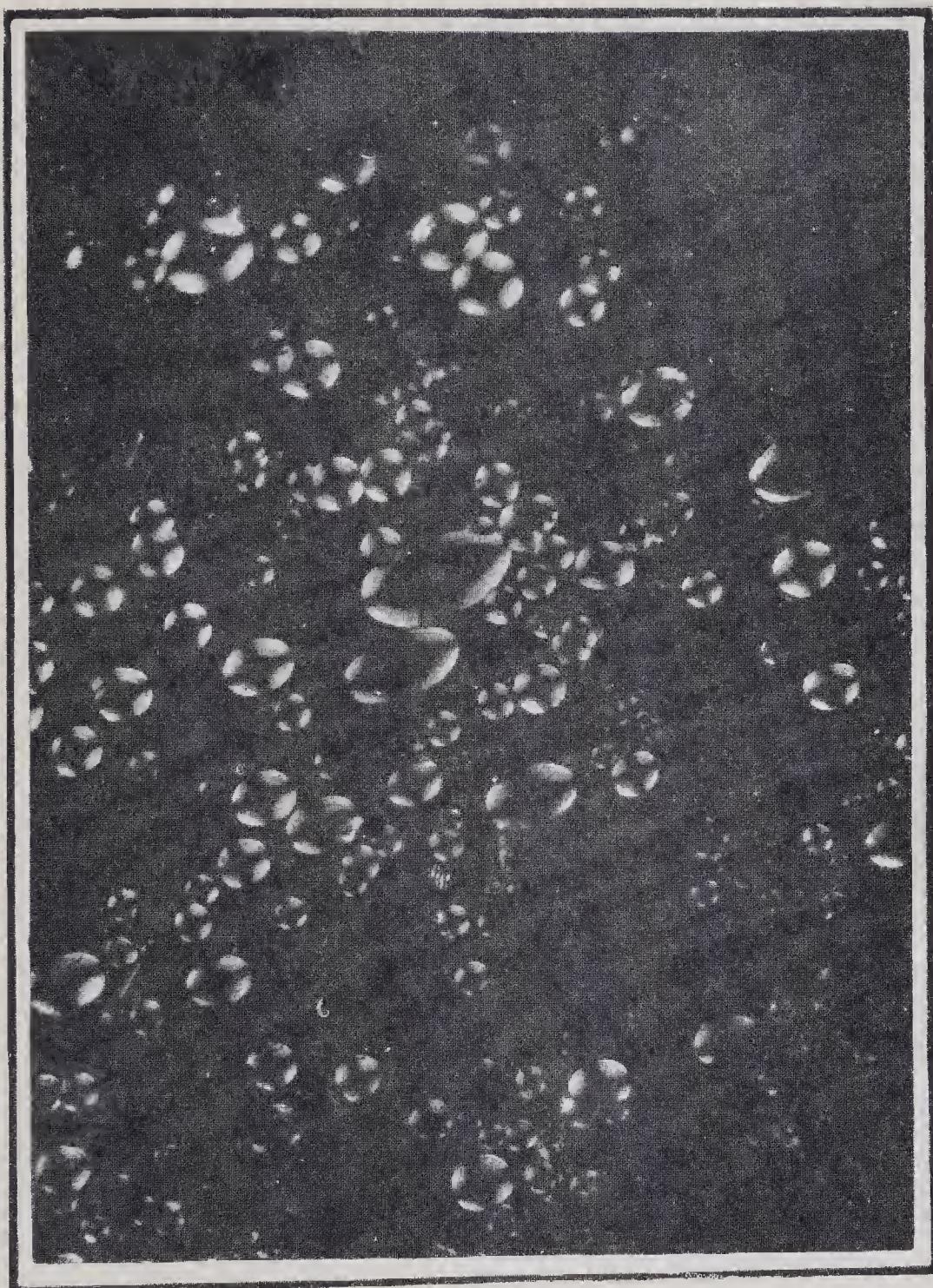
The paper is illustrated by reproductions of nine microphotographs and twelve spectrograms.

### References

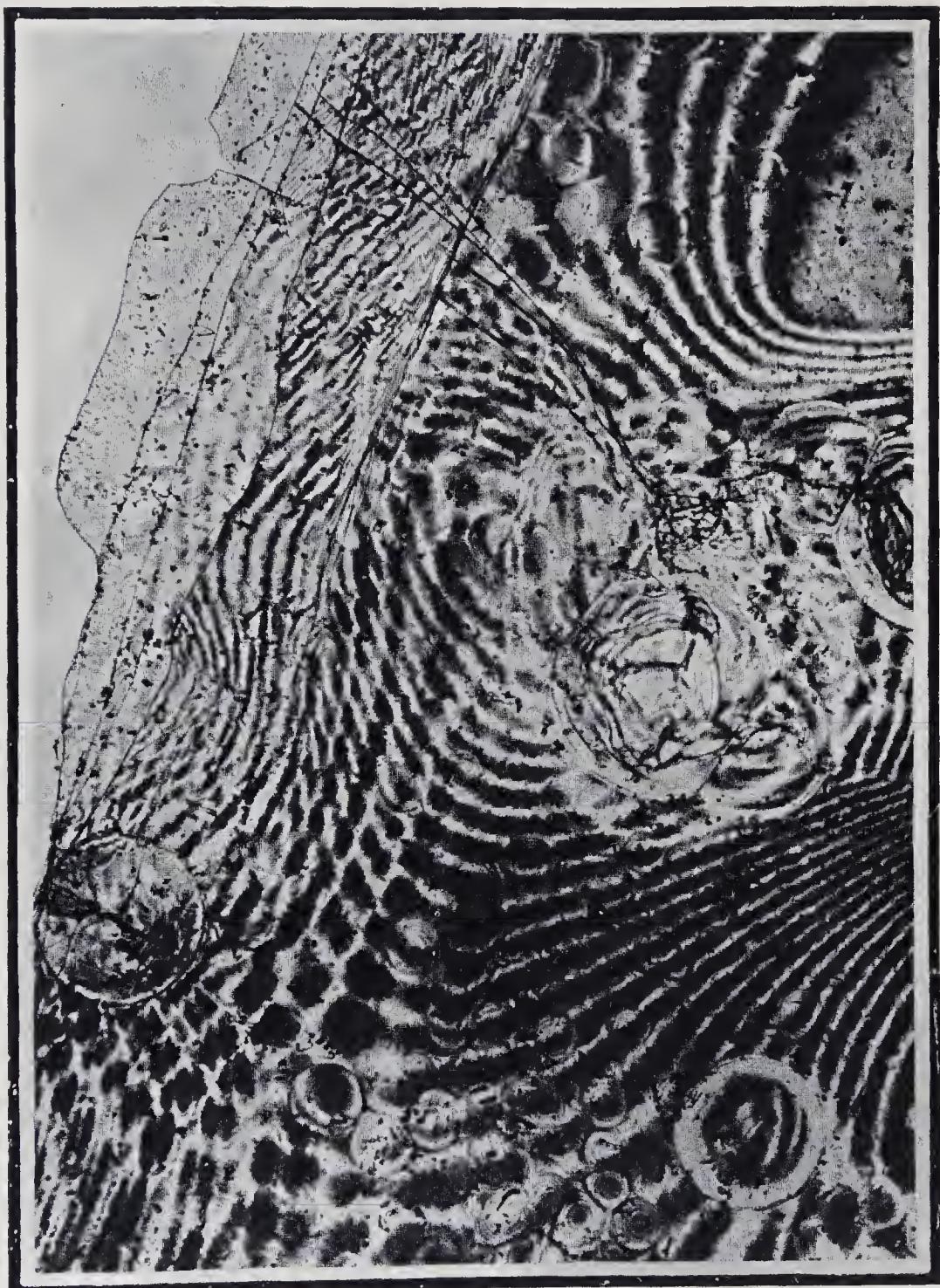
- Brewster D, *Trans. R. Soc. Edinburgh*, 1863, **23**, 193–204.  
Raman C V and Rajagopalan V S, *Proc. Indian Acad. Sci. (A)*, 1939, **9**, 371–81.  
Guillot M, *Compt. Rend.*, 1934, **198**, 2093–95.  
Coeling M B, *Koll. Zts.*, 1939, **87**, 251–72.  
Rayleigh, *Proc. R. Soc. (A)*, 1917, **93**, 565–77.



**Figure 1.** Photomicrograph of decomposed glass in monochromatic light, showing network of curved laminae.



**Figure 2.** Photomicrograph of decomposed glass in monochromatic light under crossed nicols, showing spherical and ellipsoidal cavities.



**Figure 3.** Photomicrograph of decomposed glass in monochromatic light, showing laminar edges, and multiple films of air.



Figure 4. Photomicrograph of decomposed glass in transmitted monochromatic light, showing sharply defined fringes due to intruding air films.



**Figure 5.** Photomicrograph of decomposed glass in transmitted light, showing cavities and fringes due to intruding air films.

**Plate V**

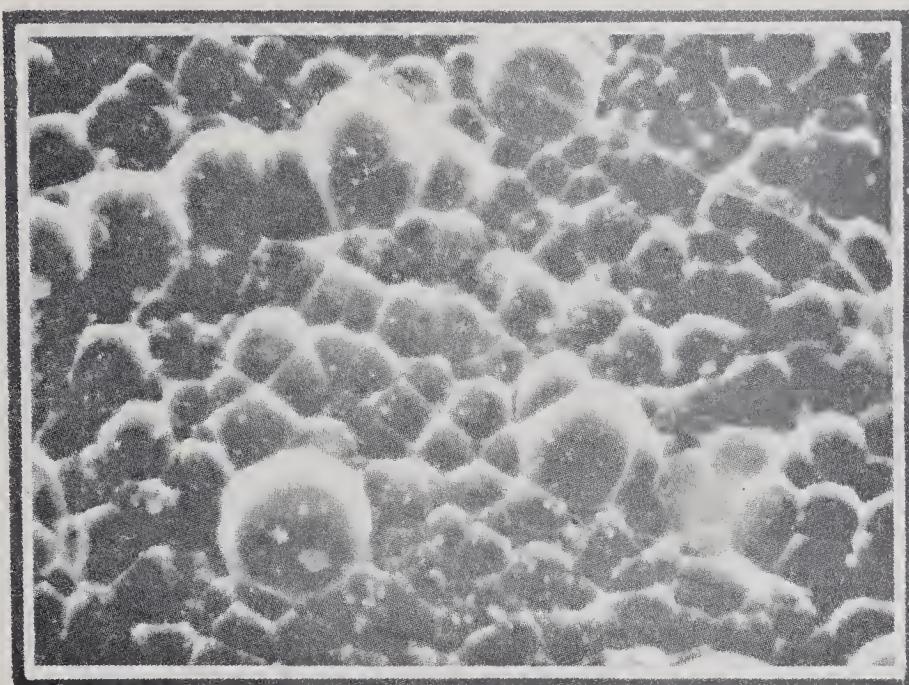


Figure 6. Lamina with hollows by reflected light.

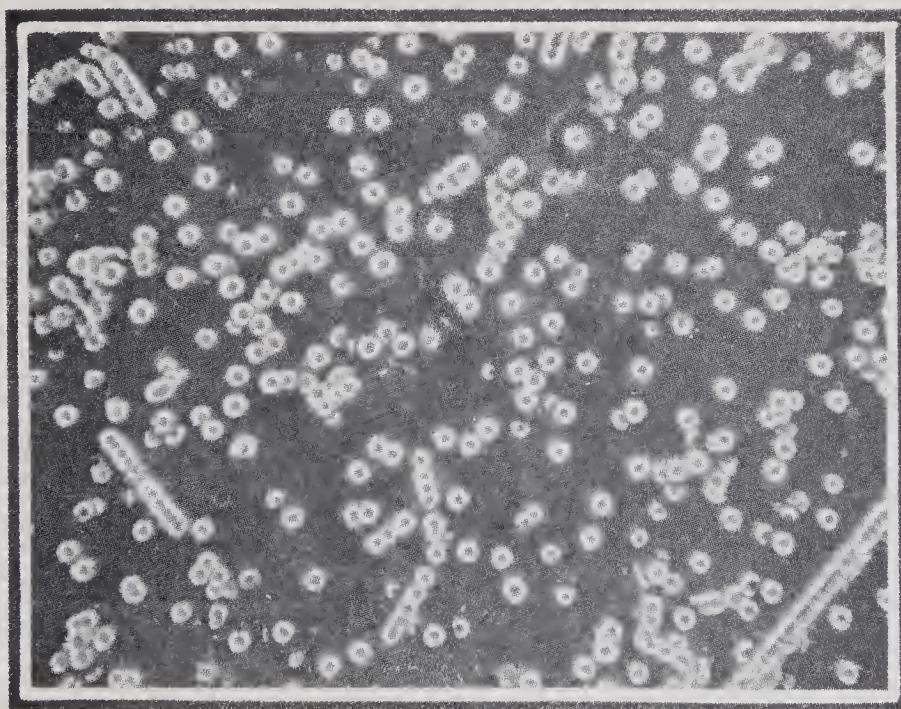


Figure 7. Lamina with hollows forming optical images of light source by reflected light.

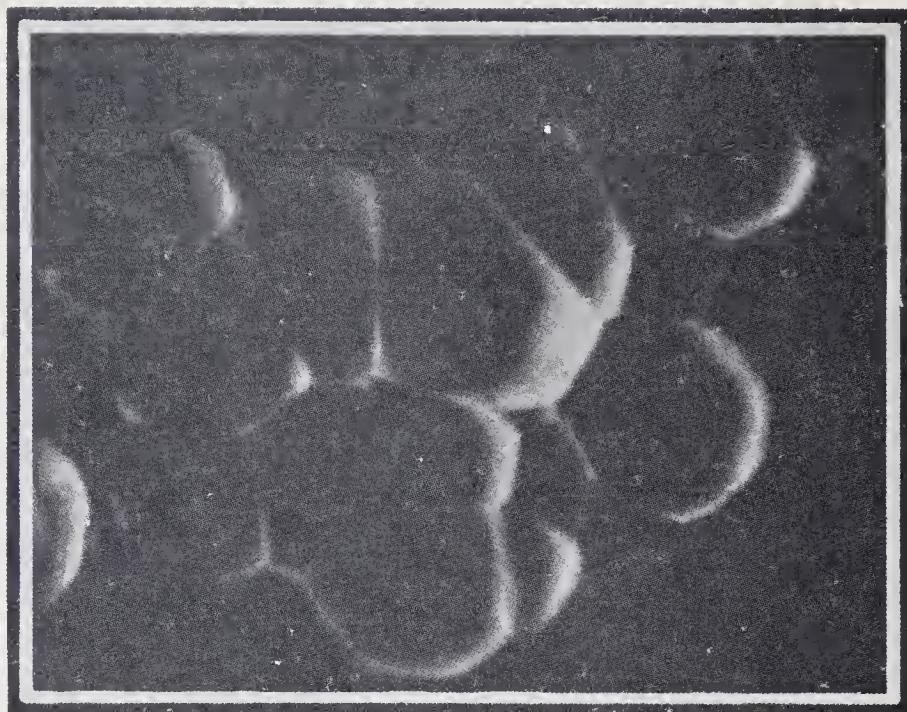


Figure 8. Lamina with hollows by reflected light.

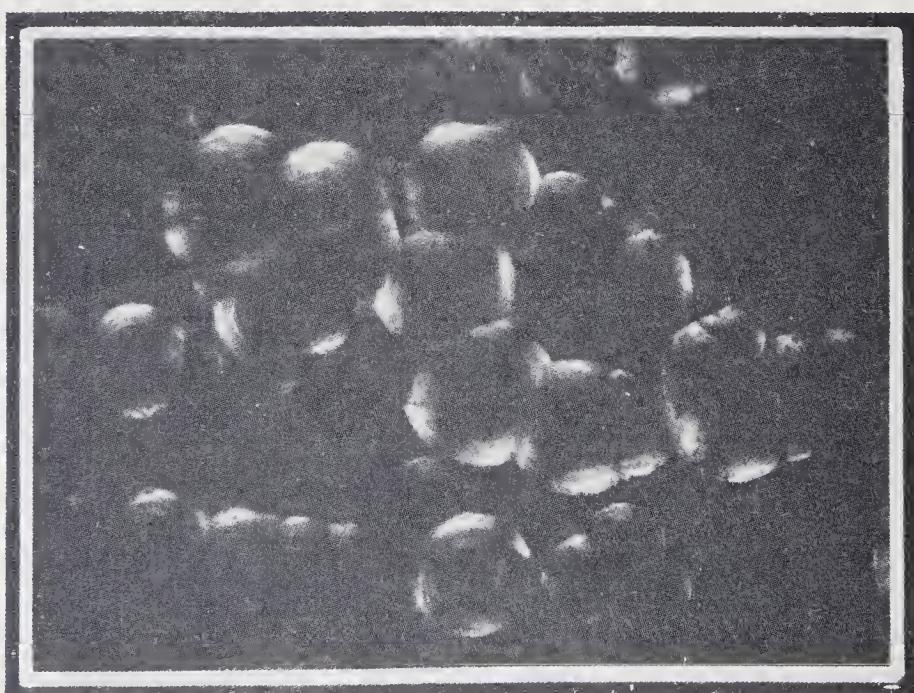


Figure 9. Lamina with hollows by transmitted light between crossed nicols.

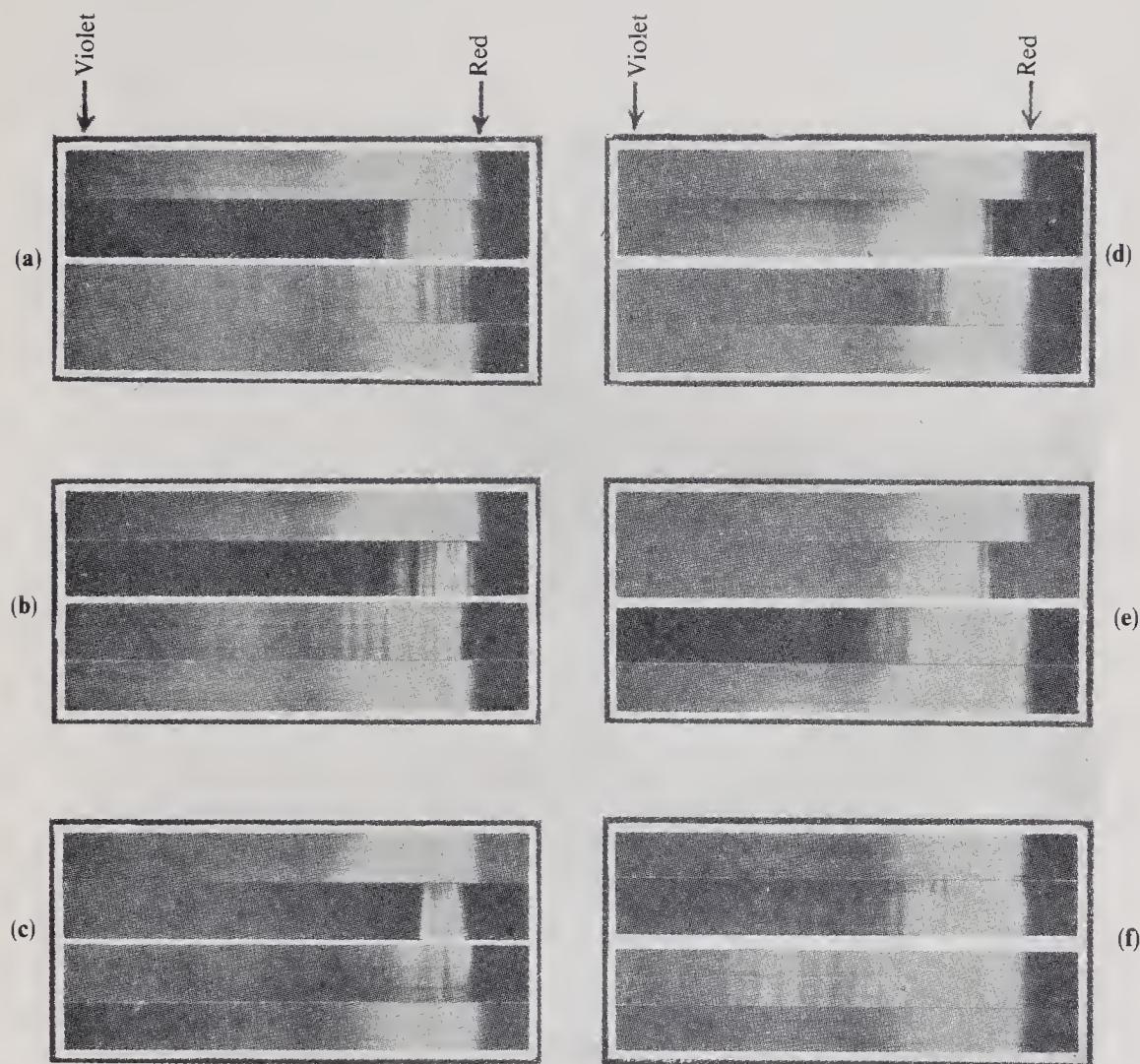


Figure 10. (a), (b), (c), (d), (e) and (f). Spectrograms of reflected and transmitted light of decomposed glass films.

## The iridescent feldspars

To the physicist interested in the structure and properties of crystalline solids, the feldspars offer themselves as a fascinating field for study and research. Being a most important group of rock-forming substances, they have naturally been the subject of numerous painstaking investigations by mineralogists. A great volume of data concerning them has accumulated, and much of this awaits interpretation in terms of structural theory. Of particular interest is the optical behaviour of the feldspars. This includes a variety of attractive phenomena for which no satisfactory explanation has hitherto been forthcoming. Amongst them may be mentioned particularly the brilliant play of colours exhibited by the species of feldspar known as labradorite, which is found not only in the locality from which its name is derived, but also in various other parts of the world. Another group of feldspars known as the moonstones has found use in jewellery by reason of a beautiful optical effect known to mineralogists as "schiller" which they display. There are also other types of feldspar which display characteristic optical effects, e.g., peristerite, murchisonite and amazonite. Labradorite and the moonstones have been the subject of two recent memoirs\* published in the *Proceedings of the Indian Academy of Sciences*. Further papers dealing with other types of iridescent feldspars are scheduled to appear in the same journal in the near future. It is felt, however, that the results so far obtained are of sufficient general interest to justify the publication of a review article in *Current Science*, presenting this field of research in its broadest aspects.

Chemical analysis shows that apart from minor impurities present as inclusions, the commoner feldspars may be regarded as admixtures of three components having a definite composition, namely the potash, soda and lime feldspars. Their mineralogical names and chemical formulae are respectively orthoclase ( $KAlSi_3O_8$ ), albite ( $NaAlSi_3O_8$ ), and anorthite ( $CaAl_2Si_2O_8$ ). In their external aspect as well as in the internal structure revealed by X-ray studies, all the feldspars possess certain features in common. Nevertheless, there are important differences. In particular, we remark that while the chemical formulae of orthoclase and albite are similar, the replacement of the monovalent alkali ion

\*"The Structure of Labradorite and the Origin of its Iridescence," by Sir C V Raman and A Jayaraman, *Proc. Indian Acad. Sci. A.*, 1950, **32**, 1–16.

\*\*"The Structure and Optical Behaviour of the Ceylon Moonstones," by Sir C V Raman, A Jayaraman and T K Srinivasan, *Ibid.*, 1950, **32**, 123–40.

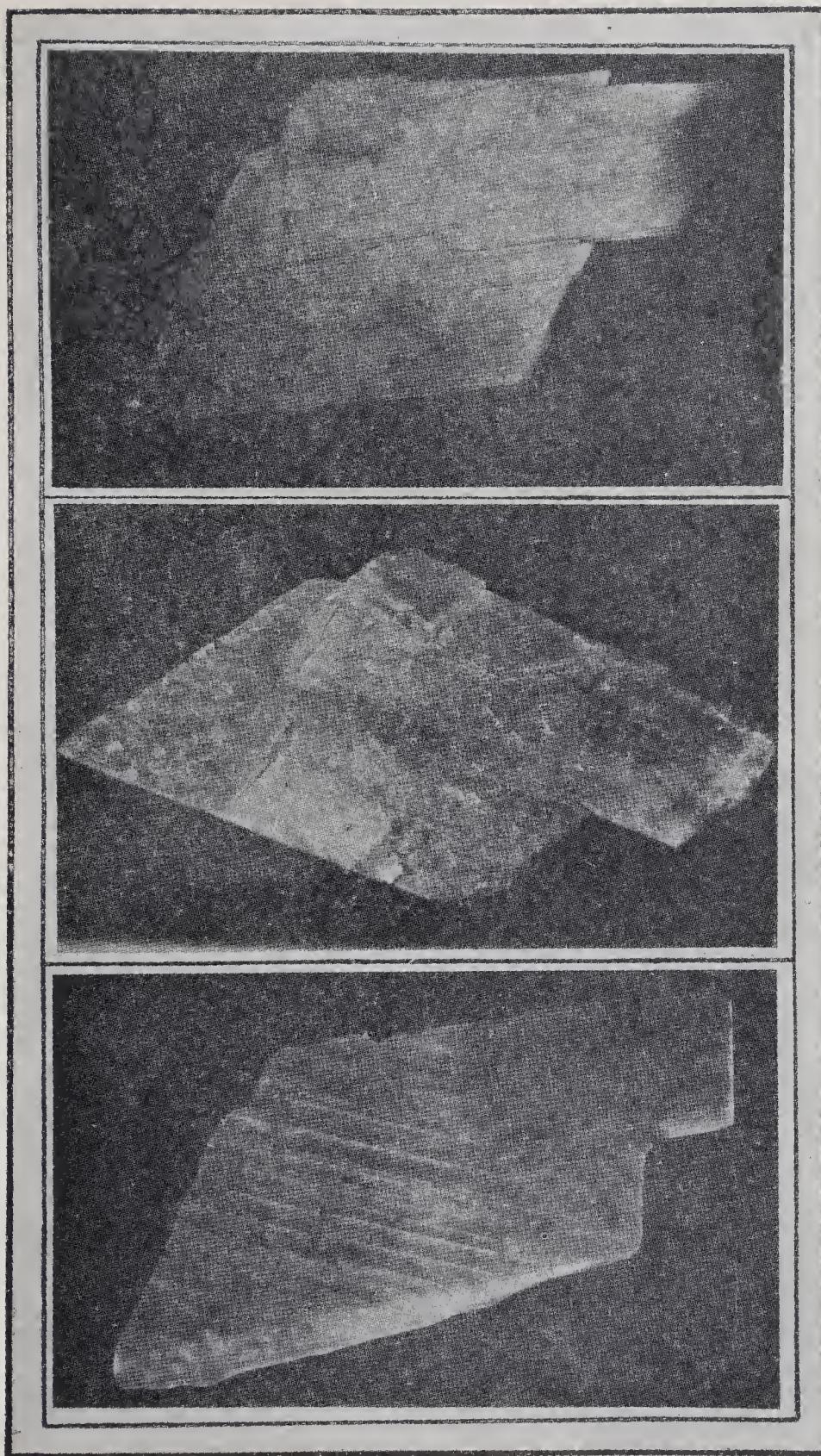


Figure 1

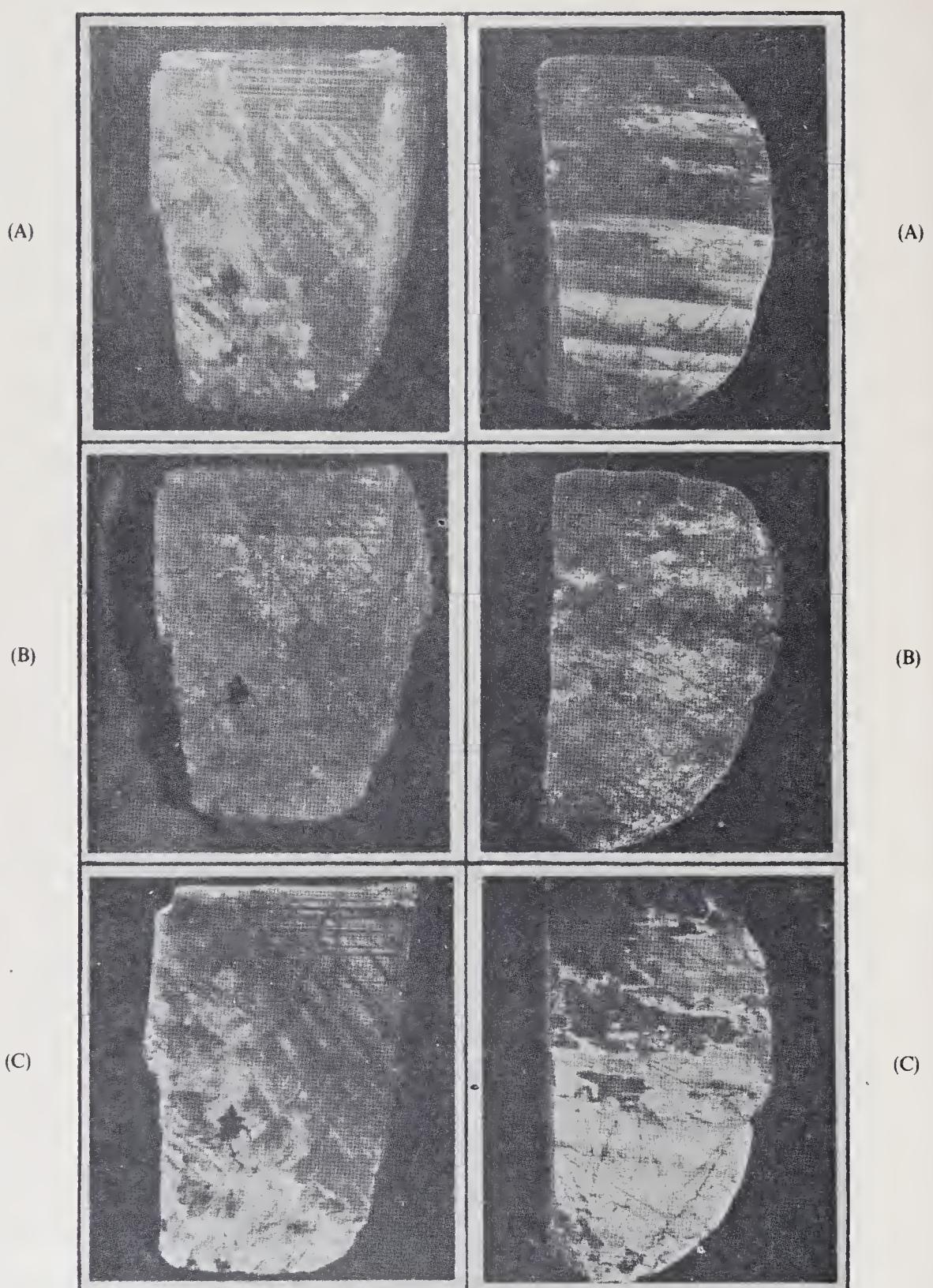


Figure 2

Figure 3

by the divalent calcium ion in anorthite is accompanied by a simultaneous replacement of a silicon atom by an aluminium atom. In spite of such replacement, albite and anorthite resemble each other in their crystal forms very closely, both being triclinic, while orthoclase is a monoclinic crystal. The explanation which has been given for this remarkable situation is that the replacement of silicon by aluminium does not involve any alteration in crystal structure, while on the other hand, the replacement of the larger potassium ion by the smaller sodium or calcium ion results in a definite change of structure.

It has been stated above that a naturally occurring feldspar usually contains all the three components. Their relative proportions, however, vary considerably. Labradorite, for instance, is principally a mixture of albite and anorthite in roughly equal molecular proportions, but contains in addition an appreciable proportion of orthoclase. The Ceylon moonstones consist principally of orthoclase, but include also a substantial proportion of albite and a small percentage of anorthite. In view of the differences in chemical composition and crystal structure of the three components in their pure state, the question naturally arises of the precise nature of their admixture in any particular feldspar as found in nature. In the two papers under reference, it has been shown that the answer to this question is furnished by the optical behaviour of the material under study. In other words, the play of colours exhibited by labradorite, and the schiller of moonstones are alike the optical consequences of the manner in which the component feldspars are distributed within the respective minerals. In the common or macroscopic sense, both labradorite and moonstones are monocrystals. But the passage of a beam of light through the mineral and the diffusion of light resulting therefrom reveal the existence of optical heterogeneity, in other words, of local variations of composition and refractive index. The observed characters of the diffused light, viz., its spectral nature, intensity, state of polarisation and distribution in different directions, and their variations with the setting of the crystal and the direction of passage of light through it, furnish us with the data needed to infer the nature of the local heterogeneities within the crystal. The explanation of the optical phenomena presented by these feldspars thereby ceases to be a matter for conjecture or speculation and rests instead on a solid basis of observation and inference.

The optical behaviour of a mixed crystal is, of course, not comparable in all respects with that of a mixture of liquids. Nevertheless, it is useful to indicate the resemblances between the optical phenomena under consideration and the diffusion of light in binary and ternary liquid mixtures. The blue schiller exhibited by the finest moonstones may, indeed, be not inaptly compared in its origin and in its spectral character with the blue opalescence which develops in a binary liquid mixture, e.g., of methanol with carbon disulphide, as its critical solution temperature is approached. The schiller is essentially a diffusion of light within the feldspar. It results from the segregation of the albite from the orthoclase in the form of tiny crystallites which so dispose themselves that the crystalline order and

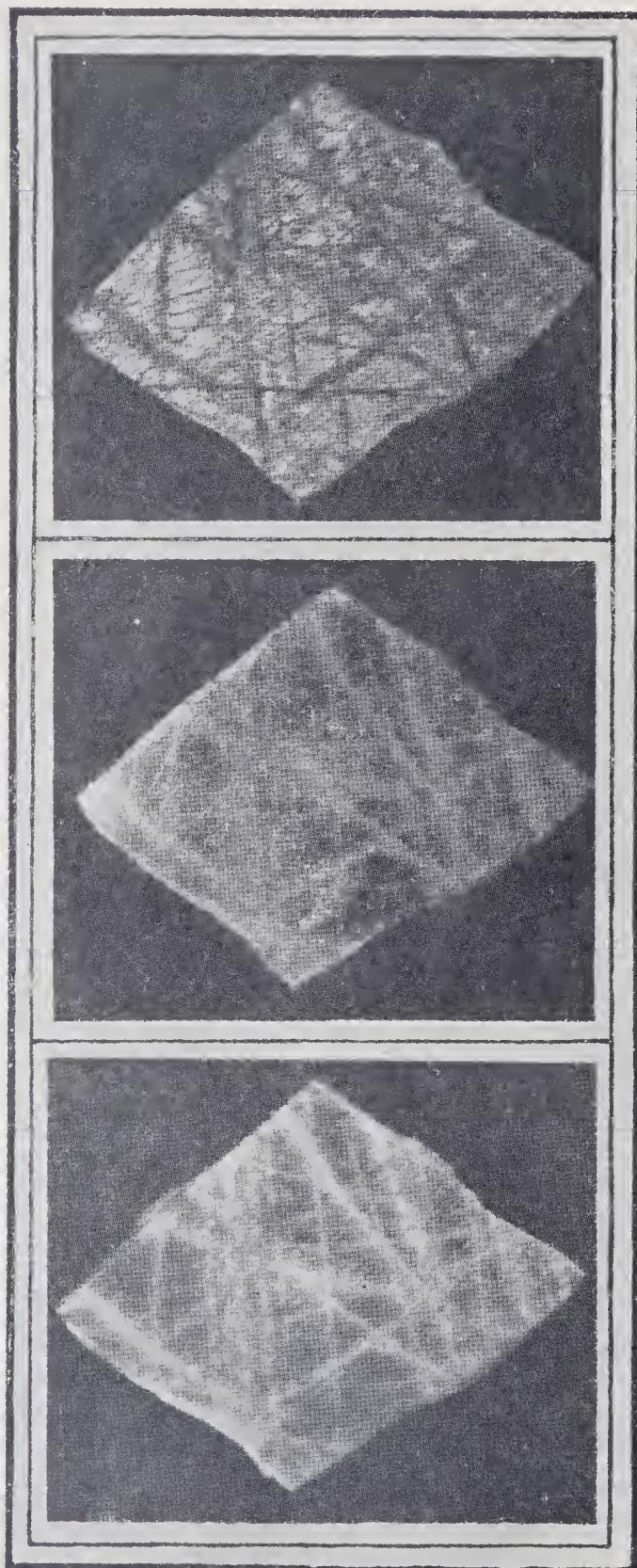


Figure 4

symmetry of the parent mass is left unimpaired. The blue colour exhibited by many specimens of labradorite may similarly be compared with the blue opalescence which develops when water is added to methanol containing benzene in solution, and the benzene tends to separate out in consequence. The diffusion of light in the labradorite which manifests as its iridescence is due to tiny crystallites of orthoclase which have segregated from the albite-anorthite mixture and set themselves in an appropriate orientation within the crystal lattice.

The interested reader will naturally refer to the original papers for further information regarding the topics dealt with above in their barest outlines. They contain a description and discussion of many facts of interest discovered in the course of the studies and which considerations of space preclude even being mentioned here. The illustrations accompanying the present article are taken from the paper on labradorite and represent four of the numerous specimens studied. As the reproductions are not in colour, they are not very effective as pictures of the beautiful phenomena actually observed. But they demonstrate a most important feature of the optical behaviour of labradorite, namely that it shows its characteristic iridescence in *two* different settings of the crystal with reference to the direction of the incident light. These settings (A and C in each figure) lie one on either side of the setting (B in each figure) at which the aventurinism due to the macroscopic inclusions is most prominently displayed. The parts of the labradorite which exhibit the iridescence in the two settings are different, being respectively the alternate layers of multiple twinning in the mineral. The distribution of these layers as well as the nature of the twinning is very different in the four specimens. This becomes evident in the iridescence displayed by them.

C V RAMAN

## The structure of labradorite and the origin of its iridescence

SIR C V RAMAN and A JAYARAMAN  
(Raman Research Institute, Bangalore)

Received July 14, 1950

### 1. Introduction

Labradorite which is a crystalline feldspar of the triclinic class is well known for the striking iridescence or play of colours which it exhibits. The phenomenon is displayed not only by specimens from the locality which gave its name to the substance, namely the coast of Labrador, but also by those from other parts of the world. This fact and the highly distinctive character of the effects observed suggest that they are in some way connected with the nature of the feldspar itself. Hintze (1897) reviewed the earlier attempts to find an explanation of the iridescence. Later investigations published about the same time by Rayleigh (1923) and by Boggild (1924) made useful contributions to the subject; but they left unanswered the fundamental questions which arise, namely, what is the material which is responsible for the iridescence of labradorite and why is it present? In the hope that a more searching examination of the phenomena than has hitherto been made might result in finding the answers to these questions, a representative collection of specimens was acquired for the crystallographic museum of this Institute. They have been carefully studied, and the investigation has revealed basic new facts concerning the iridescence of labradorite and enabled us to reach definite conclusions regarding its origin.

### 2. The chemical composition of labradorite

Mineralogists place labradorite fairly high up in the sequence of the plagioclase feldspars running from albite to anorthite. The two end-members of the series both belong to the triclinic class of crystals, and it is a well-established fact that they are isomorphous and can mix freely in all proportions to form homogeneous crystals. To describe labradorite as a mixture of albite and anorthite, in other words of soda and lime feldspars is, however, only an idealisation and not a complete picture of the reality. The chemical analyses tabulated by Hintze

(*loc. cit.*) show that labradorite contains also an appreciable proportion of potash feldspar. There are also other materials present as impurities in variable amounts, these being principally  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$ . Examination of labradorite under a binocular microscope shows the presence of inclusions of different kinds trapped at various levels within the crystal. They appear as discrete crystals with sharply defined outlines and evidently represent the impurities revealed by the chemical analysis. Their distribution within the labradorite is irregular, even in those cases in which the characteristic iridescence of the feldspar appears with remarkably uniform intensity and colour over the entire volume of the specimen. The facts stated make it highly improbable that the characteristic iridescence of labradorite is due to the presence in it of extraneous impurities or inclusions. They suggest, rather, that the phenomenon has its origin in the constitution of the feldspar itself. Our attention is thus naturally directed to the third component of the feldspar shown by the chemical analysis to be present, namely, orthoclase or potash feldspar.

### 3. The lamellar structure of the mixed feldspars

The crystallographic data and the X-ray investigations that have been made (Taylor 1934) indicate that all the feldspars possess certain structural features in common. Nevertheless, there are well-established differences amongst them, the most notable being that the feldspars in which the potash is the principal component crystallise in the monoclinic system, whereas those in which the soda and lime feldspars are the principal components form triclinic crystals. In view of its lack of isomorphism with the two other feldspars, we could scarcely expect potash feldspar to be freely miscible with them in all proportions or to form homogeneous crystals as the result of such mixture. Actually, when the results of the chemical analyses of nearly a thousand specimens of naturally occurring feldspars are plotted as points on a three-component diagram (Alling 1921), it is found that a large part of the area of the triangle is empty and that a potash-lime series of feldspars is not represented in the diagram. The occupied area consists of a belt lying along the two sides of the triangle representing respectively a soda-potash series of feldspars and a soda-lime series, its width being greatest in the vicinity of the vertex representing pure albite and narrowing rapidly as the vertices representing pure orthoclase and pure anorthite are approached. It should be emphasised that the feldspars found in nature are not invariably homogeneous crystals. Indeed, it is well known that many of the feldspars of the soda-potash series are not of that description. Amongst the feldspars of the series in which orthoclase is the major component, only those containing a relatively small proportion of albite are truly single crystals. The others are essentially intergrowths in which the monoclinic and triclinic components have separated from each other to form lamellar structures. The lamellae may be so coarse as to

be visible to the naked eye (perthites); they may also be so fine as to be visible only under a microscope or even so fine as to be optically irresolvable (microperthites).

In view of what has been said above, the question arises as to how the component of potash feldspar present in the soda-lime series of feldspars is distributed within the material, viz., whether it forms a homogeneous solid solution with the albite-anorthite, or whether it is segregated from the soda-lime feldspar and forms crystallites of orthoclase which remain embedded in the albite-anorthite matrix and distributed through its volume. The latter alternative has to be recognised at least as a possibility. The optical behaviour of labradorite would be profoundly different according as the first or the second alternative is the correct answer. In the former case, it would be a transparent colourless crystal, assuming that there are no other inclusions or impurities present. In the second case, the difference in refractivity between the orthoclase crystallites and the albite-anorthite mass in which they are embedded is considerable. Hence their presence would render the crystal an optically heterogeneous medium, causing it to exhibit various effects when traversed by a beam of light. Since labradorite does exhibit such effects, we are entitled, at least as a working hypothesis, to adopt the second of the alternatives stated and to develop its consequences for comparison with the facts of observation.

#### 4. The orientation of the lamellae

Accepting the validity of our hypothesis, we have to ask ourselves other questions, viz., what is the shape, size and orientation of the crystallites of orthoclase? Is the setting of the crystallites arbitrary and unrelated to the structure of the albite-anorthite crystal, or does it have some definite relation to it and therefore possesses some measure of uniformity?

In seeking an answer to the questions raised, the facts which have been established by X-ray investigations on the soda-potash series of feldspars give us some useful guidance. Ito and Inuzuke (1936) found that two structures are present in the microperthites, one similar to pure potash-orthoclase, the other similar to albite. Their work has been confirmed by Chao, Smare and Taylor (1939), while a further study by Chao and Taylor (1940) revealed some finer details. For our present purpose, the principal result that emerges from the X-ray studies is that the crystal axes of the two structures present in the microperthites are either coincident, or else make small angles with each other. The latter result is not unexpected, since one of the structures is monoclinic and the other triclinic. We have, therefore, ample justification for assuming that a similar situation would exist in our present problem, in other words, that the crystal structures of the orthoclase and of the surrounding albite-anorthite mass would be coherent. From a crystallographic point of view, therefore, we may, without serious error,

consider the whole of the material as a single unit in spite of its optical heterogeneity.

In the circumstances stated, it is not unreasonable to assume that the actual shape and setting of the orthoclase crystallites would bear some recognisable relationship to the lattice structure of the enclosing crystalline mass. According to Chao and Taylor (1940), the crystal structure of labradorite is itself rather complex, sheets of albite and sheets of anorthite, each a few unit cells thick, alternating along the *c*-axis. In these circumstances, it is scarcely possible even to venture a guess as how the third component, viz., the monoclinic orthoclase would dispose of itself in the lattice. We have necessarily to regard this as a matter for observational study rather than for theoretical prediction. Nevertheless, as will be shown in the following sections of the paper, the theoretical ideas set out above have various specific consequences which can be tested by observation or experiment. The complete success met with in such tests is testimony to their essential correctness.

## 5. Some consequences of the twinning of labradorite

As is well known, the plagioclase feldspars frequently exhibit multiple or repeated twinning of the albite type. The brachypinacoid or 010 face is both a plane of reflection and a plane of composition in this type of twinning; in other words, the crystal structures on either side of a composition plane are mirror images of each other. The albite type of twinning is readily recognized by the appearance of sets of parallel lines where the composition planes meet the external surface of the crystal. They are most clearly seen on the 001 faces, since these are the most perfect cleavages of the crystal and are nearly normal to the twinning planes. The visible signs of albite twinning on the 001 faces may be traced across them right up to the edges of any artificially polished surface which meets them. We shall proceed to consider how such twinning would influence the optical phenomena exhibited by labradorite.

It will be assumed that the iridescence displayed by labradorite arises from the presence in it of thin lamellae of orthoclase which reflect a beam of light travelling through the crystal by virtue of their refractive index being less than that of the surrounding albite-anorthite mass. The direction in which the light is reflected would depend on the angle of its incidence on the lamellae and hence also on the orientation of the latter within the crystal. This orientation is more or less precisely defined, being determined by physico-chemical considerations connected with the crystal structures of the three components of the feldspar. Further, the orthoclase lamellae, though optically different from the surrounding mass, are nevertheless an integral part of the crystal. Hence, if the latter is a simple albite twin, the orientations of the lamellae in the components of the twin would not be identical but would be mirror-images of each other with respect to their

composition plane. For the same reason, also, if the labradorite is a multiple or repeated twin, the orientations of the lamellae in the 1st, 3rd, 5th, etc. twinning layers of the crystal would be parallel to each other, and likewise also the orientation of the lamellae in the 2nd, 4th, 6th, etc. twinning layers, but the orientations of the lamellae in the two sets of twinning layers would be different, being the mirror images of each other in the composition planes. The thickness of the orthoclase lamellae influences their optical behaviour, including especially the colour which they exhibit. If this be the same in the 1st, 3rd, 5th, etc. twinning layers of the crystal, there is no reason why it should be different in the intervening 2nd, 4th, 6th, etc. layers. Hence, we arrive at the following inferences as necessary consequences of our theoretical views:

- A. *Every specimen of labradorite which is twinned according to the albite law and exhibits iridescence, should display the latter in two distinct settings of the specimen, if the direction of incidence of the light and the direction of observation are pre-determined.*
- B. *For the same reason, for any given setting of the specimen and a given direction of incidence of the light on it, the iridescence should be observable in two divergent directions.*
- C. *The two reflections mentioned above have their origin in different parts of the crystal, namely the two differently orientated sets of components of the multiple twin..*
- D. *The two sets of reflections should in similar circumstances exhibit identical colours.*
- E. *The settings of the crystal required for observing the two independent sets of reflections should make equal angles with the setting required to obtain a specular reflection from the composition planes of the twinning.*

Another kind of twinning which is frequently observed in the plagioclase feldspars is known as the pericline type. This species of twinning is almost invariably multiple with closely spaced components, the structures of which are derivable from each other by a rotation of the crystal about the *b*-axis through  $180^\circ$ . The composition planes of the pericline twinning in labradorite are nearly parallel to the 001 faces of the crystal, actually making an angle only  $6^\circ$  with them. The twinning manifests itself externally by parallel and closely spaced striations on the 010 faces of the crystal and is thus readily distinguishable from the albite twinning where no such striations are observed.

Reasoning analogous to that set out in the case of albite twinning leads to theoretical consequences similar to those listed above as A, B, C, D and E, except that the word "pericline" is substituted for "albite" in the description of the twinning and E is modified to read as follows:

- E'. *The settings of the crystal required for observing the two independent sets of reflections would be obtained, one from the other, by a rotation of the crystal about its *b*-axis through  $180^\circ$ .*

## 6. Comparison with the facts of observation

Our theory thus leads us to the remarkable conclusion that precisely definable relationships should exist between the kind of twinning of the albite or the pericline type, as the case may be, which a particular specimen of labradorite exhibits and the circumstances in which it displays iridescence as well as the observable characters of such iridescence. It is scarcely conceivable that any such relationships could exist unless it is the case that the material responsible for the iridescence of the feldspar is itself an integral part of the structure of the crystal. It follows that relationships indicated by the theory, if they actually exist, are a convincing demonstration of its correctness.

The specimens of labradorite at our disposal form a fairly representative collection, both in regard to the colours exhibited and in respect of their types of twinning as identified by their external manifestations. Some of our specimens display exclusively the albite type of twinning, some exclusively the pericline type, and others show both. The material examined by us is thus sufficiently extensive to prove or disprove the deductions from the theory. Actually, the observations support the theoretical inferences in the most complete and detailed fashion.

The existence of the two sets of reflections exhibiting the same colours but originating in different parts of the crystal is readily shown and the geometric relationship between them indicated by the theory simultaneously verified by the following procedure. The observer stands with his back to a window, the light from which falls on the specimen held in his hands with its polished face turned towards him. The orientation of the specimen required to display one of the coloured reflections is first ascertained by trial. It is also easy to locate the orientation in which the specimen exhibits the specular reflection from the platy inclusions lying with their faces parallel to the 010 planes in the crystal. The observer then ascertains by trial, the position of an axis such that if the specimen is rotated about it, first the coloured reflection and then the specular reflection successively come into view. *A further rotation about the same axis and in the same direction brings the second reflection into view.* If the twinning is of the albite type, the axis of the rotation needed is found to be parallel to the composition planes of the twinning: it does not coincide with either the  $a$  or the  $c$ -axis of the crystal, but makes an angle of about  $70^\circ$  with the former. If the twinning is of the pericline type, the correct procedure for viewing the two reflections successively is to rotate the crystal about its  $b$ -axis through  $180^\circ$ . But since the  $b$ -axis is not far removed from being normal to the 010 planes of the crystal, a rotation in the same direction and about the same axis as in the case of the albite twinning is found to be effective.

Except in respect of colour which is identical for both reflections, the features they display are found to be different and indeed often strikingly different. That this is due to their location in different parts of the crystal is demonstrated by the exact correspondence between the disposition of the twinning layers at the

surface through which the observations are made and the features exhibited by the iridescence. Actually, it is found that the angle at which the composition planes of twinning meet the polished face has a great influence. If they meet steeply, as in the case of pericline twinning, the iridescence exhibits alternate dark and bright bands traversing the surface, these interchanging places in the two sets of reflections. On the other hand, if the composition planes meet the external surface obliquely as in the case of the albite twinning, much depends on the disposition of the reflecting lamellae in the alternate layers of the twinned crystal. If the reflecting lamellae of one set are nearly parallel to the external face, those of the other set necessarily meet it obliquely; the reflection by the first set then appears almost uniform over the surface, while the reflection by the other set shows a banded structure. The degree of general transparency of the crystal plays a role of importance in deciding what is actually seen in any particular case; the greater the transparency, the more effective become the deeper layers in the crystal and the greater their contribution to the total observed luminosity. So much depends on the characters of the individual specimens that these details are best dealt with in describing their behaviour. This will be done later in the paper, and the particular cases illustrated in plates I to V accompanying it will be fully commented upon.

The refractions at the external surface of a specimen occurring both at entry and at emergence of the light materially influence the settings of it required for observing the internal reflections. Except, however, when the specimen has been inappropriately cut, the deviations in the course of the light rays produced by these refractions would not prevent the effects described above coming under observation. By immersing the specimen in a glass cell filled with a liquid having the same refractive index as labradorite, they may be completely eliminated. It is then possible to make a quantitative test of the geometrical relationship between the two sets of internal reflections indicated by the theory. Studies made in this way show that the settings at which the maximum intensity of iridescence is observed make an angle of  $14^\circ$  on one side or the other with that required for a specular reflection from the  $010$  planes of the crystal.

## 7. Phenomena observed with polarised light

Some rather spectacular effects are observed when labradorite is illuminated by a beam of light which has passed through a polaroid sheet and the characteristic iridescence is viewed through a second polaroid sheet; the setting of the labradorite in its own plane, the angle of incidence of the light on it, and the setting of the two polaroids with respect to each other may be varied in the experiment, with interesting consequences. Apart from their experimental interest, the results observed with polarised light have a direct bearing on the problem of the structure of labradorite and the origin of its iridescence which

forms the subject of this paper. Indeed, they afford further confirmation of the correctness of the theoretical approach made in the paper, as we shall presently proceed to show.

The reflection of electromagnetic waves which occurs at the boundary between two media is a consequence of the differences in their optical polarisabilities. When both media are crystalline and anisotropic, the intensity of such reflection would, in general, depend not only on the angle of incidence and state of polarisation of the incident light, but also on how the optic axes of the two crystals are orientated with respect to the direction of the electric vector in the incident waves. The state of polarisation of the reflected light would also depend on the same circumstances. As a consequence, the observable characters of the reflected light would, in general, exhibit a complex behaviour such as is not met with in the familiar case of optically isotropic media. In the present problem, however, we are concerned with the reflection of light at the boundary between two feldspars whose structures are similarly orientated in space, and this results in a great simplification, as we shall presently notice.

The second and third columns of table 1 show the maximum and minimum refractive indices of labradorite and orthoclase respectively, while the fourth column shows the differences between them. It will be seen that the birefringence

Table 1

	Ng	Np	Ng-Np	Ng'	Np'	Ng'-Np'
Labradorite	1.5678	1.5598	0.008	1.565	1.559	0.006
Orthoclase	1.5260	1.5180	0.008	1.524	1.518	0.006
Differences	0.0418	0.0418	0	0.041	0.041	0

is of the same order of magnitude in the two feldspars and is quite small, while on the other hand, the differences in their refractive indices are several times larger. The fifth and sixth columns show the two refractive indices Ng' and Np' in each case for flakes lying on 010, while the seventh column gives the differences between them. It will be noticed that the lower index Np' differs little from the minimum index Np in either case, and that the differences between Ng' and Np' are identical, in other words that the birefringence in flakes parallel to 010 is very similar in the two feldspars. Taking these facts into consideration, it is evident that the optical anisotropies would have a negligible effect on either the intensity or the state of polarisation of the light reflected at the boundaries of separation, which, as we have seen, make an angle of only 14° with the 010 planes in labradorite. In other words, we may, for the present purpose, treat the feldspars as optically isotropic media having refractive indices appropriate to the circumstances of each case. The following inferences are thus justified.

- (a) The intensity of the internal reflections in labradorite would be sensibly independent of the setting of the crystal, if the angle of incidence remains unaltered.
- (b) The internally reflected light would exhibit a polarisation of the normal type; this would be sensibly perfect for the Brewsterian angle of incidence on the reflecting layers, namely  $44^\circ$ , in other words, when the light is deviated through  $88^\circ$  by such reflection.

The two results stated above and especially the complete polarisation of the reflected light in a direction transverse to the incident beam indicated by the theory furnish us with an *experimentum crucis* for a test of its truth. It is satisfactory to note that the studies made by us fully confirm these results. To exhibit the polarisation effect, it is necessary to immerse the specimen in a square cell filled with a liquid having the same refractive index as labradorite, and to place it so that the light entering the cell through one face and reflected within the specimen emerges through the perpendicular face. It is also necessary to arrange that the polarisation due to the internal reflection is not modified by the birefringence of the labradorite. This may be secured by a suitable orientation of the specimen within the cell. For the same reason, it is preferable to employ a specimen that does not exhibit twinning, at least in the immediate vicinity of the area under observation. It is found that in these circumstances, the reflected light is completely quenched when observed through a polaroid set with its vibration direction in the plane of incidence.

The phenomena exhibited by labradorite when illuminated by polarised light and observed through a polariser owe their interest to the fact that they render the presence of the twinning layers adjacent to the surface as well as their inclination to the latter directly accessible to observation. The phenomena are best described when dealing with the behaviour of our individual specimens.

## 8. Spectral characters of the iridescence

When we compare the iridescence of labradorite with the colours of thin plates, we notice certain obvious similarities as well as some striking differences. A regular colour sequence is exhibited by some specimens of labradorite, recalling those shown by soap films of varying thickness or by Newton's rings. Boggild (*loc. cit.*) describes some fine examples. The colours also change with the obliquity of observation in much the same way as the colours of thin films. The spectral nature of the colours is, however, wholly different in the two cases. We do not observe with labradorite the dark and bright bands alternating in the spectrum characteristic of the interferences of thin plates; what is actually observed is a continuous variation of intensity in the spectrum. Particularly significant is Boggild's remark that the colours of the first order which are a prominent feature

in Newton's rings are wholly absent in the case of labradorite. These begin with a blue which is far richer than the faint blue of the first order, and are followed by other rich colours and not by the white observed in the Newtonian sequence.

The facts stated find a natural explanation in the ideas developed in the present paper. As we have seen, the optical heterogeneity of labradorite owes its origin to the orthoclase or potash feldspar present segregating itself from the albite-anorthite. The first stage of such segregation would evidently be the formation of very small crystallites distributed throughout the volume of the crystal. Such segregation would evidently give rise to a Tyndall effect in which the shorter wavelengths would predominate, and hence having the rich blue colour characteristic of the scattering of light by small particles. Since the particles occupy fixed positions, the diffused radiations would have specifiable phase-relations and would be capable of mutual interference. The observed effect in any direction would depend on the disposition of the particles in space. In view of the similarities in chemical composition and crystal structure between orthoclase and albite-anorthite, it is scarcely to be supposed that such disposition would be wholly random in character. If, as may reasonably be assumed, the diffracting particles locate themselves more or less accurately in sets of planes having a specific orientation within the crystal, the optical effect resulting from the passage of a beam of light would be a diffusion, the intensity of which would be greatest around a particular direction; it may be described as a diffuse reflection by the set of planes referred to. At a later stage in the segregation, the particles would be crystallites no longer small in comparison with the wavelength of light. Assuming, for the reasons discussed earlier in the paper, that they are lamellae having a specific orientation, the colour of the diffracted light would be determined by their thickness, while its angular extension would depend on their other dimensions. This second stage could scarcely be reached unless the dimensions of the crystallites are much in excess of those required to give interference colours of the first order in the Newtonian scale.

The foregoing remarks may be summed up by the statement that the colours of labradorite are neither a simple Tyndall diffusion nor a simple case of thin-film colour; they are a case *sui generis* in which the optical principles underlying both of these phenomena play a part. We may conclude this section by a brief description of some effects which we have observed and which are readily understood in the light of this statement. As both Rayleigh (*loc. cit.*) and Boggild (*loc. cit.*) have mentioned, the coloured reflections in labradorite are not sharply defined but appear spread out over a range of angles. We have noticed in our studies that the angular range of this spread is about twice as great for a blue iridescence—despite the smaller wavelengths—as for a red or an orange iridescence with its greater wavelengths. We have noticed also that when a specimen exhibiting varied colours over its area is illuminated and is slowly turned away from the setting at which the reflection is brightest, the areas of blue iridescence continue to be visible long after the other areas are dark. Further, we

have noticed in the same circumstances that the areas exhibiting these other colours show a distinct change of tint towards the blue before they are finally extinguished.

## 9. Some typical examples

In the preceding sections of the paper, references were made in general terms to the results of our observations with the specimens of labradorite at our disposal. By way of supplementing these references and to give them substance, we shall proceed to describe in some detail, the individual behaviour of a few of them.

*Specimen No. 1* is our largest and finest piece. It is a slab some 24 centimeters long, 12 centimetres broad and of thickness about a centimetre at one end, thinning off to five millimeters at the other. It was obtained through the East Coast Mineral Corporation of New York, and the locality of its origin is shown on its label as the Grenfell quarry, Nepoktulegatsuk, Tabors Island, near Nain, Labrador. Though apparently dark in colour, the material is fairly transparent and exhibits a brilliant blue iridescence on both faces. One of the faces had been polished, evidently to exhibit the effect to the greatest advantage, but the other, though quite rough, showed the same colour with scarcely less brilliance. The material on careful scrutiny shows a wavy discontinuity running through it. The central part of the slab displays a bright blue colour, while the areas to the left and the right exhibit a darker and deeper blue. Except in this respect, the iridescence is seen to possess a most remarkable uniformity over the entire area of the specimen.

Figure 1 in plate I is a photograph of the specimen when displaying its characteristic iridescence. The illumination of the slab was a few degrees away from the normal to avoid reflection from the external surface. Figure 2 is another photograph taken with the specimen turned to such a position that the aventurism due to inclusions lying in the 010 planes is prominently displayed. This effect varies enormously in its brightness over the area of the specimen, and is in fact almost entirely concentrated in and around the areas in which there are visible defects or breaks in the material. Figure 3 is a photograph exhibiting the second internal reflection observed in the specimen when it is held with the light falling on it rather obliquely, in a direction running from left to right in the picture and viewed in nearly the same direction. This reflection, unlike that reproduced in figure 1, shows a great many bands running parallel to each other across the specimen. Holding the specimen in his hand and rotating it about an axis parallel to the general direction of these bands, the observer can view successively the banded reflection, the aventurine reflection, and the uniform reflection, reproduced as figures 3, 2 and 1 respectively in plate I.

Examining the edge of the slab where the 001 cleavage could be seen, it became evident that the slab was traversed in a direction parallel to the 010 planes of the crystal by a whole series of twinning bands of the albite type. It was verified that at every one of the twinning lamellae, and exactly along the line of its meeting with the polished face of the specimen, one of the bands shown in figure 3, plate I, was located. The colour of the bands was exactly the same as that of the iridescence exhibited in figure 1 of plate I, namely bright blue in certain areas and a deeper blue in the other areas. The thinness of the twinning layers is evidently responsible for the fineness of the bands seen in figure 3. The observer readily notices that the banded reflections are more steeply inclined to the polished face of the specimen than the twinning layers themselves, though they arise in the latter. Very faint dark lines can be seen in figure 1 along the intersections of the twinning bands with the polished surface of the specimen, showing thereby that in the first reflection, these regions remain dark.

Figures 1 and 2 in plate II are photographs of the same specimen illuminated almost normally by a beam of light which has passed through a polaroid, and viewed nearly normally by the internally reflected light through a second polaroid. Figure 1 represents the case in which the two polaroids are crossed and figure 2, the case in which they are parallel. The bands seen traversing the face of the specimen in these photographs appear and disappear periodically four times in each revolution when the specimen is turned round in its own plane. It is clear that these effects arise from the birefringence of the crystal acting jointly with the birefringence of the twinning layers running through it and meeting the surface obliquely. We get bright lines in figure 1 and dark lines on figure 2 at the places where the twinning layers meet the surface, because at these places, the birefringence in the twinning layers affects the reflected light from the maximum depth in the illuminated specimen. It may be mentioned that somewhat analogous phenomena, though much less striking, may be seen when unpolarised light is incident on the slab rather obliquely and the reflected light is viewed through a polaroid. The internal reflection itself acts as a polariser in this case.

Figures 3 and 4 in plate II illustrate different kinds of inclusions observed in labradorite which are responsible for the aventurine reflections.

A few words must suffice for each of our other specimens illustrated in the Plates accompanying the paper.

*Specimen 2* is a typical example of multiple twinning of the pericline type. It exhibits a greenish yellow iridescence. Here the twinning layers meet the polished face of the specimen almost normally. Figures 1 and 3 in plate V show its two internal reflections; it is possible to make out that the dark and bright bands have interchanged places in them. Figure 2 is a photograph of the same specimen held in such a position that neither iridescence is visible.

*Specimen 3. See figures 4, 5 and 6 in plate III:* These illustrate respectively the first coloured reflection, the aventurine reflection and the second coloured reflection in the specimen. The iridescence is a golden yellow, changing to green and greenish blue at oblique incidences. The banding seen very prominently in figure 4 and less clearly in figure 6 is due to the albite twinning layers meeting the surface obliquely.

*Specimen 4. See figures 1, 2 and 3 in plate III:* This specimen exhibits a blue iridescence except towards the left where there are patches of opacity interspersed with areas of iridescence in which varied colours appear. The horizontal bands in the upper part are due to the pericline twinning, while the inclined bands towards the right owe their origin to the albite type of twinning. Figures 1 and 3 illustrate respectively the two coloured reflections, and are seen to be complementary, the bright areas in one being the dark areas in the other and *vice versa*. Figure 2 represents the aventurine reflection by the specimen.

*Specimen 5. See figures 6, 7 and 8 in plate IV:* These represent respectively, the first coloured reflection, the aventurine reflection and the second coloured reflection. The banding in figures 6 and 8 is due to the albite twinning, and the positions of the dark and bright bands in them are seen to be complementary to each other. Figure 5 in plate IV shows the same specimen viewed under incident polarised light through a second polaroid in the crossed position. It should be mentioned that this specimen exhibits very varied colours over its area; bright blue in the regions both around the dark centre and also towards its margins, with yellow, orange and red bands succeeding each other in the intervening areas.

*Specimen 6. See figures 5, 6 and 7 in plate II:* This is a small but beautiful piece which exhibits a peacock-blue iridescence with orange-yellow spots prominently in one setting (figure 5). In the other setting (figure 7), the iridescence shows peacock-blue patches which are much less intense; these appear in areas which are either completely dark or else rather faint in figure 5. Very striking also are the bright lines seen in figure 7 in the positions where the dark lines appear in figure 5. These lines represent pericline twinning bands meeting the surface steeply. Elsewhere, the specimen shows albite twinning, with one set of the iridescent laminae almost parallel to the surface and giving the strong reflection seen in figure 5, while the other set is more steeply inclined to the surface and gives the feeble effect appearing in figure 7.

*Specimen 7. See figures 1, 2, 3 and 4 in plate IV:* This is rather an extraordinary piece, showing several separate crystals in different settings firmly adhering to each other. The four photographs show its iridescence under different angles of illumination and observation. The central area shows the albite type of twinning, while two others show the pericline twinning, as is evident from the sharply

defined dark and bright bands crossing the iridescent areas. The interchange in the positions of these over the area of the crystal on the left is clearly visible on a comparison of figures 2 and 4.

In concluding this paper, we have to express our grateful thanks to those whose help has enabled us to bring this investigation to a successful conclusion. Several of our labradorite specimens were a very generous gift from Mr B W Anderson of London. Specimens of other varieties of feldspars presented to us by Professor T N Muthuswami of Madras, Dr C Mahadevan of Waltair and Mr L S Krishnamurthy of Hyderabad also proved very useful in our studies. The Director of the Geological Survey in Mysore, Dr C S Pichamuthu materially assisted us in getting access to the mineralogical literature on feldspar. Mr T K Srinivasan, Government of India, Senior Scholar in Mineralogy at this Institute, has been very helpful to us in the study of this literature.

### Summary

General considerations indicate that the phenomenon of labradorescence owes its origin to the segregation of potash feldspar as crystallites or lamellae of orthoclase which remains embedded in an albite-anorthite matrix and give rise to optical heterogeneity. The following are derived as theoretical consequences of such segregation and have been confirmed by observations made with a representative collection of specimens.

(A) Labradorite which is multiply twinned according to either the albite or pericline law or both, exhibits its characteristic reflections in two different settings geometrically related to each other by the twinning law. The two reflections display identical colours, but have their origins in different parts of the crystal, and this makes itself evident as a visible banding in one or the other or both of the reflections.

(B) The light reflected transversely to the incident beam is completely polarised.

(C) The intensity of the reflected light is independent of the setting of the reflecting layers in their own plane.

(D) The spectral character of the reflected light would approach that of a Tyndall diffusion when the crystallites are very small. Hence the colours of the first order in the Newtonian sequence would not be observed. The spectral character and the colour sequence at the later stages of segregation would also be different from those of thin films.

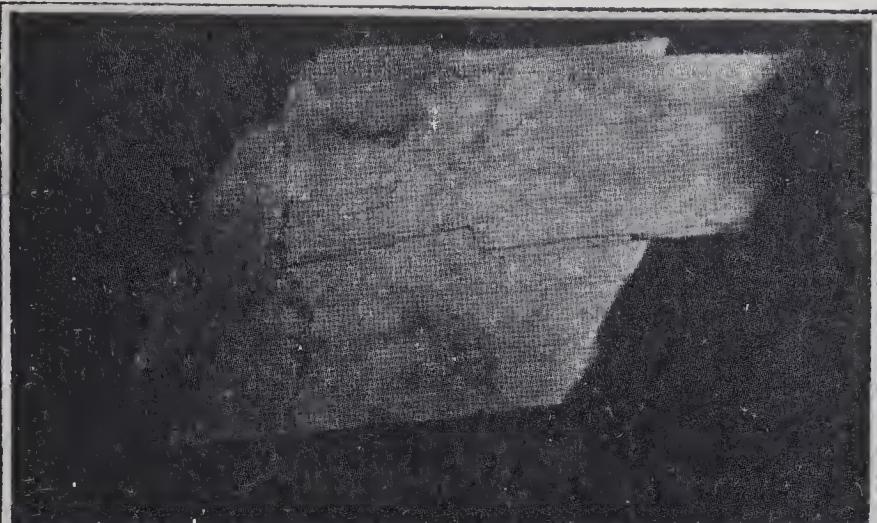
(E) The angular spread of the reflected light is greatest for the blue iridescence and less for other colours such as yellow, orange and red.

The effects arising when labradorite is illuminated and observed by polarised light are also described and explained in the paper.

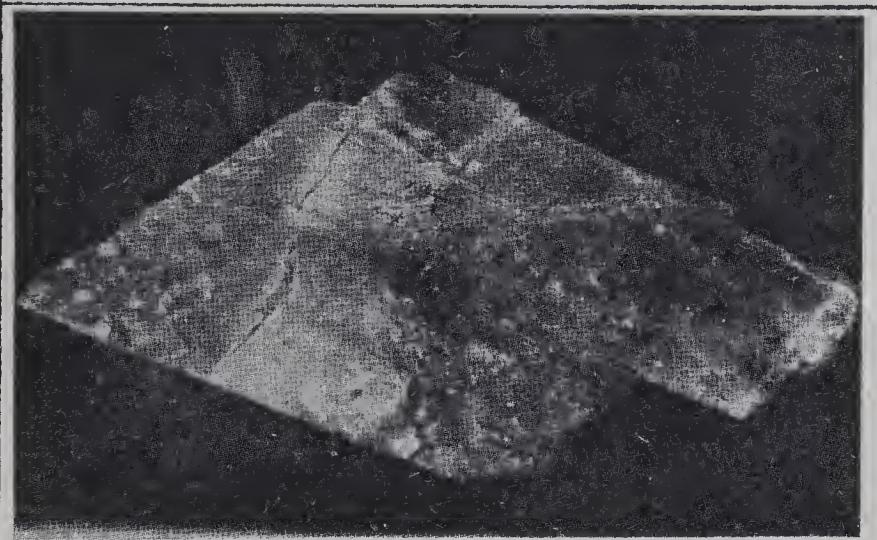
Numerous photographs reproduced in five plates illustrate the observed phenomena.

### References

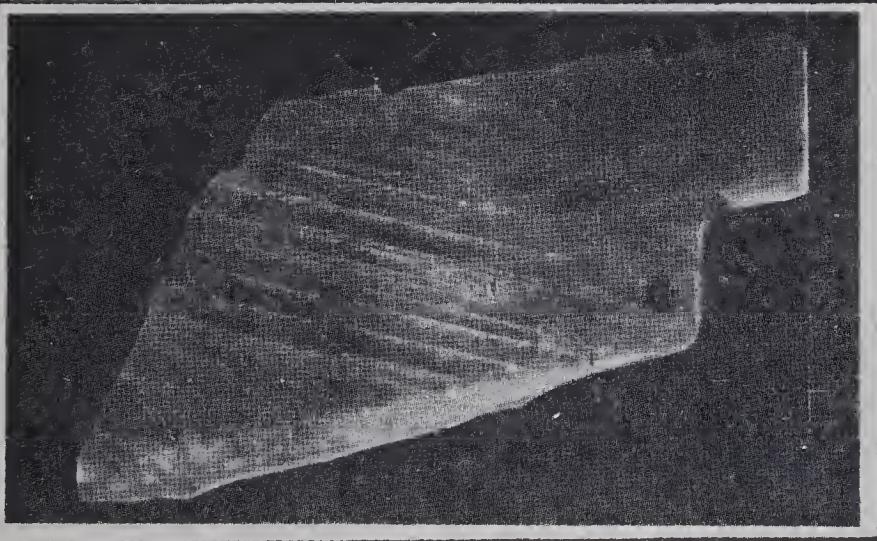
1. Alling, *J. Geol.*, 1921, **29**, 193. See also Winchell, *Optical Mineralogy*, 1932, III Edition, Part II, p. 319.
2. Boggild, *Math. fys. Meddel.*, Copenhagen, 1924, **6**, No. 3.
3. Chao, Smare and Taylor, *Miner. Mag.*, 1939, **25**, 338.
4. Chao and Taylor, *Proc. R. Soc., A*, 1940, **174**, 57.
5. Chao and Taylor, *Ibid.*, 1940, **176**, 76.
6. Hintze, *Handbuch der Mineralogie (Leipzig)*, 1897, Zweiter Band, p. 1512.
7. Ito and Inuzuke, *Z. Kristallogr.*, 1936, **95**, 404.
8. Rayleigh, *Proc. R. Soc., A.*, 1923, **103**, 34.
9. Taylor, *Ibid.*, 1934, **145**, 80.



(1)



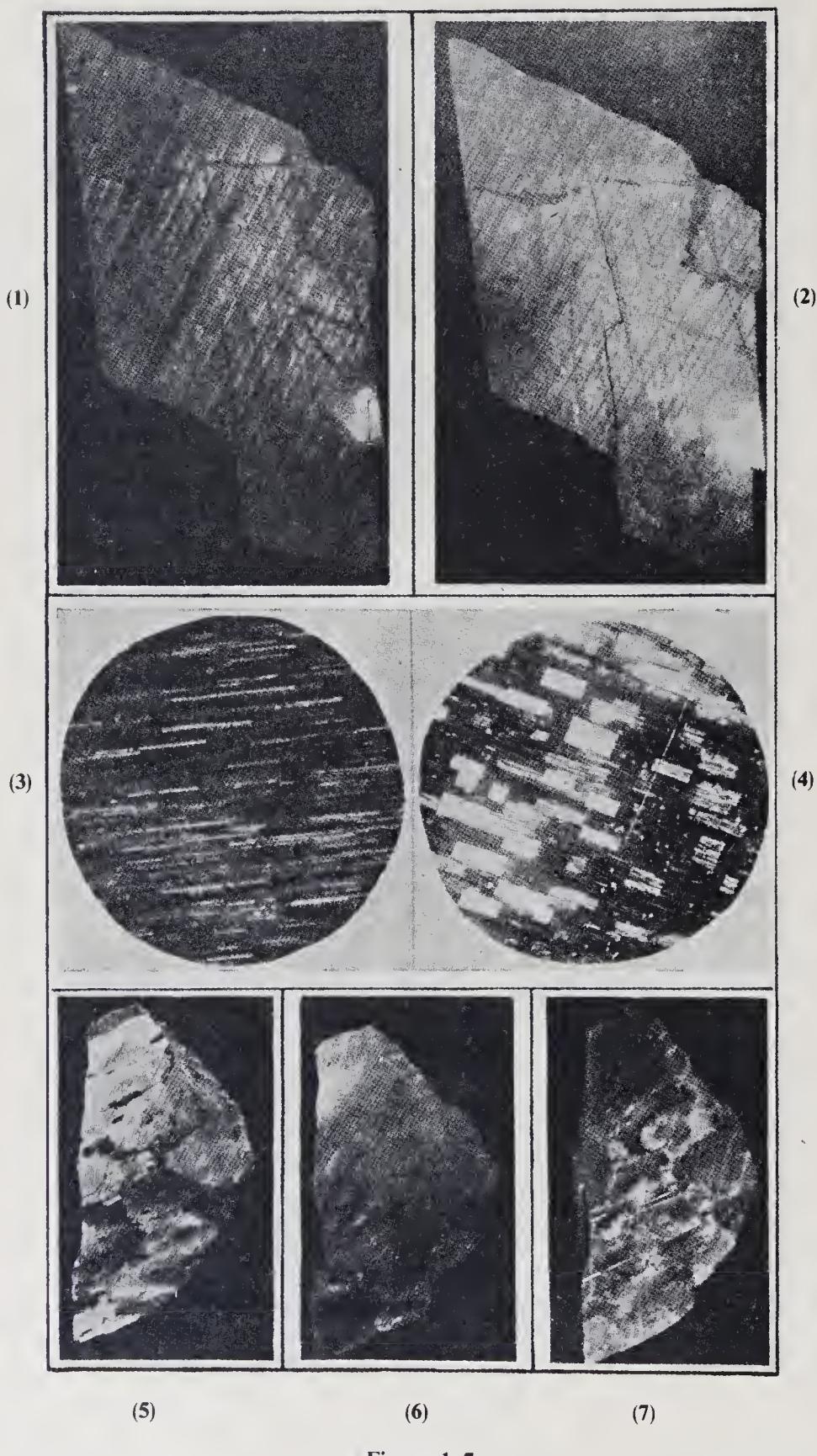
(2)



(3)

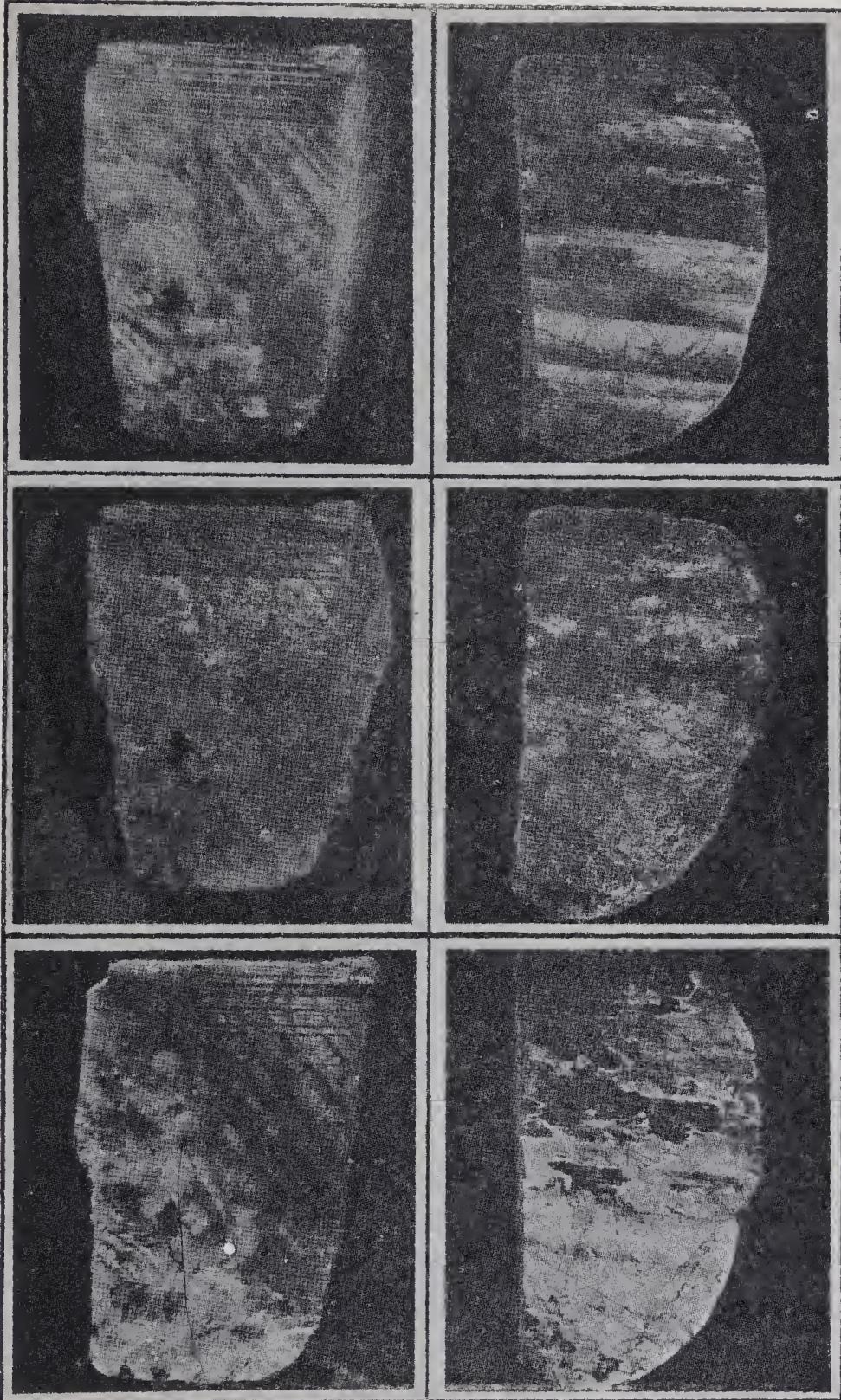
Figures 1-3

Plate I



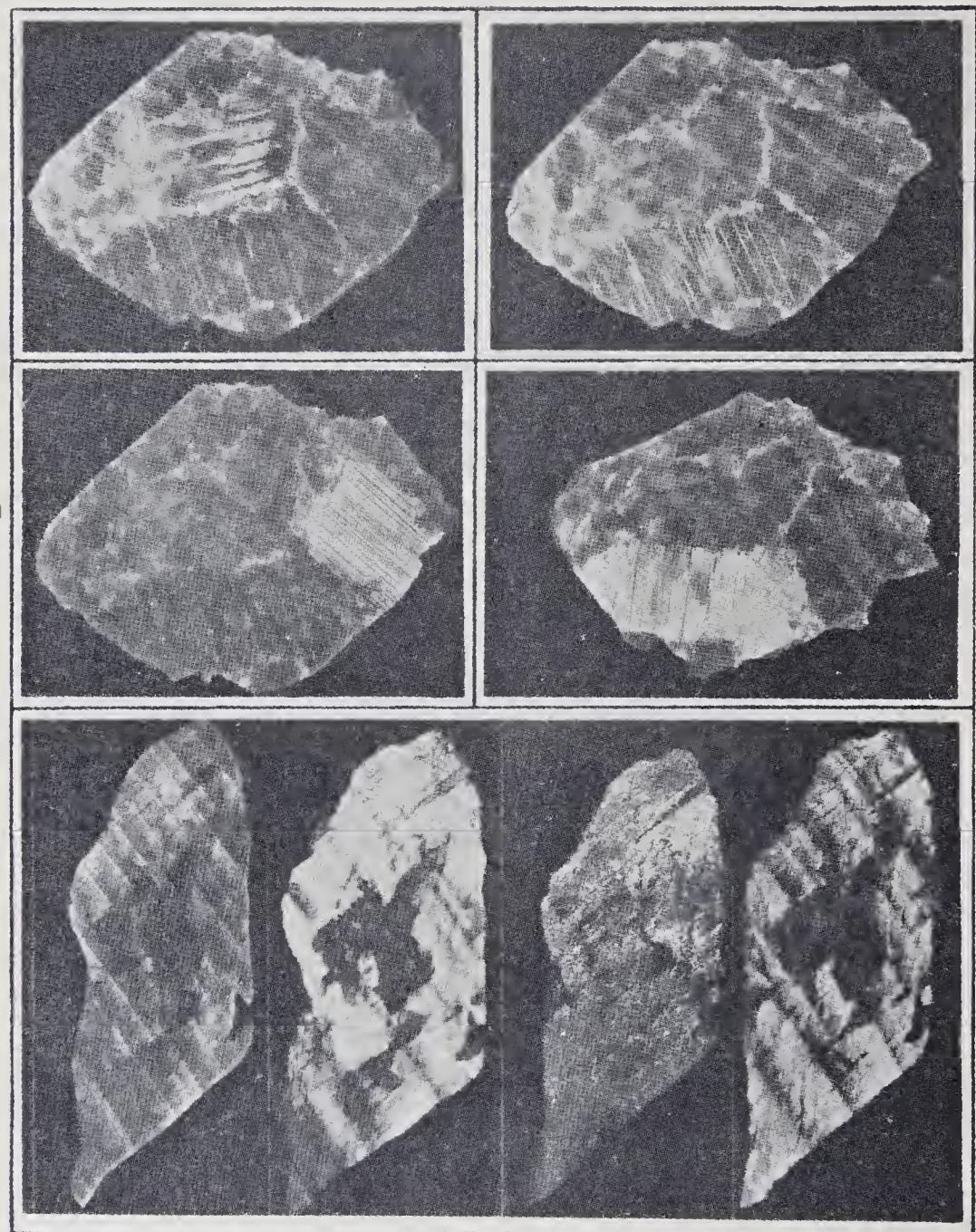
Figures 1-7

Plate II



Figures 1-6

Plate III



(5)

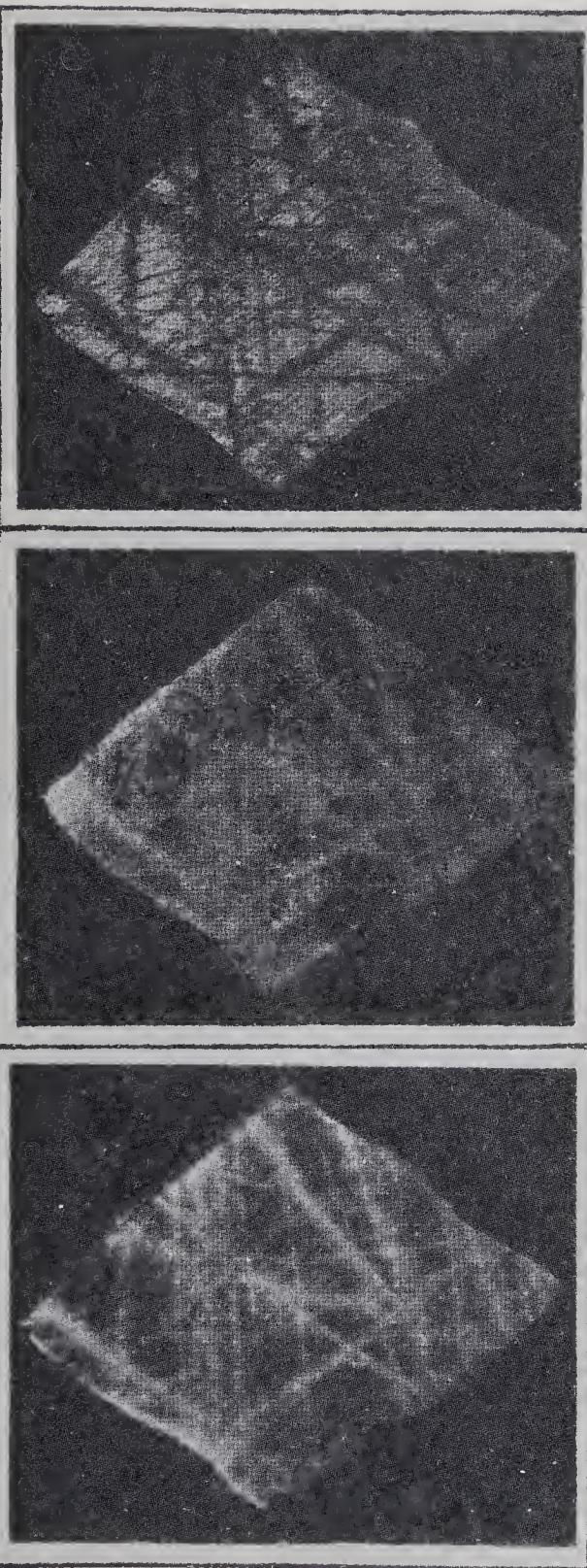
(6)

(7)

(8)

Figures 1-8

Plate IV



Figures 1-3

Plate V

## The structure and optical behaviour of the Ceylon moonstones

SIR C V RAMAN, A JAYARAMAN and T K SRINIVASAN  
(Raman Research Institute, Bangalore)

Received September 20, 1950

### 1. Introduction

As is well known, the commonly occurring feldspars have a chemical composition which may be represented as a mixture of three components, namely the potash, soda and lime feldspars. The first two components resemble each other chemically but have different crystal forms, while the second and third components are isomorphous though their chemical formulae are dissimilar. The question arises whether the feldspars formed by such admixture are in all cases truly homogeneous crystals. Optical studies may well be expected to throw some light on this issue. In a recent paper in these *Proceedings*,<sup>1</sup> it has been shown that the iridescence exhibited by labradorite results from the segregation of the potash feldspar present in the mineral from the isomorphous mixture of the soda and lime feldspars which are its principal constituents. Tiny crystals of orthoclase are formed as the result of such segregation, but they remain dispersed in the albite-anorthite phase and diffuse the light traversing the crystal, causing it to display colours which vary with the dimensions of the crystallites and their setting with respect to the incident light-beam.

The present paper is concerned with another group of feldspars which give evidence of optical heterogeneity, namely the moonstones. The published analyses show that the potash and soda feldspars are their principal constituents, the former being usually the major and the latter the minor component; a small percentage of lime feldspar is also present. The moonstones enjoy a certain amount of favour as gems by reason of a characteristic optical effect which they display and which is generally known as "schiller". The investigation described in the paper was undertaken to ascertain the nature and origin of this effect. Though there is an extensive literature on moonstones to which both mineralogists and X-ray workers have contributed, the optical phenomena exhibited by them appear to have received comparatively little attention. The need for studying them is obvious. For, any explanation of the schiller effect which is not based on, or confirmed by, the results of such study must necessarily be regarded as dubious.

## 2. Materials and methods

Following the visit by one of us to Ceylon in September 1946, some forty specimens of moonstone in the rough were received as a gift from the owner of the formation near Ambalangoda in that island where they were formerly mined. A few cut specimens also accompanied them, of which one was a particularly fine gem exhibiting a blue schiller. The material thus made available to us has been utilized in the present investigation. To supplement the same, some thirty specimens of cut and polished moonstones were purchased from a dealer in Calcutta and added to our collection. It is understood that they were from the same original source at Ambalangoda. The uncut specimens have been useful, since the cleavages characteristic of feldspar which they occasionally exhibit, enable the crystallographic orientation of the specimens to be determined, a very necessary step in the investigations. On the other hand, the rough surfaces which the uncut specimens generally possess and the internal imperfections manifest in some of them are a serious inconvenience. The polished gem stones are much better in this respect, having evidently been prepared from selected material after removal of the defective portions. By immersing the specimens under study in a cell containing liquid benzene which has nearly the same refractive index as the mineral, the disturbing effects due to reflection, refraction and scattering of light at its external surfaces are minimized. The phenomena having their origin in the interior of the specimen and arising from the passage of light through it can then be conveniently studied. Suitable methods have also had to be improvised for holding the specimen inside the liquid and altering its setting with respect to the direction of the incidence of light as required, and also for determining the orientation of the crystal in such setting.

A comparison of the numerous specimens in our collection throws into relief the striking differences in their individual behaviour. A few pieces exhibit a deep blue but comparatively weak schiller. Others show a blue schiller of decidedly greater intensity. The rest show a schiller which in the different specimens passes by insensible gradations from a blue to bluish white and then to a perfect white; the intensity increases *pari passu* and in some cases is very great. It is remarkable and obviously significant that specimens from the same locality should show such large differences in their optical characters.

## 3. Nature of the schiller effect

It is a characteristic feature of the schiller of moonstones that the phenomenon is best seen at a particular setting of the crystal determined by the direction in which the light is incident on it and the direction in which it is observed. When either the setting of the crystal or the direction of incidence of the light is altered, the direction in which the schiller is most conspicuous also shifts. The idea generally

current that the schiller owes its origin to a lamellar structure of the feldspar in which layers of orthoclase and albite alternate is based on the fact of observation just mentioned. For, such a structure would reflect light traversing the crystal in a direction varying with its angle of incidence on the planes of the lamellae. Indeed, measurements have been published<sup>2</sup> which claim to find the orientation of the postulated "schiller-planes" within the crystal in this way. It has even been claimed by one author<sup>3</sup> that examination of cleavage flakes of moonstone under low powers of the microscope when illuminated by light from a point source succeeds in revealing indications of a microperthitic or lamellar structure. Actually, however, the microscope does not reveal any noticeable structure in the typical and most interesting cases, namely the moonstones which exhibit a blue schiller. It should be remarked, further, that the coarse structure of which indications are observed under low powers of the microscope in certain other cases is *prima facie* incapable of giving rise to the optical phenomena under consideration. As already remarked, an explanation of the origin of the schiller to be acceptable should be based on the results of a detailed study of the phenomenon itself. It was with this idea that the present investigation was undertaken and it has revealed many new facts of interest. These will be set out in the proper places, but we shall proceed first to state those of which the significance in relation to the origin of the schiller is most obvious.

The effects observed with moonstones exhibiting a blue schiller are of particular interest, not only because they are the finest gems, but also by reason of the unambiguous manner in which a study of them reveals the real nature of the phenomena under consideration. As with all the moonstones studied, observations show that the schiller has a maximum intensity when viewed in a particular direction, which is related to the direction of incidence of the light in such manner that the two directions—at least roughly—make equal angles with and lie in the same plane as a particular direction within the crystal which we may designate as the schiller-axis. But the schiller can by no means be described as a reflection of light by a plane or planes within the crystal normal to the schiller-axis. Actually, it has the character of a diffusion of light spread out over a wide range of angles. This is directly evident when the light beam traversing the specimen is of sufficient intensity, as the crystal then becomes itself visible in various directions by reason of the light diffused in its interior. For instance, if the specimen is set so that the light is incident along the schiller-axis, the schiller is of maximum intensity in the direction backwards towards the source. But it has a notable intensity in various adjoining directions, and it can be seen also in the opposite or forward directions, though more faintly. Viewing the schiller in any particular direction and rotating the crystal about a chosen axis, it is found that the intensity falls off quite slowly on either side of the setting at which it is a maximum. The permissible rotation of the specimen before the schiller ceases to be visible naturally depends on the intensity of illumination and the circumstances of observation. But even with a weak illumination, the angular range is so large that the phenomenon can only be

described as a diffusion of light within the crystal. The spectral character of the blue schiller exhibited by the finest moonstones is equally revealing. It is a much richer blue than the blue of the first order in the Newtonian sequence: in other words, it does not permit of being explained as an interference colour due to reflection of light by thin films. On the other hand, it matches more or less perfectly with the deep blue colour exhibited in the diffusion of light by particles which are small in size compared with the wavelength of light. As is well known, this blue is due to the predominance of intensity of the shorter wavelengths in inverse proportion to their fourth power. Spectroscopic study of the blue schiller of moonstones reveals the same predominance of the shorter wavelengths and thus compels us to assume a physical origin for it of the same general nature.

On a superficial examination, the bluish-white or white schiller exhibited by the majority of moonstones may be mistaken for a reflection of light within the crystal, the direction in which it is most conspicuous altering with the setting of the crystal in a manner suggesting such an explanation. A careful study, however, reveals various features which are inconsistent with such a description. What is actually observed is that the concentration of intensity around a particular direction which is observed even with the specimens exhibiting a blue schiller becomes more accentuated in these cases. This is accompanied by an increase in absolute intensity and a change in spectral character towards a pure white. Nevertheless, the angular spread of the illumination which simulates a reflection in this manner is readily observable and extends over several degrees of arc. Further, it is accompanied by a diffusion of light which covers a still greater range of angles and the spectral character of which approaches more nearly that of the blue schiller. Even the specimens which normally exhibit a perfect white schiller exhibit diffusion of a sky-blue colour when the light enters the crystal along the schiller-axis and the diffusion is viewed perpendicular to it, or *vice-versa*.

It is evident from the foregoing recital of facts that despite the apparent large differences in optical behaviour of the individual specimens, the phenomena they exhibit are essentially all of the same general nature. We may summarise the factual position by the following statements:

- I. *The schiller of moonstones is a phenomenon arising from the diffusion of light within the crystal.*
- II. *The diffusion exhibits optical characters analogous to those observed in the scattering of light by small particles.*
- III. *The observed facts give no support to the hypothesis of a microperthitic or lamellar structure as the cause of the schiller.*

#### 4. Origin of the diffusion

It is obvious from what has already been stated that the schiller of moonstones is the result of optical heterogeneity in the feldspar. The most natural assumption to

make in the circumstances of the case is that the heterogeneity is associated with the known chemical composition of the mineral. Its two principal constituents, namely, the potash and soda feldspars, are similar in their chemical composition, and hence might reasonably be assumed to be capable of mixing with each other in all proportions and forming a homogeneous crystal. Against this, however, must be set the fact that the two components normally crystallise in different forms, potash feldspar or orthoclase as a monoclinic crystal, and soda feldspar or albite as a triclinic crystal. X-ray study shows that though there is a general resemblance between the crystal structures of orthoclase and albite, there are specific differences, the most significant, as indicated by table 1, being the differences in the lattice spacing along the  $a$ -axis and in the angle  $\alpha$  between the  $b$ - and the  $c$ -axes. It has been suggested that the factor which determines whether a feldspar crystallises with monoclinic or triclinic symmetry is the size of the ions which enter into the alumino-silicate frame-work of its structure. Since, however, the sodium and potassium ions are both monovalent and since the former are smaller in size, it should clearly be possible for the former to replace the latter in the framework of the lattice. In other words, we have good reasons for believing that it should be possible for soda and potash feldspars to mix and form single crystals in the ordinary or the macroscopic sense of the term, even when the former component is present in substantial amounts, possibly even as much as one-half of the entire mineral in its molecular proportion. Two questions, however, arise in this connection. Firstly, in what manner are the sodium ions disposed within the lattice, viz., whether they randomly replace the potassium ions or whether they cluster together in groups, thereby causing the soda feldspar to segregate itself locally from the potash feldspar. Secondly, what changes, if any, are produced in the alumino-silicate framework by the replacement and in particular, whether there are any local alterations in crystal structure produced by the clustering together of the sodium ions. We have also to consider the question of the part played by the third component, namely the lime feldspar, in these dispositions.

The question raised in the foregoing paragraph have an obvious bearing on our present problem. Theory indicates that the distribution of the two component feldspars within the crystal would profoundly influence its optical behaviour. Only in the particular case of a regular or orderly disposition of the sodium and potassium ions would the crystal be truly homogeneous in the

Table 1. Lattice constants

	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$
Orthoclase	8.45	12.90	7.15	90°	116° 3'	90°
Albite	8.14	12.86	7.17	94° 3'	116° 29'	88° 9'

optical sense. Even a random disposition of the ions would give rise to an observable diffusion of light. Much more striking, however, would be the consequence of a disposition of the sodium ions in groups or clusters, in other words, of a segregation of the soda feldspar in the form of tiny crystallites dispersed through the rest of the material. The local fluctuations in chemical composition which such clustering would represent and the fluctuations of refractive index consequent thereon would give rise to a strong diffusion of light, its intensity increasing in proportion to the number of such clusters, multiplied by the square of the volume of each cluster, provided that these are of sufficiently small dimensions and that they can be assumed to be randomly distributed in the available space. Granting that the diffusion of light observed in the moonstones arises in this way, we may remark on the analogy between it and the opalescence exhibited by a mixture of two partially miscible liquids, e.g., carbon disulphide and methyl alcohol at temperatures a little higher than that at which the two components begin to separate from each other. The blue colour of the opalescence of such a liquid mixture at the higher temperatures matches perfectly with the blue schiller of the finest moonstones. As the critical solution temperature of the liquid mixture is approached, there is an enormous increase in the intensity of the opalescence and also a distinct change in its spectral character as the result of the formation of molecular clusters of rapidly increasing size, until finally a white cloud of visible droplets of liquid is released. There is thus an obvious parallelism between these phenomena and the progressive variations of the colour and intensity of the schiller noticed with different specimens in the group of moonstones.

The comparison made above between the schiller of moonstones and the opalescence of liquid mixtures should not, however, lead us to assume that the phenomena are completely similar to each other in their origin and character. So far from this being the case, many important differences between them are to be expected. It may be remarked, in the first place, that in our present problem, the local fluctuations in the composition occupy fixed positions in the lattice and there is also no reason to suppose that these positions would be distributed completely at random. In consequence, there would be specifiable phase relations between the radiations diffused from different volume elements, and this would necessarily influence the observed distribution of intensity in different directions. There is also no reason for assuming that the clusters of sodium ions in the moonstone would be of spherical shape or that they would be randomly orientated. The known character of the alumino-silicate framework of the feldspars and the differences between the crystal structures of orthoclase and albite would lead us to the opposite conclusion, namely, that the soda feldspar when it segregates and forms crystallites would tend to do so in a fashion related to the structure of the crystal. The shape, size and the orientation of the crystallites thus formed would evidently determine the intensity and spectral character of the radiation diffused by them in various directions. Hence, a notable

dependence of the observed phenomena on the setting of the moonstone with respect to the direction in which the light is incident and also on the direction in which it is viewed may be expected. There is another and equally important group of differences between the present problem and that of the diffusion of light in liquid mixtures, namely, in the optical properties of the materials under consideration. The feldspars are birefringent crystals. Though their birefringence is small, we are concerned here with the *differences* in the optical polarisabilities of the medium arising from the local fluctuations in its composition, and these differences would be of the same order of magnitude as the birefringence of the feldspar. Hence, it cannot be supposed the effects under study would be of the same character for all directions of the electric vector in the light traversing the crystal. Special effects in respect of the intensity and state of polarisation of the diffused radiation are accordingly also to be expected. Altogether, it is obvious that the optical phenomena exhibited by moonstones would present a richer and more complex manifold of effects than the diffusion of light in liquid mixtures.

## 5. Relationship of the schiller to crystal structure

Reference has already been made to the "schiller-axis" in moonstones which has the property that if light traverses the crystal along that direction, the observed schiller has the maximum intensity in the backward direction, viz., towards the light source. The observations made with our specimens seem to show that the schiller axis is not noticeably different in moonstones exhibiting a blue, a bluish-white or white schiller; it is normal to the *b*-axis of the crystal and inclined to the *c*-axis at  $81^\circ$ . In other words, a plate cut perpendicular to the 010 cleavages and having its faces slightly inclined to the 100 planes of the crystal and making an angle of  $9^\circ$  with them would show the schiller most conspicuously when illuminated and viewed normally. The question arises why the diffusion of light in moonstones exhibits the maximum intensity in these circumstances. Closely related to this effect is another phenomenon observed by us which does not appear to have been previously noticed, namely, that the diffusion of light in moonstone is not symmetric about the schiller-axis but alters in intensity and character as the crystal is rotated about that axis, the directions of incidence and observation remaining the same. So striking is this non-axiality of the diffusion that its results are evident on a simple inspection of the schiller, when a cut stone is held in the hand and viewed by the light from a window, provided the shape of the stone is not such as to obscure or complicate the situation. Figures 1 and 2 in plate I illustrate the effect, the first being a moonstone with a blue schiller and the second one with a white schiller. Both the stones had been fashioned by the lapidary into a flattened spheroidal shape, the figure axis being practically coincident with the schiller-axis, so that when illuminated and viewed from the front, one would have expected the schiller to manifest itself symmetrically about

that axis. Actually, however, we see an elliptical patch of light in both cases and when the crystal is rotated, the elliptic patch turns round with it. It was verified that the longer axis of the elliptic patch was in both cases parallel to the *b*-axis of the crystal; this, as already stated, is itself normal to the schiller-axis. The effects observed with the two specimens may be described thus: the schiller has a sensible intensity over a wider range of angles in the plane containing both the *b*-axis and the schiller-axis than in a plane containing the schiller-axis and perpendicular to the *b*-axis. The same effect shows itself in a peculiar way in figure 3 in plate I which represents a moonstone which had been shaped by the lapidary into an elongated ellipsoid. Its *b*-axis was inclined to the longer axis of the ellipsoid. As a consequence, the schiller appears bent into a curve having a point of inflection at the middle.

In all the three cases described above, it is the refraction at the curved surfaces fashioned by the lapidary that enables us to observe the diffusion of light in different directions simultaneously. The same effect may be studied in a more precise fashion by immersing the specimen in benzene liquid and by a rotation about a chosen axis finding how slowly (or how rapidly) the intensity of the diffused light falls off. In every case, it is noticed that the fall of intensity is very rapid if the crystal is rotated about its *b*-axis, but relatively much slower if it is rotated, for instance, about the *c*-axis of the crystal.

The explanation of the effects described above, as well as of those already set out in section 3, is evidently to be found in a consideration of the size, shape and disposition of the crystallites of soda feldspar resulting from its segregation, since they determine the distribution of intensity of the light diffused in various directions. We proceed to consider the nature of such segregation in its relation to the structure of the crystal as a whole. We shall take it for granted that when the soda feldspar segregates, it would tend to maintain the crystal symmetry as well as the orientation of the crystal axes exhibited by the parent mass and thereby to minimise the disturbance to the crystalline order produced by the segregation. Such a result could evidently be obtained in a number of ways. The simplest would be for the soda feldspar to assume monoclinic symmetry with its axes parallel to those of the parent mass. As can be seen from table 1, this would involve only relatively small changes of the angles between the crystal axes from those of a triclinic form. An alternative would be for the soda feldspar, while retaining a triclinic structure, to mimic monoclinic symmetry by internal twinning of the pericline type in which the direction of the *b*-axis remains unaltered. In this way, the mean directions of the *a*- and the *c*-axes for the twin would be nearly the same as for the axes of the entire crystal. It is evident, however, that the latter result would be more perfectly attained, if simultaneously there is a change in the axial angles so that they approximate more closely to the values required for monoclinic symmetry. Which particular procedure is favoured would evidently be determined by the circumstances and especially by the proportion of soda feldspar present. It is not unlikely also that the lime

feldspar present may influence the choice between these different alternatives.

It is evident, however, that while there is thus a variety of possibilities for the structure of the segregated soda feldspar, a change in the lattice spacing  $a$  must necessarily occur in every case. This is a consequence of the smaller size of the sodium ion, and it is this difference which would determine the form which the crystallites would take. For, in the grouping of the cells containing the sodium ions which results from their coming together, an extension of the groups along the  $a$ -axis of the lattice would *not* be favoured. The formation of such a chain would disturb or disrupt all the chains of the alumino-silicate frame-work containing potassium ions along the  $a$ -axis with which it is linked. *Per contra*, a formation would be favoured in which the cells containing the sodium ions link themselves to others of the same kind along the  $b$ -axis or along the  $c$ -axis or more generally in the 100 planes of the crystal. The lattice spacing parallel to the  $b$ -axis differs from that parallel to the  $c$ -axis, being nearly double of it, and hence there is no reason to anticipate that a grouping of the cells containing the sodium ions along the  $b$ -axis and along the  $c$ -axis would be favoured to an equal extent. As the  $c$ -spacing is smaller, we may reasonably assume that the latter would be the more favoured arrangement. We are thus led to anticipate that the crystallites of the soda feldspar segregating from the potash feldspar would tend to extend themselves principally along the 100 planes of the crystal, and that in this plane an extension along the  $c$ -axis would be favoured more than one along the  $b$ -axis.

Optical theory indicates that as the extension of a diffracting particle or group of particles increases in a particular direction or directions, the intensity of the diffracted radiations would tend to concentrate along perpendicular directions. It follows, as a consequence of what has been stated above, that the moonstones would exhibit a schiller-axis perpendicular to the 100 planes of the crystal, in other words, normal to both the  $b$ - and  $c$ -axes of the crystal. Further, the diffusion of light would not exhibit a symmetry about the schiller-axis but would extend to larger angles in a plane containing the  $b$ -axis than in a plane perpendicular to it. It would probably not be a useful proceeding to discuss why the schiller-axis as actually observed is inclined at an angle of  $81^\circ$  to the  $c$ -axis of the crystal, instead of being perpendicular to it as deduced above. The considerations on which our argument is based are probably not deep enough to explain this small discrepancy between theory and observation. It is gratifying, however, to be able to record a direct observational proof of the explanation given above for the fact that the diffusion of light is not symmetric about the schiller-axis. Examination of several of our specimens discloses that the schiller exhibits distinct evidence of a fibrous structure running parallel to the  $c$ -axis of the crystal. A photograph showing this is reproduced in figure 4, plate I.

## 6. Intensity and polarisation of the schiller

Since the diffusion of light in its passage through the crystal is a consequence of the local variations in its refractive indices resulting from the changes of composition, its intensity would depend on the magnitude of these variations. The principal indices of albite are all greater than those of orthoclase, and the published data<sup>4</sup> show that the indices of moonstone are intermediate between them, and increase with the proportion of soda feldspar present. They are, however, in all cases, nearer the values for orthoclase than those for albite. Table 2 shows the compositions of orthoclase, of a typical moonstone from Ceylon, and of albite, and their respective refractive indices, as well as the differences between them. If we assume that the local variations in composition result in its approaching those of orthoclase and of albite respectively, the refractive indices would increase or decrease by the amounts shown in table as differences.

**Table 2.** Composition and refractive indices

Mineral	K <sub>2</sub> O%	Na <sub>2</sub> O%	CaO%	$\mu_g$	$\mu_m$	$\mu_p$
Orthoclase	15.0	0.9	0.1	1.5245	1.5228	1.5192
			diff.	0.0037	0.0029	0.0024
Moonstone	11.0	3.8	0.2	1.5282	1.5257	1.5216
			diff.	0.0110	0.0071	0.0076
Albite	0.4	11.4	0.3	1.5392	1.5328	1.5292

The maximum index  $\mu_g$  of orthoclase determines its optical polarisability in a direction parallel to the *b*-axis of the crystal, while the minimum index  $\mu_p$  gives it for a direction nearly parallel to the *a*-axis, and the mean index  $\mu_m$  corresponds to a direction in the 010 planes of the crystal nearly perpendicular to the *a*-axis, and therefore moderately inclined to the *c*-axis. In the case of moonstone, the foregoing statements would still be valid, but in the case of albite which is a triclinic crystal, they would require modification. It is evident, however, from the figures given in the table that the variations of the maximum refractive index  $\mu_g$  of moonstone, in other words of the optical polarisability along the *b*-axis, resulting from the changes in composition, would be substantially larger than the changes in optical polarisability along the two other principal directions which, as stated above, are nearly parallel and perpendicular to the *a*-axis, respectively. The changes in optical polarisability in these two other directions resulting from variations of composition would, however, be of the same order of magnitude. The diffusion of light resulting from the variations in refractive index has an intensity proportional to the square of such variations. Theoretical considerations thus lead us to the very interesting result, that the schiller of moonstones should exhibit an easily observable dependence of intensity on the state of polarisation of the light incident on it, being greater when the electric vector is parallel to the *b*-axis of the crystal and less when it is perpendicular to that axis.

When the incident light is unpolarised, the same effects would manifest themselves in a different way, the state of polarisation of the diffused light being largely determined by the component parallel to the *b*-axis.

As is well known, the light diffused in an optically isotropic medium exhibiting local variations of refractive index and traversed by an unpolarised beam of light would be plane-polarised in a transverse direction. Since the schiller of moonstones is also a diffusion of light of the same general nature, we should expect it to manifest similar polarisation effects. In observing and interpreting them, it has to be borne in mind that the crystal is itself birefringent. Hence, the radiation diffused in its interior and traversing it before emergence would undergo changes in its state of polarisation which have to be taken into consideration. This is easier when the setting of the crystal with respect to the direction of incidence of the light and the plane in which the diffused radiations are observed are appropriately chosen. As has already been remarked, the state of polarisation of the light diffused within the crystal would be influenced by the direction of the electric vector with respect to the *b*-axis of the crystal. In other words, it would exhibit a dependence on the setting of the crystal very conspicuously. There is still another point which requires to be noted; not merely the principal refractive indices but also the directions of electric vibration which they refer to are different in orthoclase and in albite. It is therefore not to be expected that the diffused radiations would, in general, be perfectly polarised in a transverse direction as in the case of optically isotropic fluctuations of refractive index, even when the setting of the crystal has been appropriately chosen. Finally, we have to remember that the extension in space of the volume elements within the crystal diffusing the light is by no means always negligibly small. In the case of the moonstones exhibiting a white schiller with a large intensity, the diffusing elements are undoubtedly of appreciable size. The state of polarisation of the light diffused by such elements would necessarily be influenced by this fact.

## 7. Comparison with the case of labradorite

The figures given in table 2 enable us to appreciate the reason for the observed differences in the optical behaviour of moonstone and of labradorite. The differences in the refractive indices of the mixture of albite and anorthite which principally constitute labradorite and the refractive indices of the orthoclase crystallites which segregate from them are greater than the average of the fluctuations in refractive indices in the case of moonstone by a numerical factor of about 7. The intensity of the light diffused by volume elements of equal size would be therefore some fifty times greater for labradorite than in moonstone. The brilliancy of the effects exhibited by labradorite despite the fact that the orthoclase which segregates in it is relatively small in quantity is thus readily understood. The circumstances in labradorite are clearly also favourable

for the segregated crystallites to appear throughout the mass with a tolerable uniformity of size, a condition necessary for the manifestation of vivid colour in the later stages of segregation. On the other hand, in the case of the moonstone, the materials under consideration, viz., the soda and potash feldspars, are present in comparable quantities and are more or less freely miscible with each other. In these circumstances, we may expect the segregated crystallites to vary widely in their sizes. Thus, except in the earliest stages when all the crystallites are small and therefore give a diffusion of a blue colour, a manifestation of vivid colour is not to be expected in the case of moonstones. There is still another striking difference between the two cases which is indicated by theory and confirmed by observation. The intensity of the diffusion in the case of labradorite is sensibly independent of the direction of the electric vector inside the crystal, and the diffused light, in consequence, exhibits a polarisation of the same character as the diffusion in optically isotropic media. As has already been remarked, a different situation is expected and actually found in the case of the moonstones.

### 8. Polarised extinction of light

There is another group of effects observed with moonstones which are of interest and importance for the elucidation of their structure. As we have seen in the foregoing pages, the diffusion of light in its passage through the moonstone is a consequence of the local variations in composition and the variations in refractive index resulting therefrom. Apart from the effects arising in this way, the Ceylon moonstones are transparent monocrystals which do not exhibit any body-colour. Hence, any loss of light which appears in the passage of a light beam through the moonstone may reasonably be attributed to the deviation of the incident energy as diffused radiation. In other words, the energy appearing as transmitted light is the incident energy less the energy diffused in various directions. It follows that the extinction of light resulting from its passage through the crystal would exhibit various features which are the counterpart of those observed in diffusion. Besides thus representing the integrated effect of the diffusion, the extinction effects usefully supplement the information given by a study of the diffusion phenomena. As examples of the correlations found between diffusion and extinction in our studies may be mentioned the following instances. The moonstones in our collection, though derived from the same source, show a wide divergence in the colour and intensity of the schiller they exhibit. The extinction phenomena likewise show a similar wide range of behaviour. Again, as the angle which the direction of the incident beam makes with the schiller-axis of a moonstone is gradually increased from  $0^\circ$  to  $90^\circ$ , large changes are observed in the angular distribution of the diffused radiation and in its aggregate intensity; the nature of these changes is related to the colour and intensity of the schiller of the specimen under study. The extinction phenomena likewise show remarkable

changes when the angle between the direction of the incident light beam and the schiller-axis is altered, these changes altering in character, as we proceed from the moonstones with a blue-schiller to those with a bluish-white and a white schiller respectively. The most interesting features of the extinction of light are the colour and the polarisation observed in various circumstances even when the incident light is unpolarised. These features are found to be closely connected with the spectral character and the polarisation exhibited by the diffusion of light and discussed earlier in the paper.

The following further details may be mentioned by way of supplementing the foregoing brief remarks. The moonstones which exhibit a blue schiller when the light is incident along the schiller-axis show a pale yellow colour by transmitted light, evidently the result of greater extinction of the smaller wavelengths in the incident light. Examination through a polariser shows that this extinction is more marked for a vibration direction along the *b*-axis of the crystal than for a perpendicular direction. This effect is evidently the counterpart of the greater intensity of the schiller for a vibration along the *b*-axis. As the schiller-axis is turned away from coincidence with the incident light beam to a perpendicular direction, the schiller becomes steadily weaker in intensity, and the extinction likewise tends to zero. Moonstones with a strong white schiller show rather different phenomena. When the specimen is held with the schiller-axis parallel to the incident light, the polarisation in the backward direction parallel to the *b*-axis is hardly observable, evidently because the crystal, in that position, throws back nearly all the light that it receives. The transmitted light is very weak and shows a yellow colour; it is found to be distinctly polarised with the *b*-axis as the direction of smaller intensity. Moonstones with a white schiller also show a remarkable type of polarised extinction when the light traverses them in a direction nearly perpendicular to the schiller axis. Here again, the setting of the *b*-axis of the crystal with respect to the direction of incidence of the light is found notably to influence the completeness of the extinction and the perfection of the polarisation of the weakly transmitted light. The special polarisation effects observed in these circumstances are rather reminiscent of those noticed in the light transmitted by a pile of glass plates held obliquely. But the diffusion of a blue colour simultaneously observed in a transverse direction and the dependence of the phenomena on the setting of the *b*-axis with respect to the plane of incidence serve to remind us that the analogy with the behaviour of a pile of glass plates is only superficial.

## 9. The X-ray evidence

The crystal structure of moonstones has been very extensively investigated by X-ray workers. We shall not here attempt anything like a complete review of the literature, but will content ourselves with referring to some of the more important investigations<sup>5,6,7</sup> in the field. It is evident that for a satisfactory correlation of

the optical behaviour of a moonstone with the facts revealed by an X-ray examination of its structure, it is necessary that the same specimens should be studied by both methods, and that the optical evidence should be as complete and detailed as the X-ray evidence with which it is sought to be compared. It is essential, for instance, to have quantitative data for the intensity and spectral character of the diffused light and their variations with the setting of the crystal and the direction of observation. Only then it would be possible to estimate the size, shape and orientation of the crystallites of the soda-feldspar which diffuse the light, and to find whether the X-ray evidence supports those findings or at least is not in disagreement with them. We may, however, permit ourselves to make a few comments. The X-ray evidence does indeed support the finding that the soda-feldspar in moonstones tends to segregate from the potash feldspar. Particularly significant are the results of a recent investigation reported in a book<sup>8</sup> by Professor Ito in which the Weissenberg X-ray diagrams of a Korean moonstone containing 7.3% of K<sub>2</sub>O, 6.9% of Na<sub>2</sub>O, and 0.7% CaO are reproduced and discussed. Though the data are not strictly comparable with those of the Ceylon moonstones, they show clearly that segregation of the soda-feldspar occurs in such a manner as to make a near approach to the structure and symmetry of the parent crystal. We may remark also on the observation by Chao, Smare and Taylor that certain specimens of moonstones show a faint schiller but give no trace of any additional X-ray reflections; there is also an observation of Chao and Taylor that in certain cases, the supplementary X-ray reflections observed are diffuse. Ito has also remarked that in a number of photographs obtained by him, the Weissenberg diagram consists of bands rather than discrete spots. It is obvious that if the segregated crystallites are sufficiently small and numerous, they could give an observable diffusion of light, but that in the X-ray patterns, the reflections given by them would be smeared out just as they would be in the case of very finely divided colloidal particles. Whether this is the explanation of the facts observed, or whether there is actually some indefiniteness in the crystal structure of the segregated soda-feldspar is a matter for further investigation. There is clearly a need for further studies in which the optical and X-ray behaviour of the specimens are examined with equal thoroughness. The position as it stands now may be conservatively stated thus: the X-ray data do not contradict the evidence regarding structure presented in this paper on the basis of their optical behaviour; on the other hand, they support the main conclusions put forward in the paper.\*

\*B V Thosar (*Philos. Mag.*, October 1945) described some observations on the spectral character, polarisation and intensity of the schiller of moonstone on the basis of which he concluded that the phenomenon is a reflection of light at the twinning planes of a microcline structure which he assumed it to possess. This view is in such complete contradiction with the facts regarding the optical behaviour of moonstone, to say nothing of the X-ray evidence, that we do not propose to traverse it in detail. Thosar's observations lack certain particulars needed to give them scientific significance. But so far as they go, they are fully explicable in the light of the considerations advanced in the present paper.

## 10. Concluding remarks

To avoid overloading the present paper, we have had to confine ourselves to a rather terse statement of the experimental facts on the basis of which the explanation of the schiller of monostone given in the paper has been developed. Much other material regarding the angular distribution of the intensity of the diffused light, its spectral character and its state of polarisation in various circumstances was gathered in the course of our studies. Some of this material was of a quantitative character, as for instance, the determination of the state of polarisation of the schiller for various settings of the crystal and for various angles of observation. Other observations, though of a qualitative character, were of scientific significance, as for instance, the fact that a "residual blue" is exhibited by moonstones giving a white schiller when the latter is extinguished by observation through a polariser. Detailed studies have also been made of the extinction of light in moonstone and of its spectral character and state of polarisation in various circumstances. To have set out all these results in detail here would have diverted attention from the main theme of the paper, namely, the genesis of the schiller as an optical consequence of the local fluctuations in its chemical composition and refractive index. We hope to be able to follow up the present communication by a paper in which the experimental facts of the subject are set out in greater detail.

In conclusion, we have to thank Mr G L Punyasoma whose generous gift of moonstone specimens from Ambalangoda encouraged us to undertake the present research.

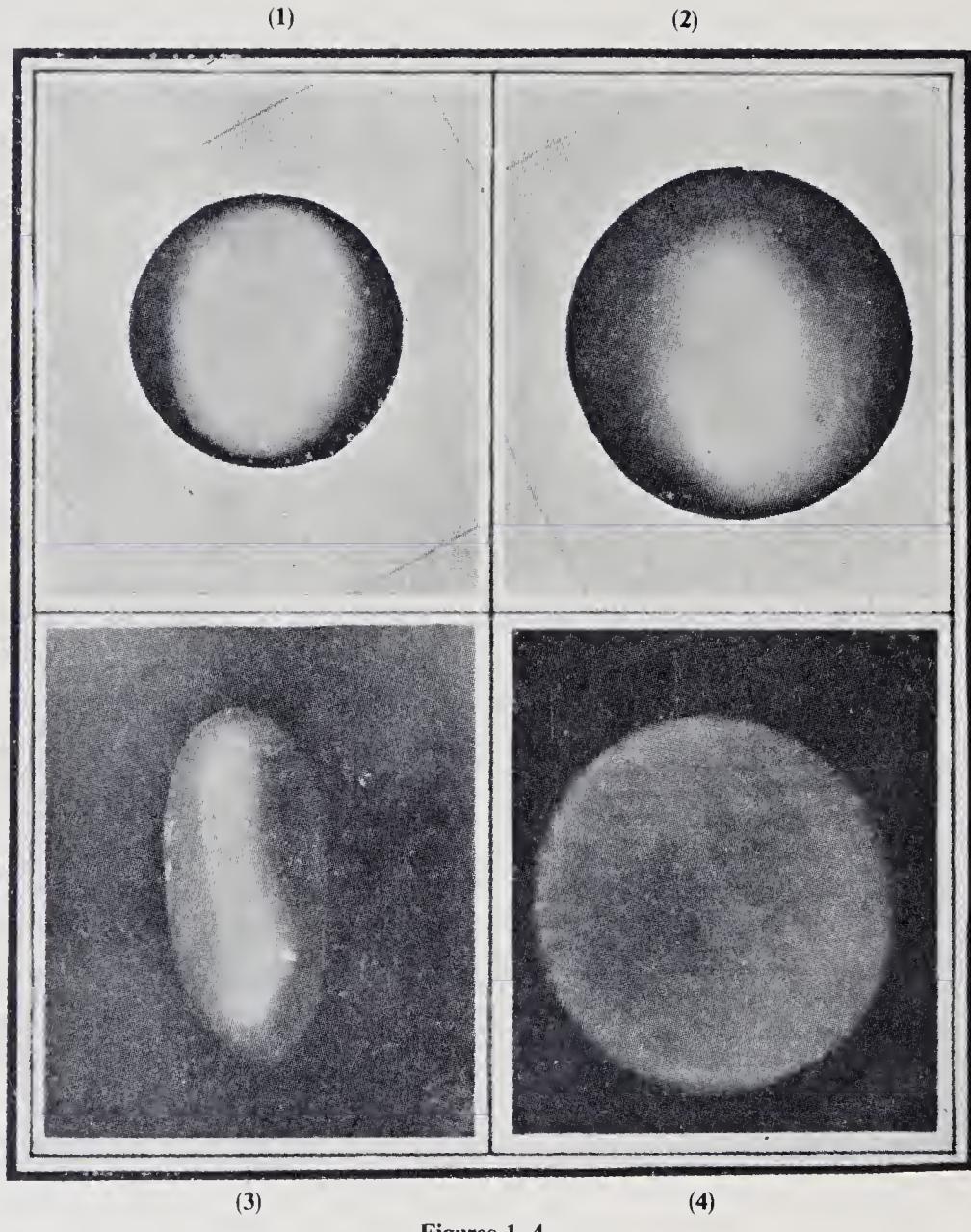
## 11. Summary

The paper describes the optical behaviour of the moonstones from Ambalangoda in Ceylon which exhibit a wide diversity in the colour and intensity of their schiller. The studies made show that the schiller is a diffusion of light within the material which is macroscopically a monocrystal but exhibits pronounced local variations in its composition and refractive index. Though the potash and soda feldspars mix together when they crystallise, the soda component tends to segregate and form tiny crystallites of which the size, shape and orientation determine the angular distribution of the diffused light, its spectral character, intensity and state of polarisation in various circumstances. The crystallites tend to appear with their greatest extension nearly parallel to the 100 planes of the crystal, the direction of the *c*-axis being preferred more than that of the *b*-axis. The distribution of intensity of the diffused light accordingly does not exhibit a radial symmetry with respect to the direction of its maximum intensity, and this lack of symmetry is conspicuously observable. The intensity of the schiller and its state of polarisation are also markedly influenced by the orientation of the electric vector

within the crystal, as a consequence of the variations of refractive index being much greater along the *b*-axis of the crystal than in perpendicular directions. The diffusion of light in moonstone is accompanied by a marked extinction, which exhibits an almost perfect polarisation in certain circumstances. An explanation is given of the striking differences in the optical effects displayed by moonstone and by labradorite in spite of the general similarity in their physical origin.

### References

1. C V Raman and A Jayaraman *Proc. Indian Acad. Sci.*, 1950, **A32**, 1.
2. Boggild *Math. Fys. Meddl.*, Copenhagen, 1924, 6, No. 3.
3. Spencer E *Miner. Mag.*, 1930, **22**, 291.
4. Spencer E *Ibid.*, 1937, **24**, 453.
5. Ito and Inuzuke Z. *Kristallogr.*, 1936, **95**, 404.
6. Chao, Smare and Taylor *Miner. Mag.*, 1939, **25**, 338.
7. Chao and Taylor *Proc. R. Soc.*, 1940, **174**, 57.
8. Tei-Ichi Ito *X-Ray Studies on Polymorphism*, Marusen Co., Tokyo, 1950.



Figures 1-4

Plate I

## The diffusion haloes of the iridescent feldspars

SIR C V RAMAN and A JAYARAMAN  
(Raman Research Institute, Bangalore)

Received for publication, 12th January 1953

### 1. Introduction

By reason of the brilliance and variety of the optical effects displayed by it and its availability in large sizes, labradorite is easily the most spectacular amongst the iridescent feldspars. The explanation of its remarkable behaviour had long remained rather mysterious and hence it was taken up for investigation at this Institute. In a paper published in these *Proceedings*,<sup>1</sup> the results of our studies made with numerous specimens of this material were described and the explanation of the optical behaviour of labradorite to which they led unambiguously was also set out. In a further paper published shortly afterwards,<sup>2</sup> the optical behaviour of the Ceylon moonstones was studied and discussed. These two cases, however, do not exhaust the list of feldspars which show interesting optical effects. Professor Ito of the Mineralogical Institute of Tokyo very kindly presented us with a collection of the small but beautifully crystallised moonstones from Korea. Through the kindness of Prof. T N Muthuswamy of Madras, we have also received a collection of quite large pieces of plagioclase feldspar from Gudur in South India exhibiting a blue or bluish-white iridescence. Some kind friends also enabled one of us to visit the pegmatite areas in the Coimbatore District in South India, and to make a collection of specimens of the orthoclase feldspar exhibiting a golden-yellow schiller found in that area. Other varieties of feldspar exhibiting "Labradorescence" are described in a memoir by Boggild.<sup>3</sup> But these were not available to us.

A feature common to all the varieties of feldspar mentioned above and studied by us is that the light entering the material and returned from its interior is not a true optical reflection but is a *diffusion of light* spread over a range of angles. The study of the features of this diffusion is of great importance for obtaining a definite idea of the structure responsible for the iridescence of the feldspar. A convenient method of carrying out such studies was devised and described by one of us two years ago.<sup>4</sup> The technique adopted is to illuminate a *small area* of the specimen by a narrow intense beam of light and to receive the radiation diffused from it on a white screen held not at too great a distance therefrom. The observations have to

be made in a darkened room, and the more intense the incident pencil of light is, the more striking are the observed effects. By altering the spot on the specimen which is illuminated, or by tilting the specimen with respect to the direction of the incident pencil of light, one can quickly observe the resulting changes in the pattern of the diffused light. The disturbing effects arising from refraction and scattering at the external surface of the specimen may be eliminated completely by immersing it in a glass cell containing a transparent liquid of suitable refractive index which is traversed by the incident beam. If, however, the external surface of the specimen has been suitably cut and polished, the disturbing effects are less troublesome and such immersion is not so essential except when the polished surface is curved, in which case the effects of refraction cannot otherwise be got rid of. In all cases, the diffusion pattern may be photographed by receiving it on a sheet of bromide paper suitably held.

## 2. The diffusion haloes of labradorite

The summary of our paper on labradorite referred to above is reproduced below *in extenso*, since the actual facts of observation as well as their theoretical explanation are clearly stated therein.

"General considerations indicate that the phenomenon of labradorescence owes its origin to the segregation of potash feldspar as crystallites or lamellae of orthoclase which remains embedded in an albite-anorthite matrix and give rise to optical heterogeneity. The following are derived as theoretical consequences of such segregation and have been confirmed by observations made with a representative collection of specimens.

(A) Labradorite which is multiply-twinned according to either the albite or pericline law or both, exhibits its characteristic reflections in two different settings geometrically related to each other by the twinning law. The two reflections display identical colours, but have their origins in different parts of the crystal, and this makes itself evident as a visible banding in one or the other or both of the reflections.

(B) The light reflected transversely to the incident beam is completely polarised.

(C) The intensity of the reflected light is independent of the setting of the reflecting layers in their own plane.

(D) The spectral character of the reflected light would approach that of a Tyndall diffusion when the crystallites are very small. Hence the colours of the first order in the Newtonian sequence would not be observed. The spectral character and the colour sequence at the later stages of segregation would also be different from those of thin films.

(E) The angular spread of the reflected light is greatest for the blue iridescence and less for other colours such as yellow, orange and red.

The effects arising when labradorite is illuminated and observed by polarised light are also described and explained in the paper. Numerous photographs reproduced in five plates illustrate the observed phenomena."

The terms "reflections" and "reflected" used in the foregoing summary of our earlier paper are rather misleading and should be replaced by "diffusion haloes" and "diffused" respectively. Indeed, the angular spread of the blue labradorescence exhibited by the finest specimens is so large that it would be erroneous to describe the phenomenon as a reflection.

Figures 1, 2 and 3 in plate I accompanying the present paper were recorded respectively with the specimen 3, and with two different areas of the specimen 5 referred to on pages 13 and 14 of our earlier paper. The photographs display in a striking manner the distinctive features of the optical behaviour of labradorite, and would have been even more striking had they been recorded and reproduced in full colour. It would then have been evident that the two haloes seen in each figure are of identical colour and that the aventurine reflection seen midway between them is white. In figures 4, 5 and 6 of plate III and figures 6, 7 and 8 of plate IV of our earlier paper, photographs of the same two specimens as viewed from different directions were reproduced. They show that both of these specimens exhibit a visibly banded labradorescence, arising from the fact that the polished face of the specimen was nearly parallel to the crystallographic B-planes and hence that the effects due to both sets of orthoclase lamellae present in the twinning layers of the plagioclase feldspar can be observed at the same setting. In the present method of study, the light diffused by these two sets of layers in different directions is recorded simultaneously, one on either side of the aventurine reflection; the latter is produced by the plates of haematite included in the feldspar and as these have their faces parallel to the B-planes, the reflection by them indicates the position of these planes. In the case of these specimens, it is noticed that when the illuminated area is caused to traverse the bands of labradorescence, the intensity of one of the diffusion haloes fluctuates relatively to that of the other. The character and intensity of the haloes and their relative positions as recorded in the figures of plate I of the present paper thus completely demonstrate the statement (A) quoted above from the earlier paper.

It will be seen further that the haloes appearing in plate I are of different sizes. Their colours as observed visually were also different. The haloes recorded in figure 1 had a golden yellow colour, in figure 2 a greenish-blue colour, while in figure 3 they were blue. This correlation of the spectral character of the labradorescence with the angular dimensions of the diffusion haloes is further confirmed by the series of five diffusion haloes photographed with other specimens and reproduced as figures 1 to 5 in plate II. Figure 1 which shows the largest halo was of a deep blue labradorescence, while the remaining haloes exhibited respectively a light blue, greenish-blue, yellow, and red colour. The progressive diminution in the angular spread of the diffusion haloes with the shift of the maximum intensity towards the red end of the spectrum (stated as

proposition E in the summary quoted above) is thus completely confirmed. We shall return presently to a consideration of its theoretical significance.

As is to be expected, the colour of the diffusion haloes changes with the angle of incidence of the light on the lamellae responsible for the labradorescence. Such incidence may be altered by a change in the setting of the specimen with reference to the incident light. The range of incidences attainable is however limited by reason of the refraction of light at entry into the specimen, by the inclination of the lamellae to the polished face, and also by reason of refraction of the diffused light at emergence. Thus, it is often the case that one of the haloes ceases to be observable at a particular setting of the crystal, and that a different setting is necessary to enable it to be seen. To avoid this difficulty, it is helpful to immerse the specimen in a cell containing a suitable liquid. The range of incidences attainable is thereby greatly increased and the change in colour of the halo with the angle of incidence of the light is more readily observable. Indeed, with this arrangement, the angle of incidence of the light on the orthoclase crystallites present in the alternate layers of the albite twinning may be so different that the two haloes appear with altogether different colours.

The other results (B) and (C) stated in our earlier paper, namely, the polarisation of the labradorescence and the independence of its intensity on the azimuth of incidence can likewise be demonstrated objectively by the present method of study. The polarisation of the diffused light is only complete in a direction transverse to the incident beam and to enable it to be demonstrated, it is necessary to immerse the specimen in a suitable liquid. The specimen should also be orientated within the cell in such manner that the depolarising effect of its birefringence is a minimum. A polaroid is then interposed between the feldspar and the receiving screen and rotated. The intensity of the diffusion halo undergoes large variations; the extinction observed is fairly complete for a deviation of  $90^\circ$  from the direction of the incident light.

The study of the diffusion haloes of labradorite thus completely confirms the findings reported in our earlier paper, and there is no need to traverse here the question of the origin of labradorescence already fully dealt with by us. It is sufficient to quote the remark made earlier that the colours of labradorite are neither a simple Tyndall diffusion nor a simple case of thin-film colours, but a special phenomenon in the elucidation of which the principles underlying both play a part. When the crystallites of orthoclase which segregate themselves from the albite-anorthite matrix are of very small size, they give rise to a Tyndall effect with the shorter wavelengths predominating and hence exhibiting a rich blue colour. On the other hand, if they are not small in comparison with the wavelength of light and are assumed on the basis of the observed facts to be lamellae having a specific orientation in the crystal, the colour of the diffracted light would be determined by their thickness while its angular extension would depend on their other dimensions. That the colour of labradorescence shows a definite correlation with the size and shape of the diffusion haloes strongly

supports the proposed interpretation. On the basis of such an explanation and the observed shape, colour and angular extension of the diffusion haloes, it is possible to make a rough estimate of the linear dimensions of the orthoclase lamellae. The figures are given below in table 1.

Table 1

Colour of labradorescence	Thickness of the crystallites	Lateral dimension	Greatest dimension
Deep blue	0·1 $\mu$	1 $\mu$	2 $\mu$
Green	0·2 $\mu$	2 $\mu$	3 $\mu$
Orange-yellow	0·4 $\mu$	4 $\mu$	5 $\mu$
Red	0·5 $\mu$	6 $\mu$	9 $\mu$

The difference between the refractive indices of the orthoclase lamellae and the surrounding albite-anorthite matrix is about 0·04. On multiplying the dimensions of the crystallites by this quantity, the retardation produced in a light wave travelling in a direction normal to the lamellae is seen to be only a small fraction of the wavelength of light, and hence one could scarcely hope to be able to distinguish the individual lamellae under the microscope. The confusion due to the presence of great numbers of them and the presence of the visible inclusions which give rise to the aventurine reflection have also to be taken into consideration. They would diminish the prospect of success in observing the individual crystallites of orthoclase even with the aid of modern phase-contrast methods. On the other hand, if the crystallites are looked at edge-wise, the possibility of discovering their presence under the microscope would be greater.

### 3. Plagioclase feldspar from Gudur (South India)

This material of which a large collection has been made for the Museum of this Institute is an opaque white feldspar. Many of the specimens however show a distinct iridescence, varying in colour from a delicate blue to a brilliant white. Only occasionally is a hint of any other colour noticeable. As cleavage faces are frequently seen, there is no difficulty in verifying that the iridescence is noticed on the exposures of the B-face of the crystal. From the character of the iridescence, it is quite clear that the material is a plagioclase feldspar. The iridescence is seen in two different settings of the crystal with reference to the incident beam and the direction of observation; the areas which appear bright in one setting are dark in the other and *vice-versa*. The angle of rotation of the specimen needed is of the same order of magnitude as in the case of labradorite. But in other respects this feldspar behaves differently from labradorite. The colours are much less saturated

and much less varied in hue. Further, whereas in the case of labradorite the change from one setting to the other is brought about by a rotation of the specimen about a line in the B-face making an angle of  $70^\circ$  with the  $a$ -axis, in the present case the rotation required is about the  $a$ -axis itself. There is also visible evidence of twinning, sometimes of the albite type, sometimes of the pericline type and sometimes of both. It seems probable from what has been stated that the chemical composition of the feldspar is principally albite and that the iridescence arises from the presence of internally segregated lamellae of orthoclase. These are inclined to the B-face as in the case of labradorite but in a different azimuth altogether.

The diffusion haloes of this variety of feldspar are readily observed. They appear in pairs, one on either side of the ordinary optical reflection from the B-face. The relative intensity of the two haloes is very variable and depends upon the position of the illuminated spot on the crystal face. The angular dimensions of the haloes are rather small and the indications are that they vary with the colour, being larger for the blue and less for the bluish-white haloes. We have not however made any quantitative measurements under appropriate conditions. It has been noticed that, as in the case of labradorite, the diffusion halo is strongly polarised when it is observed in a direction perpendicular to the incident beam.

#### 4. The diffusion halo of the Ceylon moonstones

The optical phenomenon familiarly known as schiller is exhibited by certain varieties of orthoclase feldspar, amongst which the best known are the moonstones from Ambalangoda in Ceylon of which there is a large collection in the Museum of this Institute. The optical characters of the schiller vary enormously with the individual specimens in spite of the fact that all of them come from the same area. At one extreme, we have the moonstones exhibiting a schiller of a beautiful blue colour; at the other extreme, we have those which give a schiller of great brilliance and of a perfectly white colour. In the paper which appeared earlier in these *Proceedings* and has already been referred to, the explanation of these effects was described and discussed in great detail. The conclusion reached was that the schiller is essentially a diffusion of light within the crystal and that such diffusion is a consequence of local fluctuations in the composition of the crystal. In other words, the relative proportion of the soda and potash feldspars in their composition (the latter being the principal constituent) varies from point to point. The same situation is described by the statement that the soda feldspar tends to segregate itself from the potash and form tiny crystallites which orientate themselves regularly in the lattice; by reason of the difference in refractive indices of albite and orthoclase, the crystal becomes optically heterogeneous and a diffusion of the light results. The lattice spacings of albite and orthoclase differ substantially along the  $a$ -axis and much less so along the other two axes. In

consequence, the albite crystallites may be expected to spread out principally along the *b* and *c* axes in preference to the *a*-axis. The diffusion of light would therefore tend to be non-uniform with respect to direction.

Thus, there is a parallelism between the optical effects exhibited by labradorite and by the Ceylon moonstones. But there are also notable differences which are readily intelligible in the light of the different circumstances in the two cases. The Ceylon moonstones, unlike labradorite, exhibit only a single diffusion halo, the same being elliptic in shape. The angular dimensions of the halo vary enormously with the colour of the schiller. It is very large for the moonstones exhibiting a blue schiller, smaller and brighter for those exhibiting a bluish-white schiller, and smallest and brightest with those exhibiting a pure white schiller. Photographs of the haloes in these three cases have already been reproduced in the article in *Current Science* cited as reference 4. From the angular dimensions of the halo in each case, the dimensions of the crystallites responsible for them can be roughly evaluated. The figures which are the averages derived from a large number of specimens are given below in table 2.

Table 2

Colour of schiller	Major axis	Minor axis
Blue	1·6 $\mu$	0·8 $\mu$
Bluish white	3·0 $\mu$	1·6 $\mu$
White	6·0 $\mu$	5·0 $\mu$

It may be remarked that the measurements were made with moonstones immersed in a cell of liquid and with a pencil of light traversing them in each case along the schiller axis, that is to say, along the direction in which the schiller is most prominent. Actually, the diffusion haloes may also be observed when the light traverses the moonstone in other directions. The colour and intensity of the schiller and other attendant effects alter with the angle of incidence. The study of these phenomena opens up an extensive field for research, but we do not propose to enter into the same here.

The dimensions shown in the second and third columns of table 2 are transverse to each other and to the direction of the schiller axis. The question whether crystallites of the dimensions shown could be observed directly under the microscope is one of considerable interest. A factor that needs to be considered in this connection is the difference in the refractive indices of the crystallites and of the surrounding medium. This difference for the three principal directions is respectively 0·015, 0·010, 0·010. Multiplying these by the linear dimensions shown in table 2, it is seen that the retardation in phase produced by a single crystallite with reference to the surrounding medium would lie between 0·01  $\mu$  and 0·02  $\mu$  for a blue schiller and between 0·07  $\mu$  and 0·1  $\mu$  for a white schiller. These optical

retardations are much smaller than a wavelength of light and when it is recalled that the effects of a great number of crystallites would overlap, it will be evident that there is scarcely any possibility of the individual elements responsible for the diffusion of light being distinguishable under the microscope. We are thus justified in stating that the schiller of moonstones has its origin in a heterogeneity incapable of being resolved by ordinary microscopic examination. The view put forward by some mineralogists, notably E J Spencer,<sup>5</sup> that the schiller of moonstones is due to a microperthitic or lamellar structure is thus clearly untenable. The optical irregularities reported by the same author as observable under special conditions of illumination are of much larger dimensions than those noted in table 2. They obviously cannot be responsible for the observed schiller.

### 5. The diffusion haloes of the Korean moonstones

The chemical composition of a typical moonstone from Korea has been reported by Professor Ito.<sup>6</sup> It is given as 7·32% of  $K_2O$  and 6·88% of  $Na_2O$ , while a typical Ceylon moonstone is reported to contain 11%  $K_2O$  and 3·8%  $Na_2O$ . It is not surprising in these circumstances that some differences are observed between the optical behaviour of the Ceylon and the Korean moonstones. We find the latter to fall into two categories, namely, those exhibiting a bright blue schiller and the others a bluish-white schiller. The most remarkable difference between the Ceylon and the Korean moonstones is, however, that the latter are sometimes twin-crystals and sometimes quartets. Whereas an individual crystal exhibits only a single diffusion halo, a twin crystal shows two, while a quartet shows four haloes. The first case is illustrated in figure 1 of plate III and the second case in two different settings of the moonstone in figure 2 of plate III and figure 2 of plate IV respectively. The quartet of haloes exhibited by a moonstone containing four components is illustrated in figure 1 of plate IV.

### 6. The Coimbatore moonstones

The material with which some observations were made and are reported here was collected from the Kangayam area of the Coimbatore District in South India. From its observed crystallographic characters, it would appear that it is an orthoclase feldspar. Some specimens are translucent with a pale brownish tint. Other examples are however forthcoming which are much more transparent and exhibit a pale greenish hue. These specimens have a perfect C-cleavage, and plates of the material parallel to that cleavage can therefore be obtained suitable for optical investigation. A very interesting property of the greenish moonstones is they exhibit a schiller which in many cases has a golden yellow colour, while in

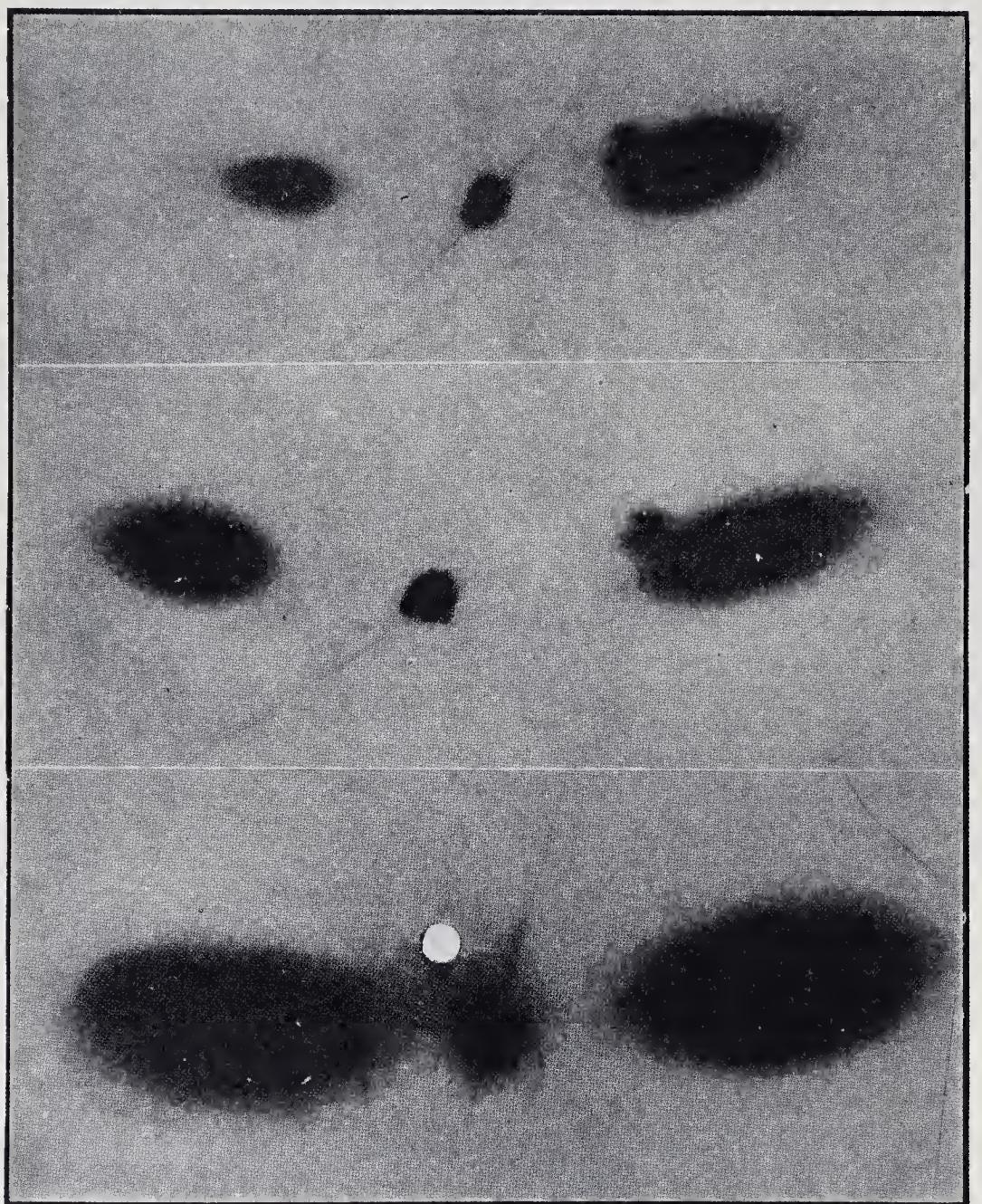
others it is yellowish-white. We have not as yet made any quantitative studies, but from general inspection, it would seem that the position of the schiller axis for this variety of moonstone is approximately the same as for the Ceylon moonstones. The character of the diffusion halo is however notably different. The halo in the present case is rather small in area and exhibits the same colour as the schiller itself. A special feature is the appearance of a bright cross whose arms pass through the diffusion halo and extend in directions perpendicular to each other. We have also noticed that when the moonstone is set so that the characteristic schiller appears in a direction transverse to the incident light, the diffusion halo is almost completely polarised. Another remarkable property of this moonstone is the polarised extinction of light which it exhibits in certain circumstances. This effect is of the same general nature as that described on pages 135 and 136 of our earlier paper on the Ceylon moonstones,<sup>2</sup> but is much more conspicuously observable.

### Summary

Labradorite, the moonstones from Ceylon and Korea and other varieties of feldspar exhibiting iridescence have been investigated, and in all cases it has been found that such iridescence is the consequence of a diffusion of light within the material and not a true optical reflection. By a suitable technique, the diffusion haloes can be photographed and from their geometric positions, colour and angular dimensions, important conclusions can be drawn regarding the structures responsible for the iridescence. The plagioclase feldspars usually show two haloes geometrically related to each other according to the twinning law. The Ceylon and Korean moonstones differ in this respect; while the former invariably shows only one halo, the latter exhibits one, two or four according to the number of components present in the individual crystal.

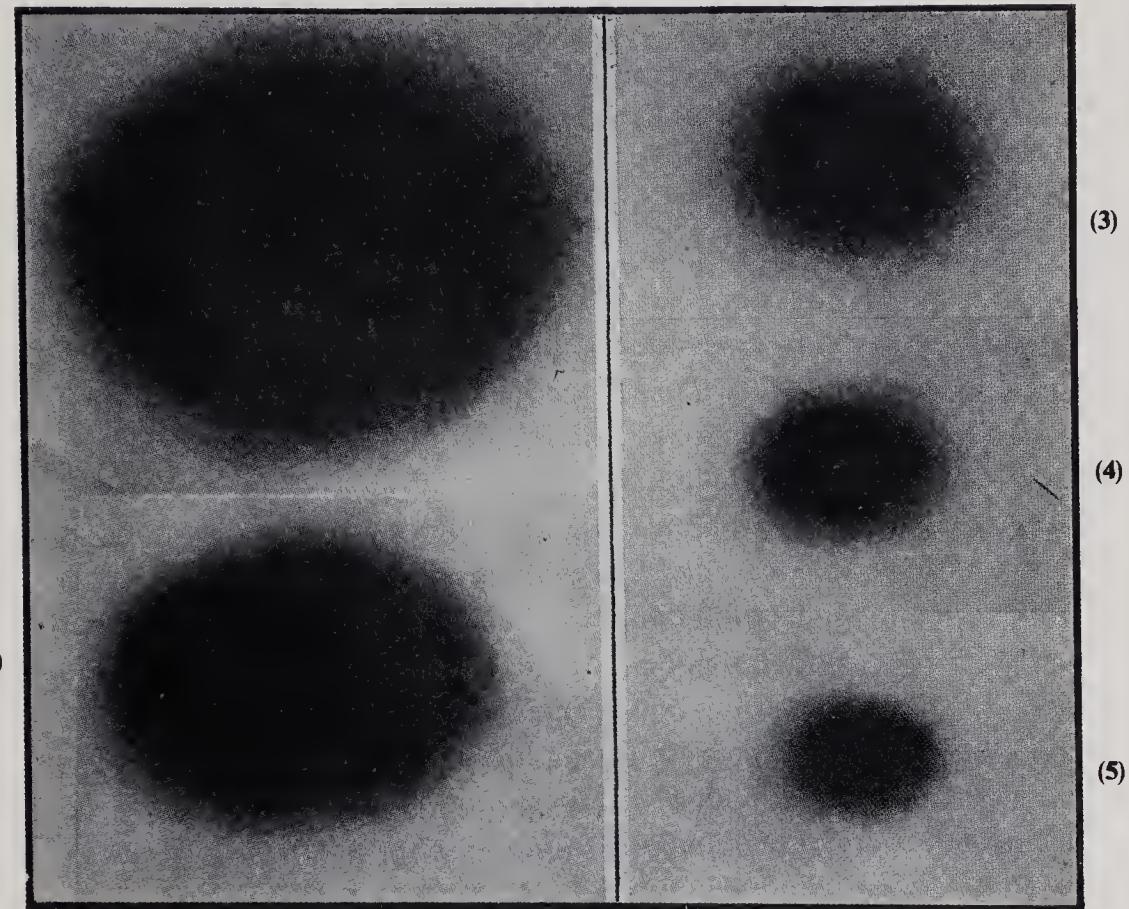
### References

1. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1950, **32A**, 1.
2. C V Raman, A Jayaraman and T K Srinivasan, *Ibid.*, 1950, **32A**, 123–40.
3. Boggild, *Math. Fys. Meddl.*, Copenhagen, 1924, **6**, No. 3.
4. C V Raman, *Curr. Sci.*, 1951, **20**, 85–87.
5. E Spencer, *Miner. Mag.*, 1930, **22**, 291.
6. Tei-Ichi Ito, *X-Ray Studies on Polymorphism*, Marusen Co., Tokyo, 1950.



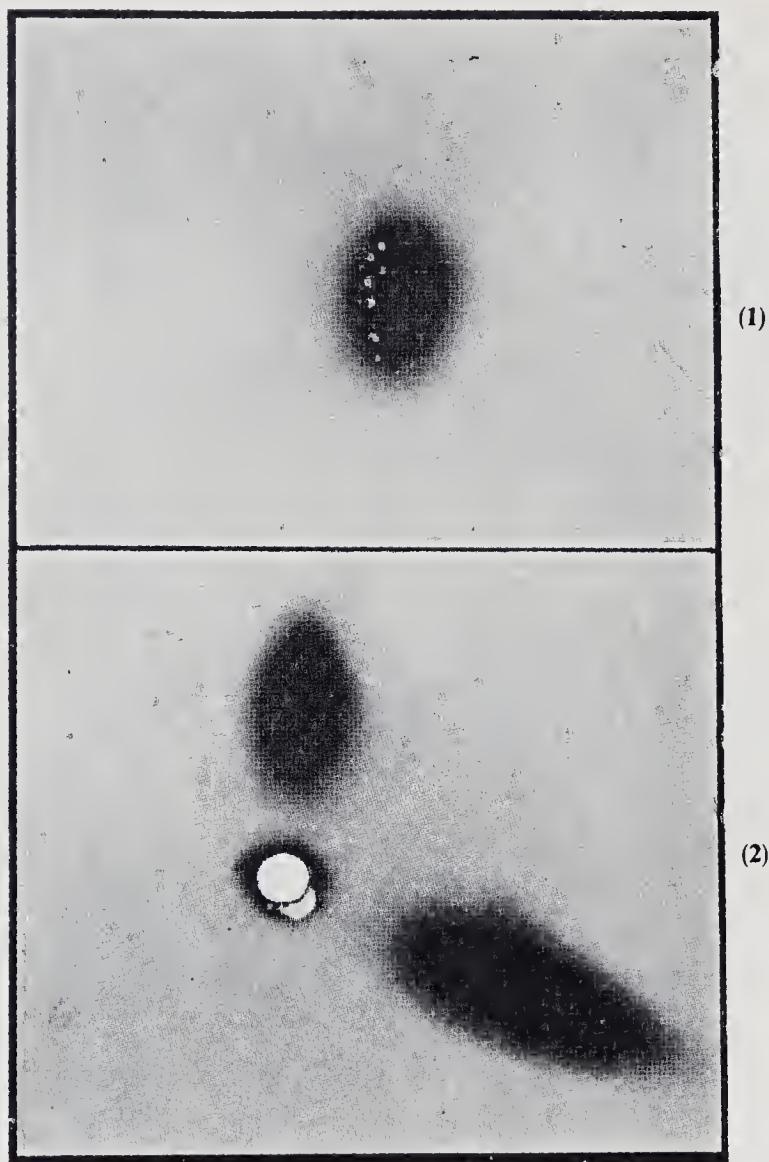
Figures 1-3. Diffusion haloes of labradorite.

Plate I



Figures 1-5. Diffusion haloes of labradorite.

Plate II



**Figures 1 and 2.** Diffusion haloes of the Korean moonstones.

**Plate III**



Figures 1 and 2. Diffusion haloes of the Korean moonstones.

## On the iridescence of potassium chlorate crystals— Part I. Its spectral characters

SIR C V RAMAN and D KRISHNAMURTI  
(Raman Research Institute, Bangalore)

Received October 27, 1952

### 1. Introduction

It has long been known that potassium chlorate occasionally crystallises in plate-like forms which display a spectacular iridescence, due to the fact that these crystals are polysynthetic twins and that the light traversing the same is reflected at the composition planes of twinning, thereby giving rise to interference effects. An extensive collection of these iridescent crystals was available to us for investigation, and an opportunity recently arose for making a detailed examination of their optical behaviour. Several surprising and interesting results have emerged from our studies, and it is proposed in the series of papers of which this is the first to describe our findings and discuss their significance.

We may usefully recall here the special features of the iridescence of potassium chlorate which drew the attention of the pioneer workers in the field and led them to the explanation stated above. When the crystals are viewed normally, the coloured reflections are absent; they develop and increase in intensity with increasing obliquity of observation, the colour changing more or less rapidly at the same time. Individual cases differ greatly in respect of the brilliancy and colour of the iridescence which they display and in respect of the sequence of changes noticed with increasing angle of incidence of the light. In all cases, however, the irrespective of such angle of incidence the coloured reflection vanishes completely for particular azimuths of the plane of incidence, disappearing twice in each complete revolution as the crystal tablet is rotated in its own plane. A specially noteworthy feature is that the coloured reflection when examined through a spectroscope appears in many cases as a narrow monochromatic band or else as a number of such bands. These bands shift towards shorter wavelengths in the spectrum and simultaneously broaden out to a notable extent as the angle of incidence is increased. The light transmitted by the crystal exhibits effects complementary to those observed by reflected light.

## 2. Spectral characters of the iridescence

It appeared to us important to obtain a series of spectrograms with selected crystals exhibiting the character of the reflected and of the transmitted light in varying circumstances of observation, viz., over a wide range of angles of incidence, extending from nearly zero upwards, as also over a range of azimuths of incidence extending from that at which the reflections vanish to that at which they attain maximum intensity. One may expect on theoretical grounds to find an increase in the spectral width of the bands of reflection when the azimuthal angle measured from the former position increases from zero to  $90^\circ$ , the angle of incidence of the light remaining the same. This effect has actually been observed by us. Surprisingly enough, however, other and even more striking changes in the nature of the spectra are noticed when the azimuthal angle is changed without changing the angle of incidence.

The spectrograms reproduced in the plates accompanying this paper were obtained with five crystals selected for the reason that all of them at nearly normal incidence of the light exhibit a monochromatic reflection in the visible region of the spectrum. The source of light used was a metal filament lamp run with a heavy current and the spectrograms were recorded with Hilger glass instruments. The crystals were mounted in Canada balsam between two thin prisms of glass facing opposite ways, thereby eliminating the usual reflection from the external faces. We shall refer to the five crystals as A, B, C, D and E respectively. At nearly normal incidence they exhibit respectively deep red, indigo blue, orange red, greenish yellow and green iridescence.

*Crystal A:* At nearly normal incidence, this has a reflection maximum in the visible spectrum at about  $\lambda 6500$  in the red having a total width of 100 A.U. In the ultra-violet it shows a reflection maximum at about  $\lambda 3290$  having a width of about 20 A.U., thereby making it evident that the band in the red corresponds to a first-order reflection. Figure 1 in plate I shows a series of spectrograms of the light in the visible region reflected by this crystal; the plane of incidence was that of maximum intensity of reflection and the seven successive spectrograms show the effect of increasing the angle of incidence by steps from about  $5^\circ$  to  $55^\circ$ ; the exposure times were adjusted suitably so that all the spectra were satisfactorily recorded on the same plate. Figure 2 in plate I reproduces a similar series of spectrograms, the azimuth of incidence being however kept constant and nearly that at which the reflections vanish. Longer exposures had naturally to be given for figure 2 than for figure 1.

Examining these spectra, a striking feature is that the principal reflection maximum is accompanied by an extended trail of subsidiary maxima of relatively feeble intensity. The distribution of intensity of these subsidiary maxima shows a notable asymmetry about the principal maximum. They are both more numerous

and more intense on the side of longer wavelengths; on the side of shorter wavelengths, the intensity falls off rapidly to zero.

A comparison of figures 1 and 2 in the plate clearly shows that in both cases, the width of the principal maximum increases with increasing obliquity of incidence. On the other hand, it is clear that such increase is definitely less in figure 2 where the azimuthal angle is small instead of being  $90^\circ$  as in figure 1. To illustrate this further, a series of spectrograms have been recorded keeping the angle of incidence nearly constant at about  $55^\circ$  and varying the azimuthal angle by successive steps from nearly  $0^\circ$  to  $90^\circ$ . This series is reproduced as figure 1 in plate V and exhibits a notable increase of the width of the principal maximum in the series. On the other hand, the subsidiary maxima do not exhibit any such widening. Likewise, in the two series of spectrograms taken with increasing obliquity and at a constant azimuth there is no obvious increase in the width of the subsidiary maxima. The increasing dispersion of the instrument in the region of shorter wavelengths results, however, in a corresponding progressive alteration in their apparent width.

### 3. Splitting of the reflection maxima

We now turn to the spectrograms reproduced in plates II, III and IV which were recorded with crystals B, C and D respectively on the same general plan as those of crystal A reproduced in plate I. Before referring to the features appearing in these spectra, some particulars should be mentioned concerning these crystals. Crystal B gives at nearly normal incidence a reflection maximum at about  $\lambda 4780$  and 20 A.U. wide; another reflection maximum appears at about  $\lambda 3225$  with a spectral width of only 8 A.U., from which it is clear that the band in the visible corresponds to a second-order reflection. Crystal C gives at nearly normal incidence a reflection maximum at  $\lambda 6150$  about 40 A.U. wide. In the violet region, a second maximum at about  $\lambda 4155$  with a width of 12 A.U. is observed. These two evidently correspond to the second and third order reflections respectively. Crystal D gives a principal maximum at  $\lambda 5350$  about 20 A.U. wide. This is probably a first-order reflection.

As in the case of crystal A, two series of spectrograms were recorded with each of the crystals B, C and D; in the first series the azimuthal angle was  $90^\circ$  while in the second series it was nearly zero. In each series the angle of incidence was altered by steps from  $5^\circ$  to  $55^\circ$ . A comparison of figures 1 and 2 in the plates referring to each of these crystals shows a striking difference in the nature of the spectra in the two series. When the azimuthal angle is small, the principal maximum of reflection splits symmetrically into components which drift away from each other and also towards shorter wavelengths with increasing angles of incidence. On the other hand, in the spectra recorded at an azimuthal angle of  $90^\circ$  the principal maximum of intensity does not split but merely widens out and

drifts towards shorter wavelengths. Simultaneously, however, an additional component or "ghost" appears on either side of the principal maximum in the spectrum but well removed from it. These ghosts or companions broaden and become more intense with increasing obliquity of incidence and the entire triplet simultaneously drifts towards shorter wavelengths. The widening of the central maximum of the triplet in one series of spectra is of the same order of magnitude as the separation of the two components of the doublet in the second series. While this general description covers the effects observed with three crystals, there are some differences in detail, to which attention may be drawn.

*Crystal B:* As in the case of crystal A, a trail of subsidiary bands accompanies the principal maximum of reflection. These are most clearly seen in the series of spectra reproduced as figure 1 in plate V. One notices that the bands are very fine and numerous. However, they exhibit periodic variations of intensity which convey the impression that a second set of broad bands are superposed thereon.

In order to exhibit the change-over in the nature of the spectra in passing from the azimuthal angle  $0^\circ$  to  $90^\circ$ , a third series of five spectrograms were recorded in which the obliquity of incidence was kept nearly constant at about  $45^\circ$  and the azimuthal angle altered by steps. These are reproduced as figure 2 of plate V from an inspection of which it will be seen that the two components of the reflection maximum in the doublet series coalesce together so as to form the broad central band in the triplet series, while simultaneously, the outer components of the triplet appear and increase in width and intensity.

*Crystal C:* As will be seen on a comparison of the figures in plates II and III, the general features of the principal reflection maxima exhibited by crystals B and C are similar; the components for crystal C appear rather closer together than for crystal B. It is of interest to note that the doublets and triplets into which the maxima split are to be observed also in the third order reflection appearing towards the violet end of the spectrum. The subsidiary maxima in the spectra of crystal C are somewhat closer than in the case of crystal A but much farther apart than those of crystal B. Their distribution in intensity is very regular and does not show the peculiar features observed in the last-mentioned case.

*Crystal D:* The components of the triplet are not single but exhibit much detail. It is noteworthy that the components of the reflection maximum in the doublet spectra likewise exhibit a structure. Indeed at oblique incidences, we actually notice in figure 2 of plate IV that the reflection maximum has split into four broad components instead of two as in the case of crystals B and C. The subsidiary maxima in the spectra of this crystal are sharp and numerous, and do not exhibit the regularity of spacing noticed in the case of the other crystals.

#### 4. Transmission spectra

As is to be expected, the transmission spectra in all cases are complementary to the reflection spectra. When the azimuthal angle is nearly zero the reflections and hence also the extinctions are very weak, and only the strongest of the latter are recorded, if at all, in transmission. More detail is however observable in the transmission spectra corresponding to the azimuths of incidence at which the reflection has a maximum intensity.

Figures 1 and 2 in plate VI and figures 1 and 2 in plate VII are a series of transmission spectra recorded with crystals A, B, C and D respectively at an azimuthal angle of  $90^\circ$ , and at varying obliquities of incidence. It will be seen on a comparison with the figures in plates I to IV that they reproduce only the strongest features in the corresponding reflection spectra. In particular, the triplets of the principal maxima exhibited by crystals B, C and D are also to be seen in transmission.

On account of their extreme weakness, the subsidiary maxima are scarcely to be seen in the transmission spectra. Figures 1 and 2 in plate VIII however show for comparison the reflection and transmission spectra of crystal E at varying angles of incidence and at an azimuthal angle of  $90^\circ$ . This crystal shows at nearly normal incidence a maximum of reflection at about  $\lambda 5350$  and about 150 A.U. wide, and this widens and drifts towards the violet at increasing angles of incidence. The close correspondence in the positions and intensities of the subsidiary maxima of reflection and extinction can be clearly made out from the figures. Figure 3 in plate VIII shows the enormous increase in the intensity of the reflections given by this crystal with increasing azimuthal angle. It will be noticed however, that the positions of the subsidiary maxima remain practically unaltered. Studies made with this particular crystal at very oblique incidences show that both in reflection and extinction, there is a notable widening of the principal band as the azimuthal angle is increased from  $0^\circ$  to  $90^\circ$ .

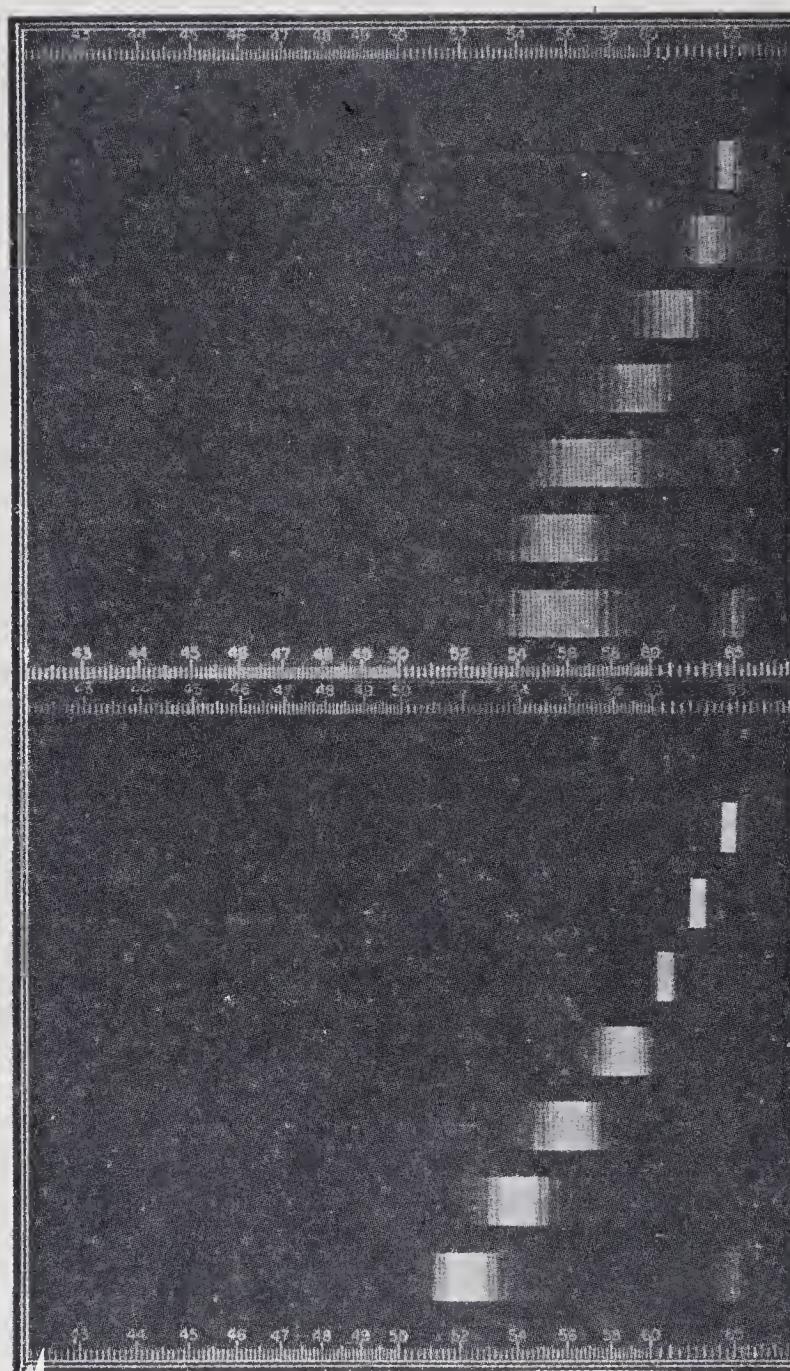
#### 5. Discussion of the results

Studies described more fully in the second paper of this series have shown that the components of the doublet and the outer components of the triplet recorded with crystals B, C and D are strongly polarised, and related effects have also been observed with crystal A. A detailed discussion of the experimental facts reported in the present paper has therefore to be deferred till we have described and discussed the polarisation effects. The appearance of subsidiary maxima accompanying the strong monochromatic reflections is however intelligible in the light of the general theory of the optical behaviour of stratified media. Reference may be made in this connection to two recent papers in these *Proceedings* by G N Ramachandran dealing with the spectral character of the reflection of light from

stratified media and the analogous theory of X-ray reflections in crystals. The spectrograms reproduced in the present paper recall in a striking manner the theoretical curves for the spectral distribution of intensity appearing in the first of the two papers by Ramachandran, quoted above. As has been stressed by him, the spectral width of the principal reflection maximum for a regularly stratified medium is determined by the absolute reflecting power of a single stratification and not by the total number of stratifications present, if the latter be large enough. The experimental findings regarding the effect of varying the azimuth of incidence brought to notice in the present paper fall into line with this indication of the theory.

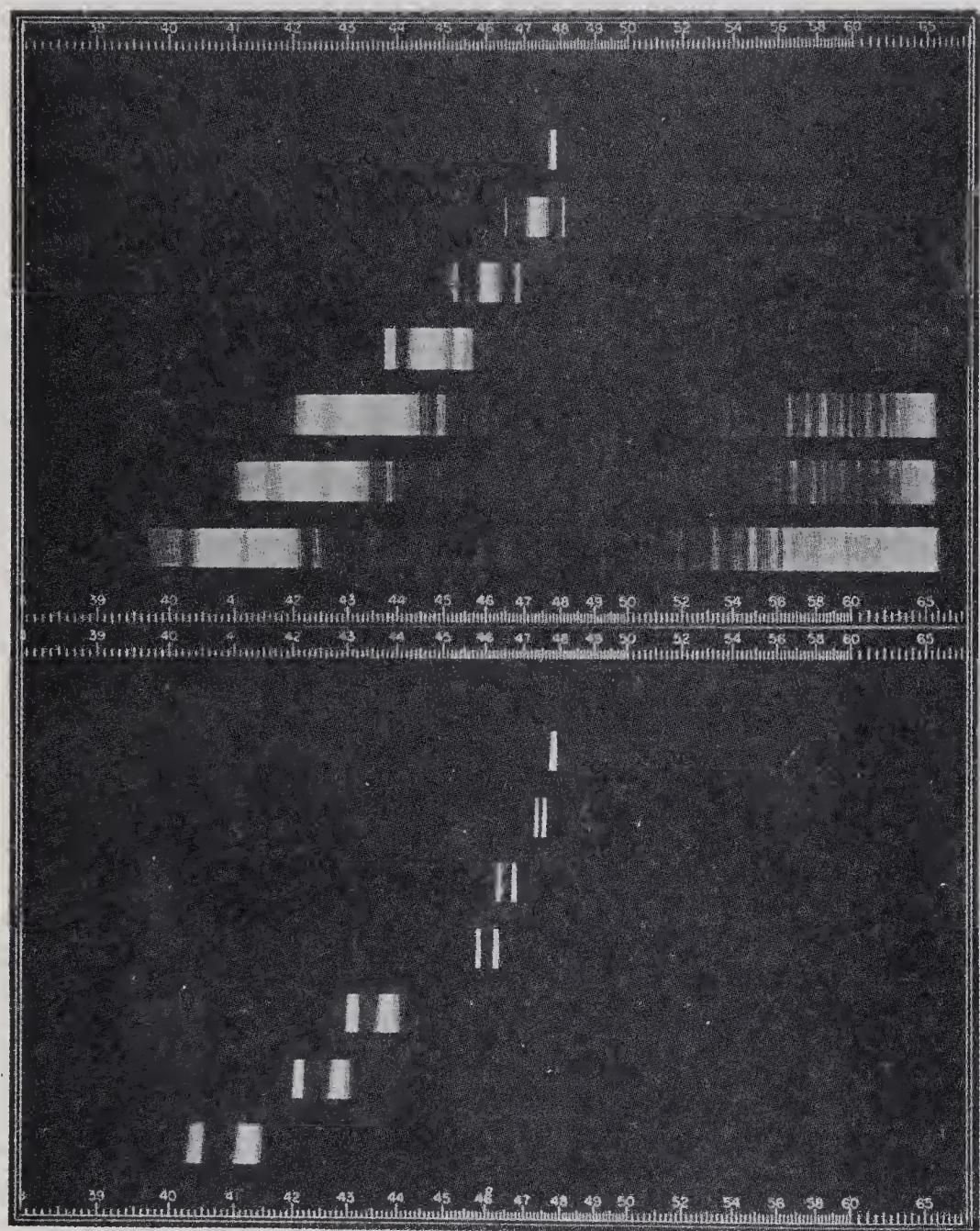
## 6. Summary

Spectrograms obtained with five iridescent crystals of potassium chlorate at varying azimuths and obliquities of incidence have been obtained and are reproduced with the paper. Some of the results observed are explicable in terms of the general theory of the optical behaviour of a regularly stratified medium, viz., (a) the appearance of a whole series of subsidiary bands accompanying the principal maxima and distributed asymmetrically about them and (b) the variation of the spectral width of the principal maximum with change of azimuthal angle and obliquity of incidence. Other striking effects are however also observed which are not so explicable, viz., when the azimuthal angle is nearly zero, the principal band splits into a doublet the components of which drift apart progressively and also shift towards shorter wavelengths with increasing obliquity of incidence. When the azimuthal angle is  $90^\circ$  the crystals exhibit the principal maximum as a triplet, the central component of which has a width of the same order of magnitude as the separation of the doublet in the preceding case, while its outer components are much further apart.



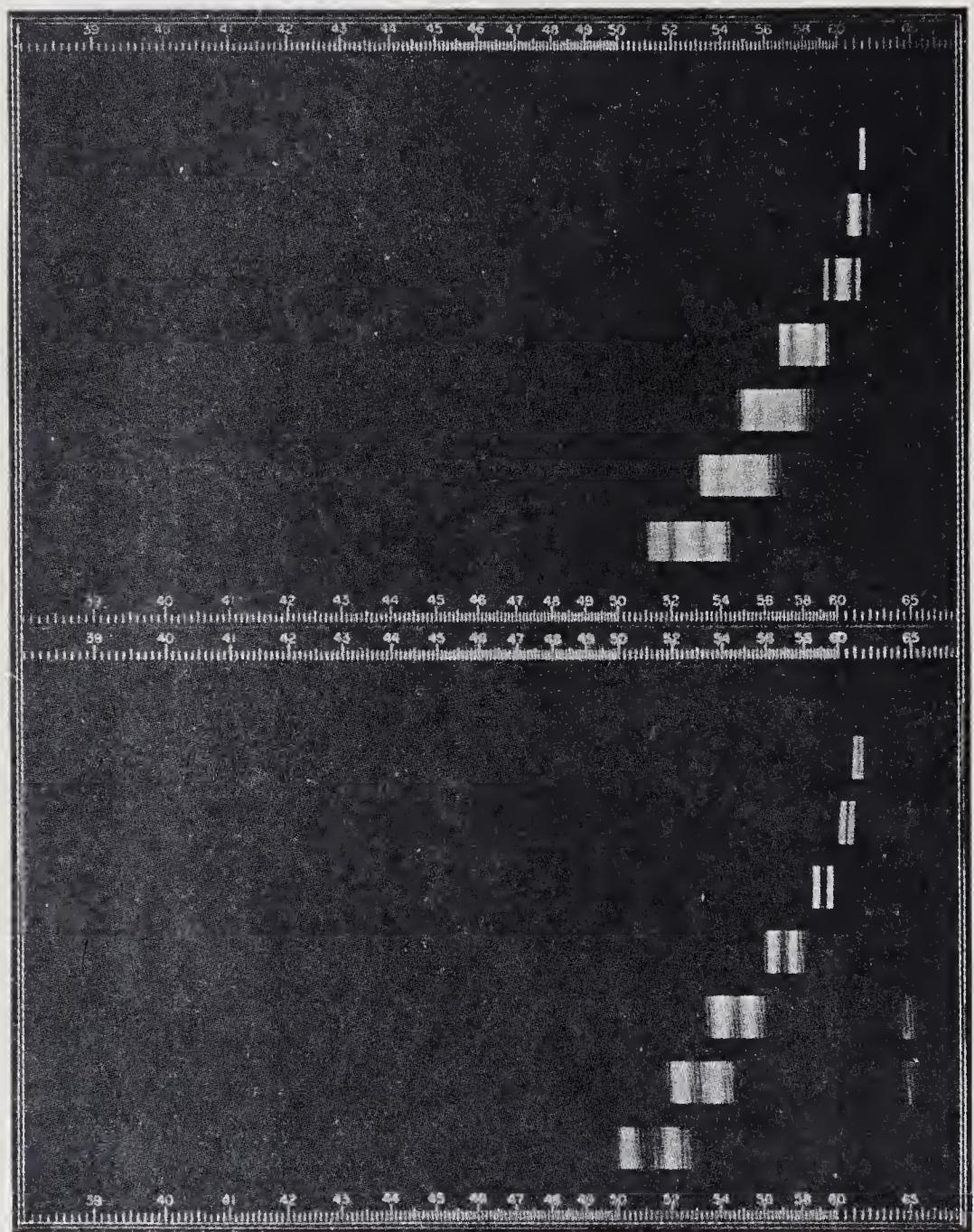
Figures 1 and 2

Plate I



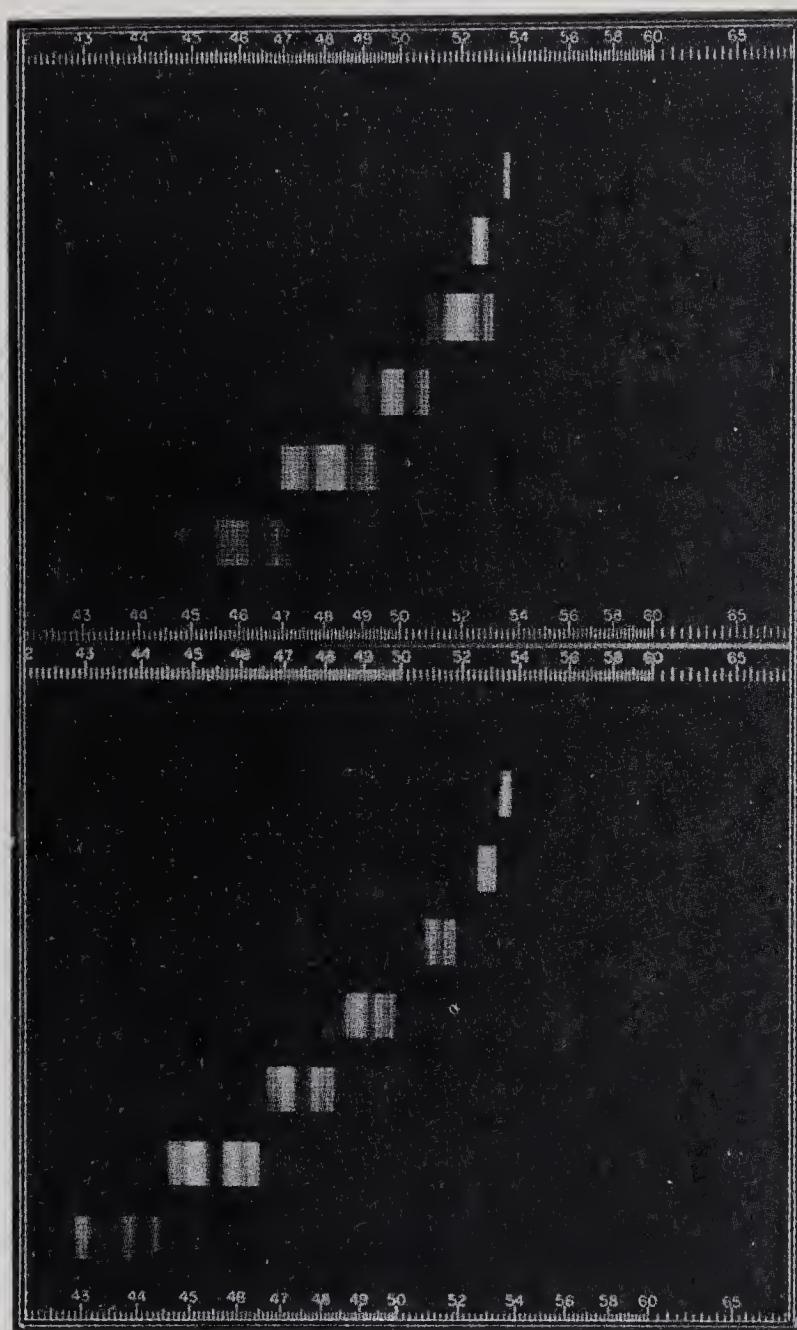
Figures 1 and 2

Plate II



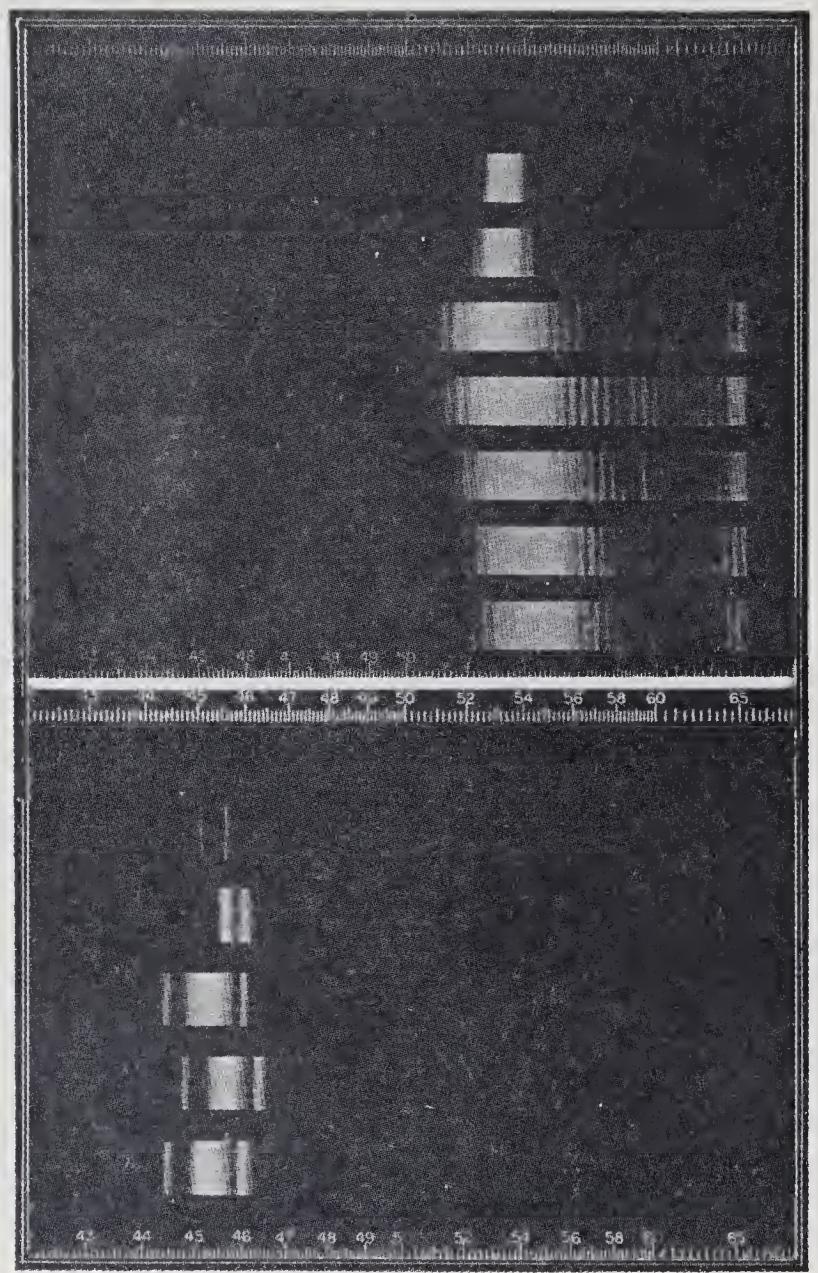
Figures 1 and 2

## Plate III



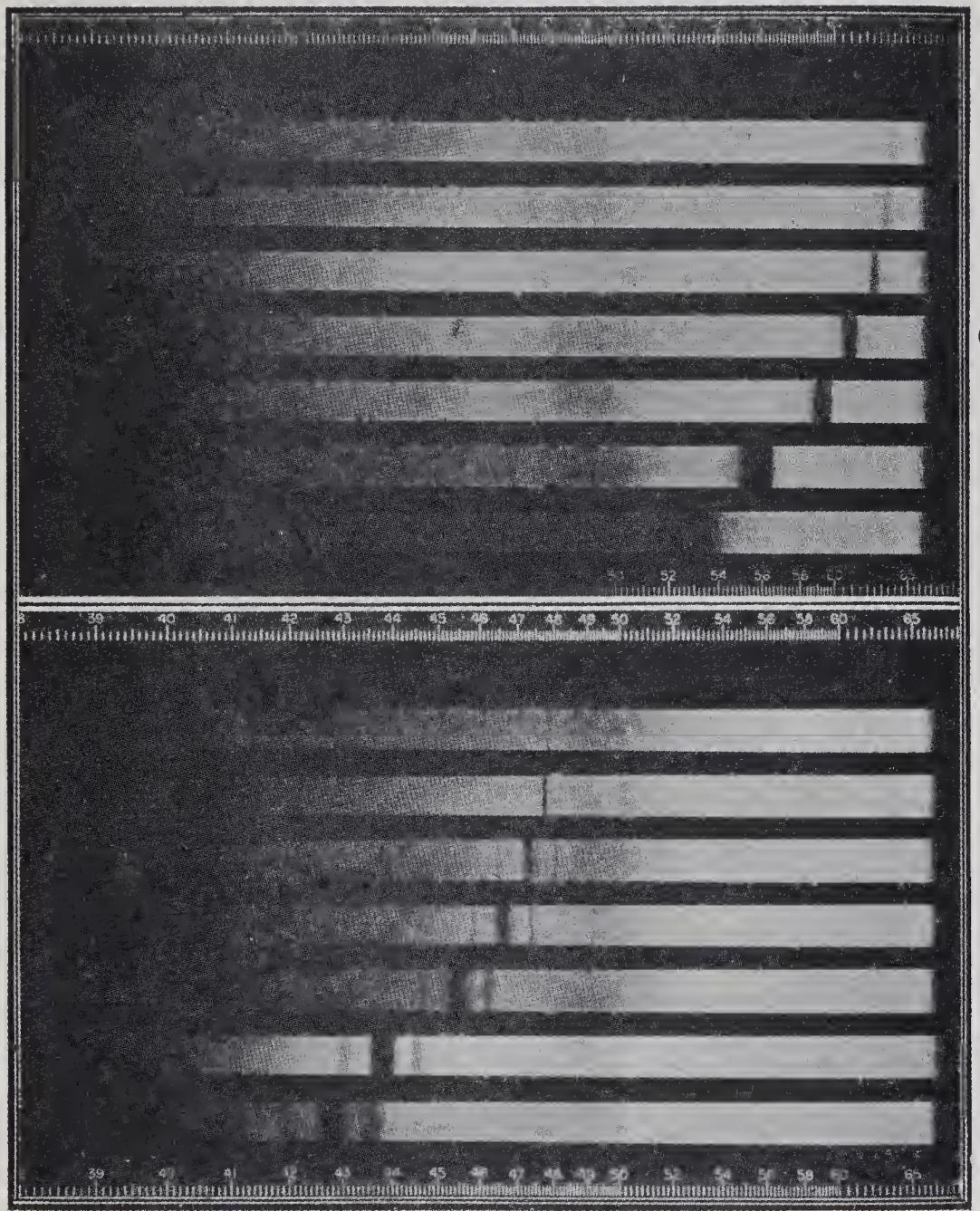
Figures 1 and 2

Plate IV



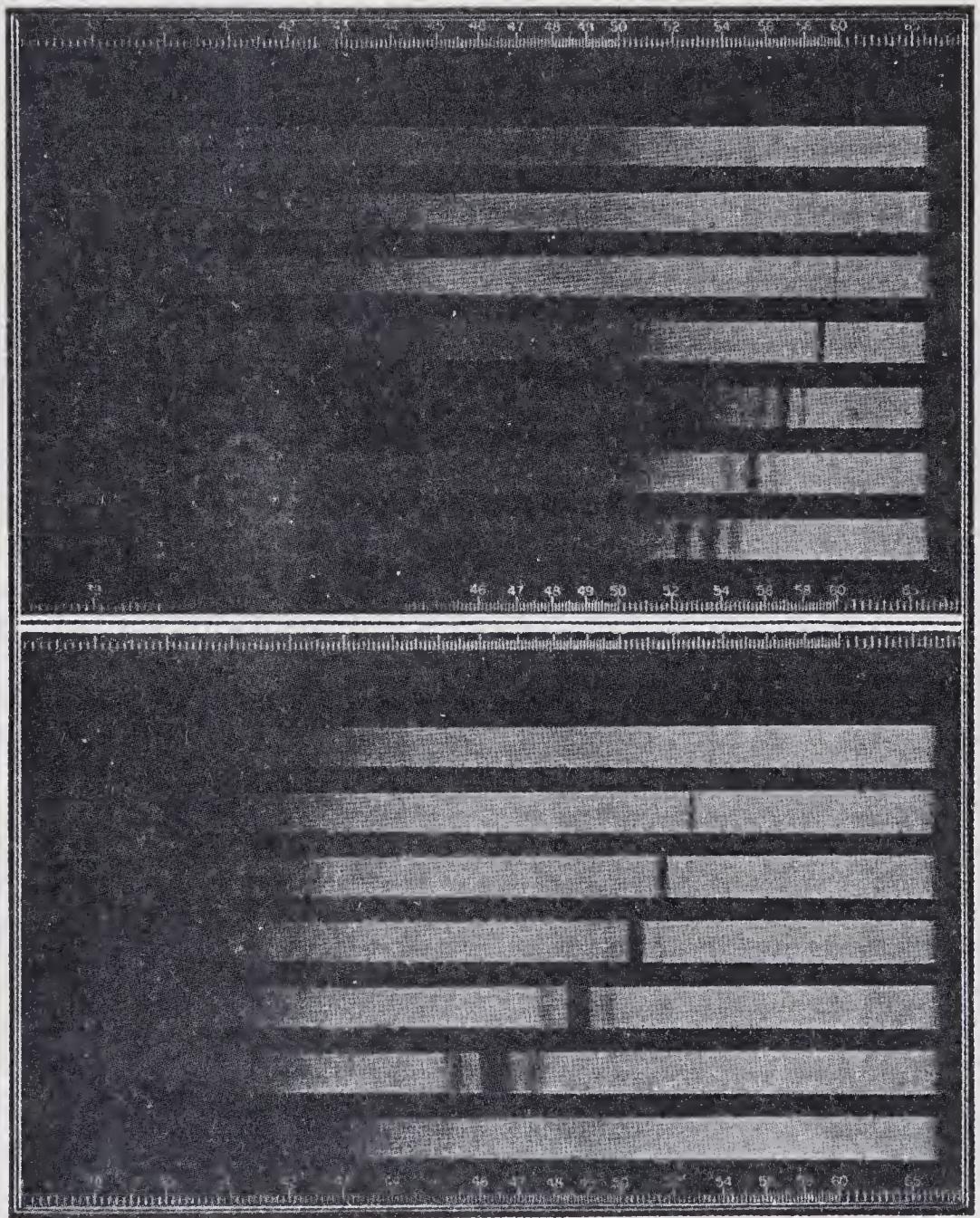
Figures 1 and 2

Plate V



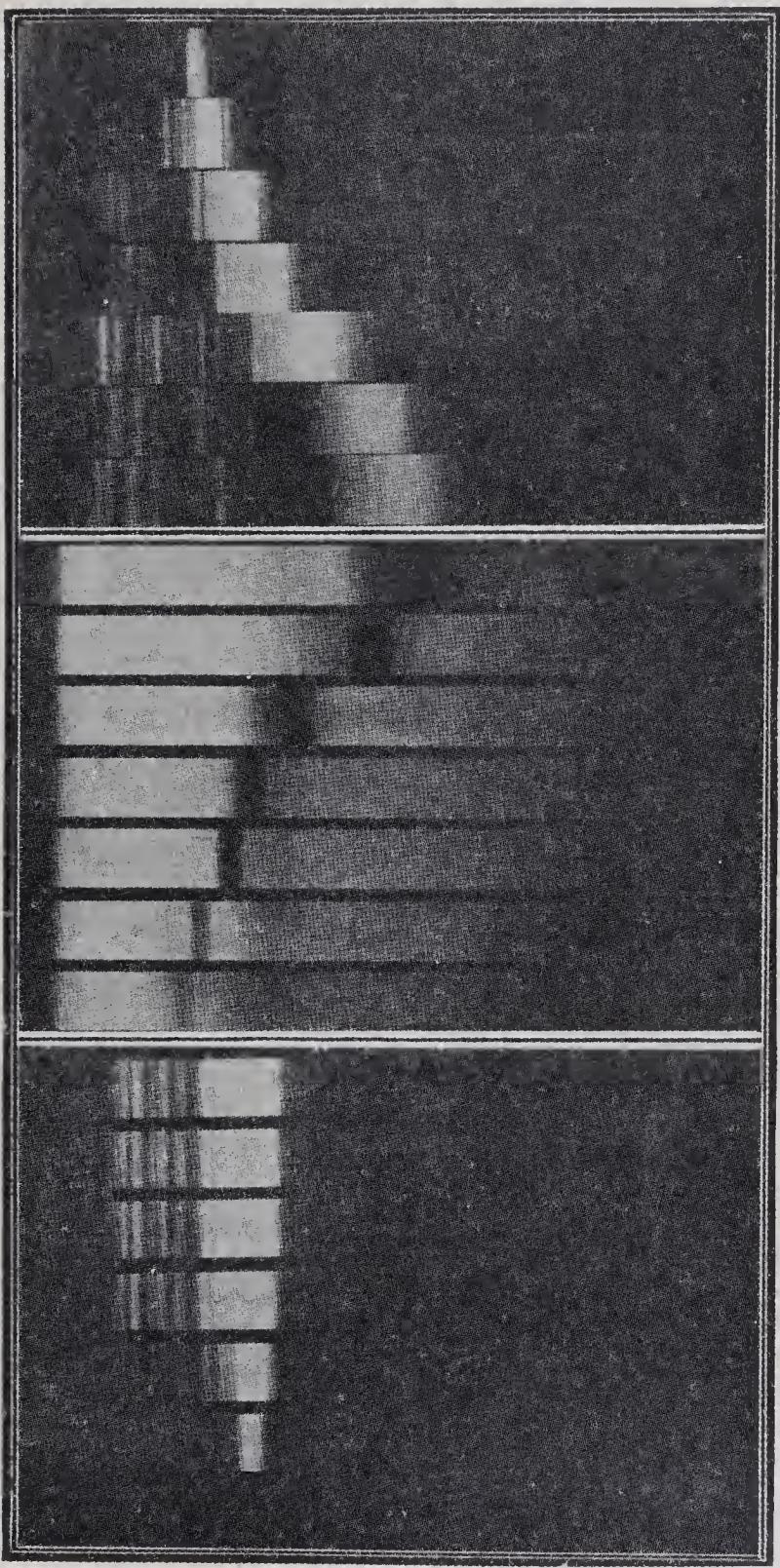
Figures 1 and 2

Plate VI



Figures 1 and 2

## Plate VII



**Figures 1-3**

**Plate VIII**

## On the iridescence of potassium chlorate crystals— Part II. Polarisation effects

SIR C V RAMAN and D KRISHNAMURTI  
(Raman Research Institute, Bangalore)

Received October 29, 1952

### 1. Introduction

A remarkable fact about the iridescence of potassium chlorate is that examples are frequently forthcoming in which the reflections are monochromatic, indicating a high degree of regularity of the stratifications as well as the presence of a great number of them. As we have seen in the preceding paper, an examination of the reflection spectra of such crystals reveals features that are in accord with the general theory of the optical behaviour of a regularly stratified isotropic medium. Nevertheless, it is not to be supposed that such a theory would suffice to explain all that is actually observed in the present case. Indeed the iridescence is itself a consequence of the birefringence of the medium coupled with the fact that the alternate layers of it are differently orientated. It follows that a proper theory has necessarily to be based upon a consideration of the propagation of light through a birefringent medium and of the specific characters of a reflection at a twin plane boundary.

### 2. Crystal form and birefringence

Potassium chlorate crystallises in the holohedral class of the monoclinic system; in other words the crystal has both a two-fold rotation axis and a plane of symmetry perpendicular to it. An examination of the tablet-shaped iridescent crystals in convergent polarised light readily enables one to convince oneself that the two-fold rotation axis and the plane of symmetry are oriented alike for all the components of the twinned crystal and that the former is parallel to the external faces of the tablet and that the latter is perpendicular to it. When the tablet is viewed normally between crossed polaroids and rotated in its own plane, two positions of extinction are obtained; in both these positions, when an extended source of light is viewed through the combination, a dark straight isogyre is seen crossing the field from end to end. It follows that the plane of observation marked

out by this isogyre contains two of the principal optical vibration directions, while the third is perpendicular to it. In other words, the symmetry plane containing two of the principal vibration directions is normal to the face of the tablet, while the other principal vibration direction coinciding with the two-fold rotation axis lies in that face. Observations made with rhombus-shaped tablets show that the two-fold axis bisects the acute angle of the profile, while the symmetry plane bisects the obtuse angle in it.

The detailed discussion of the theory of twin-plane reflection given by Rayleigh in his pioneer investigation on the subject is based on the assumption that the crystal is feebly birefringent. This however is far from being actually the case for potassium chlorate. The three principal refractive indices of the crystal for sodium yellow light, are given in the literature as 1.5241, 1.5174 and 1.4099, and the crystal is thus strongly birefringent. On the other hand, one would not be far wrong in describing the substance as a close approximation to a uniaxial crystal in its optical behaviour. The angle between the two directions of single wave-velocity is given in the literature as 27° for sodium yellow light.

### 3. The vanishing of the reflection in the symmetry plane

Very simple considerations indicate that the reflection at the twin-plane boundaries should vanish—as is actually the case—when the plane of incidence coincides with the plane of symmetry.

The location of the principal optic directions in the symmetry plane is shown in figure 1, OX and OY referring to the upper side and OX' and OY' to the lower side of a twinning plane. The third vibration direction OZ is perpendicular to the plane of the paper. Since the upper and lower halves of the diagram are mirror images of each other, it follows that the coefficient of reflection at the boundary for any given angle of incidence would be the same whether the incidence is from above or from below. On the other hand, it follows as a consequence of the principle of reversibility that the reflection coefficients should be of opposite sign according as the wave is incident on one side or the other of the boundary. As these two results are inconsistent, it follows that the reflection coefficient should vanish for all angles of incidence and all states of polarisation of the incident light, in the case under consideration.

### 4. The polarisation of the reflection by a twin plane

The foregoing result may be interpreted physically in terms of the polarisation of the medium produced by the field of the light wave traversing it. If the vibration be perpendicular to the plane of symmetry, the polarisation is obviously the same on both sides of the boundary; there being no discontinuity, there is no reflection. The same situation subsists when the direction of vibration is in the symmetry

plane and the incidence is normal. For oblique incidences, the polarisation does indeed exhibit a discontinuity at the boundary, but this lacks a component transverse to the direction of travel of a reflected wave and hence there is no reflection.

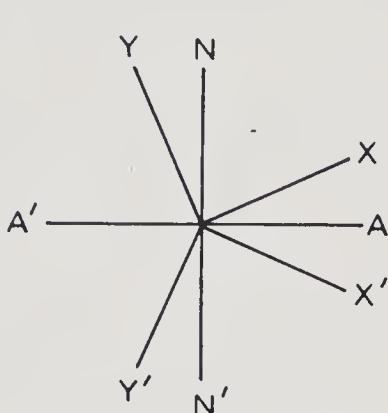


Figure 1

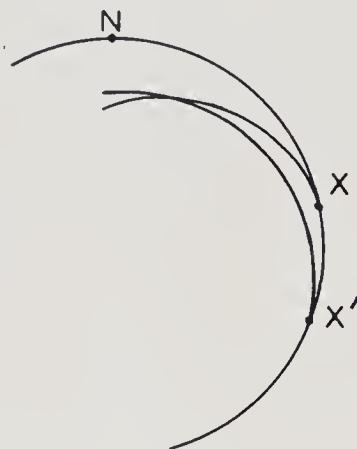


Figure 2

The foregoing considerations assist us to derive in a very simple manner the characters of the reflection at the composition plane of twinning when the direction of travel of the incident light-waves in the medium does not lie in the symmetry plane but makes a small angle with it. The latter condition allows the azimuths and obliquities of incidence to be varied subject only to the restriction that if the azimuthal angle is large, the angle of incidence should be small. In all such cases, the reflection would necessarily be weak and the incident and transmitted waves would therefore differ but little in amplitude. The corresponding directions of vibration would however be different on the two sides of the boundary, and the reflection occurring at the latter would be the result of a sudden change in the direction of the polarisation at the boundary and not of a discontinuity in its magnitude.

In figure 2, the normal to the boundary and the principal vibration directions OX and OX' on either side of it are shown as points N, X, X' on a great circle. Two other great circles have been drawn through X and X' containing respectively the directions of travel of the incident and transmitted waves. These circles cut each other at a small angle and the possible directions of vibration may be assumed to be either parallel or perpendicular to them, since the optical behaviour of potassium chlorate closely approximates to that of a uniaxial crystal with OX or OX' as the optic axis. The vector difference in the polarisation on the two sides of the boundary which results in a reflection is transverse to the mean direction of the polarisations due to the incident and transmitted waves. Hence, we deduce

that if an ordinary wave is incident on the twin-plane boundary, it is reflected as an extraordinary wave and *vice versa*.

The validity of the result stated above is restricted to the cases considered in which the twin-plane reflection is weak in comparison with the incident and transmitted waves. More generally, a discontinuity in magnitude as well as in direction of the polarisation at the boundary would have to be considered. There would then be both an ordinary and an extraordinary reflected wave and not merely one or the other. If, for example, the plane of incidence is perpendicular to the symmetry plane, only in the particular case of nearly normal incidence of the light, and not at all incidences, could we expect the special law of polarisation stated above to be valid.

### 5. The case of nearly normal incidence

As already remarked, potassium chlorate is strongly birefringent and the refractive indices for waves incident nearly normally are very different for the two possible directions of vibration, namely, 1·52 and 1·47. In these circumstances it is distinctly surprising that the crystals give at such incidences, a single sharply defined monochromatic reflection or a series of such reflections. The reason for this is to be found in the special law of polarisation shown above to be valid for such incidences. Considering a pencil of light incident on the crystal, it divides into two beams travelling with very different velocities, the ordinary ray with the lower velocity and the extraordinary ray with the higher velocity. However, the ordinary ray is reflected at the successive twin boundaries and travels backwards as an extraordinary ray with the higher velocity, while similarly the extraordinary ray is reflected and travels back as an ordinary ray with a lower velocity. Hence the total light path is to a very close approximation the same in both cases, and we observe sharply defined monochromatic bands in the spectrum of the reflected light which give no indication that the stratifications giving rise to them are of a strongly birefringent material.

### 6. Explanation of the triplet bands

The situation stated above is radically altered when the light is incident obliquely in a plane perpendicular to the symmetry plane. For, in this case, an ordinary wave travelling downwards is reflected back both as an ordinary wave and as an extraordinary wave, while similarly the extraordinary wave is reflected back both as an ordinary wave and as an extraordinary wave. Hence we have four distinct trains of reflected waves, the light paths traversed by the first two of which are so widely different that we can expect them to manifest themselves independently in the spectrum of the reflected light, viz., (i) incident and reflected as ordinary

waves, (ii) incident and reflected as extraordinary waves, and (iii) and (iv) incident as ordinary and reflected as extraordinary waves or vice versa. For the reasons stated above, the first and the second groups may be expected to appear as monochromatic reflections well removed from each other on either side of a central group comprised of the third and fourth set of reflections. These outer components would be of vanishingly small intensities when the incidence is nearly normal, but would gain in this respect as the incidence is made more oblique. The third and fourth groups would by reason of the geometric symmetry, have identical optical paths and would therefore not be spectroscopically separable.

### 7. Explanation of the doublet bands

The case in which light is incident obliquely in an azimuth nearly coinciding with the symmetry plane may now be considered. Here, as we have seen, an ordinary wave is reflected only as an extraordinary wave and vice versa. The light paths however lie on opposite sides of the normal to the face of the crystal. Hence, unless the alternate components of twinning are all of equal thickness, the total light path of a wave entering as an ordinary and reflected back as an extraordinary wave would not be the same as that of a wave entering as an extraordinary and reflected back as an ordinary wave. In these circumstances, the wavelengths for which the reflections reinforce each other would not be the same in the two cases, and the monochromatic reflection observed at nearly normal incidences would split into a doublet, and the doublet separation would increase progressively with increasing obliquity of incidence. As the reflections are weak, the components of the doublet may be expected to be fairly sharply defined. A further remark may be made. Since the appearance of the doublet is a consequence of the optical paths on the two sides of the normal being different, a rotation of the crystal through  $180^\circ$  about the normal should result in a reversal of the situation; the extraordinary and the ordinary reflections would interchange their positions in the spectral doublet when the crystal is rotated through  $180^\circ$ .

### 8. Some observational facts

We now return to the theoretical result deduced in section 4 above, viz., that in certain circumstances an ordinary wave incident at a twin plane boundary is reflected as an extraordinary wave and vice versa. An observational test of this may be readily made. A bright source of light is viewed by reflection in the crystal set at such an azimuth that the coloured reflection vanishes and the setting is then altered a little so that it reappears. It is then found that if the incident light be unpolarised, the reflected light is also unpolarised, indicating that the reflection

coefficients are equal for the ordinary and the extraordinary waves. If however the incident light is plane-polarised in such manner that only either the ordinary ray or the extraordinary ray traverses the crystal, the coloured reflection is also plane-polarised but in a reciprocal fashion; it is quenched if the polariser and analyser are set in parallel positions, but comes through if they are crossed.

As is well known, a strongly birefringent crystal transforms a beam of plane-polarised light traversing it into elliptically polarised light which would not be quenched by an analyser set in any position. In the particular case under consideration, however, this difficulty does not arise, since the plane of incidence is nearly coincident with the symmetry plane of the crystal which contains two of the optical vibration directions while the third is perpendicular to it; the ellipticity introduced in these circumstances is therefore negligible. Its disturbing effect can however be made evident by setting the polariser so that the vibration direction is neither parallel nor perpendicular to the plane of incidence. It is then found that the reflection cannot be quenched at any setting of the analyser.

The foregoing considerations suggest that for a complete study of the laws of twin-plane reflection at all azimuths of incidence, it is necessary to use very thin plates in which the iridescent layer is not overlaid by untwinned material. Observations made with such crystals further confirm the theoretical results deduced in section 4 above and show that in the particular case when light is incident in a plane perpendicular to the symmetry plane, the special law of polarisation is only valid if the incidence of light on the crystal is nearly normal. The observations suggest that at more oblique incidences the vibration in the reflected light is neither parallel nor perpendicular to that in the incident waves. Such a result becomes readily intelligible when it is recalled that at such incidences the reflected light includes both an ordinary and an extraordinary component and not merely one or the other (*vide* section 6 above).

In his theoretical paper on the reflection of light at a twin-plane in a crystal, Rayleigh showed that when the plane of incidence is perpendicular to the plane of symmetry, the polarisation of the reflected ray would be reversed in the act of reflection; in other words if the incident light is polarised in the plane of incidence, the reflected light would be polarised in the perpendicular plane and vice versa. The theoretical derivation was based on the assumption that the birefringence of the crystal is very weak. This assumption is however not in agreement with the facts for the case of potassium chlorate. It is therefore not surprising that Rayleigh was unable to confirm the theoretical prediction by observations except in the particular case of nearly normal incidence.

## 9. Polarisation of the spectral components

The remarks in the foregoing section refer to the behaviour of the reflected light when examined without the aid of spectral analysis. We shall now pass on to

consider the very interesting polarisation effects exhibited by the spectral components of the reflected light in various cases. The facts of observation will be succinctly described and the reader will have no difficulty in verifying that they afford a striking confirmation of the origin of the spectral components given earlier in this paper. It should be understood that the circumstances of observation are invariably those described in the second paragraph of section 4. When reference is made to a polariser or an analyser, it is to be understood that their vibration directions are set such that they are either parallel or perpendicular to the plane of incidence as the case may be.

*The case of nearly normal incidence:* The unresolved maximum in the spectrum of reflected light is unpolarised if the incident light is unpolarised. If the incident light is polarised, the unresolved maximum is polarised in the *reverse* fashion and is therefore extinguished by an analyser set *parallel* to the polariser.

*The triplet bands:* The outer components of the triplet described in section 6, when observed with incident unpolarised light are found to be plane-polarised in two mutually perpendicular directions. One or the other component is extinguished when viewed through an analyser appropriately set. If the incident light is polarised in one or another of two perpendicular directions, one or the other of the two components is found to be extinguished. The surviving outer component is also extinguished if viewed through an analyser in the *crossed* position. The central band of the triplet behaves in a fashion similar to the unresolved maximum referred to above in the case of normal incidence.

*The doublet bands:* With incident unpolarised light, the components of the doublet described in section 7 are plane-polarised in mutually perpendicular directions. In this case, if the crystal be turned round through  $180^\circ$ , the planes of polarisation of the two components are interchanged. With incident polarised light, one or the other component is extinguished. The surviving component is also extinguished if the analyser is set *parallel* to the polariser.

## 10. Description of the plates

The spectra reproduced in plates I and II illustrate the polarisation effects briefly described above. They were obtained with the crystals designated as A, B, C and D in part I of the present series of papers and whose spectra were illustrated in the plates accompanying that paper. For convenience of reference the crystal used and the setting in which it was placed have been entered at the head of each vertical column in plates I and II. In setting I, the plane of incidence was

normal to the plane of symmetry and the angle of incidence was small. In setting II, the plane of incidence was nearly coincident with the plane of symmetry and the angle of incidence was large. P entered in the horizontal row of the figure denotes that the incident light was polarised, but that no analyser was employed, while A denotes that the incident light was unpolarised while the reflected light was analysed. If both P and A are entered, it signifies that incident light was polarised and that the reflected light was analysed. The angle which the direction of vibrations of the polariser and the analyser respectively, make with the plane of incidence have been entered after the letters P and A.

The following special remarks may be made.

*Figure A I:* The pictures of this crystal with polariser or analyser alone have not been reproduced as they were all similar to each other. The picture appearing in plate I was taken with both polariser and analyser. Notice that the reflection is weak when the polariser and analyser are parallel and strong when they are crossed.

*Figure A II:* Note the change in spectral width and the spectral shift of the reflection with the change in position of the vibration direction of the polariser or the analyser alone. Note also that the reflection vanishes when the polariser and analyser are parallel and that it appears when they are crossed.

*Figure B I:* Note the plane polarisation of the outer components of the triplet and fact that they almost disappear when the polariser and analyser are crossed and that one or the other of the outer components reappears strongly when they are parallel. The central band becomes very weak when they are parallel, whereas it comes out strongly when they are crossed.

*Figure B II:* Note the nearly perfect polarisation of the components of the doublet and that one or the other appears when polariser and analyser are crossed whereas both of them disappear when they are parallel.

*Figure C I:* The same remarks given for figure B I apply to this figure also.

*Figure C II:* The same remarks given for figure B II apply to this figure also.

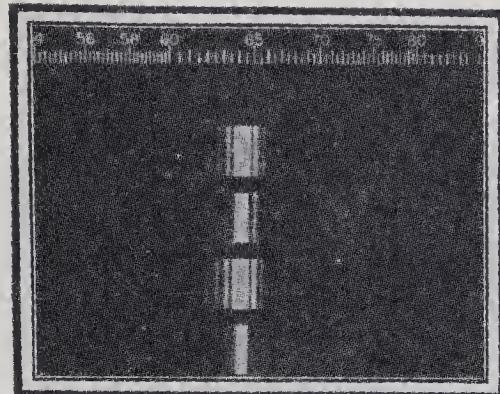
*Figure D I:* The outer components of the triplet are themselves double. Otherwise the same remarks apply to this figure as in the case of figures B I and C I.

*Figure D II:* Each of the components is now double and the two subsidiary components behave in opposite ways. Otherwise the remarks are the same as in the case of B II and C II.

## 11. Summary

A simple explanation is given why the reflections vanish when the light is incident in the symmetry plane of the twinned crystals. Physical considerations enable the law of polarisation for twin-plane reflections to be derived for directions of incidence adjoining the plane of symmetry. It is further shown that the spectral character of the reflections stands in the closest relationship with the polarisation law thus derived. An explanation is given for the appearance of doublets and triplets respectively in the spectra observed when the incidence is oblique and the azimuth of such incidence is nearly zero and  $90^\circ$  respectively. It is a necessary consequence of the theory that the outer components in these two cases should be plane-polarised, in one case in the reciprocal fashion and in the other case normally. The theoretical results are strikingly confirmed by observations on the polarisation of the spectral components. Photographs are reproduced illustrating these effects.

A I



(1)

P0 A90

P0 A0

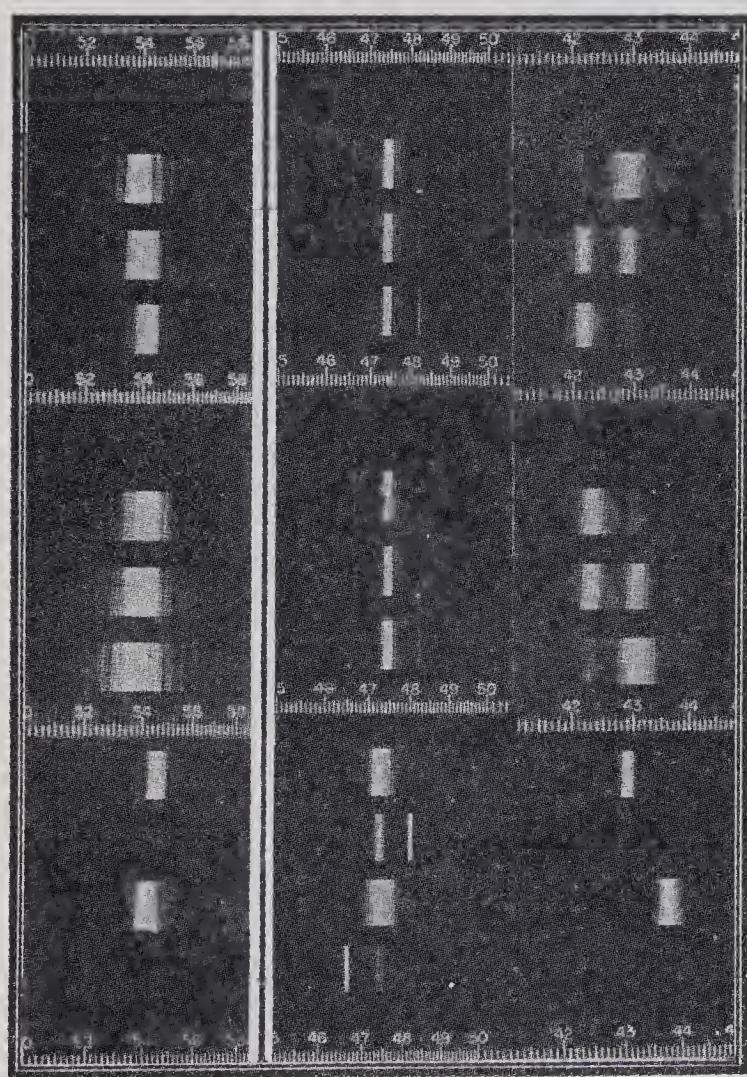
P90 A0

P90 A90

A II

B I

B II



(2)

P90

P45

P0

A90

A45

A0

P0 A90

P0 A0

P90 A0

P90 A90

Figures 1 and 2

Plate I

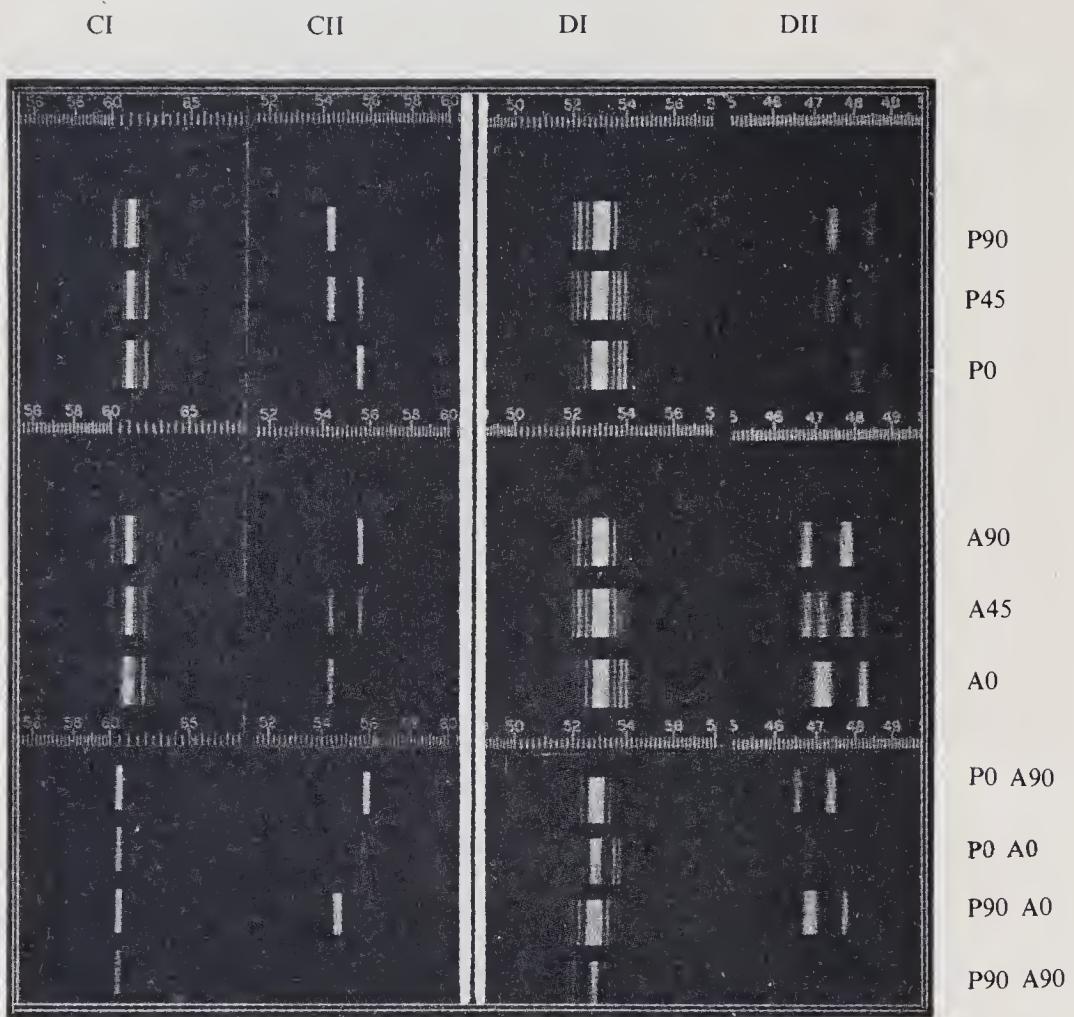


Figure 3

Plate II

## On the iridescence of potassium chlorate crystals— Part III. Some general observations

SIR C V RAMAN and D KRISHNAMURTI  
(Raman Research Institute, Bangalore)

Received November 3, 1952

### 1. Introduction

In the two preceding parts we have discussed the optical behaviour of a few selected crystals which could be regarded as ideal or nearly ideal specimens exhibiting highly monochromatic iridescence. It is not without interest however to consider the subject from a wider standpoint. It is proposed in the present part to report briefly on the optical phenomena observed by us in our studies with a rather extensive collection of specimens. The availability of the material was due to the circumstance that some years ago a chemical manufacturing concern at Bangalore was engaged in the large-scale production of potassium chlorate. Arrangements were made with them for a systematic collection of the iridescent crystals that occasionally formed in the crystallising vats.

A good way of exhibiting a collection of the iridescent crystals is to place the same on a flat circular disc of black glass held horizontally and which could be rotated about a vertical axis. The reflected colours can be viewed under the diffuse illumination provided by a large window. The variety and brilliance of the tints and their rapid change with the obliquity of observation then become strikingly evident; and the disappearance and the reappearance of the iridescence of each specimen twice in each revolution of the disc can also be exhibited. This arrangement, however, does not eliminate the dilution of the iridescence by the reflection of white light from the two surfaces of the crystal. This can only be secured by mounting the plates in Canada balsam between two prisms of glass. The liveliness of the colours is thereby vastly improved and the arrangement is also suitable for exhibiting the transmission colours in a very striking manner. It is also the most suitable arrangement for a critical spectroscopic study of the reflected or transmitted light. The simple technique of immersing the specimen in a watch glass containing xylene, the outside of which has been dead-blacked, however suffices for a rapid visual examination of numerous specimens. Indeed it may be used also for obtaining a photographic record of their spectra.

## 2. Characters of the iridescence

The majority of the specimens are rhombus-shaped tablets, but hexagonal-shaped plates are also not infrequently met with. An impressive feature is the fact that though the individual crystals exhibit the widest diversity of colours by reflection, such colour is usually quite uniform over the area of a particular crystal. Occasionally however, one finds plates which exhibit iridescence of one colour over part of the area and either no iridescence at all or else an iridescence of a different colour or intensity over the rest of it; the dividing line between the two parts in such cases is usually sharp but rather wavy. Straight boundaries are however occasionally observed.

It is possible at first sight to believe that a particular specimen is non-iridescent and yet to discover on closer examination that it exhibits the characteristic reflections. This can happen, for instance, when the reflection is at the violet end of the spectrum at nearly normal incidence and moves out of the visible with oblique observation. It may also happen that the crystal has a series of monochromatic reflections in the visible spectrum the integrated effect of which is merely white light. There are cases also where the characteristic reflection moves into the visible spectrum and results in visible colour only when the crystal is viewed obliquely.

A systematic examination of the specimens was made to find whether any of the tablets have stratifications so fine that the first order reflection appears only in the ultra-violet. These were looked for by photographing a continuous spectrum of white light transmitted obliquely through the specimen. Though many crystals were examined, no such case was met with. *Prima facie* there seems to be no reason why such fine stratifications cannot appear, and it is possible they were not found merely because they had been passed over when the material was collected. On the other hand, crystals were forthcoming with stratifications so widely spaced that thirteen successive orders of reflections are observed between  $\lambda 6600$  and  $\lambda 3200$ . This would mean that the order actually observed at the red end would be the twelfth, the first order being far out in the infra-red and that the actual spacing of the stratifications would be about  $2.7 \mu$ . On the other hand, a crystal showing a first order in the violet say at  $\lambda 4200$  would have a spacing of  $0.14 \mu$ .

## 3. Variations of its spectral nature

In plate I, figures 1 to 8 are illustrated the reflection spectra taken at nearly normal incidence of a series of eight crystals, beginning with a specimen which shows a single reflection (probably a first order) at  $\lambda 4275$ , followed by others showing a large number of reflection maxima up to thirteen. It is generally the case that if a crystal exhibits a series of monochromatic reflections, the

monochromatism becomes sensibly more perfect in the higher order reflections seen in the ultra-violet. This feature is readily noticeable in several of the spectra reproduced in plate I. It is also generally characteristic of monochromatic reflections that their intensity is far larger than that of the subsidiary maxima accompanying them, so much so that the latter are recorded only with prolonged exposures. We have however come across several cases in which a crystal gives a series of reflection maxima forming a regular sequence, but in which we do not observe the regularities referred to above. Some examples of this kind are reproduced as figures 6, 7 and 8 in plate I. It will be seen in these three pictures that the reflection maxima are rather diffuse, each of them visibly exhibiting several components distinctly resolved from each other and that the structure of the individual reflections is not always the same. Further, the subsidiary maxima may often attain a notable intensity and show a lack of regularity in their distribution. This feature is very conspicuous in figure 8, plate I. A natural explanation of the facts observed is that the stratifications are not perfectly equidistant in these cases but are subject to errors in spacing which may be either random or periodic.

Another interesting feature which is occasionally noticed is that some of the orders are unusually strong and others unusually weak in comparison with their neighbours, e.g., the reflection at  $\lambda 5800$  appearing in figure 6 in plate I is very strong, whereas the order at  $\lambda 4850$  is weaker than the orders on either side of it. Similarly in figure 4, plate I, the orders appearing at  $\lambda 4350$  and at  $\lambda 4900$  are far stronger than the orders appearing on either side at  $\lambda 3950$  and  $\lambda 5600$  respectively. The latter is so weak that the principal maximum and the subsidiary maxima on either side are of nearly comparable intensity. Another example of the same kind is the reflection appearing at  $\lambda 4130$  in figure 5, plate I, which is much weaker than the orders at  $\lambda 3920$  and  $\lambda 4380$  respectively on either side. One more illustration is furnished by figure 7 in plate I in which the reflection appearing at  $\lambda 4475$  is far stronger than the orders at  $\lambda 4050$  and  $\lambda 5000$  respectively on either side, the latter being extremely weak. A natural explanation for these facts is to be found in the different thicknesses of the alternate layers of the polysynthetically twinned crystal. The ratio of these thicknesses would determine the relative intensity of the different orders of reflection.

#### 4. Multiply-periodic twinning

In the course of our studies also, several examples were met with in which instead of a single series of sharply defined reflection maxima, regularly spaced groups of such reflection maxima were obtained, the successive orders exhibiting almost identically similar features. Four such spectra are reproduced as figures 1 to 4 in plate II. The similarity of the successive groupings is particularly conspicuous in figure 4 in that plate, though it may be readily recognised in the others as well.

In figure 1 in plate II the principal feature observed is a strong band centred at  $\lambda 6000$  with other features on either side of it. The corresponding order in the violet is rather weak and exhibits a strong central band at  $\lambda 4050$  and weak bands at  $\lambda 3820$  and  $\lambda 4350$  respectively which are hardly visible in the reproduction.

Two alternative views may be put forward regarding the structures responsible for such spectra. One is that each specimen contains several separate layers of iridescent material, each of which gives its own series of monochromatic reflections of different orders. While this view cannot be summarily rejected, it is rather difficult to reconcile with all the observational facts and it would, in particular, require a considerable thickness of the crystal to contain all the separate lamellae required by such an explanation. Another view which appears to merit consideration is that the twinning in such crystals is multiply-periodic, in other words, that two or more sequences of equidistant planes exist side by side in the same layer. Such a structure would naturally give rise to complex groups of lines in the spectra instead of a single series of monochromatic reflections.

Finally, mention should also be made of cases which depart still further from the ideal structures giving monochromatic reflections. They give spectra in which the bulk of the intensity is concentrated in particular regions of the spectrum but not in the manner characteristic of regularly ordered stratifications. Examples of spectra of this type are reproduced as figures 5 to 8 in plate II.

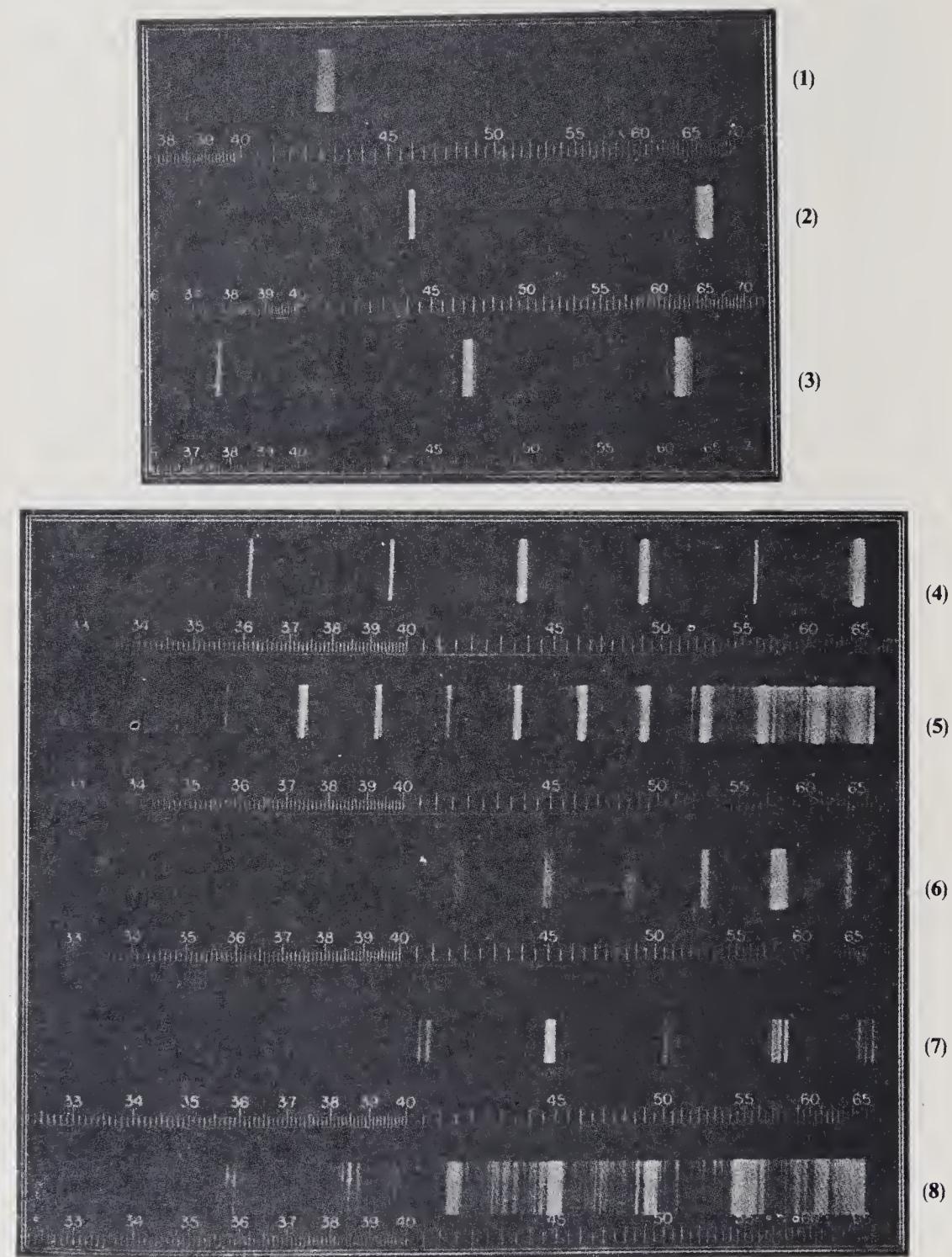
## 5. Summary

The paper describes the results of a study of an extensive collection of material. The spacing of the stratifications giving rise to monochromatic reflections has been found to range from  $2.7 \mu$  to  $0.14 \mu$ . The monochromatism becomes sensibly more perfect in the reflections of higher orders. Variations in intensity from order to order are also noticeable and these are ascribed to the alternate lamellae in the twinning being of different thickness. Instead of a single series of monochromatic reflections, regularly spaced groups of reflection maxima are also observed in some cases. The components in each group of such reflections may be wide apart or else may be closely spaced. The nature of the stratifications in these cases is discussed.

## References (In chronological order)

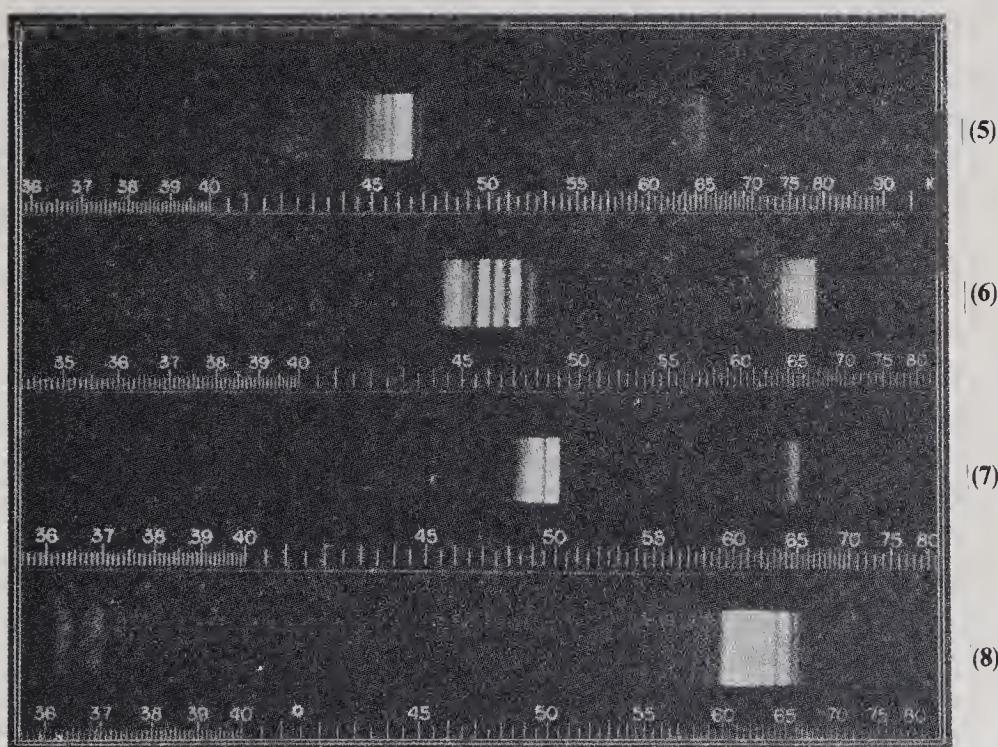
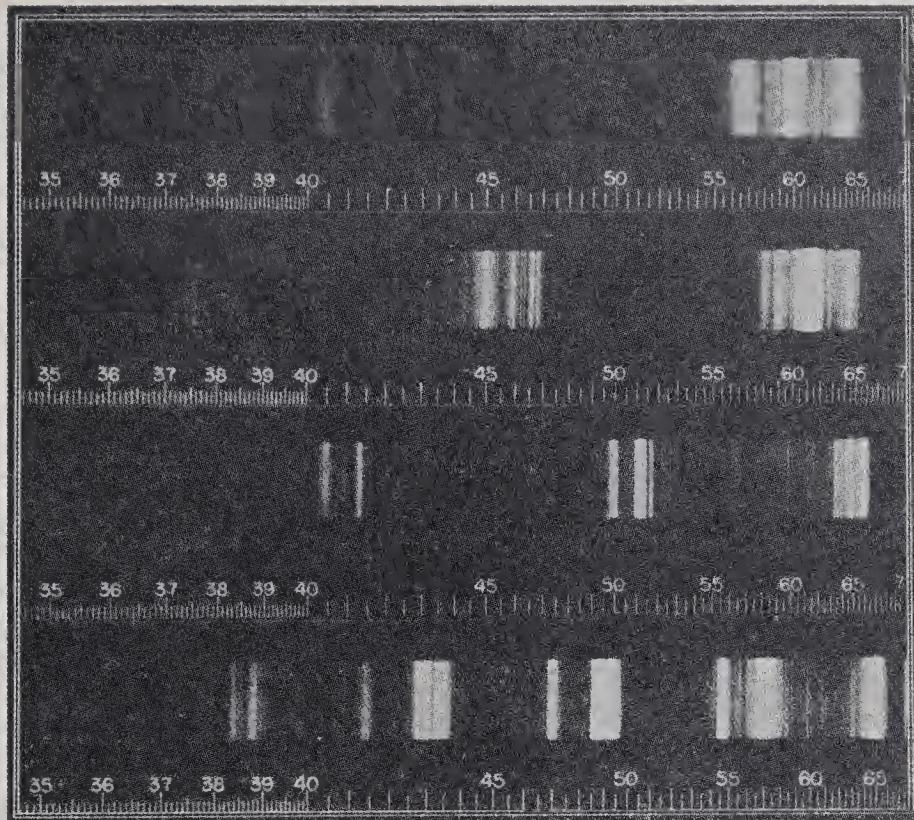
- Stokes G G, *Proc. R. Soc.*, 1885, **38**, 174.
- Rayleigh I, *Philos. Mag.*, 1888, **26**, 241.
- Rayleigh I, *Ibid.*, 1888, **26**, 256.
- Wood R W, *Ibid.*, 1906, **12**, 67.
- Rayleigh I, *Proc. R. Soc.*, 1917, **A93**, 565.

- Ramdas L A, *Proc. Indian Assoc. Cultiv. Sci.*, 1923, **8**, 231.  
Rayleigh II, *Proc. R. Soc.*, 1923, **A102**, 668.  
Subrahmanian R V, *Proc. Indian Acad. Sci.*, 1941, **A13**, 467.  
Ramachandran G N, *Ibid.*, 1942, **A16**, 336.  
Ramachandran G N, *Ibid.*, 1944, **A20**, 100.  
Cairo, Euler and Fricke, *Abh. Braunsch. Wiss. Ges.* 1951, **3**, 21.



Figures 1-8

## Plate I



Figures 1-8

Plate II

## On the polarisation and spectral character of the iridescence of potassium chlorate crystals

SIR C V RAMAN and D KRISHNAMURTI  
(Raman Research Institute, Bangalore)

Received November 27, 1952

### 1. Introduction

In a series of three recent papers in these *Proceedings*, we described and discussed the results of studies made with material selected from the rather extensive collection of iridescent crystals of potassium chlorate at our disposal. In particular, we dealt with the spectral character and polarisation of the iridescence of five selected crystals the optical behaviour of which indicated a high degree of regularity in their structure. Since then, we have made observations with a dozen other crystals of the same kind over a wider range of azimuths and obliquities of incidence than previously. A fairly complete picture of the phenomena has emerged from these studies. It is proposed in the present paper to describe our findings and to illustrate the same by a new set of spectrograms obtained with a typical specimen.

### 2. Some theoretical considerations

Potassium chlorate is a strongly birefringent crystal and the reflections which give rise to the iridescence owe their origin to the fact that the alternate layers of the polysynthetically twinned crystal are orientated differently from the rest. It might seem in these circumstances that a theoretical treatment of the problem would be very complicated. Fortunately, however, there are circumstances which considerably simplify the situation. In the first place, all the layers in the polysynthetic crystal have a common symmetry plane and a common axis perpendicular to it which coincides with the direction of maximum optical polarisability. Then again, while potassium chlorate is actually a biaxial crystal, its optical behaviour is not very different from that of an uniaxial crystal. In dealing with the problem, therefore, one can use the phraseology appropriate to an uniaxial crystal, and speak of an ordinary and an extraordinary beam, the directions of vibration in which are determined by the position of the optic axis

(which is the direction of least polarisability) relatively to the direction of the wave-normal.

A beam of unpolarised light incident on the face of the crystal divides upon entry into two beams of light, viz., the ordinary and the extraordinary beams polarised in perpendicular planes. In the particular case when the directions in which these beams traverse the crystal lie in the symmetry plane, the ordinary and the extraordinary beams retain their character as such in their entire course through the crystal. In such a case, of course, there is no reflection at the twin-plane boundaries. So long as the directions of propagation do not deviate largely from the symmetry plane, we are justified as a first approximation in assuming a similar situation to subsist, viz., that an ordinary beam remains an ordinary one and an extraordinary beam as extraordinary throughout. Similar assumptions may also be made in the same circumstances about the beams of light arising from the internal reflections. In other words, it will be assumed that light reflected as an ordinary or as an extraordinary beam retains this character until its final emergence from the crystal.

As has already been shown in the second of our earlier papers, the state of polarisation of a light beam traversing the crystal and reflected at a twin-plane boundary changes from the ordinary to the extraordinary and vice versa in the act of reflection, irrespectively of the angle of incidence, provided that the directions of the incident and reflected beams do not deviate greatly from the plane of symmetry, and the reflections are in consequence very weak. More generally, an ordinary beam is reflected both as an extraordinary and as an ordinary beam, while similarly an extraordinary beam is reflected both as ordinary and as extraordinary. The strength of the second component relatively to the first in each case would be determined jointly by the azimuth and by the obliquity of incidence, and may reach considerable values if the azimuthal angle as well as the angle of incidence are large.

### 3. Spectral character of the reflections

Thus, in general, we have four sets of reflected beams generated at each of the twinning plates in the crystal and finally emerging from it. For convenience we can refer to them as the  $o-o$ ,  $o-e$ ,  $e-o$  and  $e-e$  reflections, the first letter indicating the state of polarisation in the incident light and the second in the reflected light. In general, also, the total optical path traversed in all these four cases would be different, and hence the wavelength for which the intensity of reflection is a maximum at any given angle of incidence, would be different for these four beams. Thus, in general, we should have four different reflection maxima in the spectrum; all the four would be plane-polarised, but in different ways. Since the ordinary index is substantially greater than the extraordinary index, it follows that the  $o-o$  reflection maximum would have the greatest wavelength of the four and that the

$e-e$  reflection maximum would have the smallest. Between them would lie the  $o-e$  and the  $e-o$  reflection maxima.

An explanation is necessary here to indicate why the positions of the  $o-e$  and the  $e-o$  reflection maxima in the spectrum would not in general be identical. The direction of minimum optical polarisability in potassium chlorate makes an angle of  $38^\circ$  with the normal to the surface of the plate. The refractive index of the ordinary ray is approximately independent of the directions of the incident and reflected beams within the crystal. But this is not the case in respect of the extraordinary index, which would be greater for the incident beam and less for the reflected beam or vice versa according as the light is incident on one side or the other of the normal to the plate. The position in this respect is reversed when we consider the alternate layers of the twinned crystal, since in the latter the direction of minimum polarisability is situated on the opposite side of the normal. There is thus a compensation which would be complete if the alternate layers in the polysynthetically twinned crystal are of equal thickness. In such a case the total optical paths for the  $o-e$  and the  $e-o$  reflected beams would be identical, and instead of a quartet of reflection maxima in the spectrum we would in general have only a triplet. There is no reason however for assuming that the periodic twinning of the crystal is always or even frequently of the special type referred to above. A regular periodic twinning is consistent with the alternate layers being of different thickness. In such a case it would follow that the total optical path for the  $o-e$  reflection is greater than the path for the  $e-o$  reflection, or vice versa.

#### 4. Some consequences of the theory

The considerations set forth above have several verifiable consequences. In the first place, if the azimuth of incidence is  $90^\circ$ , i.e., if the plane of incidence be normal to the plane of symmetry and the reflections are hence of maximum intensity, the incident and reflected beams lie symmetrically on either side of the normal, and hence the  $o-e$  and the  $e-o$  paths are necessarily identical irrespective of the angle of incidence and the nature of the twinning. Hence it follows that in this particular azimuth and irrespective of the angle of incidence, the  $o-e$  and the  $e-o$  reflections would overlap and the quartet of reflection maxima would be reduced to a triplet.

A second verifiable consequence of the theory is the effect of rotating the crystal in its own plane through two right angles. As the result of such rotation, the directions of travel of the incident and reflected beams with reference to the orientations of the optic axis within each layer of the crystal would be reversed. Hence the  $o-e$  and the  $e-o$  reflection maxima should also reverse their positions in the spectrum and such reversal should take place in a continuous manner, the two reflections approaching each other and coinciding when the azimuthal angle is  $90^\circ$ , and thereafter separating again when the crystal is rotated further. That an interchange between the  $e-o$  and the  $o-e$  reflections is thus brought about would

be indicated by a corresponding interchange in the plane of polarisation of these reflection maxima in the spectrum.

Another verifiable consequence is that the separation of the  $o-o$  and the  $e-e$  reflections of the spectrum would vary from specimen to specimen and in particular cases actually vanish, whereas the  $o-o$  and the  $e-e$  reflections would be widely separated in the spectrum in all cases, and their planes of polarisation would not be reversed when the crystal is turned round through  $180^\circ$ .

It follows from what has been stated earlier that the  $o-o$  and  $e-e$  reflections would vanish completely if the azimuth of incidence is nearly coincident with the plane of symmetry, and this is irrespective of the angle of incidence. Thus, for such azimuths, the quartet of reflections would reduce to a doublet the components of which would be polarised in perpendicular planes, the separation of the components also varying from specimen to specimen. The separation of the doublets should also increase with the angle of incidence. But the simultaneous spectral widening of the reflection maxima would not be very conspicuous in view of the small reflecting power at such azimuths of incidence.

Observed at nearly normal incidence, the  $o-o$  and the  $e-e$  components would vanish in all cases. If in addition the azimuth of observation is  $90^\circ$ , the  $o-e$  and the  $e-o$  components would also coincide. Thus instead of a quartet of reflection maxima, we would obtain a single and fairly sharply defined maximum in the spectrum. At more oblique incidences, the  $o-o$  and the  $e-e$  components would make their appearance; for any given angle of incidence, their intensity would be greatest when the azimuth of observation is  $90^\circ$ , whereas they would vanish when the azimuthal angle is  $0^\circ$  as already remarked. At intermediate azimuths, they may be expected to be visible but less conspicuously. When the azimuth of incidence is  $90^\circ$ , the  $o-e$  and the  $e-o$  components would appear overlapping each other in the same position. Hence at this azimuth the single sharp maximum which is seen at nearly normal incidence alters into a triplet when the incidence is made more oblique.

From what has been stated above, it follows that neither at an azimuth  $0^\circ$  nor at an azimuth  $90^\circ$  would the quartet of reflection maxima indicated by the theory be observable. The most favourable case for viewing it is when the azimuth of incidence is neither too small nor too large, and the incidence should also be fairly oblique, as otherwise the separation of the  $o-e$  and the  $e-o$  components may be too small to be detectable.

## 5. Description of the spectrograms

The various features set forth above are illustrated in the series of spectrograms reproduced as figures 1 to 4 in plate I and as figures 1 to 4 in plate II. These were recorded with a crystal which at nearly normal incidence exhibited a highly monochromatic iridescence at  $\lambda 5665$  with a spectral width of about 25 A.U. A

reflection of higher order is recorded at the same incidence at  $\lambda 4280$  while a reflection of lower order comes into view at the extreme red end of the spectrum at oblique incidences. From these facts it is readily deduced that the reflection at  $\lambda 5665$  is of the third order. The actual values of the azimuthal angle of incidence ( $\phi$ ) measured from the plane of symmetry and of the obliquity of incidence ( $\theta$ ) measured from the normal to the surface are indicated against each of the spectrograms in the figures.

Figure 1 in plate I reproduces a series of seven spectrograms taken at an azimuthal angle of about  $5^\circ$ , the angle of incidence increasing in steps from  $5^\circ$  to  $65^\circ$ . It will be seen that the reflection maximum is recorded as a doublet the components of which drift apart from each other and also towards shorter wavelengths with increasing obliquity. If the increasing dispersion of the instrument in the region of shorter wavelength is taken into account, it will be seen that there is hardly any increase in the spectral width of each component with increasing obliquity of incidence. Fairly large exposures of the order of half an hour had to be given to record the doublets. This exposure, though considerable, fails to bring out the true secondary spectrum. Figure 2 in the same plate exhibits the polarisation of the doublet. The two spectrograms in the figure were recorded with equal exposures, a nicol being placed in front of the slit of the spectrograph with its vibration directions respectively vertical and horizontal. It will be seen that in the one case the component on the longer wavelength side has been extinguished while in the other the component on the shorter wavelength side has disappeared. Figure 3 in the same plate exhibits the reversal in the position of the two components produced by rotating the crystal through  $180^\circ$  in its own plane, the arrangements being otherwise identical with those used for recording figure 2.

Figure 4 in plate I shows the typical quarter spectrum. It will be seen that the two central components are both much wider and much more intense than the two outer ones. The latter indeed remain quite sharp even at oblique incidences whereas the former have widened out notably. A whole series of subsidiary maxima can be distinctly seen in the spectrograms recorded at the more oblique incidences. In the same figure the central doublet of the reflection of the higher order has come out weakly in two of the spectrograms, and it will be seen that they are much sharper and more clearly separated than in the lower order reflection.

The seven spectrograms reproduced as figure 1 in plate II were recorded at an azimuthal angle of  $60^\circ$ . It will be seen that the increased azimuthal angle has brought about a notable increase in the intensity of the outer components as well as a diminution in their sharpness. Likewise, the two central components have broadened out so much so that at moderate obliquities they are hardly separated from each other. The separation is however clearly seen in the second order reflection appearing near the violet end of the spectrum. At the more oblique incidences the two central components though greatly broadened, are clearly separated. They are however so broad that they have masked the outermost

components. The secondary maxima are clearly seen in many of the spectrograms.

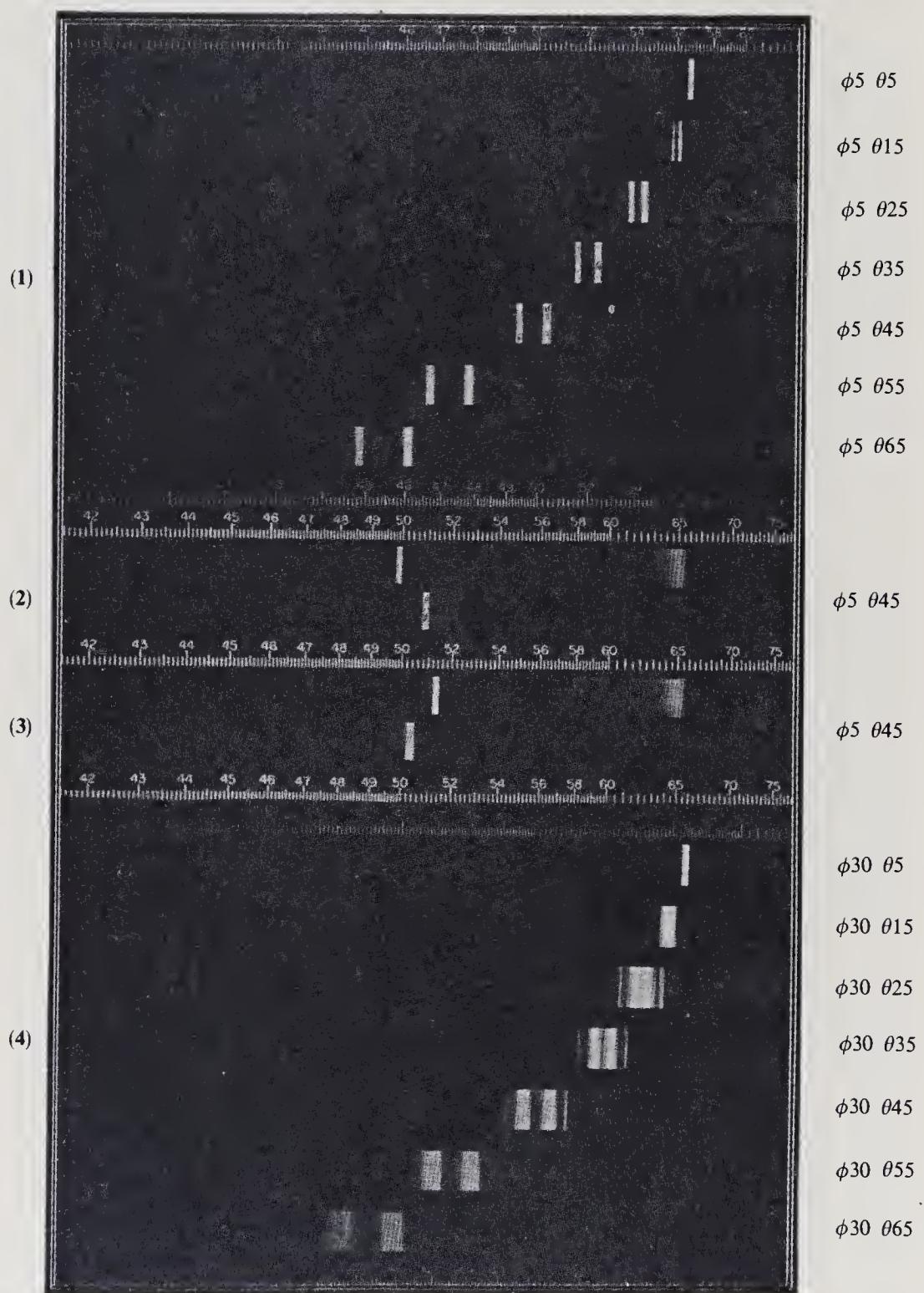
Figure 4 in plate II shows the triplet spectrum recorded at an azimuthal angle of  $90^\circ$ . The appearance of the outer components and the increase in their intensity and width as well as of the central component at increasing obliquities of incidence are clearly shown. Figure 2 in the same plate exhibits the polarisation of the outer components of the triplet and the lack of polarisation in the central component. The spectrograms shown in that figure were recorded by placing a nicol in front of the slit of the spectrograph with its vibration directions respectively vertical and horizontal and giving equal exposures. Figure 3 was recorded under identical conditions except that the crystal was turned round in its own plane through  $180^\circ$ . It will be noticed that the components have now *not* interchanged their positions.

## 6. Summary

It is shown from theoretical considerations and confirmed by the spectrograms reproduced in the paper that the sharply defined monochromatic reflection observed at nearly normal incidences splits up into a quartet in the general case of any arbitrary azimuth and obliquity of incidence. The outer components disappear thereby reducing the quartet into a doublet when the azimuthal angle is small. But if the azimuthal angle be  $90^\circ$  the two central components merge and the quartet reduces to a triplet. When the crystal is rotated in its own plane the two central components of the quartet come together, overlap and move out again in the same direction, thereby giving rise to a reversal of their polarisation characters. They owe their origin to the alternate layers of the polysynthetically twinned crystal being of unequal thickness.

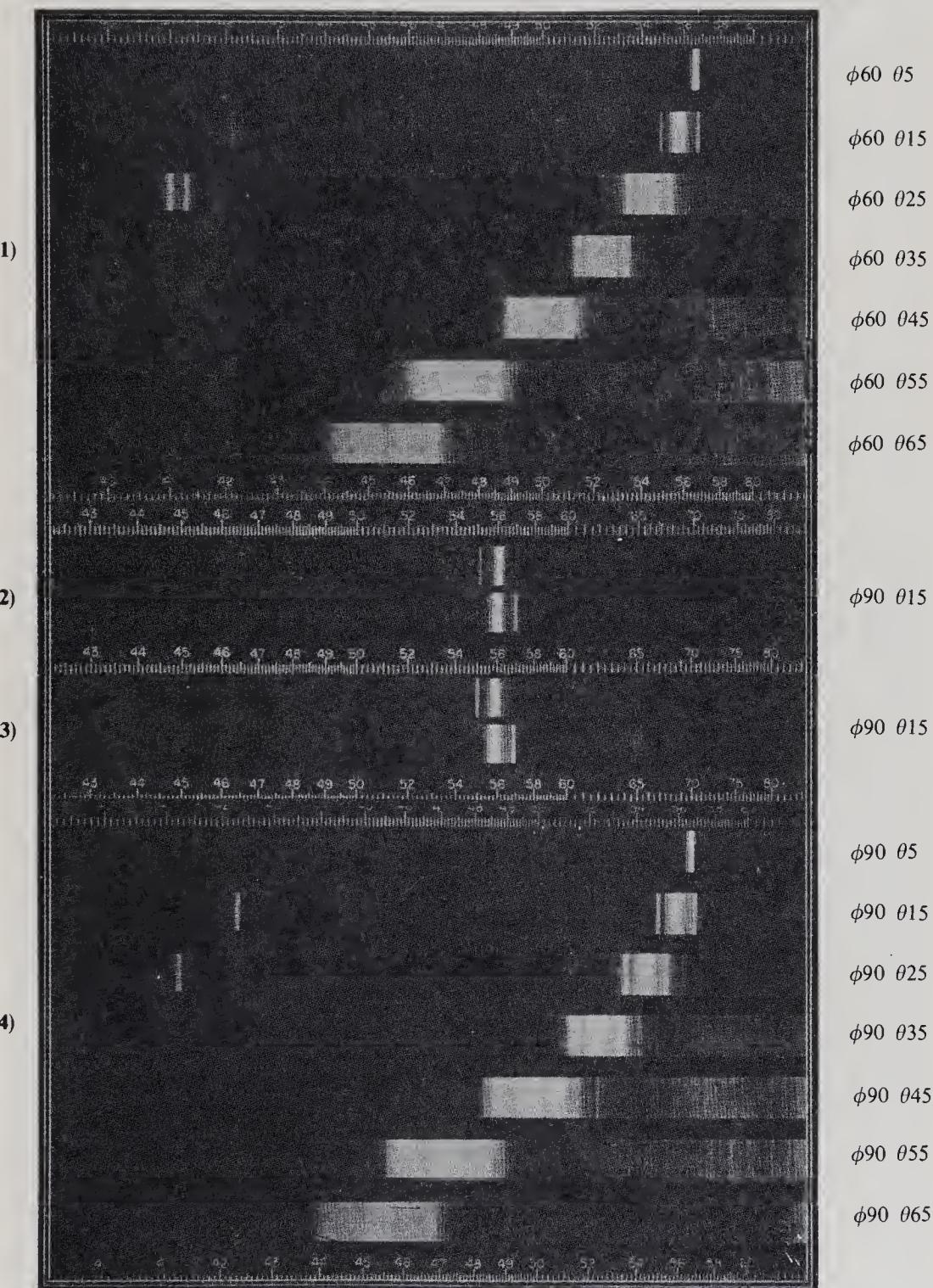
## References

Raman C V and Krishnamurti D, *Proc. Indian Acad. Sci., A* **36**, 315, 321, 330, 1952.



Figures 1-4

Plate I



Figures 1-4

## Plate II

## The structure and optical behaviour of iridescent crystals of potassium chlorate

SIR C V RAMAN and D KRISHNAMURTI  
(Raman Research Institute, Bangalore)

Received September 20, 1953

### 1. Introduction

The iridescent crystals of potassium chlorate which exhibit monochromatic extinctions and reflections form admirable material for a study of the optical behaviour of regularly stratified media. The fact that we had at our disposal a fine collection of these crystals led us to undertake a thorough study of the phenomena which they exhibit, and this brought to light a feature of importance which had been overlooked by the earlier investigators in the field, viz., the variation of the spectral character of the iridescent reflections with the azimuth of the plane of incidence, and also revealed the existence of discrete polarised components in the spectra of such reflections. Our findings were reported in a memoir published in the November 1952 issue of these *Proceedings*. Shortly afterwards we found it possible to develop theoretical considerations which satisfactorily accounted for the facts. These, together with some further experimental results, were published in the following issue of the same *Proceedings*. A summarising article also appeared in *Current Science* for December 1952.

Fresh developments have since resulted from further investigations undertaken by us. The most striking of the new results which we wish to report in the present paper is the discovery of the *geometric patterns of reflection and extinction* which iridescent crystals of potassium chlorate exhibit when an extended source of monochromatic light is viewed by reflection at or transmission through the crystals. Typical examples of such patterns are reproduced in figures 3 to 10 in plate II and plate III accompanying the paper. They show at a glance the whole group of phenomena reported in our earlier papers. Two further topics of interest are also dealt with in the present paper. A study of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope with monochromatic light reveals a rich variety of forms which are of interest in themselves and also help to elucidate the structure of the polysynthetic

twins. Finally, the paper also records the interesting fact that the iridescent crystals of potassium chlorate function as diffraction gratings and give polarised spectra when traversed by a beam of light in a direction parallel to the composition planes of twinning.

We have thought it advisable in preparing this paper to deal with the subject in such manner that it would be intelligible even to one who had not studied our earlier publications.

## 2. The structure of the polysynthetic twins

Potassium chlorate is a strongly birefringent crystal belonging to the holohedral class of the monoclinic system and possessing a two-fold axis of symmetry as well as a plane of symmetry normal to that axis. The crystals are usually forthcoming in tablet-shaped forms. Examination of an untwinned crystal of that form on the stage of a polarising microscope makes it evident that the faces of the tablets contain the two-fold axis of symmetry and are perpendicular to the plane of symmetry. The iridescent crystals also appear in tablet-shaped forms and similar observations made with them indicate that they are polysynthetically twinned in such manner that all the components have a common direction for the two-fold axis of symmetry and a common plane of symmetry, and further that the alternate layers of the structure are so related that they can be obtained one from the other by a rotation of  $180^\circ$  about the normal to the faces of the tablet.

The foregoing description of the iridescent crystals as inferred from their optical behaviour is very elegantly confirmed by the two X-ray diffraction patterns reproduced as figures 1 and 2 respectively in plate I, the first referring to an untwinned crystal and the latter to an iridescent tablet, the crystal in each case having been set precisely normal to the X-ray beam. We are indebted for these beautiful records to Mr A Jayaraman of this Institute. It will be seen that the pattern of the untwinned crystal is symmetric about a line running diagonally across the picture through its centre, and that on the other hand, the pattern of the iridescent crystal exhibits geometric symmetry about two directions, one of which is the same as for the untwinned crystal while the other is perpendicular to it. The number of spots seen in the pattern of the iridescent crystal is, except along the axis of two-fold symmetry of the structure, twice as large as for the untwinned crystal.

## 3. Nature of the twin-plane reflections

The clue to an understanding of the optical effects exhibited by the iridescent crystals is furnished by considerations regarding the intensity and state of polarisation of the light reflected at the composition planes of twinning. Such

reflections cannot arise if the plane of incidence of the light coincides with the plane of symmetry; for, the well-known optical principle of reversibility indicates that the reflection coefficients should be of opposite sign for incidence on the two sides of the boundary, whereas the structures on either side being mirror images of each other, the coefficients should necessarily be the same in both cases—contradictory assertions which are reconcilable only when the coefficient is itself zero. But the reflections would reappear, though only feebly, when the plane of incidence deviates even slightly from the plane of symmetry. Such reappearance being a consequence of a difference only in direction and not of magnitude of the optical polarisations on the two sides of the boundary, there would ensue a rotation of the plane of polarisation of the incident light through  $90^\circ$  in the act of reflection. In other words, a light wave polarised in the plane of incidence would be reflected as a wave polarised in a perpendicular plane; and *vice-versa*. With increasing deviation of the plane of incidence from the plane of symmetry the two streams of light with reversed polarisation thus arising would rapidly gain in intensity, while at the same time the two streams of reflected light polarised in the same manner as the components in the incident light wave, which are absent in the first instance, would come into evidence and ultimately reach a strength comparable with the reflections of the other type. Thus, there would, in general, be four streams of reflected light emerging from the crystal, two with reversed and two with normal polarisation, their relative and absolute intensities being determined by the plane of incidence as also by the angle of incidence in that plane.

#### 4. Spectral character of the reflection

The considerations set forth above enable us to infer the spectral character of the integrated reflection given by the entire crystal when observed with incident white light. For any given angle of incidence, the intensity of reflection would be a maximum for the wavelength at which the reflections by the successive stratifications reinforce each other by reason of agreement in phase. Since there are, as we have seen, four reflected streams of light, there would, in general, be also four wavelengths of maximum intensity in the spectrum resulting therefrom, their positions being determined by the respective optical paths. Each principal maximum would be accompanied by a set of secondary maxima in the region of wavelengths for which the reflections by the successive stratifications only partially reinforce each other. Of the four principal maxima of intensity, two would be polarised in the normal manner and two in the reversed fashion. Their relative intensities would vary with the angle which the plane of incidence makes with the plane of symmetry. When this angle is small, there would only be two maxima of the latter type, while if the angle is large all four would appear with comparable intensities.

It can easily be shown that when the plane of incidence is perpendicular to the plane of symmetry, the optical paths for the two streams of light which emerge after reflection with reversed polarisation would be identical irrespective of the angle of incidence; for, in such a case, considerations of symmetry permit us to exchange the paths of the incident and reflected streams of light and thereby reverse the roles which they respectively play without altering the total optical paths. It follows that two out of the four maxima of intensity of reflection would then overlap and appear in the same position of the spectrum. It can be shown further that if the alternate layers in the twinning are of equal thickness, the optical retardations for the two streams of light emerging after reflection with reversed polarisation would also be identical in all cases. There would then be three maxima of intensity at the most and not four. Thus the presence of four spectral maxima would be evidence that the alternate layers of the twinning are *not* of equal thickness; the greater their difference the wider would be the spectral separation of the components exhibiting reversed polarisation.

## 5. Stratified media in monochromatic light

Instead of allowing a pencil of white light to fall upon the medium in some specified direction and viewing the transmitted or reflected light through a spectroscope, a different procedure which in some respects proves itself to be far more convenient and powerful is to allow diffuse monochromatic light to be incident on the medium simultaneously in all directions and to view the reflected or transmitted light without spectroscopic aid. It is useful in this connection to recall the well known interferences exhibited in similar circumstances of observation by a plane-parallel glass plate, or better still, by a sheet of a birefringent crystal such as mica: interferences appear which in the case of an isotropic plate are concentric circular rings, whereas in the case of a birefringent plate two distinct sets of rings appear which to a first order of approximation are both elliptic in shape. In the case of a regularly stratified medium we are concerned with the integrated effect of the reflections by a whole series of regularly-spaced laminae: their resultant effect would evidently be to give a total reflection in the directions along which all of them reinforce each other by reason of agreement in phase. For any particular order of interference, such directions would lie along the generators of a cone whose cross-sections would be circles if the stratified medium is isotropic, and ellipses if it is birefringent. Since as we have seen, there are four streams of reflected light arising from within the twinned crystal of potassium chlorate, there would be four cones of total reflection of elliptic shape, two having the normal type of polarisation and two of the reversed type. Further, each cone of total reflection would have running parallel to it on either side a series of fainter cones due to the secondary maxima of interference.

Likewise, in the transmitted light we would have for each order of interference, four cones of maximum extinction accompanied by their respective secondaries.

## 6. Geometric patterns of reflection and extinction

Very simple arrangements suffice for observing the phenomena indicated above. A translucent sheet of plexiglass is illuminated from behind by a sodium vapour lamp or alternatively by a mercury arc. The crystal is held as close as possible to the observer's eye or to the lens of the camera. If the illuminated screen be viewed through the crystal, the extinction bands of the latter are seen in the field of view; with sodium light they appear as dark bands on a bright field, while with the mercury arc which is a multichromatic source the extinction bands exhibit subtraction colours. The reflection spectra of the crystal, on the other hand, appear as bright curves on a dark field. With the mercury arc, the reflection patterns for its different radiations are seen well separated from each other; even the patterns due to the two yellow rays are seen clearly resolved. With some of the crystals also, more than one set of reflection and extinction patterns is observed, evidently corresponding to different orders of interference.

A great variety of patterns could be observed visually, their angular dimensions as well as the nature of the pattern depending very much on the particular crystal employed. A characteristic feature observed in all cases is that the pattern vanishes in the symmetry plane of the crystal and is seen with maximum clearness in the perpendicular plane. Besides the primary extinction or reflection bands the secondaries accompanying them could also be seen. The simplest type of pattern and one which is frequently observed is that of two semi-circular crescents facing each other with their tips narrowing to sharp points near their terminations in the symmetry plane of the crystal.

In plate II, figures 3 and 4, we reproduce the extinction patterns and in figures 5 and 6 the reflection patterns for a typical and most general case where, as will be seen from the figures, there are four principal bands. In figures 4 and 6 the portions of the patterns near the symmetry plane are reproduced, while figures 3 and 5 exhibit the portion of the pattern near the perpendicular plane. It will be seen that the two outer bands which have a more or less constant angular separation become sharper and also fade off in intensity as we approach the symmetry plane. On the other hand, the two inner components are most widely separated and also sharper in the vicinity of the symmetry plane: they approach each other and cross at the perpendicular plane.

Of the four components of the extinction and reflection bands, two are polarised with their vibration directions parallel to the symmetry plane and two others perpendicular thereto. This state of affairs is demonstrated by the four photographs reproduced as figures 7, 8, 9 and 10 respectively in plate III, the two former referring to the extinction and the two latter to the reflection pattern of the

crystal. The figures were recorded by placing a polaroid sheet between the wide-angle lens and the photographic film, the polaroid being orientated with its vibration directions respectively parallel and perpendicular to the symmetry plane. It will be seen that in each case two out of the four bands in the pattern have vanished, leaving the other two in possession of the field. It should be mentioned that the birefringence of the untwinned layers of the crystal gave no trouble as they were placed so as to face away from the camera lens while the iridescent layer faced towards it.

It should be mentioned that reflection and extinction patterns of varied character are also observed in monochromatic light using crystals in which the stratifications due to twinning are far from being regular. They are however much less conspicuous than in the case of the specimens possessing a periodic structure which exhibit intense monochromatic iridescence.

## 7. Comparison with the spectroscopic observations

In the plates illustrating our earlier papers, the spectrograms reproduced had been grouped together for each particular crystal so as to exhibit the effect of varying the angle of incidence of the light. This arrangement was not altogether satisfactory, since the effect of varying the azimuth of incidence, keeping the angle of incidence constant is much more interesting from the standpoint of optical theory. The geometric patterns of reflection and extinction observed with monochromatic light exhibit the latter effect in a very vivid manner and we have now found it possible to illustrate the same effect also with the aid of spectrograms in which the angle of incidence is kept constant while the azimuth is varied in steps.

Figures 11, 12, 13 and 14 in plate IV reproduce the spectrograms of the light reflected by a particular crystal. The angle of incidence is progressively increased as we pass from one figure to the next in the series, while in each figure the angle of incidence is kept constant and the azimuth of incidence is varied in steps, commencing from a setting nearly coinciding with the plane of symmetry and ending with one perpendicular to it. Figures 15, 16 and 17 in plate V reproduce similar sets of spectrograms for a second crystal. Figure 18 in plate V refers to a third crystal in which the spectra exhibit the effect of the change of azimuth very clearly and is of particular interest since it was the identical crystal with which the geometric reflection patterns in figures 5 and 6 of plate II have been recorded with sodium light and their polarisation exhibited in figures 9 and 10 of plate III. Comparison of the reflection patterns observed with monochromatic light with the spectral patterns obtained with white light for various azimuths of incidence reveals a remarkably perfect concordance. The transition from a doublet near the plane of symmetry to a quartet and thence to a triplet in the perpendicular plane are shown equally well in both sets of figures. The

variations in the sharpness and intensity of the components and the secondaries accompanying them are also very clearly seen in both.

We should also mention that we have made visual observations of the reflection and extinction patterns of the two other crystals whose reflection spectra have been reproduced in plates IV and V. It will be noticed that the character of the spectra recorded for these two crystals are very different in appearance. Differences of the same nature have also been observed by us in the corresponding reflection and extinction patterns.

### 8. The conoscopic patterns

The interference figures exhibited by twinned crystals in convergent polarised light are of considerable interest and are discussed in some detail in the well known treatise of Pockels on crystal optics. The illustrations of such patterns reproduced as plates in his book appear to have been obtained by the rather artificial procedure of putting a plate of untwinned crystal on the mirror of a Norremberg's doubler; the two components of the synthetic twin thus obtained are necessarily of equal thickness. However, both simple and multiple twins of potassium chlorate are forthcoming in great variety as tablet-shaped crystals, and the material thus available is particularly well suited for such observations. All that is necessary is to mount the crystals with Canada balsam between a microscope slide and a thin cover-slip and to view the same on the stage of a polarising microscope. Two special settings of the specimen are of interest; in one setting the symmetry plane is parallel to the vibration-direction of either the polariser or the analyser, while in the other setting, it bisects the angle between them. In the former setting, a dark isogyre appears along the trace of the symmetry plane, while in the latter this is absent.

As potassium chlorate is strongly birefringent, it is desirable to use the monochromatic light furnished by a sodium vapour lamp, though some features of interest may be seen even with white light. In the observations with monochromatic light the iridescent crystals may be naturally expected to exhibit their extinction patterns superposed on the patterns due to birefringence, and we have found this to be actually the case. The configuration of the extinction patterns is not essentially altered by reason of the observations being made between crossed polaroids. But some curious features are noticeable in and around the regions where the patterns of birefringence and extinction cross each other; into a description of these features we do not propose here to enter.

The conoscopic figures of twinned potassium chlorate assume their simplest form when the crystal consists of only two components. They may then be described as a superposition of the birefringence patterns of the individual components, but as the result of such superposition two other sets of figures are also seen in the field which may be designated as the *differential* and *summational*

*patterns* respectively. If the components of the twin are of equal thickness, the entire pattern is symmetrical with respect to the direction of the normal to the plate. If, on the other hand, the components are of unequal thickness, their individual patterns are naturally different, and their differentials and summationals drift away to one side and the pattern becomes unsymmetrical. In the normal setting of the crystal the differentials are very prominent, while in the diagonal setting the summationals dominate the picture. The former consist of a set of parallel lines, while the latter are closed curves approximately elliptic in shape. The differentials represent interferences of a lower order and may be seen as coloured bands in the appropriate parts of the field with incident white light. The foregoing remarks are illustrated in plates VI and VII for four specimens numbered I, II, III and IV respectively, each in the two settings already specified. For these photographs we are indebted to Mr T K Srinivasan by whom they were recorded in the course of an unpublished investigation at this Institute.

It is not to be expected that the conoscopic figures observed would always be of the comparatively simple types illustrated in plates VI and VII. A form of pattern frequently noticed is that which resembles that of an untwinned crystal, but in which the successive bands exhibit periodic fluctuations of intensity. Four patterns of this type are reproduced in plate VIII. These again were recorded by Mr T K Srinivasan in the course of his examination of numerous specimens with a petrographic microscope. The detailed interpretation of these patterns awaits further investigation.

## 9. The twinned crystals as diffraction gratings

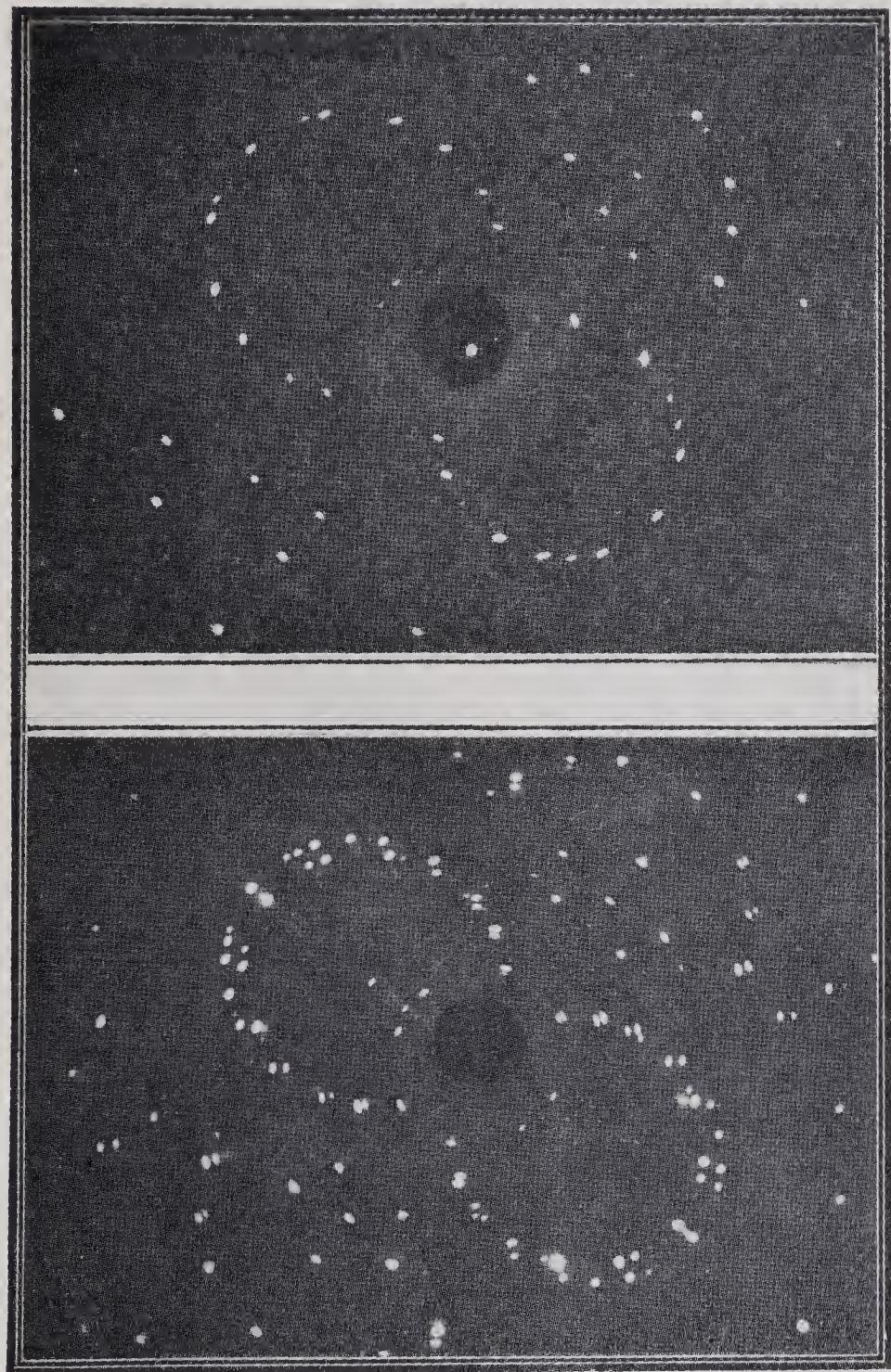
Optical theory indicates that a regularly stratified medium can in appropriate circumstances also function as a diffraction grating and exhibit the phenomena arising therefrom. Several examples could be cited as illustrations of this statement. It is therefore not without interest to record the fact that the polysynthetically twinned crystals of potassium chlorate have actually been observed by us to exhibit such effects. For this purpose it is necessary to use a crystal in which the stratifications are not excessively fine and, in order to eliminate boundary effects as far as possible, to immerse the crystal in a cell containing liquid paraffin or other suitably chosen liquid of which the refractive index approximates to the mean index of potassium chlorate. The crystal is set in the cell in such manner that a pencil of light entering the crystal at one edge and traversing it in a direction parallel to the composition planes of twinning emerges through the opposite parallel edge and is received on an observing screen. The cleavages of potassium chlorate are good and hence with the arrangements described, disturbing effects other than those arising from the lamellar structure of the crystal are not serious.

We have made observations in the manner described above with three specimens and noticed that the emergent pencil of light is spread out by diffraction over a wide range of angles on either side of the direction of the undeviated pencil. With incident white light, coloured spectra are observed, whereas with monochromatic light the field exhibits a great many interference bands with local concentrations of intensity such as would be exhibited by a diffraction grating. The most remarkable feature, however, is that the diffraction bands observed are markedly polarised but in different ways, some concentrations in the field appearing bright for one position of the polaroid while the others disappear and *vice-versa*.

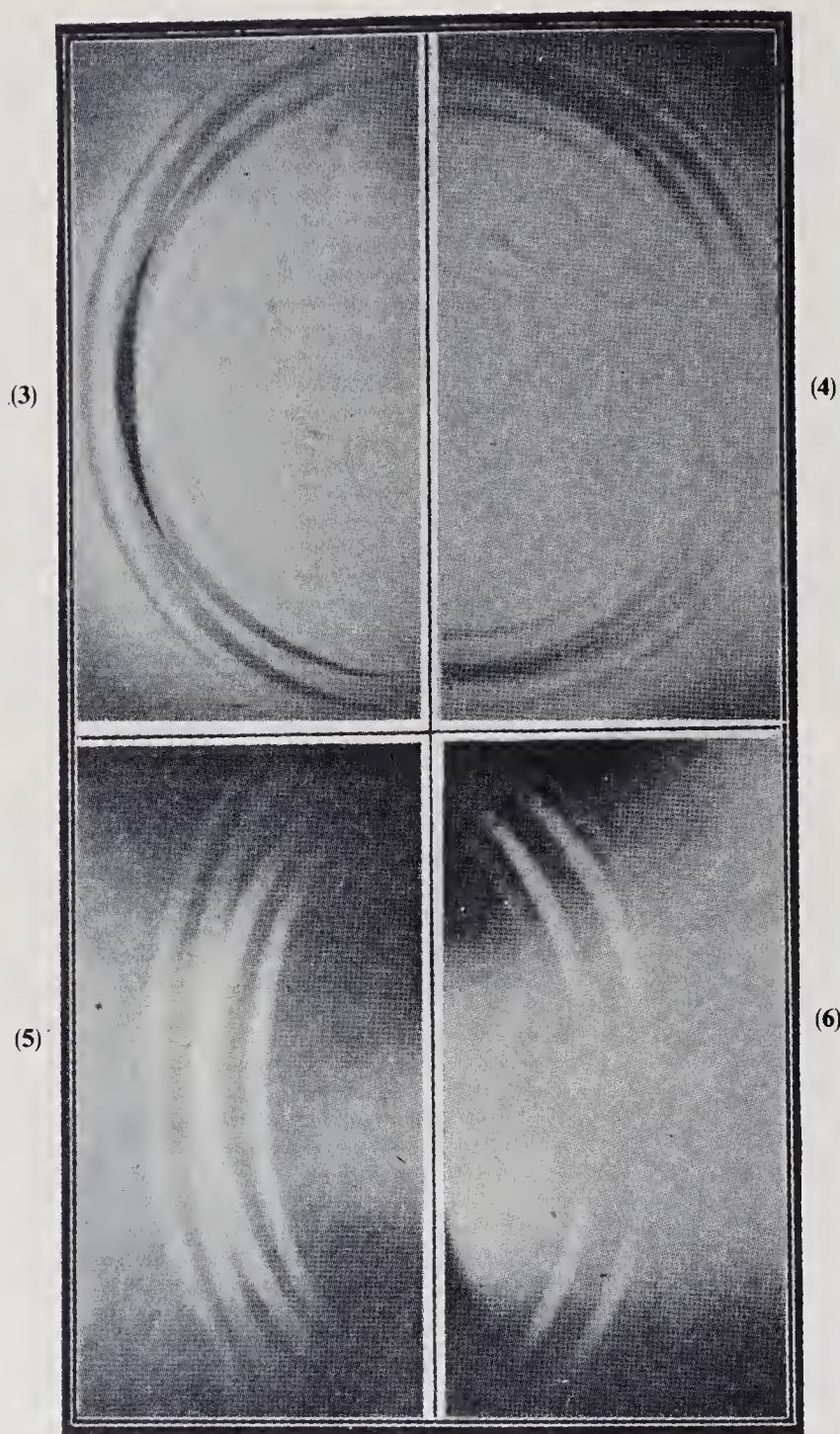
In a general way an explanation of the results observed by us is not far to seek. It is evident that except in the particular case when the light traverses the crystal along the lines of intersection of the planes of the lamination with the symmetry plane of the structure, the alternate layers of the twinning present optically different orientations to the light waves traversing them. As a consequence, the two vibration directions as well as the optical paths of the light wave would be different in the alternate layers. In these circumstances the crystal would necessarily function as a phase-change diffraction grating, the resultant spectra exhibiting polarisation effects of the character observed. Since the path differences involved are fairly large, it is necessary to use incident monochromatic light in order to reveal the resulting phenomena completely.

## 10. Summary

Iridescent crystals of potassium chlorate exhibit geometric patterns of reflection and extinction respectively when a field of diffuse monochromatic light is viewed by reflection at or transmission through the crystal. The patterns consist in general of four closed curves, two of which are polarised with their vibration directions parallel to the plane of symmetry of the crystal and the two others perpendicular thereto. The configuration of the patterns exhibits a perfect concordance with the spectral character of the reflections or extinctions observed with incident white light at corresponding azimuths of incidence and thus furnishes a complete picture of such spectral behaviour. Photographs of the geometric patterns are reproduced with the paper as also of the conoscopic patterns exhibited by the iridescent crystals on the stage of a polarising microscope. The paper also reports the observation that the twinned crystals of potassium chlorate function as diffraction gratings and give polarised spectra when light traverses them along their composition planes of twinning.

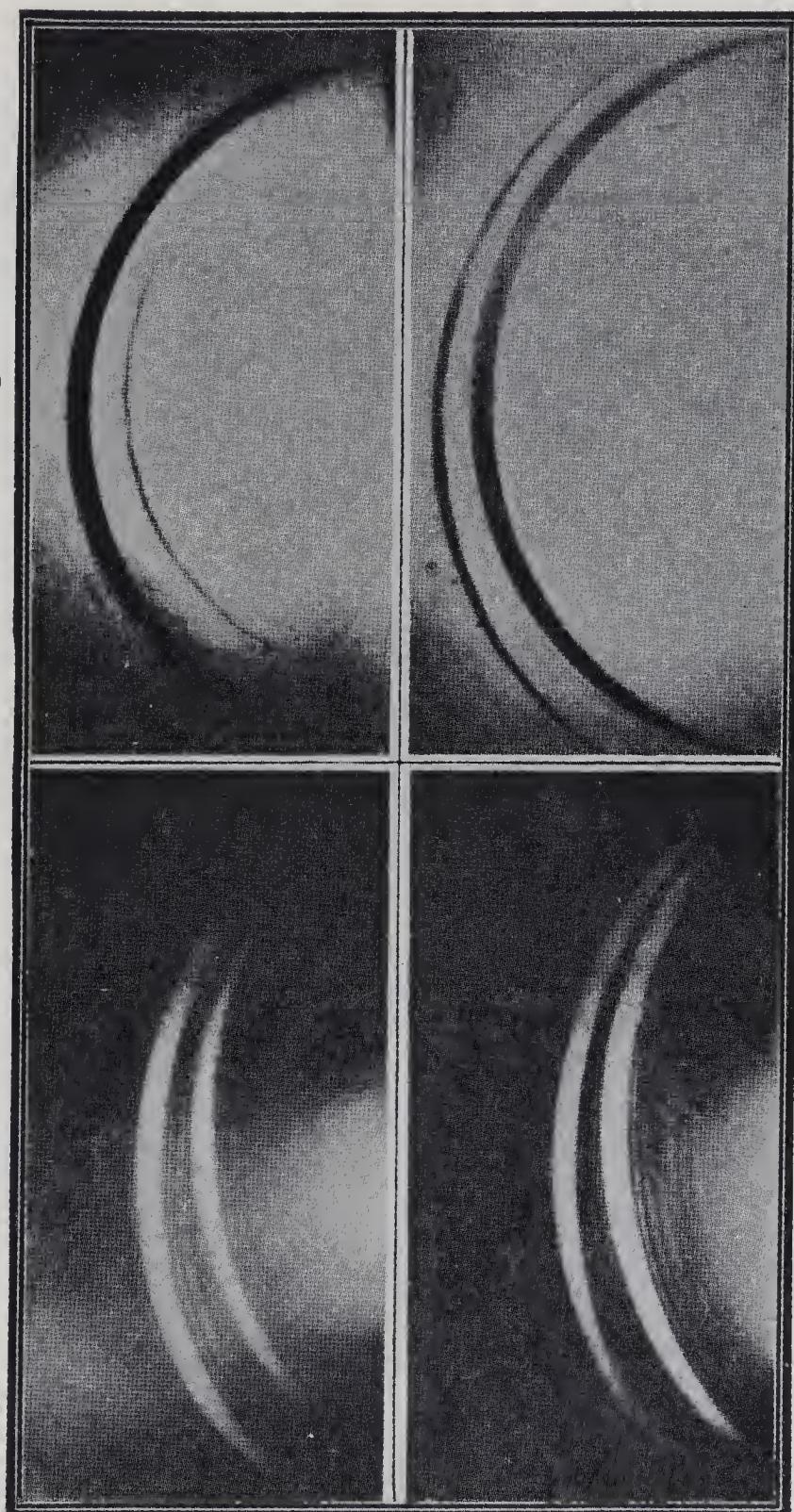


**Figures 1 and 2.** X-ray diffraction by untwinned and by iridescent crystals.

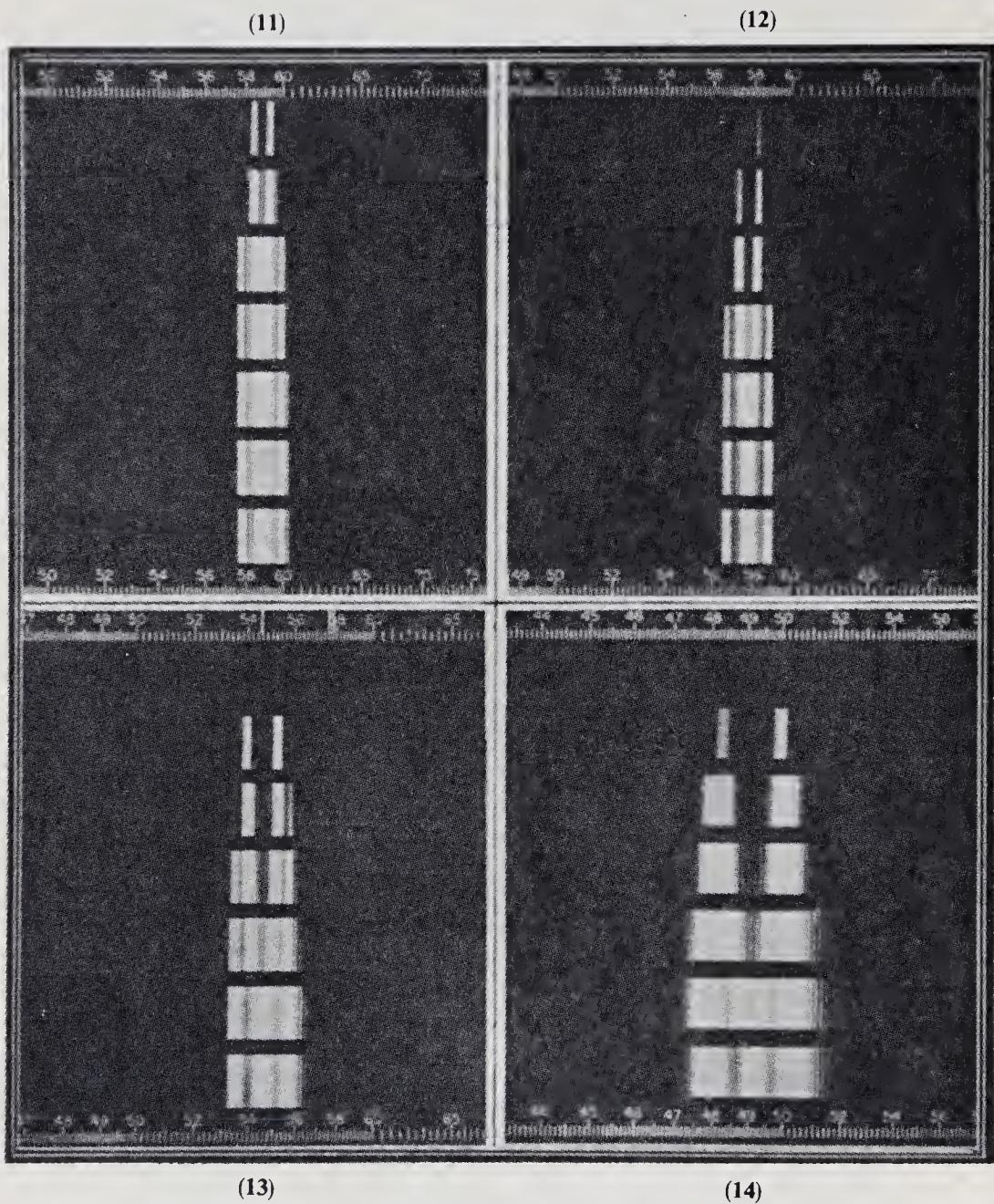


Figures 3–6. Geometric patterns of extinction and reflection.

Plate II



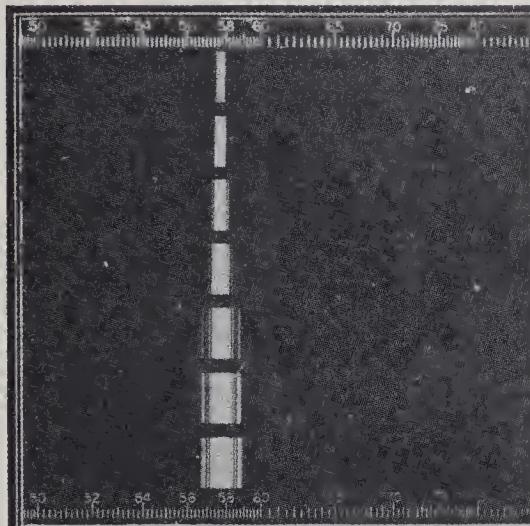
Figures 7–10. Polarisation of the patterns.



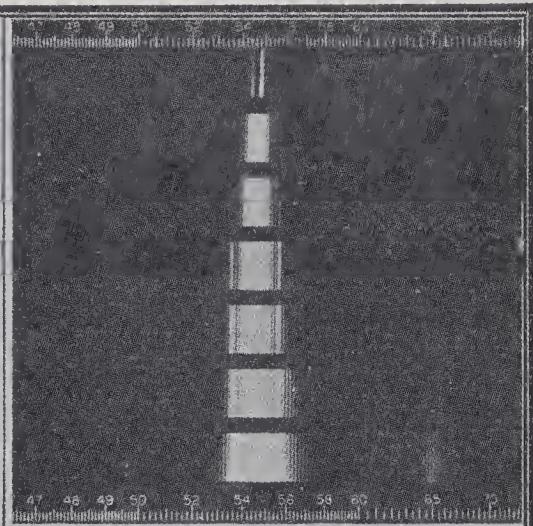
Figures 11-14. Reflection spectra of iridescent crystals.

Plate IV

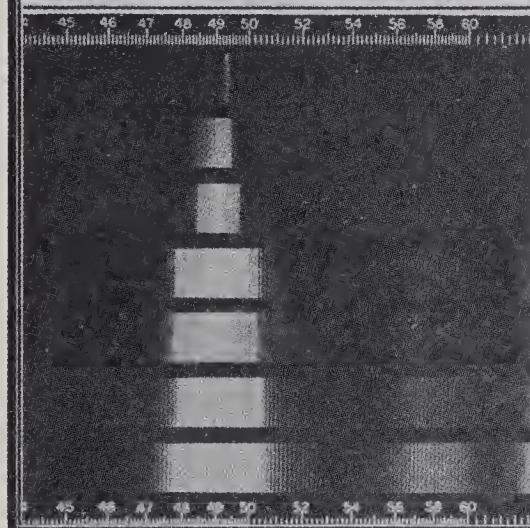
(15)



(16)



(17)



(18)

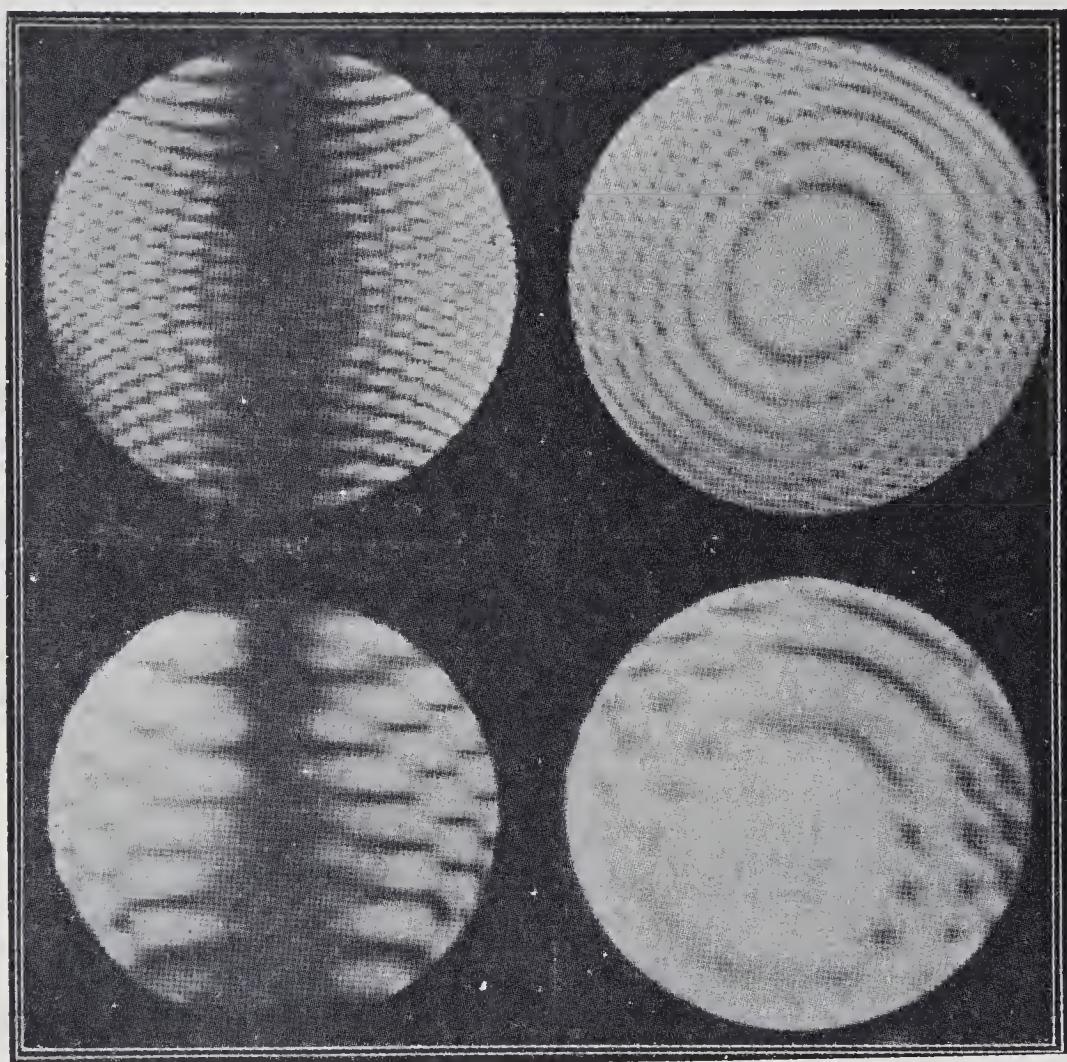


Figures 15–18. Reflection spectra of iridescent crystals.

Plate V

Normal Setting

Diagonal Setting

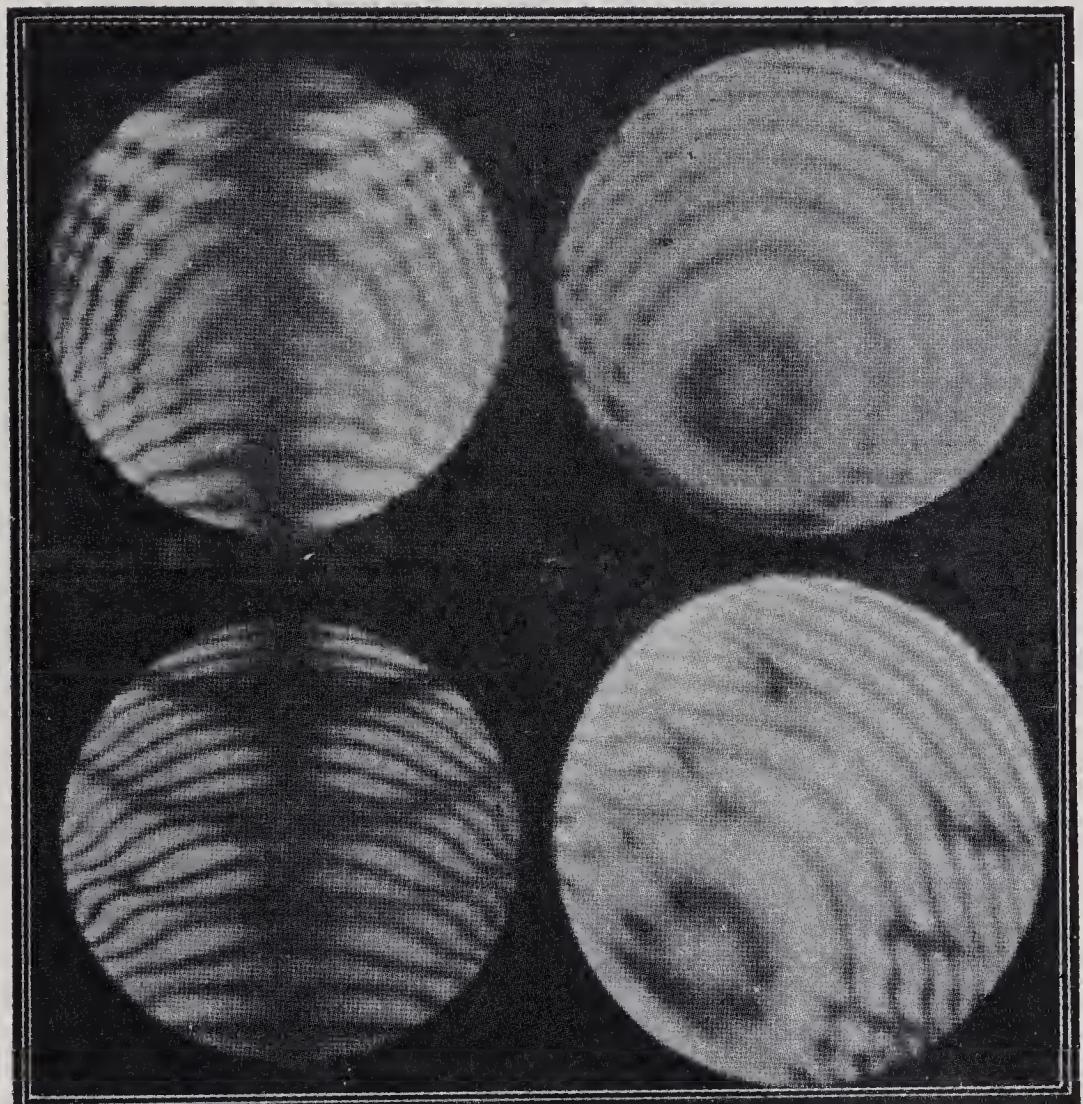


Symmetric conoscopic patterns.

Plate VI

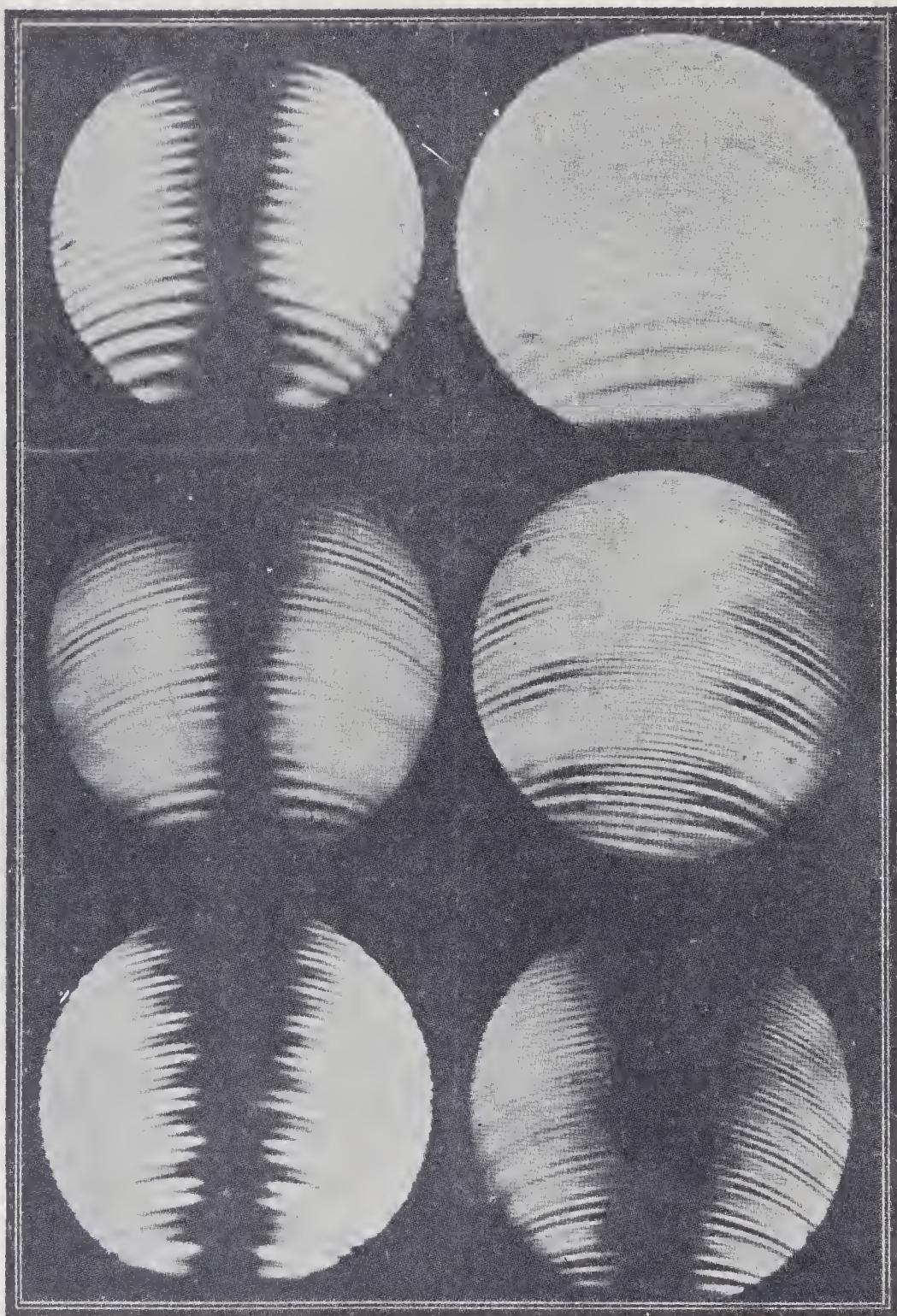
Normal Setting

Diagonal Setting



Asymmetric conoscopic patterns.

Plate VII



Conoscopic patterns of iridescent crystals.

# The structure of opal and the origin of its iridescence

SIR C V RAMAN and A JAYARAMAN  
(Raman Research Institute, Bangalore)

Received August 5, 1953

## 1. Introduction

Mineralogists designate as opal a whole group of naturally occurring substances which have silica as their principal chemical constituent, this being usually accompanied by a small but variable percentage of water; they distinguish opal from chalcedony by its lower density. It will be obvious that not all the substances thus designated are necessarily identical in their ultimate physical constitution. The designation of opal is here used in a restricted sense; we are concerned with the species of opal which exhibit certain characteristic optical effects, the origin of which forms the subject of the present paper. Even as thus circumscribed, the category includes substances showing a diversity of optical behaviour. At one extreme, we have the so-called precious opals displaying their characteristic brilliantly coloured internal reflections, and at the other extreme, we have the material known as hyalite which looks very much like ordinary glass. Intermediately, we have other varieties exhibiting distinctive features of their own.

The present investigation was undertaken with the aim of elucidating the origin of the characteristic iridescence of precious opal. Almost inevitably, however, we were led to extend our studies to hyalite and other forms of opal. Our observations showed that the optical behaviour of these materials exhibits certain relationships with each other, indicating certain general structural similarities amongst them. Our X-ray studies have also enabled us to throw some light on the nature of these structures and to put forward an explanation of the iridescence of opal. It may be remarked here that in spite of the great volume of literature which has grown up around the subject, the origin of this well-known phenomenon has so far remained a mystery.

## 2. Hyalite exhibiting diffraction haloes

The material at our disposal included a piece of transparent hyalite (I). This had been shaped by the lapidary into the form of a thick double-convex lens with a

sharp edge of division between its two surfaces. The diameter of the lens was 11 millimetres and its thickness 6 millimetres. The density of the material was 2·04 and its refractive index as determined by the usual methods was 1·442. Photographs of the specimen (marked as I) are reproduced in plate IV, figures 5 and 6, the illumination being respectively transverse and parallel to the direction of observation.

Seen edgewise in diffuse light, the hyalite exhibited a bluish-white opalescence, but this was not very noticeable when it was viewed normally. If, however, a small bright source of light was viewed *through* the specimen, the image of the source formed by the lens-shaped body was seen to be surrounded by a diffraction halo exhibiting vivid colours. To elucidate this effect, the specimen was immersed in a flat-sided glass cell containing a mixture of dichloro-ethylene and xylene which was adjusted to have the same refractive index as the hyalite. A bright narrow pencil of light traversed the specimen and after emergence from the cell was received on a viewing screen. Surrounding the central bright spot due to the primary beam appeared a bluish white corona, and beyond this again a brightly coloured diffraction halo. The angular diameter of the halo for red light was 30°. Indications of a second halo appeared further out and clearly separated from the first.

A photograph of the effects described above (marked I) is reproduced in figure 1, plate I. The area illuminated by the primary beam is heavily overexposed, while *per contra* the exposure was inadequate to record the second outer halo. The first halo is however clearly seen. It is not quite circular but has a hexagonal shape. The photograph was taken with the beam of light passing normally through the lens-shaped hyalite. The general nature of the phenomenon was however not notably influenced by the setting of the piece within the cell.

### 3. Hyalite exhibiting diffraction spectra

The second specimen (II) which we shall now consider is a material of the same nature as that described in the preceding section, its density being 2·01 and the refractive index 1·441. It had been shaped by the lapidary into a double-convex lens of ellipsoidal form 21 millimetres long, 14 millimetres wide and 9 millimetres thick, a well-defined edge separating its two sides. Under diffuse illumination, the hyalite exhibited a faint milkiness with only a hint of iridescence in its interior. The image of a bright narrow source of light viewed through the piece did *not* exhibit the halo described above for our specimen I. However, in directions inclined at angles ranging from 20° upwards to the direction of the source, brilliant patches of colour were seen inside the specimen. These became more numerous and vivid as the direction of observation was made more oblique. They reached their maximum brilliancy in directions nearly transverse to the incident

light. On the other hand, only vague indications of colour were noticeable in directions lying backwards towards the source.

The significance of the phenomena described above became clear when the specimen was immersed in a flat-sided cell containing liquid, and a brilliant narrow pencil of light sent through it was received on a viewing screen. A whole series of elongated diffraction spectra pointing radially outwards from the direction of the central spot were then seen on the screen, a region surrounding the centre however remaining clear. The spectra appeared over a field of angular radius of  $90^\circ$ . It was, therefore, not possible to photograph the entire group on a single flat plate. The spectra nearest to the direction of the incident beam could, however, be recorded. A photograph thus obtained (marked II) is reproduced in figure 1, plate I.

The enormous difference in the appearance of the specimen (marked II) when illuminated in directions transverse and parallel to the direction of observation will be evident on a comparison of figures 5 and 6 in plate IV. In the former, the whole specimen appears filled with brilliantly coloured patches of light of characteristic shape, while in the latter it appears quite dark.

#### 4. Hyalite exhibiting monochromatic reflections

The third specimen (III) in our collection of which we shall now describe the optical behaviour had a density of 2.03 and a refractive index of 1.442. It had been shaped by the lapidary so that one surface was a highly convex ellipsoid and the other a very flat one, the two being separated by a well-defined edge. The specimen exhibits very beautiful effects when it is illuminated by the light from a brilliant source of small angular extension and is viewed by the observer with the source of light behind him and the specimen held with the highly convex surface facing him. The whole specimen then appears filled inside with brilliant sparkling spangles of colour whose position alters as the specimen is turned round. On the other hand, when a light source is viewed through the specimen, nothing whatever is seen except the transmitted light which is pale yellow in colour. Under diffuse illumination the specimen exhibits a distinct brownish-yellow body-colour which is overlaid by a great number of variously coloured patches of light seen within its volume.

On immersing the specimen in a flat-sided cell containing liquid and sending a narrow pencil of light through it, nothing is seen on the screen in the forward directions. If, however, a white screen with a hole cut to allow the incident pencil of light to pass through it is placed between the source of light and the cell, the internal reflections by the specimen appear as monochromatic spots of light on the screen. It is not possible to photograph all of them on a flat film owing to the large range of angles involved, and only those appearing in directions nearly

opposite to that of the incident beam are recorded. Such a photograph (marked III) is reproduced in figure 1, plate I. Two photographs of the specimens (marked III) are reproduced in figures 5 and 6 of plate IV. The internal reflections are much more evident in figure 5 than in figure 6.

A fourth specimen of hyalite (IV) in our collection may also be mentioned here, since we have made use of it in our X-ray studies. It is a small faceted piece shaped by the lapidary into the form of a brilliant with a sharp edge encircling it. The specimen exhibits a very pretty orange-red body colour. It could, however, easily be mistaken for a piece of coloured glass. When immersed in liquid and traversed by a powerful beam of light, one could glimpse patches of internal iridescence. The density of the piece was 2.03 and its refractive index 1.441.

It may be remarked that all the four specimens described above exhibit no noticeable luminescence under ultra-violet illumination.

### 5. The X-ray diffraction patterns

As already remarked, all the four specimens included in the present study had been shaped into forms having a sharp edge girdling them. It was, therefore, possible to record their X-ray diffraction patterns merely by allowing a fine pencil of X-rays to graze any chosen point on this edge and receiving the diffracted X-rays on a photographic film. The width of the X-ray pencil and its position relative to the edge were adjusted so as to record the pattern with satisfactory definition. The radiation employed was that from a copper target filtered through a nickel foil. The technique employed was tested by using edges of agate; the diffraction rings of cryptocrystalline quartz were then found recorded as sharply defined lines in the correct positions.

The records made with our hyalite specimens using a flat camera are reproduced in figure 2, plate II, the distance from edge to plate being 4 cm. The patterns recorded with a cylindrical camera of 6 cm radius are reproduced in figure 3, plate III. The numbers entered against each photograph indicate the particular specimen used.

Various authors<sup>1,2,3</sup> have claimed that the X-ray pattern of opal is identical with that of high cristobalite. Apart from the difficulty of understanding why the high-temperature form should remain unchanged at the low temperatures, the result reported by those authors leaves the origin of the optical effects displayed by opal unexplained. It seemed to us therefore necessary that a critical comparison should be made of the X-ray patterns of our specimens with those of high and low cristobalite respectively. With this aim and for purposes of comparison with our specimens, we have made use of a porcelain-like material found associated with some specimens of agate collected by one of us near Indore in Central India. The density of this material ranges between 2.30 and 2.35 and its

X-ray patterns show it to be low cristobalite mixed with a little tridymite. On heating the material to 300°C., the cristobalite changes reversibly to the hightemperature form, as is shown by its altered X-ray pattern. In figure 4, plate IV the pattern of our hyalite (No. IV) is reproduced in juxtaposition with the patterns of the comparison material recorded at the high and low temperatures respectively.

From a scrutiny of the photographs reproduced in plates II, III and IV, it is evident that though the X-ray patterns of our specimens exhibit certain similarities with high cristobalite, there are some significant differences demanding attention.

A. The principal ring of hyalite exhibits two components distinctly resolved from each other. This effect is particularly clear in the photographs reproduced in plate II. In strongly exposed pictures, the ring exhibits an unsymmetrical broadening.

B. The rings other than the first appearing in the patterns also exhibit large variations in sharpness which are uncorrelated either with the angle of diffraction or with the intensity of the line.

C. Several diffuse bands are present in the patterns of the hyalites which are not seen in the comparison photographs.

## 6. Interpretation of the results

The experimental facts set forth above preclude us from describing opal as being merely a cryptocrystalline form of high cristobalite. The doubling of the principal ring indicates, on the other hand, that the material is composite and consists of two distinct phases distributed throughout its volume. A reasonable explanation of the observed features is forthcoming if these two phases are identified respectively with high and low cristobalite. In particular, the doubling of the principal ring appears as an immediate consequence of the fact that the spacings for high and low cristobalite are different, being 4.11 Å and 4.04 Å respectively.

The lower symmetry of low cristobalite results in its X-ray pattern exhibiting many more spacings than that of high cristobalite.<sup>4,5,6</sup> Indeed, while the latter shows only 12 lines with spacings greater than 1 Å, the former shows 43 lines in the same region. Many of the latter lie very close to each other and their intensities are also small. Diffuseness of the rings resulting from the smallness of the crystallites in the material would therefore influence the pattern of low cristobalite with its numerous closely-packed faint lines to a much greater extent than in the case of high cristobalite which has relatively fewer and brighter lines. Indeed, they would in such circumstances, appear in the former case as diffuse bands instead of discrete lines as in the latter case. The presence of low cristobalite in the material would, if the particle sizes are small, thus be readily capable of being overlooked.

## 7. The optical evidence

The conclusion deduced above from the X-ray data that opal includes two distinct crystalline species of silica in its physical make-up may be also inferred from its optical behaviour.

The optics of stratified media is sufficiently well understood to enable us, from a study of the spectral character of the light reflected and transmitted by such a medium, to infer the number and nature of its stratifications. For a high degree of perfection in the monochromatism of the reflections to be possible, it is necessary that the stratifications should be regular in their spacing as well as in their optical character, and further that great numbers of the stratifications should be present. It is also necessary that the reflecting power of an individual stratification is small. For, if the reflecting power of an individual stratification were large, the first few alone of the stratifications would function, and the reflections would necessarily cease to be monochromatic.

It is well-known that the coloured reflections given by precious opal are highly monochromatic and that the light transmitted by them also exhibits monochromatic extinctions. Two further observations that we have made are significant in this connection. In the first place, we have noticed that the internal reflections of opal are perfectly polarised when observed in a direction making an angle of  $90^\circ$  with the incident beam. We have also noticed that a reflection which is highly monochromatic when observed at or near normal incidence retains this character even when it is shifted towards shorter wavelengths by making the incidence oblique. The optical behaviour of opal thus compels us to recognise the existence of a remarkably perfect periodicity in its structure. It also emerges from the observations that the difference in the refractive indices of the alternate layers is small and yet precisely the same throughout the stratifications. The only reasonable hypothesis that could be put forward to account for these facts is that the alternate layers consist of two distinct and specific modifications of silica.

The conclusions set forth above are supported by the observations described earlier on the optical behaviour of the specimens of hyalite in our collection. Though the individual specimens exhibit distinctive features, it is clear that the phenomena observed have a common origin, namely, the existence of regular optical stratifications within the material; the differences observed arise from the spacing of the stratifications and the dimensions of the individual domains in which they appear not being the same for all the specimens. Thus, hyalite in spite of its apparent dissimilarity in appearance belongs optically to the same category as precious opal.

It may be remarked in conclusion that the density of low cristobalite is 2.32 and its refractive index 1.484, whereas the density of high cristobalite is 2.27 and the refractive index calculated therefrom is 1.468. The difference between the two refractive indices is sufficiently small to be reconcilable with the observed characters of the internal reflections. That the density of our hyalite specimens is

distinctly lower than that which might be anticipated on the basis of their structure may be ascribed to the presence in them of ultra-microscopic cavities partly or wholly filled with water. Their existence makes itself evident in a distinct turbidity of the material, a phenomenon which is quite distinct from the optical effects having their origin in the regularly stratified structure of the silica.

## 8. Summary

A study of the optical behaviour of iridescent opal indicates very clearly that the silica present in the material has a regularly stratified structure in which the alternate layers differ in refractive index, such difference being small but the same throughout the stratifications. A critical examination of the X-ray diffraction patterns of cryptocrystalline hyalites exhibiting optical phenomena identical with or analogous to those of precious opal confirms this finding and enables the two species of silica present in association with each other and giving rise to these phenomena to be identified respectively with high and low cristobalite. The different optical effects exhibited by a stratified medium when the spacing of the stratifications and the extent of the domains in which they are present are varied have been observed with different specimens of hyalite and are illustrated in the paper by a series of photographs.

## 9. References

1. Levin I and Emil Ott, *Z. Krist.*, 1933, **85A**, 305.
2. Dwyer E P and Mellor D P, *J. R. Soc., New South Wales*, 1934, **68**, 47.
3. Buerger M J *Phase Transformation in Solids*, John Wiley and Sons, 1951, pages 206–09.
4. Wycoff R W G *Z. Krist.*, 1925, **62**, 189.
5. Nieuwenkamp *Ibid.*, 1935, **92A**, 82.
6. Jay A H *Miner. Mag.*, 1944, **27**, 54.

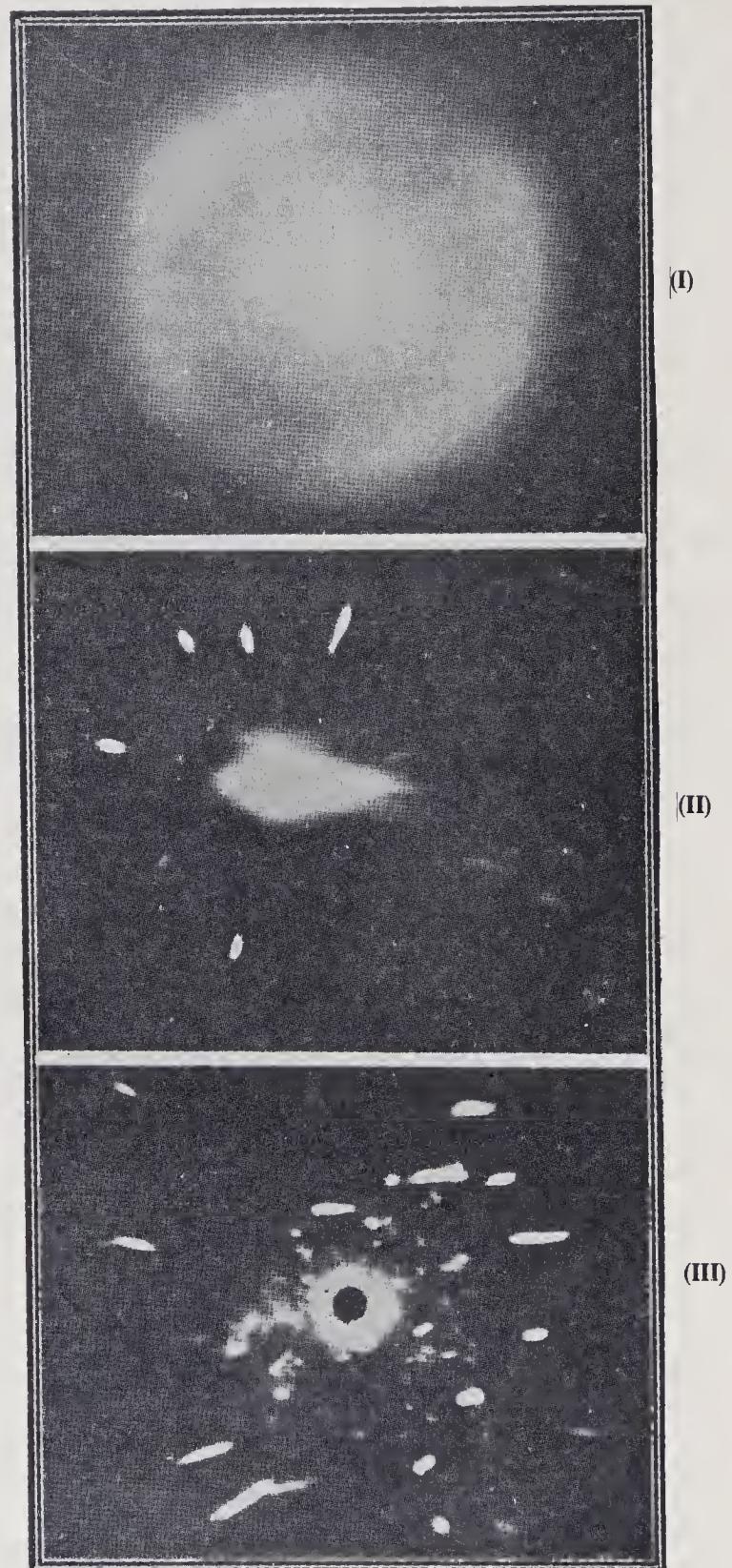
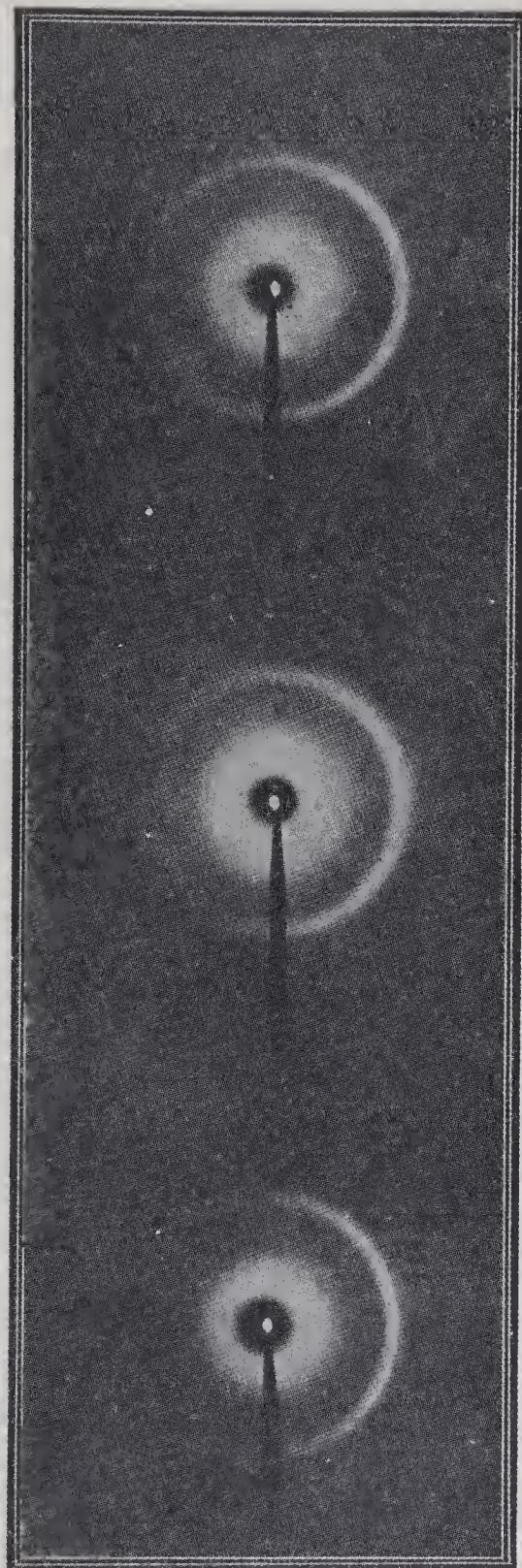


Figure 1

Plate I



(IV)

(II)

(III)

Figure 2

Plate II

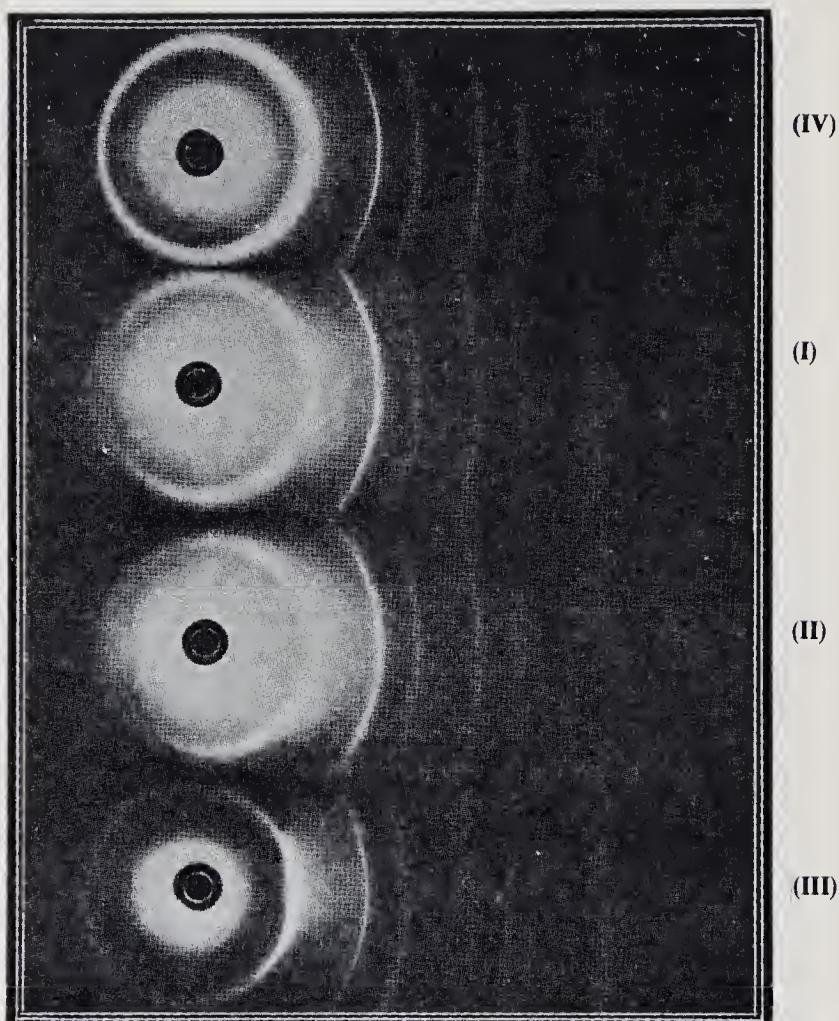
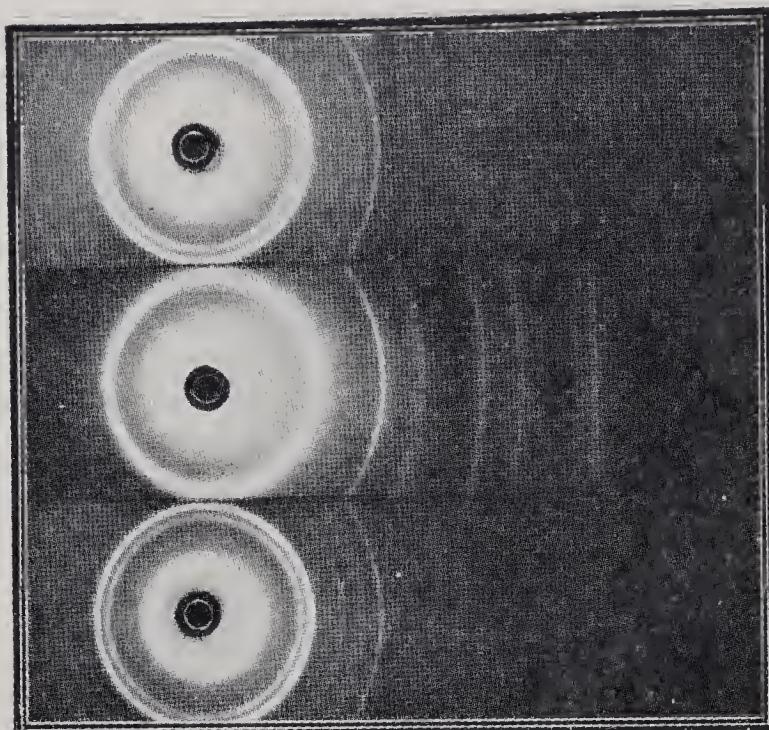
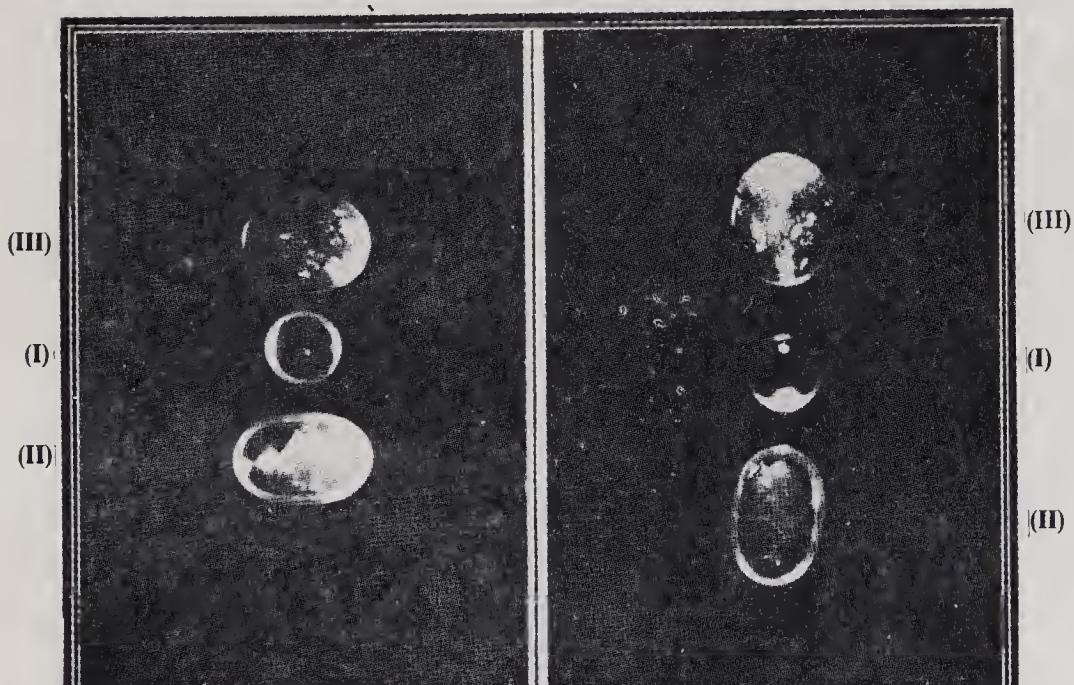


Figure 3

Plate III



(4)



(6)

Figures 4–6

Plate IV

# The structure and optical behaviour of iridescent opal

SIR C V RAMAN and A JAYARAMAN

(Memoir No. 42 of the Raman Research Institute, Bangalore)

(Received November 11, 1953)

## 1. Introduction

The remarkable and very beautiful effects exhibited by iridescent opal have long been known and have made it one of the most admired of gems. In the finest specimens, the play of colour takes the form of localised internal reflections exhibiting hues of extraordinary brilliance and saturation which vary from place to place over the area of the gem and change in a surprising manner with the angle of incidence of the light. Not the least part of the beauty of a fine opal is the orange-red colour of the transmitted light which may be seen reflected back by the rear surface of the gem and then appears all the more vivid by reason of its contrast with the greens and blues so frequently seen in the iridescence. Spectroscopic examination reveals that the internal reflections and the corresponding extinctions in the transmitted light are highly monochromatic. From this, it is evident that they are consequent on the presence within the material of regularly stratified layers in great number. Indeed, the existence of such stratifications is not just a hypothesis. When a gem-opal is examined through a microscope which has arrangements for illuminating the object from above the stage and viewing it by the internally reflected light, the lamellar structure of the material becomes immediately evident. In not a few cases, geometric patterns of a very striking character are observed (see figures 1 to 4 in plate I).

A reasonable hypothesis which would fit the observed character of the stratifications as well as the optical effects to which they give rise is that iridescent opal consists of alternate layers of two crystalline modifications of silica of slightly different refractive index. In a recent paper<sup>1</sup> in these *Proceedings*, we presented evidence which supports this hypothesis derived from a study of the X-ray diffraction patterns of hyalite which is a material having a composition similar to that of gem-opal and exhibiting optical phenomena of a similar nature. Further studies have since been carried out by us in which X-ray cameras of higher resolving powers were used and the resulting photographs were precisely measured. They have enabled us to reach the definite conclusion that the two modifications of silica present in hyalite are respectively low-tridymite and high-

*cristobalite*. X-ray studies have also been made by us with common opal which occurs in massive form with a waxy lustre. These have led to a similar conclusion regarding the nature of the latter material.

The X-ray patterns of gem-opal are diffuse, thereby making it less easy than in the case of the crypto-crystalline materials hyalite and common opal to identify the nature of the atomic groupings which appear in the alternating layers of its lamellar structure. Nevertheless, a careful examination of the patterns leaves little room for doubt that, as in the case of the iridescent hyalite, we are concerned with two modifications of silica present side by side in it, one of them having a structure resembling that of low-tridymite and that the other that of high-cristobalite. Comparative studies of the optical behaviour of hyalite and of gem-opal made by us confirm this finding and establish this as the origin of the iridescence exhibited by these materials.

## 2. The crypto-crystalline forms of silica

As is well known, agate and chalcedony are massive forms of silica which X-ray studies show to consist of crystallites of quartz. The latter are frequently grouped together in specific orientations, thereby giving rise to the characteristic banding of the material, as has been shown by us in a recent paper.<sup>2</sup> *Prima-facie*, one may expect that two other crypto-crystalline forms of silica should also be forthcoming in nature consisting respectively of low-tridymite and low-cristobalite. The latter expectation, at least, is found to be fully justified. Some years ago, a white and compact porcelain-like material was collected by one of us on the open terrain not far from Indore in Central India. It was usually found associated with agate, but occasionally also appeared as separate masses. The density of the material has been determined and lies between 2.32 and 2.35, thus excluding the possibility of its being chalcedony. The density approximates closely to the known value for low-cristobalite, and examination by X-ray diffraction methods confirms this identification. On heating the substance to about 300°C, it transforms completely to high-cristobalite, and on cooling reverts again to low-cristobalite. These findings are illustrated in figures 12(a) and (b) in plate IV which show respectively the X-ray patterns of the material at the low and at the high temperature. The pattern was first recorded at the high temperature and later at the room temperature. Measurement of the photographs confirms the identification of the material with cristobalite.

It is clear from the X-ray patterns that the cristobalite is present in the material

randomly orientated. The most significant result that emerges is that high-cristobalite is unstable at ordinary temperature even when in a fine state of subdivision and reverts immediately to low-cristobalite.

### 3. The structure of common opal

Another material examined by us in detail is common opal with a waxy lustre, two large lumps of which were purchased from a mineral dealer in New York. The material is translucent in thick layers, but in smaller thicknesses of the order of a millimeter transmits light freely. The density of the material is 2.02 and its refractive index 1.440. On heating to about 800° C, it becomes opaque and white and also loses about 10% of its weight, presumably due to the loss of adsorbed water. An X-ray diffraction pattern was recorded in the usual manner, using a fine rod prepared from the material with a cylindrical camera of 3 cm radius. This is reproduced in figure 13(b) in plate V. Figures 13(a) and (c) in the same plate are X-ray diffraction patterns respectively of high-cristobalite and low-tridymite, recorded under identical conditions. The low-tridymite was taken off a burnt-out silica brick and then finely powdered; the high-cristobalite is the same material as that described in the preceding section.

A careful comparison of the three patterns reproduced in plate V is highly instructive. Particularly noteworthy is the fact that the principal ring of common opal is of considerable width, this being approximately the same as the total width covered by the triplet of lines appearing in the pattern of low-tridymite, while on the other hand, the principal ring of high-cristobalite is single, sharp and well defined. But in other respects, the patterns of common opal and of high-cristobalite exhibit a close similarity. But even so, there are recognisable differences. While the rings of high-cristobalite are all sharp and fairly intense, those of common opal are definitely weaker and also rather diffuse though to varying extents. The pattern of the opal also exhibits a much more intense small-angle scattering than that of high-cristobalite. A continuum of varying intensity is also present in the pattern of the opal which is absent in the case of high-cristobalite. On careful scrutiny, a close correspondence is revealed between the intensity of the continuum in the pattern of common opal and the integrated intensity of the groups of lines appearing in the corresponding parts of the low-tridymite pattern.

All the facts set forth above indicate that common opal is a material in which high-cristobalite and low-tridymite co-exist in intimate juxtaposition.

### 4. The structure of hyalite

In our earlier paper which appeared in these *Proceedings* for August 1953, the X-ray diffraction patterns of four specimens of hyalite were reproduced. The pattern

of specimen no. I which was recorded with a 3 cm radius camera is reproduced again as figure 14(b) in plate VI. For comparison with it, the patterns of high-cristobalite and low-tridymite recorded under identical conditions are once again reproduced in plate VI as figures 14(a) and 14(c) respectively. Apart from the circumstance that only one side of the pattern of the hyalite has been recorded, it will be seen that it closely resembles the pattern of common opal appearing in figure 13(b) in plate V, except that the outer rings are generally rather sharper and more intense in the case of the hyalite. Hence, the remarks made above regarding common opal apply *mutatis mutandis* to the case of hyalite.

To make the position clearer, the pattern of hyalite no. IV which had a very sharp edge has been recorded once again with X-ray cameras of higher resolving power. A picture taken with a camera of 5.73 cm radius and an exposure of seven hours is reproduced as figure 9 in plate III. Three prints of a pattern of the same specimen recorded with a camera of 19 cm diameter and an exposure of twelve hours are reproduced as figure 10 in the same plate. It is very clearly seen in both pictures that the principal ring in the pattern is a triplet, with a strong central component. Both the positions and relative intensities of the components of the triplet are explicable if the pattern is recognised to be a superposition of those of high-cristobalite and low-tridymite. This will be evident from table 1 where the respective *d*-values of the more prominent lines have been tabulated. The table also makes it clear that the suggestion made in our earlier paper that the X-ray pattern of hyalite is a superposition of the patterns of high- and low-cristobalite is untenable.

## 5. The structure of gem-opal

The density of gem-opal ranges between 2.1 and 2.2, and its refractive index between 1.45 and 1.46. The density and the refractive index of hyalite are respectively 2.0 and 1.44 respectively, these lower values being related to those for gem-opal at least approximately in the manner demanded by the Gladstone-Dale formula. The principal difference between gem-opal and hyalite is that while the latter, as we have seen, gives a well-defined X-ray diffraction pattern, the pattern of the former is diffuse and resembles that of vitreous silica, though there are recognisable differences. Figures 11(a), (b), (c), (d) and (e) in plate IV are X-ray diffraction-patterns recorded with a camera of 5.73 cm diameter and the filtered radiation from a molybdenum target of the materials indicated respectively against each figure. Figures 11(a) and (e) are of two different specimens of gem-opal, while the other figures refer respectively to silica gel, vitreous silica and the natural silica glass from the Sand Sea in the Libyan Desert collected by Dr L J Spencer. At a first glance, all the patterns seem to be similar, but a more careful scrutiny reveals significant differences. Remarkably enough, the difference is greatest as between gem-opal and vitreous silica. In the patterns of opal the two

outer rings are seen clearly separated from each other and from the next inner ring, whereas with the vitreous silica, the two outer rings have nearly coalesced, and the next inner ring has joined up with the bright central area. The differences between the opal and the silica gel on the one hand, and between opal and the Libyan glass on the other, are of a less striking character. It should be remarked that in the case of all four materials, there are two outer bands of low intensity which can be scarcely glimpsed in the reproductions. The *d*-values calculated for the principal ring and for the five outer bands for the case of gem-opal are respectively 4.1 Å, 2.05 Å, 1.45 Å, 1.20 Å, 0.97 Å and 0.80 Å.

Table 1. *d*-values in Angstroms with intensities

Low-cristobalite	High-cristobalite	Hyalite	Low-tridymite
—	—	4.32 (moderate)	4.32 (intense)
—	4.13 (intense)	4.12 (intense)	4.10 (strong)
4.04 (intense)	—	—	—
—	—	3.9 (weak)	3.82 (strong)
3.12 (moderate)	—	—	—
—	—	—	—
2.85 (moderate)	—	—	—
2.48 (strong)	2.52 (strong)	2.51 (strong)	2.49 (moderate)

The use of the short-wave molybdenum radiation and a camera of small radius results in obscuring much of the visible detail in the inner parts of the pattern. The latter are much clearer when recorded with the filtered radiation from a copper target. Two pictures, namely those of gem-opal and of silica glass, taken with  $\text{CuK}_\alpha$  radiation and a flat camera with a film to specimen distance of 4 cm are reproduced as figures 8(a) and 8(b) respectively in plate III. The density of gem-opal being rather less than that of vitreous silica which is 2.22, one might have thought that the principal ring of opal should have a smaller angular diameter and give a larger *d*-value than that of silica glass. The actual position is the reverse, as can be seen on a careful comparison of the two figures. It will also be noticed that the first diffraction ring of gem-opal is definitely sharper and of greater intensity relatively to the region inside it than for silica glass.

Using the  $\text{CuK}_\alpha$  radiation and an X-ray camera of 3 cm radius with adequate exposures, the complete pattern of gem-opal can be satisfactorily recorded and shows features of great interest. Unfortunately, however, owing to the weakness of the outer bands relatively to the principal halo, it is difficult to copy it in a satisfactory manner for reproduction. Hence we have to content ourselves here with a description of the observed features. One can clearly see in the

photographs besides the principal ring and a strong continuum stretching out from it, a distinct concentration of intensity along a ring with a  $d$ -value of  $2\cdot50 \text{ \AA}$ , besides the other bands with smaller  $d$ -values which are the same as those recorded with molybdenum radiation. The pattern in fact is essentially similar to that of hyalite reproduced as figure 14(b) in plate VI, provided that one supposes that the rings appearing in the latter had broadened out sufficiently to become a set of diffuse bands. The continuum seen in the hyalite pattern between its first and second rings is a conspicuous feature also in the pattern of the gem-opal as recorded with the  $\text{CuK}_\alpha$  radiation.

Thus, the X-ray data point clearly to the conclusion that the structure of gem-opal is essentially the same as that of hyalite; except that the crystallites are now much smaller, thereby tending to make the material simulate a vitreous solid.

The essential similarity between hyalite and gem-opal indicated by the X-ray data is supported by other facts of observation. One of the most striking features observed with gem-opal is the appearance of visible stratifications in it. These are very conveniently observed with the aid of an 'Ultropak' microscope. In this arrangement, a conical beam of light is directed from above the stage on to the surface of the specimen and the latter is viewed by the light reflected from its interior and returned to the objective of the microscope. A great variety of geometric patterns are observed, a few particularly striking examples of which are reproduced as figures 1, 2, 3 and 4 in plate I. Figures 1 and 4 refers to exactly the same portion of a particular specimen but under slightly different conditions of illumination. Figure 2 refers to another area on the same opal. Figure 3 is a particular area on the finest gem-opal in the collection of this Institute. It will be seen from these pictures that the stratifications run in several directions simultaneously and in fact the entire material is honeycombed by them. The material is divided up into layers parallel to one, two or even three sets of parallel planes crossing each other. It is to be noted that hyalite also shows visible evidence of internal stratifications. One may refer for example, to the picture of our specimen II under transverse illumination reproduced as figure 5 in plate IV of the earlier paper in which triangular patches shining by reflected light are clearly to be seen. The essential similarity of the structures of opal and hyalite is thus made clear.

## 6. Observations with monochromatic light

In examining the optical behaviour of regularly stratified media, the use of monochromatic light is very helpful. We shall proceed to recount some observations made with opals, respectively in the light of a sodium vapour lamp and of a mercury arc.

The finest opal in the collection of this Institute is a square tablet which in

diffuse daylight exhibits bright green, blue or violet flashes of internal reflection. In the light of a sodium vapour lamp, however, this brilliance disappears and the gem is seen transformed to an insignificant and unsatisfactory object exhibiting numerous defects, including especially a cloudiness over part of its area on one face in which no iridescence is visible even in diffuse daylight. Every one of the opals in the collection of the Institute which exhibits a green or blue iridescence resembles in the light of a sodium lamp a piece of common but rather turbid glass. Such disappearance of the iridescence is intelligible in the light of optical theory, for a regularly stratified medium ceases to reflect at any incidence if the wavelength  $\lambda$  of the light is greater than  $2\mu t$ , where  $\mu$  is the mean index and  $t$  is the spacing of the stratifications.

The opals which show up so badly in the light of the sodium lamp present a very different appearance in the light of a mercury arc. The difference between the mercury arc and diffuse daylight is however conspicuous in the colour exhibited by the internal reflections, as also in the colour of the transmitted light. The former shows less variety than in daylight, while, on the other hand, the transmitted colours are more lively, being less diluted by the light of longer wavelengths present in daylight.

In our earlier paper,<sup>1</sup> we described and illustrated the optical effects exhibited by hyalite which were individually different in our three specimens I, II and III. The first showed a diffusion halo around the direction of the transmitted light, the second a set of radially directed diffraction spectra, while our specimen III behaved much like an opal and showed a great number of individual monochromatic reflections backwards towards the source of light, many of which are of a red colour. Examined in the light of a sodium lamp, hyalite no. III showed many sparkling reflections from its interior which disappeared and reappeared in other positions as the specimen was turned round.

It is clear from the facts that the optical effects exhibited by transparent hyalite and by iridescent opal form a continuous sequence in which there are three stages. In the first stage, the stratifications are too widely spaced to result in internal reflections, but give rise to diffraction haloes or diffraction spectra in forward directions. In the second stage, the stratifications are too closely spaced to give diffraction effects in forward directions, but result in reflections backwards towards the source. Finally, we have a third stage when the stratifications are too closely spaced to give any effects at all, unless the wavelength of the light is sufficiently small. In the crypto-crystalline hyalites, we would naturally expect the first stage to be commonest, and the second stage less common. In the gem-opals, on the other hand, where the material is approaching the vitreous condition, the stratifications may be expected to be much finer and the third stage therefore attained, unless the wavelength of the light is chosen sufficiently small. We do indeed have opals which exhibit a bright yellow or red iridescence. But those with a green, blue or violet iridescence are commoner, indicating that the more closely-spaced stratifications are favoured.

## 7. The reflection patterns of opal

In studying the optical behaviour of opal rather more closely, we may adopt one of two different methods. In the first method, we view the opal directly or through a microscope, illuminating it from one direction and viewing it in another, and vary these directions. The second method is the same as that described in our earlier paper. We illuminate the opal by a intense narrow pencil and the light reflected backwards is received on a white screen held not too far away from the specimen, a small aperture in the screen permitting the illuminating pencil to pass through and fall on the opal. The complete pattern of reflected, diffracted or scattered light returned by the opal is then visible on the screen.

Observations made in the manner described disclose a great variety of effects in different cases. With some specimens, we observe a bright spot or a group of bright spots constituting a reflection-pattern properly so-called. There are also cases in which no pattern appears but only a diffuse area of light on the observing screen, its colour being the same as that of the observed opalescence of the specimen. Opals giving brilliant localised reflections give, in general, complex patterns composed of bright spots, bright coloured streaks of light and brilliant diffraction spectra crossing each other in different directions, the whole pattern altering rapidly as the opal is moved with respect to the illuminating pencil of light. Even those opals which are not of much value as gems, exhibiting colour only in tiny specks or spots on a non-iridescent background, give interesting patterns of various kinds.

It would take us too far from the main purpose of the paper to describe or discuss the reflection patterns of opal in greater detail. We may, however, make a brief reference to the behaviour of a particularly interesting specimen in our collection. This is a so-called "black-opal" in other words, a layer of opal on a background of opaque ferruginous material. When it is illuminated by a narrow pencil of sunlight, the pattern seen on the viewing screen is a single bright streak of light covering a wide range of angles and exhibiting the usual sequence of colours seen in a diffraction spectrum. The distribution of intensity in the spectrum is however anomalous, a concentration of intensity appearing at one place and a dark gap elsewhere, the position of the former altering with the inclination of the reflecting surface to the incident pencil of light. Examination of the specimen under the microscope reveals the presence of parallel striations over its area. These presumably represent the stratifications of the opal meeting the surface of the specimen obliquely. That in these circumstances a diffraction spectrum appears and not a simple reflection is scarcely surprising.

## 8. The spectroscopic facts and their significance

Figures 5 and 6 in plate II reproduce some spectroscopic records of the reflection of light by some specimens of gem-opal, a beam of white light being

allowed to fall at nearly normal incidence on a restricted area of the specimen and after reflection being received on the slit of the instrument. Particularly remarkable is the spectrum reproduced in figure 5(d). It shows a single monochromatic reflection in the red, the spectral width of which is only about 20 Å. Figures 6(a), (b), (c), (d), (e) and (f) are a series of reflection spectra recorded with a single specimen of opal immersed in a cell containing liquid paraffin, the angle of incidence of the light being varied by steps from nearly normal incidence to about 50°. The exposures with which the spectra were recorded were not the same in all cases, and hence it is not possible to attach any quantitative significance to the spectral width as seen in the reproductions. In a general way, however, it is evident that there has been no noteworthy increase in the spectral width of the reflection in spite of the wavelength at which it appears having been shifted from 5820 Å to 4930 Å with the increasing angle of incidence.

Figures 7(a), (b) and (c) in plate II are the extinction spectra of three different gem-opals in the collection of the Institute. They were recorded by the simple device of holding the specimen against the slit of the recording spectrograph and allowing the light from a filament lamp 50 cm away to enter the slit after passing through the specimen. The photographs exhibit the extinctions produced by the entire thickness of the opal which was about 3 millimeters in each case. They represent the joint effect of the sets of stratifications present at different depths and possibly also differently inclined to the path of the light-rays through the opal. The spectrograms exhibit a great variation in the effects recorded at different points along the slit of the instrument. Well-defined extinctions usually about 100 Å wide appear in the blue-green region, accompanying which are seen streaks of transmitted light extending towards the violet end of the spectrum. In other regions, there appears a general cut-off of the shorter wavelengths and a free transmission of the longer wavelengths. These facts will be readily understood in the light of the remarks made earlier in this paper.

The theory of the reflection of light by a regularly stratified medium has been elaborately discussed in these *Proceedings* by G N Ramachandran.<sup>3</sup> As has been shown by him, the degree of monochromatism of the reflections by such a medium cannot be indefinitely increased by increasing the number of its stratifications, their spectral width having a minimum limiting value which depends only on the reflecting power of an individual stratification. If such reflecting power be large, the monochromatism would necessarily be very imperfect; *per contra*, if high monochromatism is actually observed, it indicates that the reflecting power of an individual lamination is small. These conclusions have an important application to the case of opal. They indicate that the difference in refractive indices of the alternate layers of the stratifications in opal is quite small. Further, such variation is strictly periodic and of the same magnitude throughout an individual set of stratifications.

## 9. The nature of the stratifications

The considerations set forth above suffice by themselves to exclude the explanations of the iridescence of opal which appear in the earlier literature of the subject. It is likewise not possible to entertain the idea that the presence of adsorbed water in opals is responsible for their iridescence, as it would then be necessary to assume that the adsorbed water is so distributed as to give rise to a regular periodic variation in refractive index of small magnitude, an assumption for which there is no *prima facie* justification. We have made some observations on the effect of heating opals to temperatures sufficiently high to drive out all adsorbed water. This drastic treatment usually results in a disintegration of the opal, but the iridescence as such remains unaffected. We are thus forced to recognise that the iridescence of opal is a consequence of the inherent structure of the silica in the material.

The densities of low-tridymite and of high-cristobalite are not very different and their refractive indices would therefore differ just sufficiently little to account for the observed behaviour of opal if they exist as separate layers side by side. The same difference could equally account for the observed cloudiness of opal in many cases if the distribution of the two materials were irregular in such cases.

As is well known, high-cristobalite is a form of silica which is stable over a wide range of temperatures, but which reverts to low-cristobalite below 300° C. The presence of high-cristobalite admixed with low-tridymite in opal may be reasonably accounted for by assuming that its association with low-tridymite, which is itself a stable form at ordinary temperature, confers on it the requisite stability. Since the two materials have the same chemical composition and nearly the same density, and since their structures have the silicon-oxygen tetrahedra as a common factor, there is no inherent difficulty in making such an assumption. Since the two structures are not identical, the materials would naturally tend to segregate and form layers so disposed with respect to each other as to present the maximum possible degree of continuity in the chains of valence bonds between the silicon and oxygen atoms extending through the material. Since the structure of low-tridymite is pseudo-hexagonal while that of high-cristobalite is cubic, geometric patterns in which the two structures alternate may be expected to arise, as is indeed actually observed in opal.

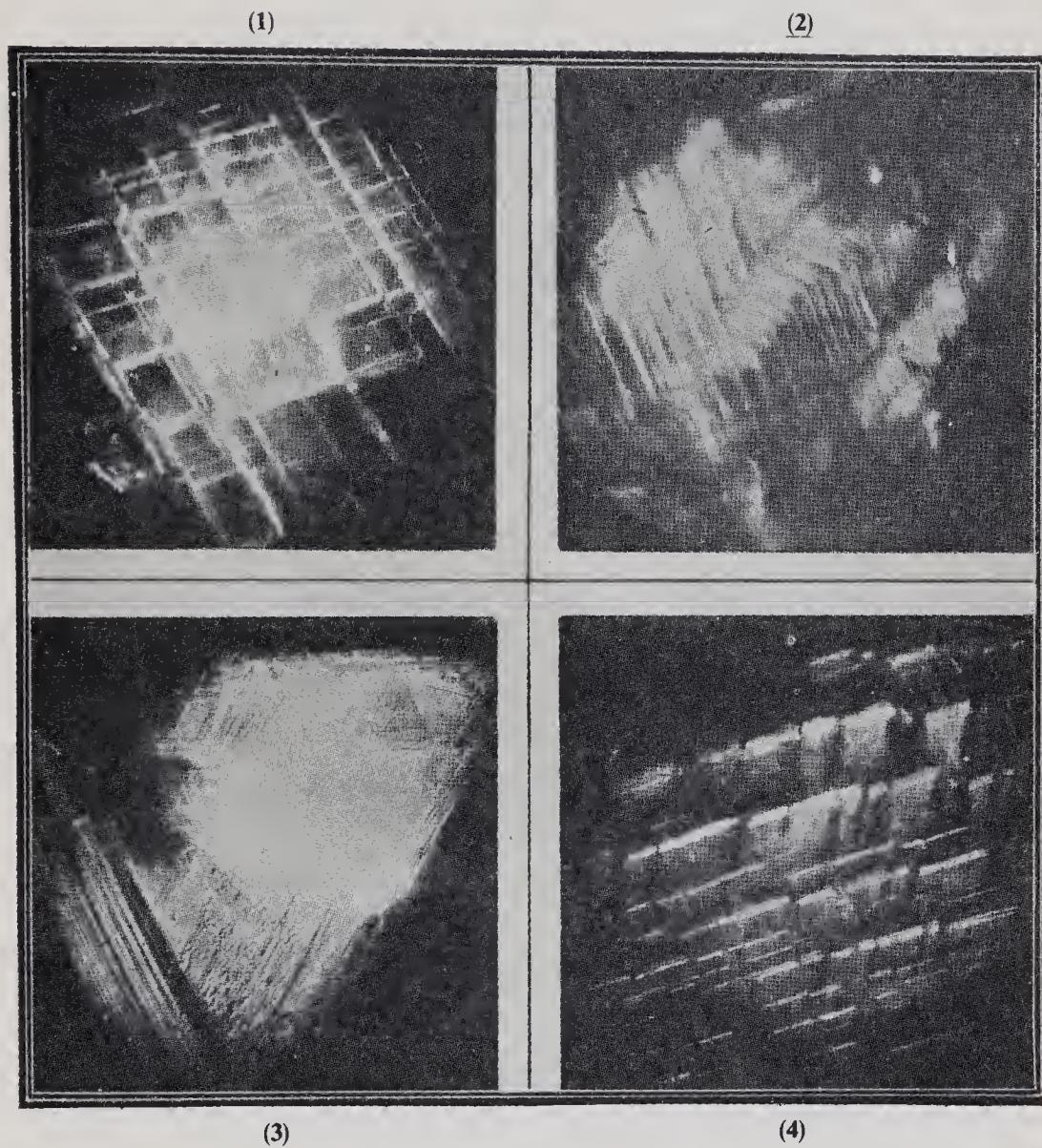
## Summary

The X-ray investigation of the structure of the cryptocrystalline hyalites reported in an earlier paper has now been revised using cameras of higher resolving power. Precise measurements of the resulting photographs reveal that low-tridymite and high-cristobalite are present associated with each other in this material. Investigation of the structure of common opal exhibiting a waxy lustre leads to

similar results. From a detailed examination of the diffuse X-ray patterns given by gem-opals as well as a comparative study of the iridescent hyalites and opals, it is concluded that in both of these materials, the presence of alternating layers of high-cristobalite and low-tridymite is responsible for the iridescence.

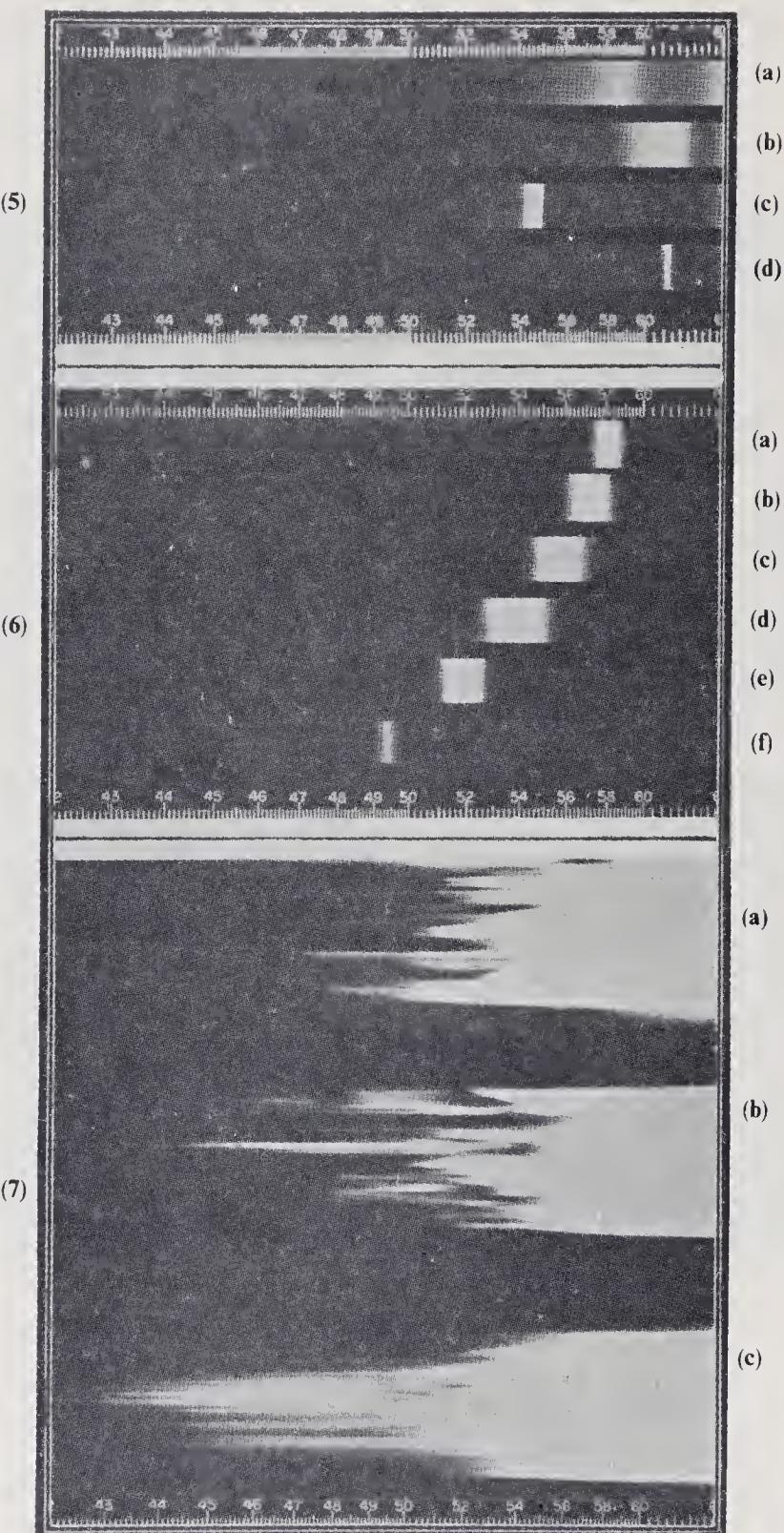
### References

1. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1953, **38A**, 101.
2. C V Raman and A Jayaraman, *Ibid.*, 1953, **38A**, 199.
3. G N Ramachandran, *Ibid.*, 1942, **16A**, 336.



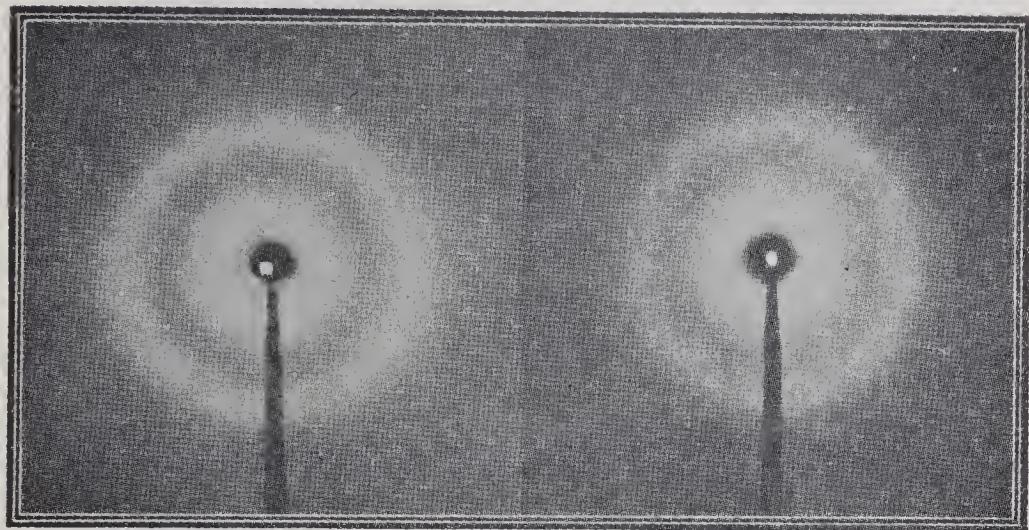
Figures 1–4. Lamellar structures in precious opal.

Plate I



Figures 5–7. Reflection and extinction spectra of precious opal.

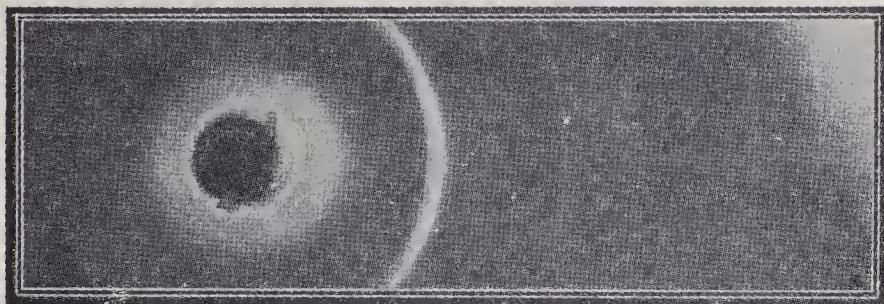
(a) Precious opal



(b) Silica glass

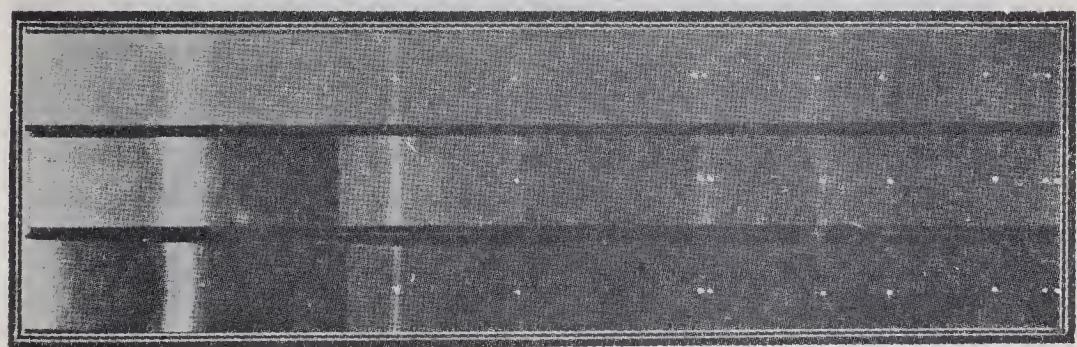
(8)

Hyalite IV



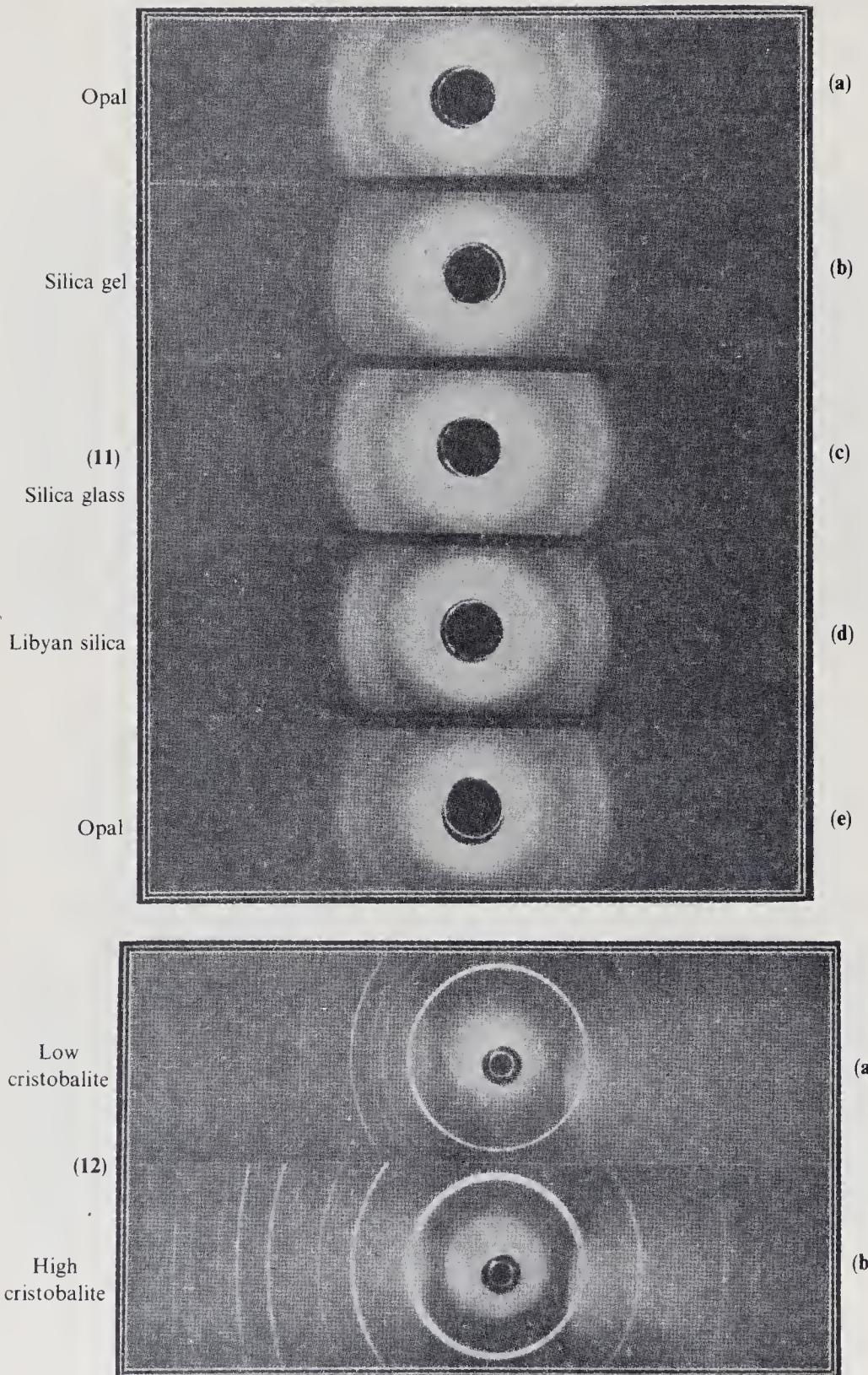
(9)

Do



(10)

Figures 8-10. X-ray diffraction patterns.



**Figures 11 and 12.** X-ray diffraction patterns.

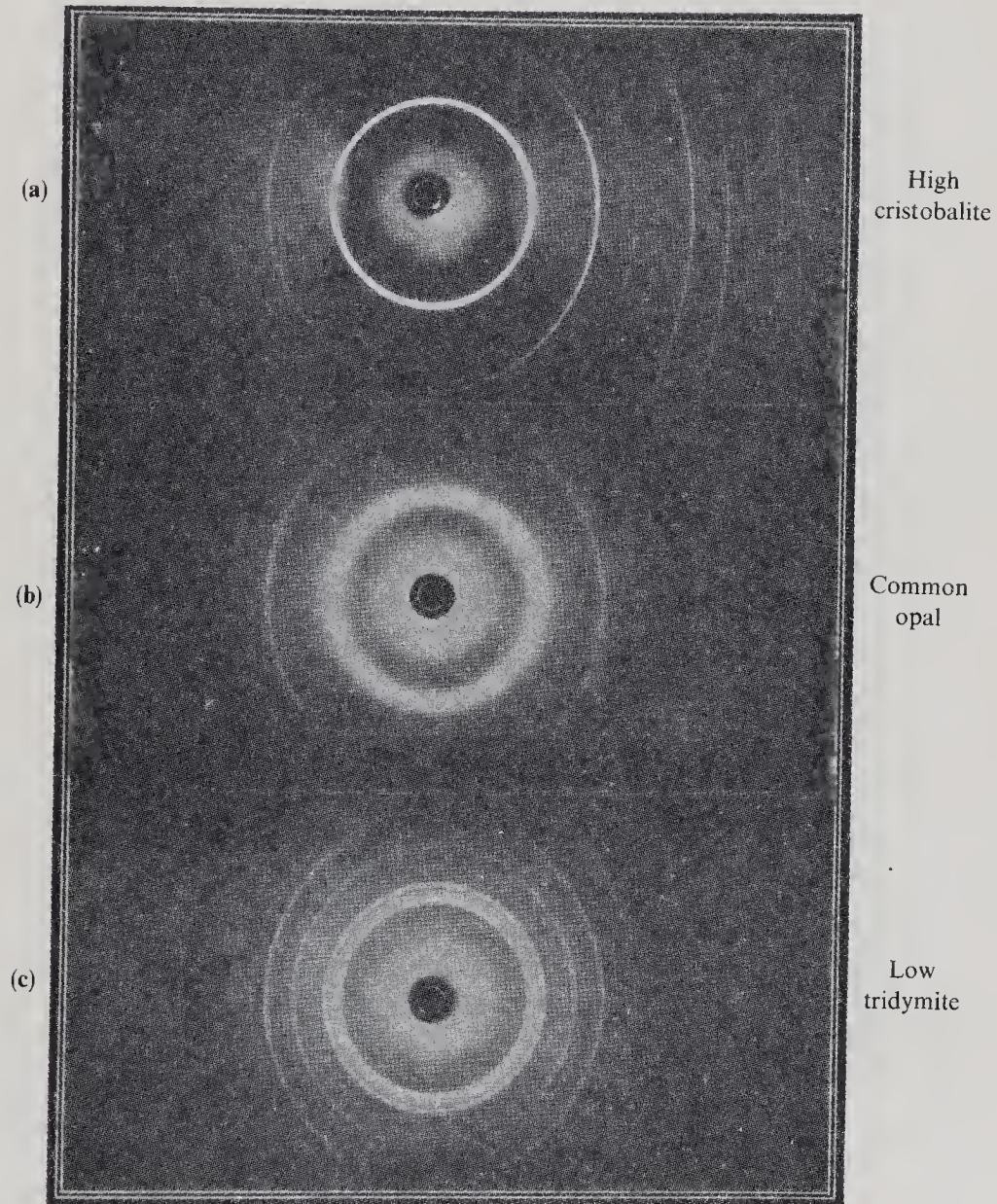


Figure 13. X-ray diffraction patterns.

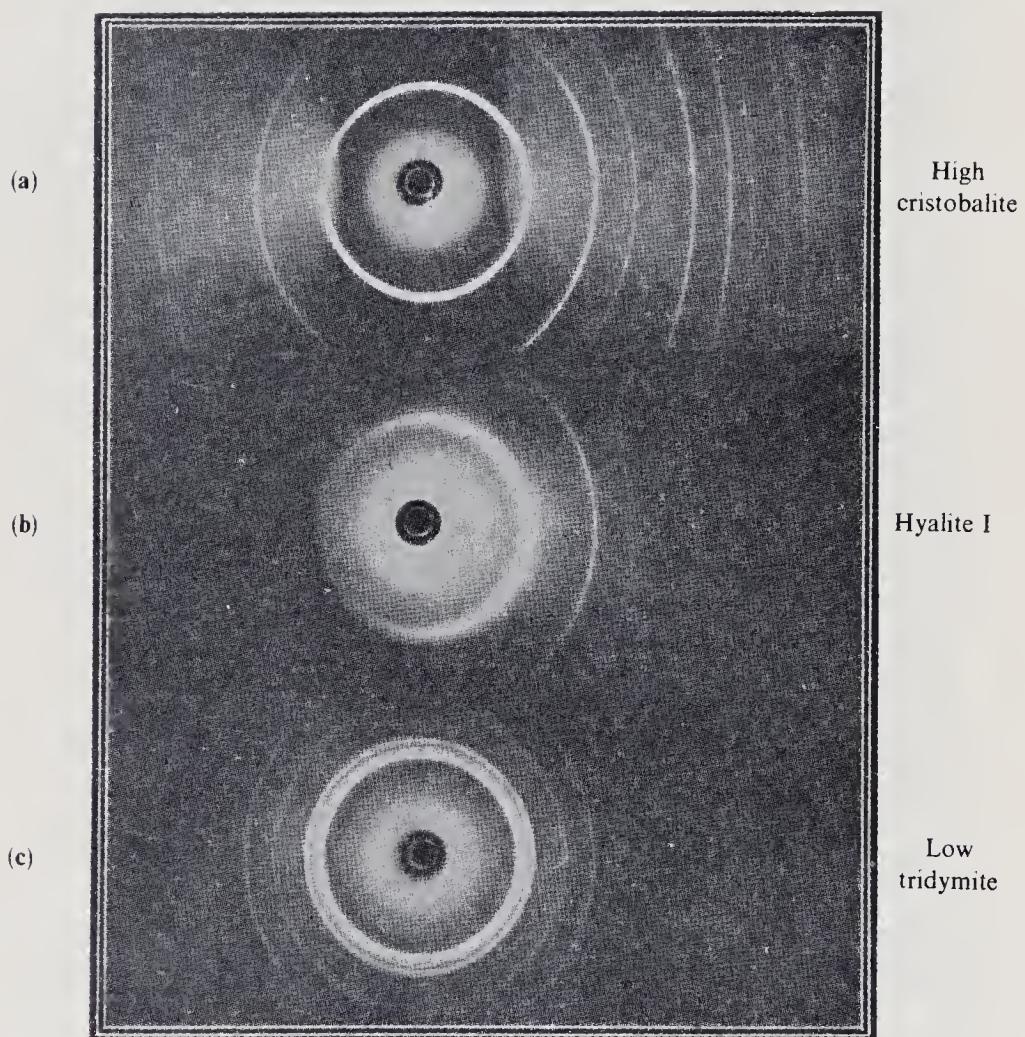


Figure 14. X-ray diffraction patterns.

Plate VI

# The structure and optical behaviour of pearls

SIR CV RAMAN and D KRISHNAMURTI

(Memoir No. 49 from the Raman Research Institute, Bangalore)

Received May 5, 1954

## 1. Introduction

The pearl holds a unique position amongst gems by reason of its natural beauty which needs no enhancement at the hands of the lapidary. It is also distinguished from the rest of them by the fact of its origin within the living body of a mollusc. For these reasons, it is a product of great and general interest. The aim of the present paper is to lay bare and express in the language of science the effects which pearls display and for which they are so highly admired.

The investigations here reported may be regarded as a sequel to a recent paper<sup>1</sup> by us in these *Proceedings* which concerned itself with iridescent shells. It was shown in that paper that the birefringence of nacre notably influences the spectral character of its iridescence. Further, it was shown that the discrete structure of the material results in characteristic diffusion phenomena which, no less than the iridescent reflections, make themselves evident in the observed optical behaviour of the shells. In view of the general similarity in nature of the material composing pearls and of the nacre in iridescent shells, it is to be expected that analogous effects would be observed in both cases. The spherical or nearly spherical shape of a pearl has however to be considered in this connection. Further, neither the structure of the material nor the nature of the stratifications is necessarily identical in the two cases. In the present paper, observations are presented bearing on these questions. The most noteworthy outcome of the investigation is to show that the diffusive properties of the material composing pearls play a major role, which is indeed no less important than the reflection of light by the stratifications, in making pearls the beautiful objects that they are.

## 2. The birefringence of pearls

It is well known that in the production of cultured pearls, a sphere of extraneous material (usually mother-of-pearl) is inserted within the mollusc, as a result of which, it deposits a whole series of layers in the course of years around the nucleus

thus provided. By cutting a cultured pearl in two halves, it is easy to remove the nucleus and obtain two hemispherical shells of the deposited material. These shells are in a very useful form for a study of the optical characters of the substance composing pearls.

Placing such a hemispherical shell between crossed polaroids and viewing it normally along its axis through a magnifying lens against a source of light, one observes an interference figure (see figure 15 in plate IV) which is very similar to the conoscopic figure of a plate of a biaxial crystal seen under the polarising microscope. It is remarkable that such a figure is observed in *parallel light* in the present case. The explanation of it is the hemispherical shape of the shell coupled with the fact that its optic orientation everywhere follows the curvature of the surface. Hence, when traversed by a parallel beam of light, the interference figure is localised at or near the curved surface of the shell. If the hemisphere is rotated round its axis, the isochromatic lines in the figure are observed to rotate with it, while the isogyres pass through a cycle of changes. If, on the other hand, the hemispherical shell is rotated around a diameter, the entire pattern drifts along the surface of the shell but remains substantially unaltered.

Another simple and effective way of exhibiting the birefringence is to grind one of the hemispherical shells cut from a cultural pearl to a flat surface on both sides and to mount the plate thus obtained in canada balsam between glass coverslips. Since the stratifications in the material are curved, a specimen thus prepared and mounted reflects light like a spherical shell. However, when held up against a lighted window, it becomes evident that the plate has a circular bevelled edge where the original spherical surface meets the parallel plane faces. This bevelled edge acts like a circular prism, and since the material is doubly refracting, two concentric rings of light are seen around a source of light when the latter is viewed through the plate (see figure 1, plate I). On tilting the specimen, the two circles become eccentric with respect to each other (see figure 3, in plate I). On further tilt, both the rings of light become elliptic, the outer one much more so; the two ellipses touch each other at one end of the major axis and are widely separated at the other end (see figure 5, plate I). At such oblique settings the rings also exhibit distinct colours due to dispersion. That these effects arise from the birefringence of the material is confirmed by viewing the rings of light through a polaroid. It is then noticed that the rings are extinguished in certain regions which shift around as the polaroid is rotated (see figures 2, 4 and 6 in plate I). In the case in which the source of light is viewed normally through the plate, the rings are extinguished at the ends of two diameters which are mutually perpendicular to each other.

### 3. The structure of the pearly layers

The shells of the bivalves<sup>2</sup> exhibit conoscopic figures closely resembling that reproduced as figure 15 in plate IV. It follows that the orientation of the

aragonite crystallites is very similar in the two cases. In other words, the crystallites in pearls have their *c*-axes more or less exactly normal to the laminations, while their *a* and *b* axes also have fairly defined orientations in the plane of the laminations. This is confirmed by X-ray diffraction studies, all that is necessary being to send a fine pencil of X-rays along the axis of the hemispherical shell and to record the results on a flat film. Two such photographs recorded at this Institute by Mr A Jayaraman are reproduced as figures 7 and 8 in plate II. The former was obtained with the filtered X-radiation from a copper target and the latter with unfiltered molybdenum radiation. In both records, we notice that the bright arcs have a finite spread, thereby indicating that the orientations of the *a* and *b* axes in the plane of the stratifications have a tolerably large range of variation. It may likewise be assumed that the direction of the *c*-axis is also sensibly variable, as has been established by X-ray methods<sup>3</sup> in the case of the bivalve shells. Comparison of figure 8 with the figures reproduced in the papers of Rama Swamy quoted show that the fluctuations in the orientation of the *a* and *b* axes are of the same order of magnitude in the two cases.

When a bright source of light is viewed normally through a thin plate of an iridescent shell having its faces parallel to the stratifications, a characteristic diffusion halo is observed; for the bivalves, this consists of a diffuse central spot overlying the source and two other diffuse spots lying one on either side of it<sup>1</sup>. The observation indicates that the aragonite crystallites are arranged in parallel rows along the lines of growth of the shell; the spacings of the rows calculated from the separation of the diffuse spots agrees with that directly observed with thin sections examined under the microscope<sup>2</sup>. If the material in cultured pearls had a similar structure, we should expect to be able to observe it when thin layers are examined under the microscope and also to see similar diffusion haloes. These anticipations are to some extent supported by the results of observation. We do indeed find that thin plates of the material under a microscope exhibit a fibrous structure in the plane of the laminations. We are also able to observe in some cases, diffusion haloes similar to those of the bivalve shells (see figure 13 in plate IV). On the other hand, in other cases, a different form of diffusion halo is observed, consisting of a pattern of six diffuse spots arranged in the form of a hexagon and surrounding the central diffuse spot; two of these spots at the end of a diameter are brighter than the rest (see figure 14 in plate IV). In the deposition of pearly material round a spherical nucleus, it is difficult to see why any particular direction on the surface should be favoured. It is therefore a little surprising that parallel rows of crystals, as in bivalve shells, are found in many cases. *Per contra*, it is not surprising that in other cases a halo indicative of a grouping of the crystallites in hexagonal order in the plane of the laminations is observed.

#### 4. The optical behaviour of pearls

*Some general remarks*—The appearance which any object presents to an observer is determined by the manner in which it is illuminated and by the particular way in which the light falling on the object is returned to the eye. Consider, for example, a case in which the object under examination is a polished metallic sphere held at some distance from an open window and viewed by the observer against a black background. The more perfectly polished the sphere is, the less would be the intensity of the light scattered by its surface. All that the observer would see in these circumstances is a well-defined image of the lighted window formed by reflection at the convex surface, while the sphere itself would hardly be visible. It is clear from this example that the possession of a high reflecting power by a spherical body would not by itself make it appear an attractive object.

The reflection of light by a pearl, however, occurs not solely or even principally at its surface. A whole series of spherical laminations participate, and since the material is optically heterogeneous, the reflections at the successive layers would be accompanied by a strong diffusion which would appear spread out over a range of solid angles, instead of forming a well-defined image of the luminous object. Hence, unless the source of light be of very small angular dimensions, its reflected image would be overlaid by diffuse light, and hence prevented from its being readily observed; *per contra*, the illusion would be created that the pearl is itself a lustrous and brilliant object. It is thus evident that the diffusion of light in directions approximating to that of regular reflection contributes notably towards making the pearl an attractive gem. The diffusion in other directions also plays an important role, as will appear later.

*The reflection-diffraction spectra*—With our earlier paper, we reproduced several photographs of the reflection-diffraction spectra of iridescent shells. These were recorded by allowing a narrow pencil of light to fall on the surface of a shell and receiving the reflected and diffused light on a photographic film held a few centimetres away. The photographs show very clearly that the diffraction of light by the corrugations at the external boundary and the reflection of light by the internal stratifications form a single coherent series of spectra, the iridescence usually appearing as the last of the series on one side. A similar phenomenon can also be observed with pearls when a magnifying lens is focussed on the image of a distant source of light formed by reflection at the surface of the pearl. A series of spectra are then seen in focus whose separation depends on the angle at which the stratifications meet the surface; if they were strictly parallel to the surface, the spectra would all overlap and we would observe only a single coloured image of the source. More generally, however, the spectra are seen clearly separated.

*The diffusion-halo of reflection*—Surrounding the reflected image of the source (or the whole group of reflection-diffraction spectra) is observed a phenomenon

which may be designated as the diffusion-halo of reflection. The structure of this halo varies to some extent from specimen to specimen. It is most clearly seen when the external surface is truly spherical and the stratifications are parallel to the surface, so that we observe only a single image of the source formed by reflection and exhibiting the characteristic iridescence. Through this image runs a straight band of light terminated by two diffuse spots and exhibiting over its length approximately the same colour as that of the iridescent reflection. This band is encircled by two coloured arcs lying on either side of it and exhibiting a tint complementary to that of the iridescence. The obvious analogy between this and the diffusion haloes by transmitted light reproduced as figures 13 and 14 in plate IV makes it clear that its origin is to be sought for in the discrete structure of the stratifications reflecting the light. The reason why the reflection halo exhibits complementary colours in the different parts of it is not difficult to fathom. The most prominent features of the halo are those due to light selectively reflected and diffracted by the upper layers of the stratifications and hence exhibiting the characteristic colour of the iridescence. The rest of the light thus filtered out would penetrate deeper into the stratifications and would be returned by diffusion, thereby appearing spread out over a wider range of angles, and this would exhibit the complementary colour.

*Some illustrative examples*—Figures 9 and 10 in plate III illustrate some of the observations set out in this and the preceding section. They are photographs respectively of a natural and of a cultured pearl illuminated in each case by two filament lamps set one on either side of the pearl. The cultured pearl appearing in figure 10 was a rather perfect specimen of spherical shape. On the upper right of that picture can be seen a small bright spot being the coloured image of the source formed by reflection and this appears surrounded by an extended area of diffuse radiation. Lower down in the picture can be seen the image of the second lamp surrounded by a rather complicated pattern of diffused light.

The natural pearl which appears in figure 9, though larger than the cultured pearls in our possession and far more expensive, had a rather irregular shape, and the optical effects exhibited by it were rather irregular. In the patch of light seen in the upper right hand side of the picture, the long streak and the diffuse spot separated from it record the reflection-diffraction spectrum exhibited by that part of the surface. These features appear surrounded by a strong patch of diffuse light. In the lower part of the same picture, effects of the same general nature due to the second source of light appear.

*The whispering gallery effect*—The photographs reproduced as figures 9 and 10 in plate III were recorded with the pearls placed on a sheet of black glass and in a dark room with blackened walls. Nevertheless the whole of the pearl shows up quite clearly. Not only are the spherical margins clearly seen, but they are actually somewhat brighter than the central regions of the pearl. Closely connected with

the explanation of these facts is the very remarkable phenomenon illustrated in figures 11 and 12 of plate III, recorded respectively with a cultured and a natural pearl. In figure 11 the pearl was illuminated tangentially on the side remote from that in which it was observed. Nevertheless it will be seen that the rear face is seen brilliantly illumined, the edges in particular being very bright. In figure 12, the pearl was illuminated at a part of the surface a little to the rear of that visible in the photograph. Nevertheless it can be seen that the entire periphery of the sphere appears lit up, the part on the right much more so.

The explanation of these effects is evidently related to the phenomenon of the lateral or transverse diffusion of light in nacre described and illustrated in a paper<sup>4</sup> published in these *Proceedings* twenty years ago. It was there shown that light penetrates nacre by diffusion through far greater distances parallel to the laminations than perpendicular to them. It is clear that a similar effect is operative also in the case of pearls. Light diffuses in directions parallel to the spherical laminations through considerable distances with relatively little loss, thereby enabling the pearl to be lit up and become visible in areas where no light falls directly.

*The spectral character of the iridescence*—Owing to the spherical shape of the pearls and the relatively small sizes available, the recording of the spectrum of iridescence presents some difficulties. The angle of incidence of the light would vary rapidly from point to point on the surface of the pearl and so also the spectral character of the iridescence. Hence it would be necessary to severely restrict the aperture of the incident beam and of the reflected beam as well. The iridescence exhibited by pearls varies considerably in its hue and saturation from specimen to specimen. The pearls taken up for examination were naturally those that exhibited the most vivid colours. Even in their cases, however, the results were rather disappointing. Complex spectra exhibiting a great many maxima of illumination, some stronger than the rest, were recorded. Further, the spectrum also showed large variations in different areas of the same specimen. See figures 16(a), (b), (c) and (d) in plate V recorded with a cultured pearl and figures 17(a), (b) and (c) in plate VI recorded with a natural pearl. These were obtained with the light beam incident normally on the specimen.

It would seem from these facts that the stratifications in pearl are somewhat different in nature from those in nacre. It appears not improbable that they consist of distinct groups of layers, each having a separate spacing and not a single continuous sequence. However, this is only a surmise which has to be tested out by further study of different specimens and a careful comparison with the nacre from the same species of mollusc.

*Effect of birefringence on the iridescence*—In spite of the complicated nature of the spectra, it has been found possible to establish their bifurcation at oblique incidences due to birefringence, as has already been done by us with nacre.

Figures 16(e), (f) and (g) are the spectra of a cultured pearl recorded respectively with vibrations perpendicular to the plane of incidence, with vibrations in the plane of incidence and with the vibrations unpolarised. The shift of the bands as between figures 16(e) and 16(f) is readily seen, while figure 16(g) is clearly a superposition of both. Figures 17(d), (e) and (f) are similar records obtained with a natural pearl and analogous effects are there noticed.

Figures 16(h), (k) and (l) in plate V obtained with a cultured pearl exhibit an interesting effect. They were recorded in circumstances similar to those of figures 16(e), (f) and (g) but with the beam incident on the surface of the pearl at an angle of about  $60^\circ$ . As in all other cases, the sphere was kept immersed in liquid paraffin to minimise disturbing effects at the external surface. It will be seen that the iridescence is almost completely polarised with its vibration direction perpendicular to the plane of incidence. Surprisingly enough, this effect was observed to persist over a wide range of angles of incidence.

*Transmission spectra*—Figure 18 in plate VI shows the spectra of the light transmitted by the hemispherical shell obtained from a cultured pearl, the incidence being normal in (a), (b) and (c) and a few degrees away from normal in (d), (e) and (f). The three spectra in each group were recorded respectively with light having its vibration direction perpendicular to the plane of incidence, the same lying in the plane of incidence and with the vibrations unpolarised. It will be noticed from the pictures that there is a noteworthy extinction of the component in the plane of incidence at oblique incidences, a phenomenon clearly analogous to that already noticed by us in the case of nacre.

## 5. Summary

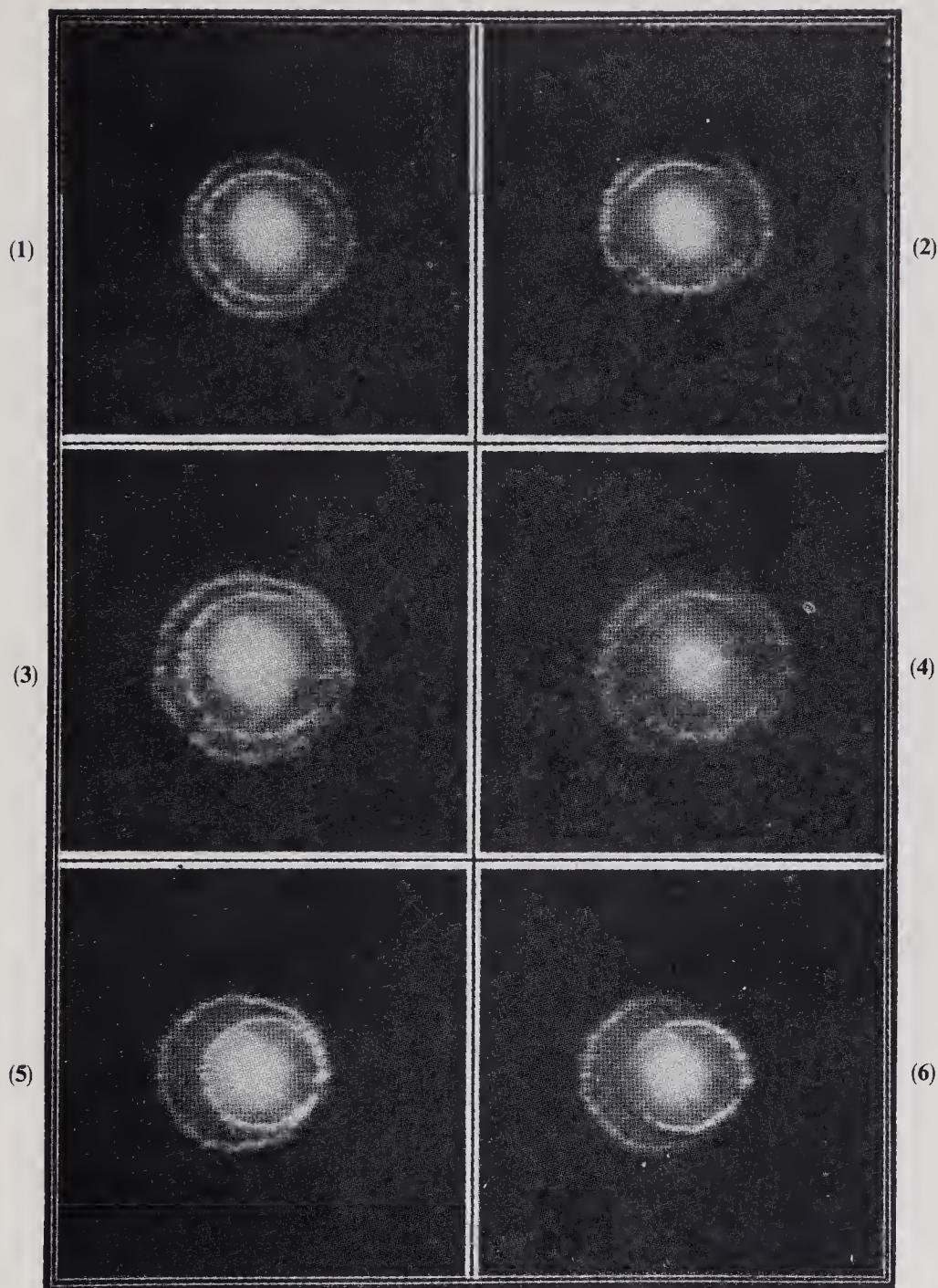
The paper embodies a study of the structure of the material composing pearls and of the optical effects which they display. The following topics are dealt with: (1) birefringence, (2) X-ray-diffraction patterns, (3) the reflection-diffraction spectra, (4) the diffusion haloes of reflection and transmission, (5) the whispering-gallery effect, (6) the spectral character of iridescence and the influence of birefringence thereon, (7) the transmission spectra. The most noteworthy result of the investigation is to show that the diffusive properties of nacre play a major role no less important than that of the reflection by its stratifications in the optics of pearls.

## Bibliography

A detailed account of the origin and structure of pearls will be found in F Haas' book *Bau Und Bildung Der Perlen*, (Leipzig, 1931). See also W J Schmidt's *Die Bausteine Des Tierkörpers* (Bonn 1924), pages 166–169.

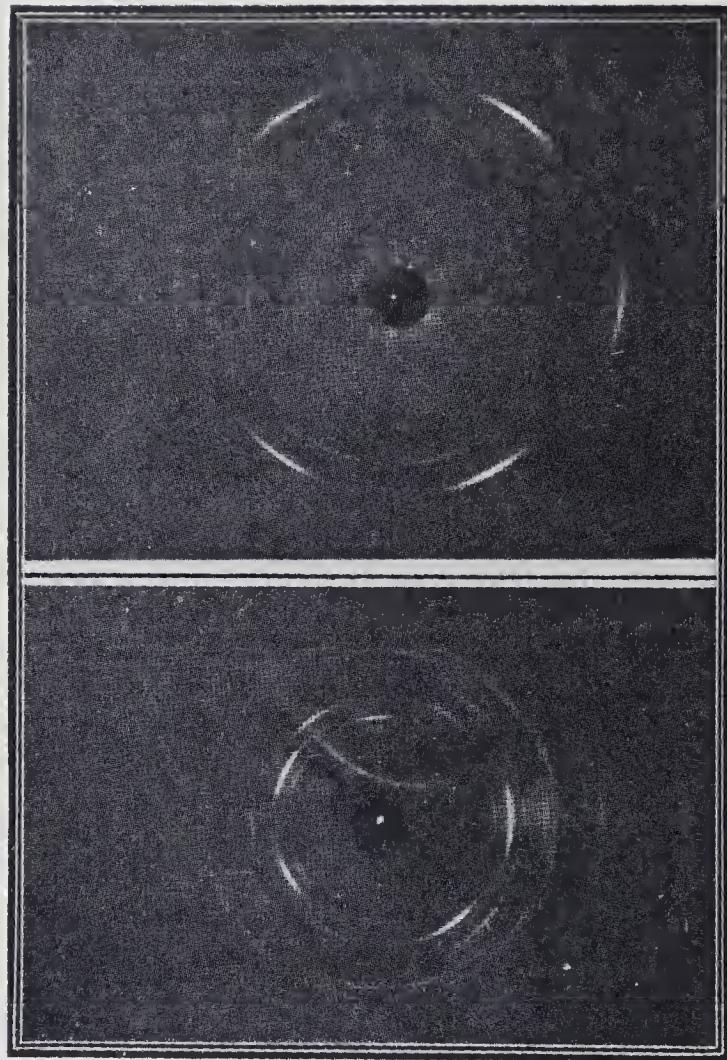
The culturing of pearls is an important Japanese industry and several laboratories in that country are at present investigating its problems and have published papers dealing with various aspects of the subject which are collected together in Bulletin No. 1 of the Nippon Institute for Scientific Research on Pearls (1953). The following papers are those referred to in the text.

1. Raman, C V and Krishnamurti, D, *Proc. Indian Acad. Sci.*, **A39** 1 (1954).
2. Rajagopalan, V S, *ibid.*, **A3** 572 (1936).
3. Rama Swamy, S, *ibid.*, **A1** 871 (1935); **2A** 345 (1935).
4. Raman, C V, *ibid.*, **A1** 859 (1935).



Figures 1-6

Plate I



Figures 7 and 8

Plate II

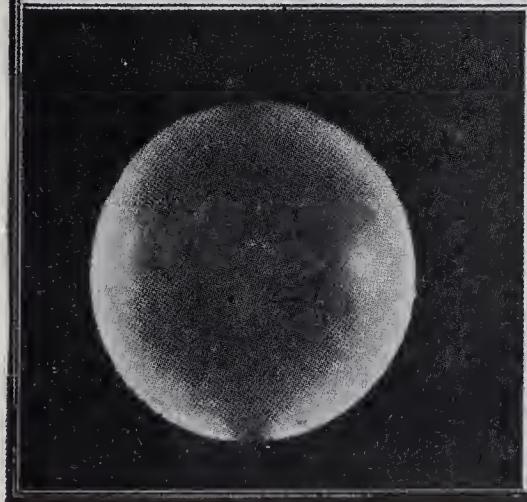
(9)



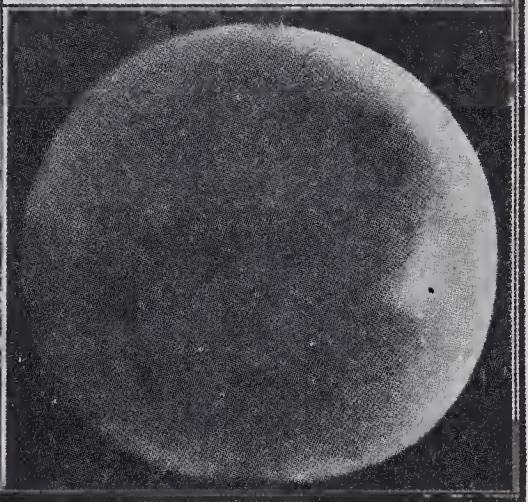
(10)



(11)

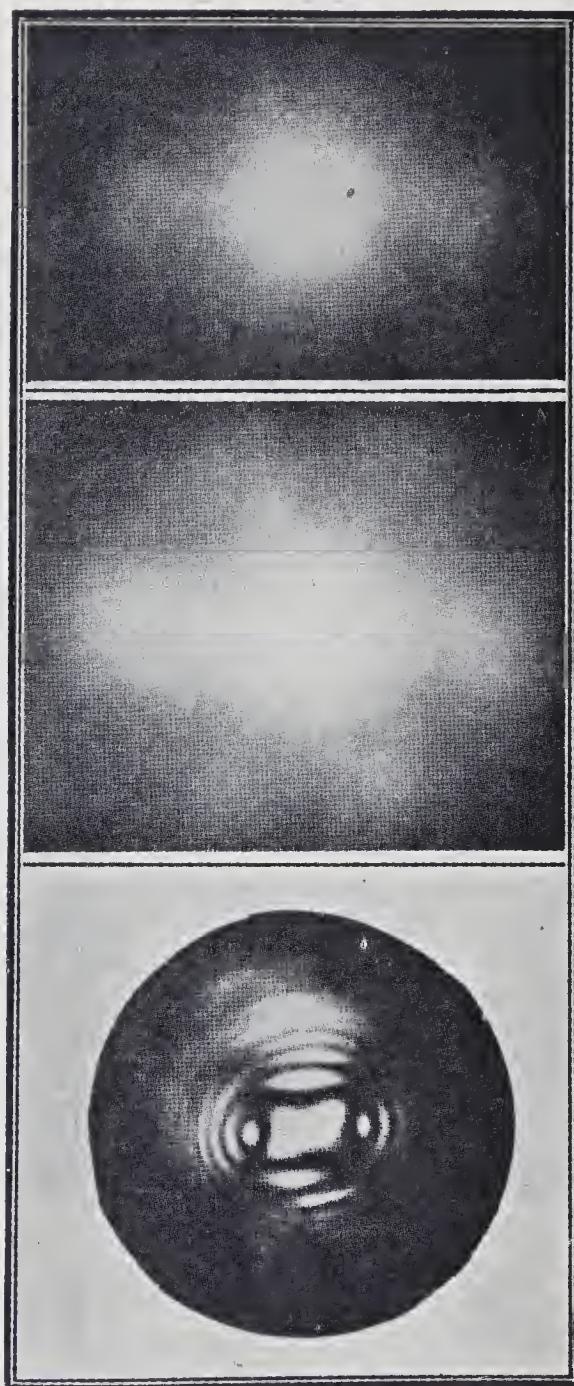


(12)



Figures 9-12

Plate III



Figures 13-15

Plate IV

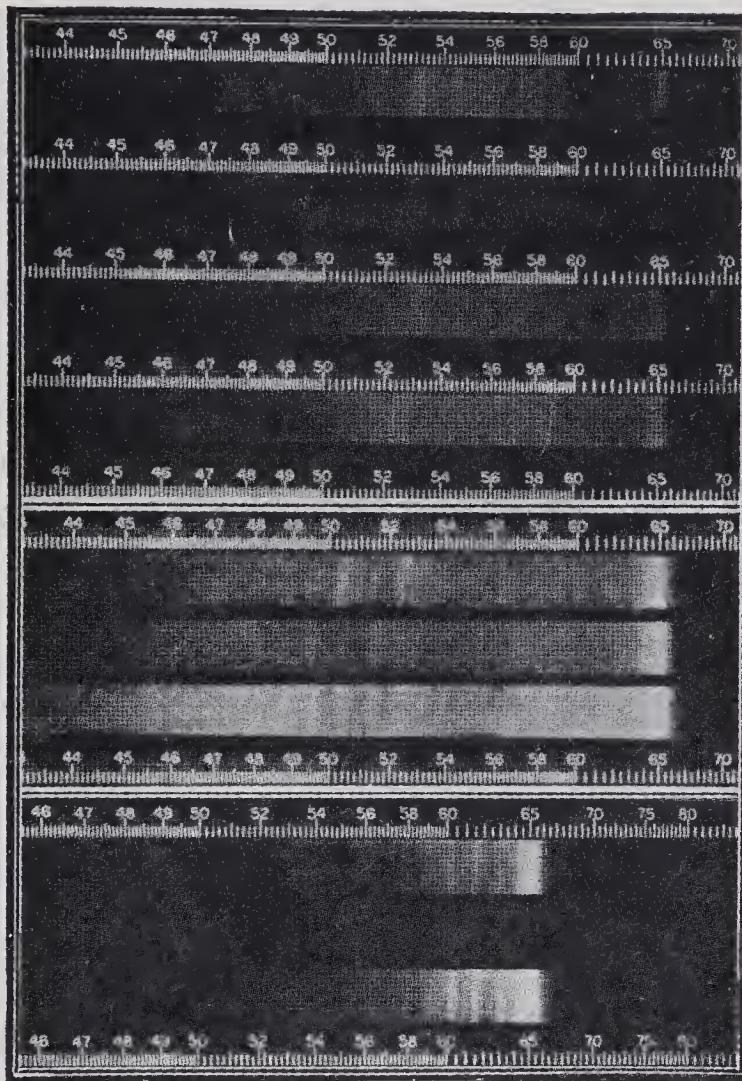


Figure 16

Plate V

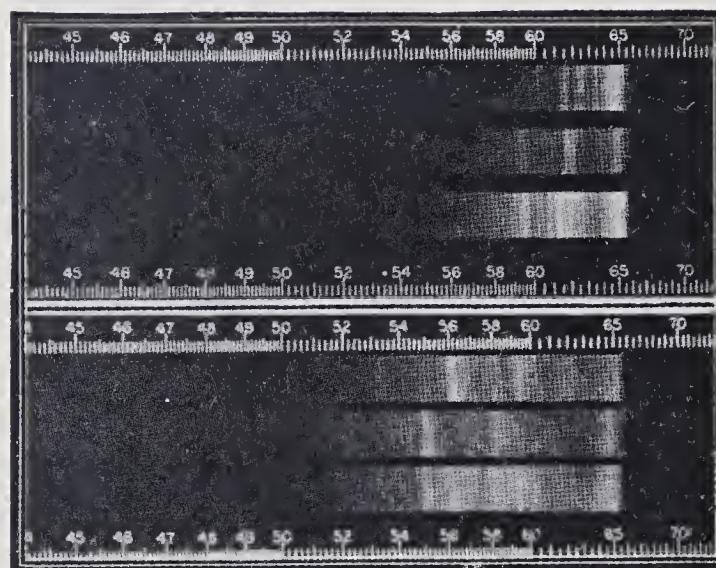


Figure 17

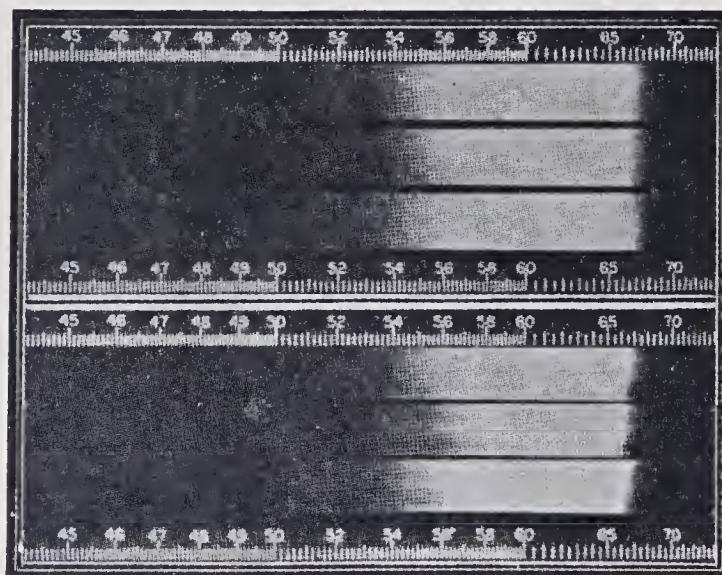


Figure 18

## Plate VI

## Optics of the pearl

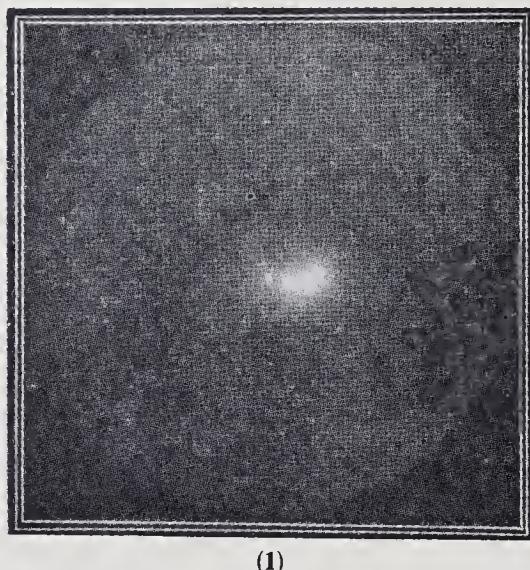
The pearl stands in a class by itself as a gem-stone which does not need the services of a lapidary to enhance its natural beauty. The characteristic of the pearl most admired is its lustre, though other features such as shape, size and colour are also important. A precise understanding of the optics behind its loveliness is therefore a matter of more than ordinary interest. The inadequacy of the explanations of it given in the text-books on gemmology becomes apparent on a critical examination.

Natural pearls are very expensive, and this is sufficient to discourage anyone who might feel inclined to investigate their structure and optical behaviour. Fortunately, however, the cultured pearls produced by the Japanese industry offer to the student a wealth of material of excellent quality at a modest price. As is well known, their production is the result of an operation by which a spherical pellet of calcareous substance is introduced into the body of the pearl oyster. In the course of years, the mollusc deposits a great many layers of pearly substance around the nucleus thus provided. Since the latter is a polished sphere, the deposited layers are also very regular and smooth. Indeed, it is the case that cultured pearls are optically superior to the more expensive natural pearls. By cutting a cultured pearl into halves, the nucleus can be taken out and the hemispherical shells of pearly material thus detached are in a very suitable form for physical examination. Many interesting observations can be made with them as has been described in a recent paper<sup>1</sup> by the present authors.

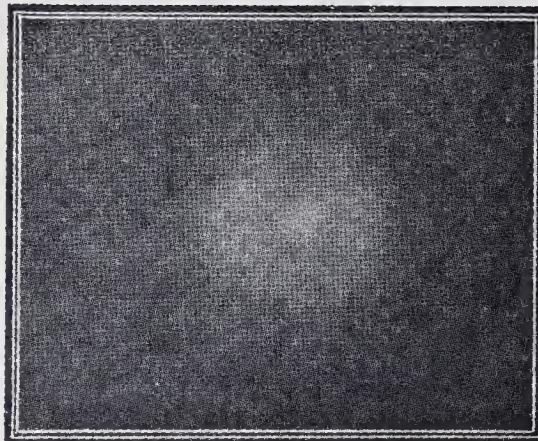
Very simple methods of observation suffice to reveal some highly significant facts regarding the optical behaviour of pearls. A small aperture backed by a brilliant source of light is placed a few feet above the head of the observer and the pearl is held in the path of the strong beam of light thus provided. It is then viewed by the observer through a hand magnifier. The optical effects then observed fall roughly into three groups, viz., (a) the reflection-diffraction spectra consisting of focussed images of the light source, (b) a chromatic diffusion halo surrounding these images and extending over the surface of the pearl over a considerable area, and (c) a general diffusion visible right up to the periphery of the pearl. We shall proceed to describe each of these phenomena in detail and discuss their origin and significance.

If, as is the case with perfect pearls, the layers of nacreous material are parallel to the external surface, they would conspire to give a single reflected image of the source exhibiting colour as a result of interference between the effects of the successive layers. If, on the other hand, the layers meet the surface obliquely, the

latter would present the aspect of an echelon grating. It has been shown by us<sup>2</sup> that in the case of mother-of-pearl the light diffracted at the surface as also that reflected by the internal stratifications appear together as a set of diffraction spectra forming a regular sequence. In the present case as well, similar results are noticed when the illuminated pearl is viewed in focus through a magnifier. The separation of the successive orders of spectra is usually very small, but occasionally they can be seen distinctly separated. Figure 1 is a photograph



(1)



(2)

**Figures 1 and 2**

obtained with a natural pearl in a particular setting. Three spots in a line can be seen; the sharpest appearing at the centre is the spectrum of zero order; the second is the diffraction spectrum of the first order, while the third spot is the characteristic iridescence appearing as the spectrum of the second order.

We now proceed to consider the second of the effects mentioned above, viz., the chromatic diffusion halo. This phenomenon which does not appear to have been noticed earlier has been briefly described by us.<sup>1</sup> It is characteristic of pearls and plays a fundamental role in their optical behaviour. Its observable features are notably influenced by the shape of the pearl, by the inclinations of the stratifications to the external surface and by the degree of optical perfection of the latter. The chromatic halo takes its simplest form in the ideal case of a spherical pearl in which the stratifications are strictly parallel to the external surface. It then appears as a diffuse circle of light with fainter outlying regions surrounding the iridescent reflection; there is a concentration of intensity in the halo near the opposite ends of one diameter. The predominant colour of the halo is complementary to the colour of the iridescence. A photograph of the halo in this typical case is reproduced as figure 2. A slight asymmetry of the intensity on the two sides is usually noticed, and this is very prominent when the successive orders of the reflection-diffraction spectra are widely separated. The colour of the diffusion halo may then be quite different on the two sides of it.

The observed effects indicate that the diffusion halo has its origin in the internal stratifications of the pearl and not at its external surface; this is indeed clear from the fact that its colour is complementary to that of the iridescence. The origin of the halo is to be sought for in the fact that the material of the pearl consists of individual crystallites of aragonite imbedded in a network of conchyolin. Each crystallite would diffract the light waves incident upon it in various directions, the iridescence appearing in the direction in which the diffracted radiations from the crystallites in any given layer are in agreement of phase. In other directions, they would give rise to a cone of diffuse light.

Figure 3 illustrates a remarkable effect exhibited by pearls. It is a photograph

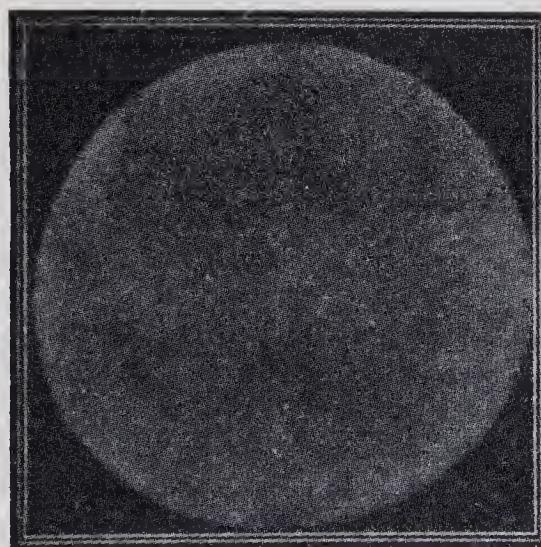


Figure 3

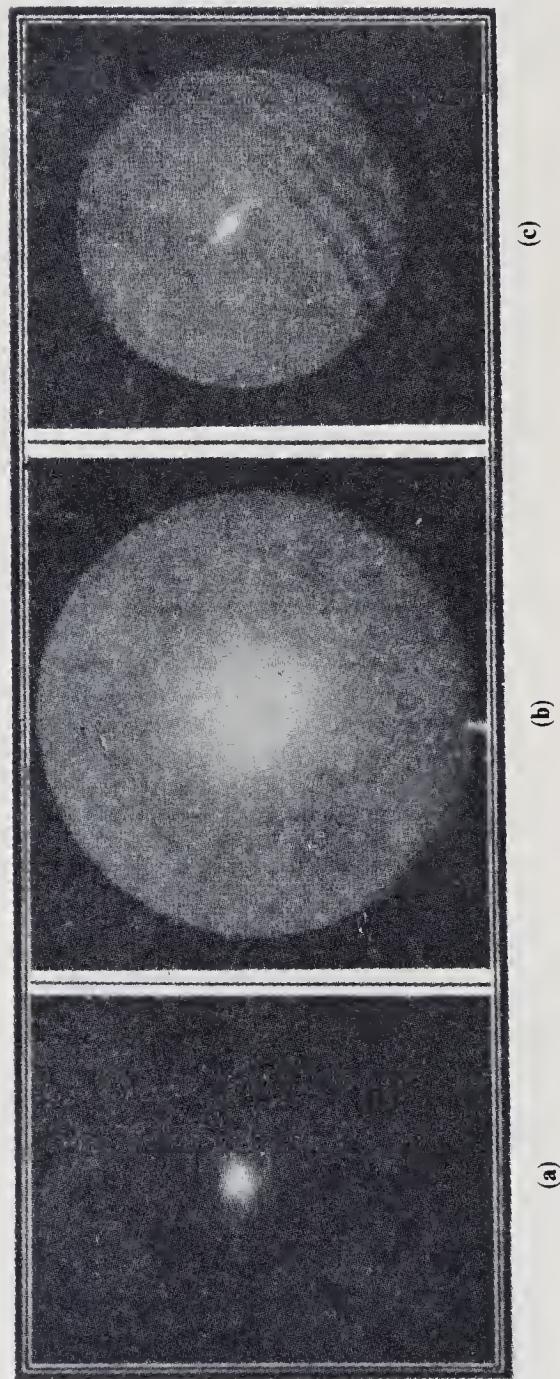


Figure 4

of a natural pearl illuminated centrally over a very narrow region on the side *opposite* to that from which it was observed and photographed. It will be noticed that the entire pearl is thereby rendered visible, the periphery appearing brighter than the central region. It is evident that the light falling normally on the rear surface of the pearl has travelled around following the laminations of its structure, and not *through* the pearl. A similar effect is observed in all cases, irrespective of the direction in which the illuminating pencil falls on the pearl or the particular area on which the incident light falls.

We shall now turn to the role which the three effects described above respectively play in the optical behaviour of pearls. Figures 4(a), (b) and (c) reproduce photographs showing respectively (a) a polished steel sphere, (b) a cultured pearl, and (c) a polished spherical segment of mother-of-pearl removed from a cultured pearl. All the three objects were illuminated and viewed in the same fashion, viz., normal to their respective surfaces, the original source of light being of small angular dimensions. But the appearance of the three objects is totally different. In the case of the steel sphere, we see a well-defined optical image of the original source, but the sphere remains invisible except in the immediate neighbourhood of the image of the source where a faint illumination is visible due to the imperfect polish of the surface. In the case of the mother-of-pearl as well, the optical image of the source is a prominent feature, but is much feebler than in the case of the steel sphere. On the other hand, the mother-of-pearl is itself visible by reason of the light diffused in the material.

Writers on gemmology usually attribute the beauty of the pearl to two distinct effects, viz., the reflection of light from the interior of the pearl and the diffraction of light at its exterior surface. The latter effect would be non-existent in the case of a perfect pearl. Moreover, the angular separation of the various orders of the reflection-diffraction spectrum is so small, that with an extended source of light they need not at all be considered as distinct phenomena. Further, the reflection of light at a spherical surface would not suffice to make it visible, much less to make it an attractive object. It is evident therefore we have to look elsewhere for an explanation of the beauty of the pearl. This is to be found in the superposition of the reflected light and the chromatic diffusion halo. Such superposition would necessarily occur when the source of light is of extended area, and since their colours are complementary, their joint effect would be to make the pearl seem to the observer to be a silvery white and lustrous object, quite unlike a polished sphere which only exhibits the reflected images of external objects. The impression that the pearl is a lustrous object would be further enhanced by the diffuse light emerging from the shadowed areas on which no light is directly incident. The brilliance of the periphery would further enhance the general effect by enabling the entire pearl to be clearly seen.

We may sum up the situation by the statement that the coloured reflection of light by the stratifications of the nacre is not by itself an adequate explanation of the beauty of the pearl; the special properties of the material which manifest

themselves in the chromatic diffusion halo and in the propagation of light parallel to the stratifications play the leading role in making the pearl appear a lustrous and attractive object.

C V RAMAN  
D KRISHNAMURTI

---

<sup>1</sup>Raman C V and Krishnamurti D, *Proc. Indian Acad. Sci.*, 1954, **39A**, 215.

<sup>2</sup>Raman C V, *Ibid.*, 1954, **39A**, 1.

# On the chromatic diffusion halo and other optical effects exhibited by pearls

SIR C V RAMAN and D KRISHNAMURTI

(Memoir No. 52 from the Raman Research Institute, Bangalore)

## 1. Introduction

The present paper concerns itself with the optical phenomena observed when a pearl is illuminated by a light-source of small angular dimensions and is viewed in the reverse direction. They were briefly reported upon in these *Proceedings*<sup>1</sup> but will be described and discussed rather more fully in the present communication. It appears worthwhile doing this, for, as was explained in the earlier paper, it is these phenomena that make the pearl appear so attractive an object when illuminated by extended light-sources.

As is well-known, the material of the pearl consists of an immense number of tiny crystals of aragonite held in an encompassing network of conchyolin. In the previous paper, the details of this structure and its optical behaviour have been discussed in detail and it is therefore not necessary to traverse the same ground here. The photographs reproduced as figures 21 and 22 in plate V are however of interest, as they illustrate the conclusions there stated. Figure 21 is an enlarged view of the shell of a cultured pearl as observed between crossed polaroids in parallel light. It was prepared by grinding down a fragment of the shell into a flat thin plate and mounting it in canada balsam between glass cover slips. From the birefringence pattern seen in the photograph, it is evident that the material consists of successive layers of approximately spherical shape superimposed on each other. However, the extinctions are far from being uniform, nor are the rings regularly spaced, thereby indicating that neither the optic orientation of the crystallites nor the spacing of the successive layers is completely regular. Figure 22 exhibits a small region of the same preparation as seen under a microscope between crossed nicols in parallel light; the approximately linear arrangement of the crystallites is well shown.

## 2. Some general observations

It is obvious that a material consisting of discrete crystallites would be optically turbid and would strongly diffuse the light traversing it. The explanation usually

given of the lustre of pearls as due to internal reflection and/or diffraction at the surface ignores this feature and is totally inadequate. Actually, we observe three distinct effects: (a) the reflection and diffraction of light by the stratifications; (b) a chromatic diffusion halo which surrounds the direction of reflection; and (c) a diffusion of light through large angles consequent on a "whispering gallery effect". It is the co-operation of these three phenomena that results in the characteristic lustrous appearance of the pearl.

Figures 1, 2, 3 and 4 in plate I illustrate all the three phenomena referred to above. They are photographs of a natural pearl illuminated by a light-source of small angular dimensions and viewed in the reverse direction. The pearl was not perfectly spherical and in consequence, the four figures which were recorded in slightly different settings of the pearl show recognisable differences. In figure 1, we observe a single spot at the centre and this is surrounded by a diffuse halo. In figures 2, 3 and 4 we observe two, three and four bright spots respectively, as also a diffuse halo which has its maximum intensity in the vicinity of the last of the spots. Outside the halo, there is a general luminosity which has its maximum intensity at or near the spherical periphery, thereby making the latter appear very clearly visible.

Before we proceed to describe and discuss these effects in detail, it should be remarked that they have their analogues in the phenomena observed and described by one of us many years ago<sup>2,3</sup> in the case of the iridescent molluscan shells. But there are differences consequent on the fact that we are now concerned with strongly curved layers instead of plane or nearly plane stratifications.

### 3. The reflection-diffraction spectra

The optical effects arising at the surface of a stratified medium depend on the angle at which its layers meet the external surface, as also upon the actual configuration of that surface. In the particular case when the stratifications are perfectly parallel to the external face, the incident light-waves would be reflected at that face and also at each of the boundaries between the successive strata. Since these surfaces are curved in the present case, such reflections would result in a well-defined image of the source being visible when the pearl is viewed through a suitably held lens. The image would exhibit colour consequent on the mutual interference of the reflections from the successive boundaries.

If the stratifications of the material meet its surface at an angle, the external boundary would present the aspect of a diffraction-grating, and if it is sensibly corrugated, would give rise to a series of diffraction spectra with more orders on one side than on the other. As was shown in the case of iridescent shells and illustrated by a series of photographs in a recent paper by the present authors,<sup>4</sup> the sequence of spectra thus resulting would include the light internally reflected by the layers of the material as one of them, usually the last of the series. Further,

the order of that spectrum would be the order of the interference of the reflections from the successive strata. In the present case, we are concerned with a convex diffraction grating and the spectra to which it gives rise would be focussed by a lens to a series of spots or streaks.

The foregoing consequences of the theory are in agreement with what is actually observed and are illustrated by figures 1, 2, 3 and 4 in plate I already referred to. In the case of cultured pearls of good quality, the stratifications are usually so nearly parallel to each other and to the external surface that the separation of the different orders in the reflection-diffraction spectrum is very small. Careful focussing is then necessary to enable them to be seen clearly separated.

#### 4. Nature and origin of the chromatic halo

We may here appropriately refer to the phenomenon<sup>3</sup> of the body colour exhibited by nacreous iridescent shells when illuminated and observed in directions other than of the internally reflected light. This body colour is most vivid in directions not too remote from that of the internal reflection and then exhibits a complementary tint. It fades away in intensity and also changes colour as the direction of observation is further removed from that of regular reflection. The angle of incidence of the light on the surface of the material influences the colour of the internal reflection as also the body colour, but their complementarity when viewed in adjacent directions persists.

The chromatic diffusion halo exhibited by pearls is a phenomenon of the same general nature as the body-colour of nacreous shells referred to above, but the shape of the pearl and the curvature of its reflecting layers have important consequences. When the pearl is illuminated by a light-source of small angular dimensions and is viewed in the opposite direction, the angle of incidence of the light on the surface alters progressively from the centre outwards, and the light rays reaching the observer also make increasingly larger angles with the normal to the surface. Hence, what is observed would be an ensemble of effects; at the centre, the internal reflection would appear as a bright spot, and surrounding it would appear the body colour with its intensity and tint changing progressively from the centre outwards consequent on the changing angles of incidence and observation.

The foregoing analogy between the chromatic diffusion halo of pearls and the body colour exhibited by iridescent nacre enables us to predict various features of the former phenomenon. The diffusion halo should in the immediate vicinity of the reflected light exhibit the complementary colour. Then again, the larger the pearl the greater would be the apparent size of the halo as observed on its surface. If the pearl is not spherical in shape, but has a different curvature in different planes, we should expect the halo to spread further out from the centre in the

plane of least curvature. Complications may also be expected if the stratifications of the material are not parallel to its external surface. For, instead of a simple reflection we would then have streams of diffracted radiations emerging in different directions and these would be superposed on the diffusion halo, thereby modifying the effects observed. Hence, the chromatic diffusion halo is best studied with pearls in which the separation between the various orders of the reflection-diffraction spectrum is either zero or very small.

The origin of the chromatic diffusion halo is evidently to be sought for in the fact that the reflecting layers in the pearl are not optically continuous but consist of individual crystallites of aragonite held together in a network of concholin. Each crystallite would therefore function as a diffracting particle, and the light returned by an individual layer would not be confined to the direction of geometric reflection, but would be spread out over a cone whose angular dimensions would be determined by the size and shape of the individual crystallites. The distribution of intensity of the diffracted rays within such cone would necessarily also be modified by the interference of the rays diffracted by adjacent crystallites. The manner in which the crystallites are disposed in the individual layers would therefore also have to be considered. The grouping of the crystallites in parallel linear rows which appears to be a common feature in cultured pearls (see figure 22, plate V) is a factor which needs to be taken into account in this connection. We may, in fact, expect to find that the arrangement of the crystallites in parallel and roughly equidistant rows would give rise to specific features in the chromatic diffusion halo, as it actually does in the diffusion haloes observed in transmitted light.<sup>1</sup> Finally, we have also to consider that the light emerging from the material is not a simple summation of the light diffused by successive layers. The progressive changes in phase and intensity of the incident light as it advances into the material and the mutual interferences of the radiations diffused backwards by the successive layers would have to be taken into consideration. Indeed, it is only on some such lines that we could hope to explain the complementarity of colour in adjacent directions of the reflected and diffused radiations.

## 5. Some illustrative examples

Reproductions in natural colour would be necessary to exhibit the beauty of the chromatic haloes of pearls in a satisfactory manner. However, by using panchromatic films and when necessary also colour filters, it has been possible to obtain pictures which show a fair degree of photographic contrast and exhibit the characteristic features of the halo. Twelve such photographs showing typical examples are reproduced as figures 9 to 20 in plates III and IV. Individual figures amongst them illustrate the various features referred to above. For example, the influence of the shape of the pearl on the configuration of the halo is

shown clearly by the circular haloes reproduced in figures 9, 10 and 13 which were obtained with spherical pearls. On the other hand, figure 11 which exhibits an elliptic halo was recorded with a spheroidal pearl, its major elongation being in the same direction as the elongation of the halo itself. Figure 14 which was recorded with a barrel-shaped specimen exhibits a certain amount of parallelism with the shape of the pearl. A characteristic feature which frequently appears is a bar of diffuse radiation along a diameter of the halo having the same colour as the iridescence, while the curved arcs on either side exhibit the complementary colour. A distinct concentration of intensity is also generally seen in such cases at the two ends of the bar. Figures 11, 15 and 16 exhibit these features and it seems highly probable that they are a consequence of the arrangement of the crystallites of aragonite in linear rows perpendicular to the direction of the bar observed.

A certain measure of optical perfection in the stratifications of the pearl and of its surface is necessary in order that the halo be regular and exhibit vivid chromatic effects. Irregularities show up quite prominently in the character of the diffusion halo. A typical example is figure 19 which shows a patchy appearance. Cases are also not lacking in which the halo exhibits comparatively little colour. In such cases the reflection also exhibits little iridescence, suggesting that these features are interrelated.

The diffusion of light which manifests itself in the chromatic halo clearly plays an important role in the general appearance of a pearl. It extends over a substantial area of the pearl and hence when the illuminating source is also of extended area, the reflected and diffused streams of radiation overlap. Thus, an observer would no longer perceive sharply defined images of the external luminous objects but would instead regard the pearl itself as a lustrous object. The complementarity of the colours of the reflected and diffused radiation would compensate each other and result in a silvery white lustre.

## 6. The whispering gallery effect

Figures 5, 6, 7 and 8 in plate II recorded with a natural pearl exhibit a noteworthy phenomenon characteristic of pearls. They illustrate the fact that light incident on the surface of the pearl in any direction diffuses around within the material in the plane of the stratifications with very little loss.

Figure 5 illustrates a case in which a narrow pencil of light was incident normally on the pearl and the latter was viewed from the remote side in the opposite direction. It will be seen that the pearl nevertheless appears luminous, the periphery being much brighter than the centre. Hence the effect observed does not arise from a penetration of the light *through* the body of the pearl.

In figure 6, the light was incident almost normally on the surface of the pearl in a direction transverse to that in which it was observed. The actual area of illumination was small and was located just behind the bright edge seen in the

figure. It is evident from the photograph that the light has travelled along the periphery of the pearl in all directions transverse to the direction of incidence of the light. The slow fall in intensity of the apparent luminosity of the pearl as we move away from the illuminated spot is a noteworthy feature.

In figure 7, the illuminating pencil grazed the surface of the pearl horizontally at a point a little to the rear of the top of the picture. A remarkable feature of this photograph is that it exhibits no very marked asymmetry of illumination to the right and to the left. The fall of intensity of the luminosity from the top to the bottom of the picture is quite slow.

Figure 8 was photographed in the same circumstances as figure 5 except that the illuminating pencil grazed the surface of the pearl instead of falling on it normally. Here again, it is significant that there is little difference in intensity between the right and left halves of the picture.

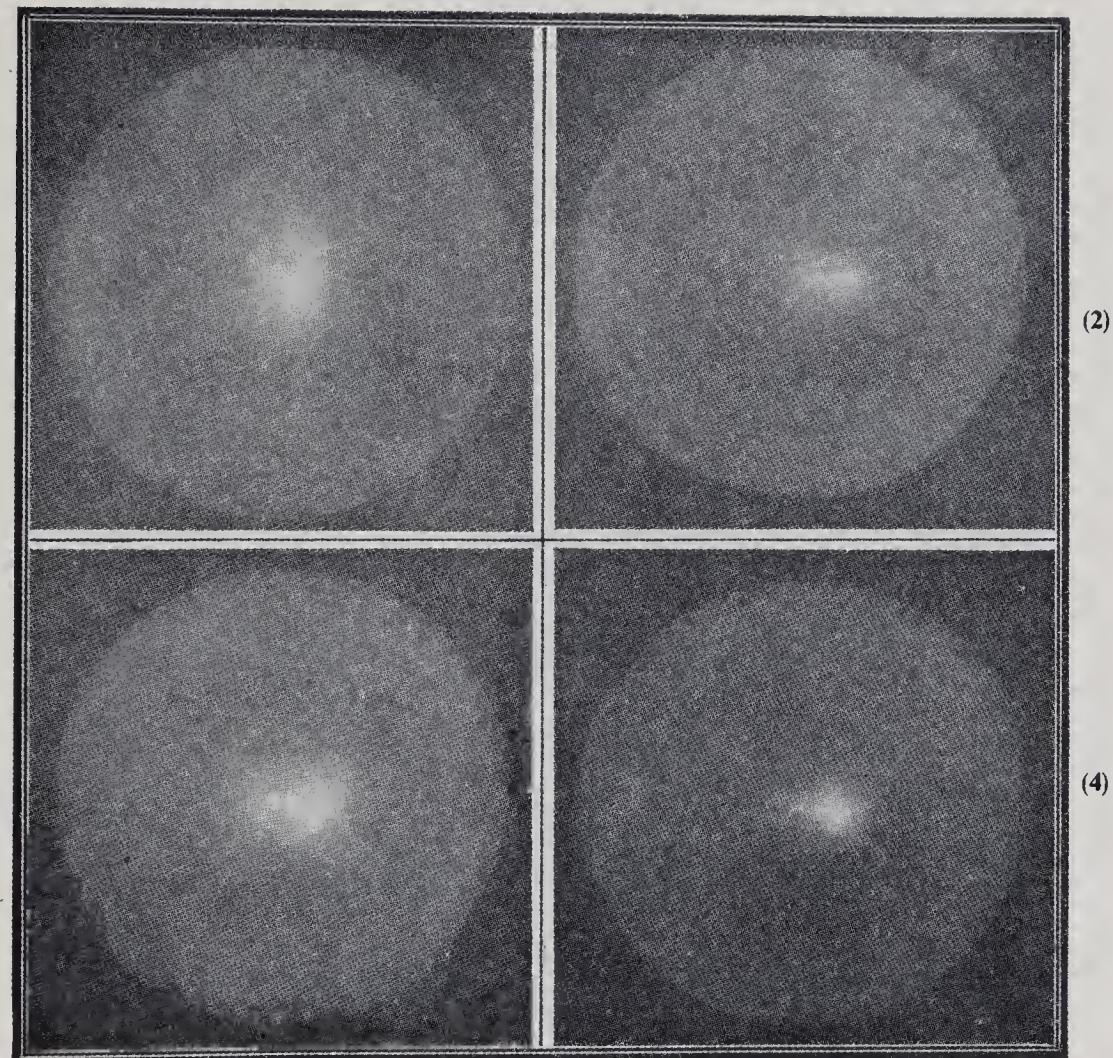
The spherical shape of the pearl plays a not unimportant role in these phenomena, but it is not the essence of the matter. Long ago, it was shown by one of us<sup>3</sup> that when light falls on a plane nacreous shell, it diffuses far more freely in directions parallel to the stratifications than normal to them. We need not here enter into an explanation of this fact, but will content ourselves with pointing out that essentially the same property of the nacreous substance operates in the case of pearls, enabling light falling in any direction on any part of the surface to find its way around with relatively small attenuation, thereby making the pearl visible even in regions where no light is directly incident.

## 7. Summary

The paper discusses the origin and character of the coloured diffusion halo exhibited by pearls surrounding the reflected image of a light source seen at their surface. Twelve photographs illustrative of various types of halo are reproduced. Other aspects of the optical behaviour of pearls are also described and discussed with illustrative photographs.

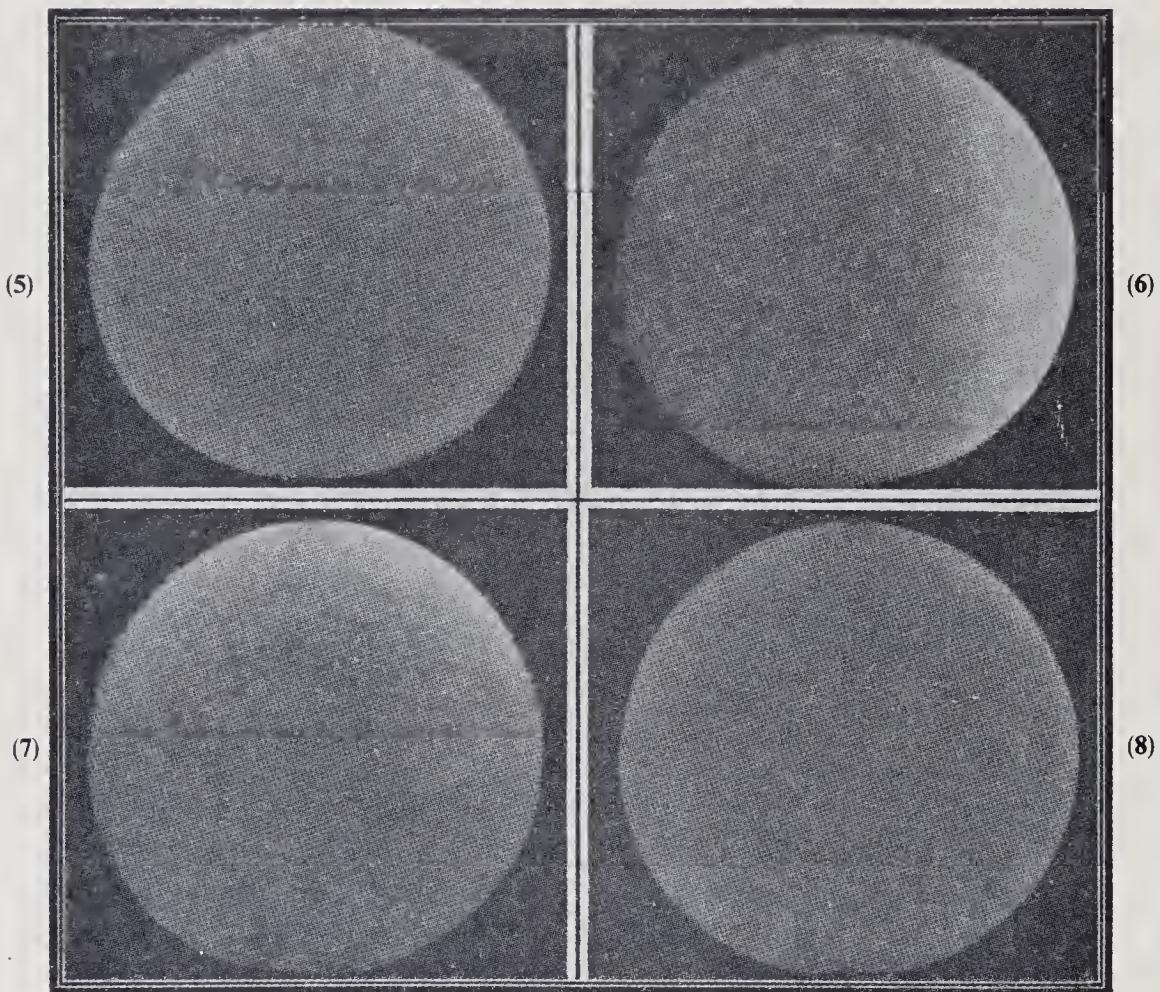
## References

1. Raman C V and Krishnamurti D, *Proc. Indian Acad. Sci.*, 1954, **39A**, 215.
2. Raman C V, *Ibid.*, 1935, **1A**, 574.
3. *Ibid.*, 1935, **1A**, 859.
- 4: Raman C V and Krishnamurti D, *Ibid.*, 1954, **39A**, 1.



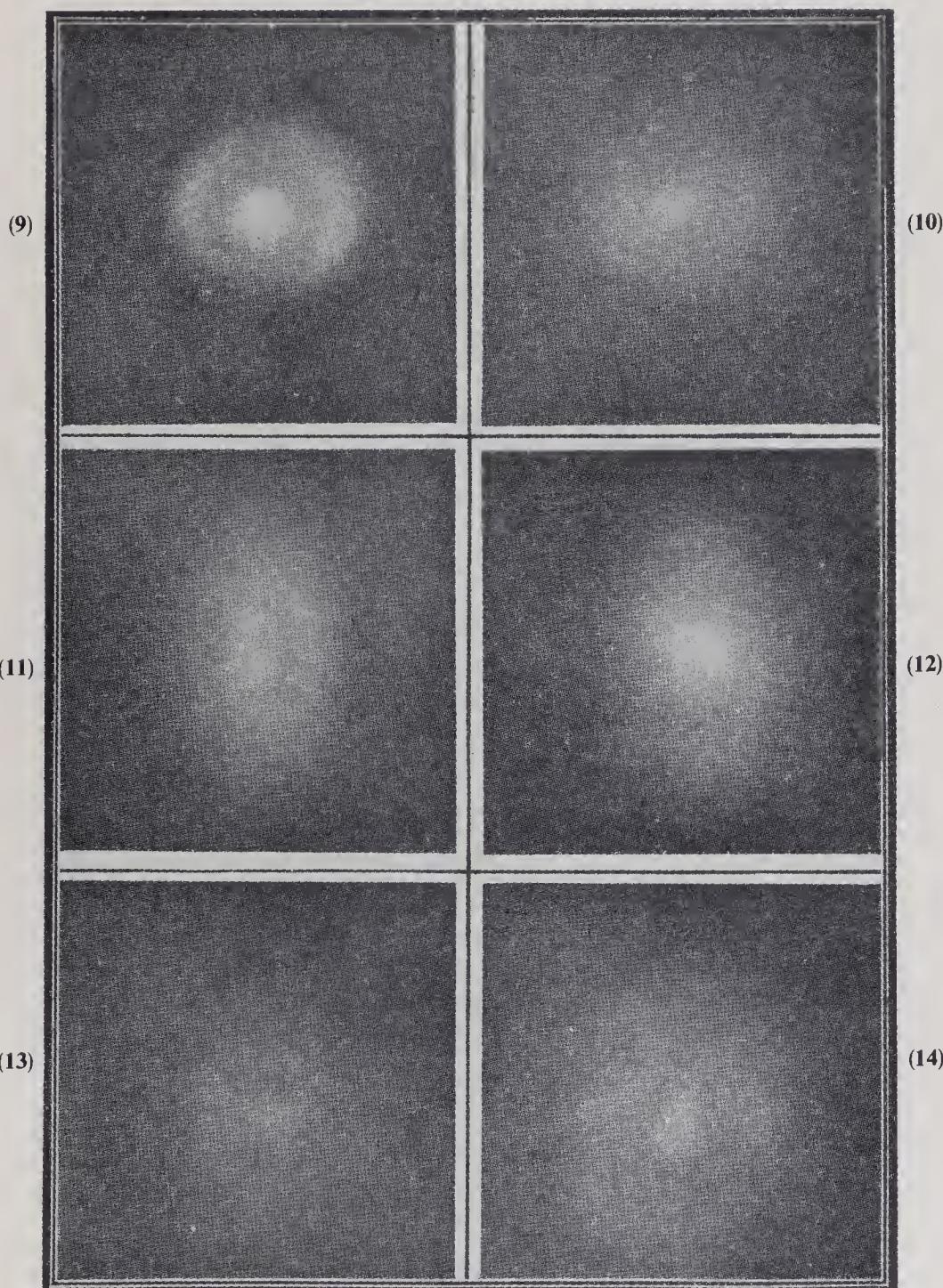
Figures 1-4. The reflection-diffraction spectra of a natural pearl.

Plate I

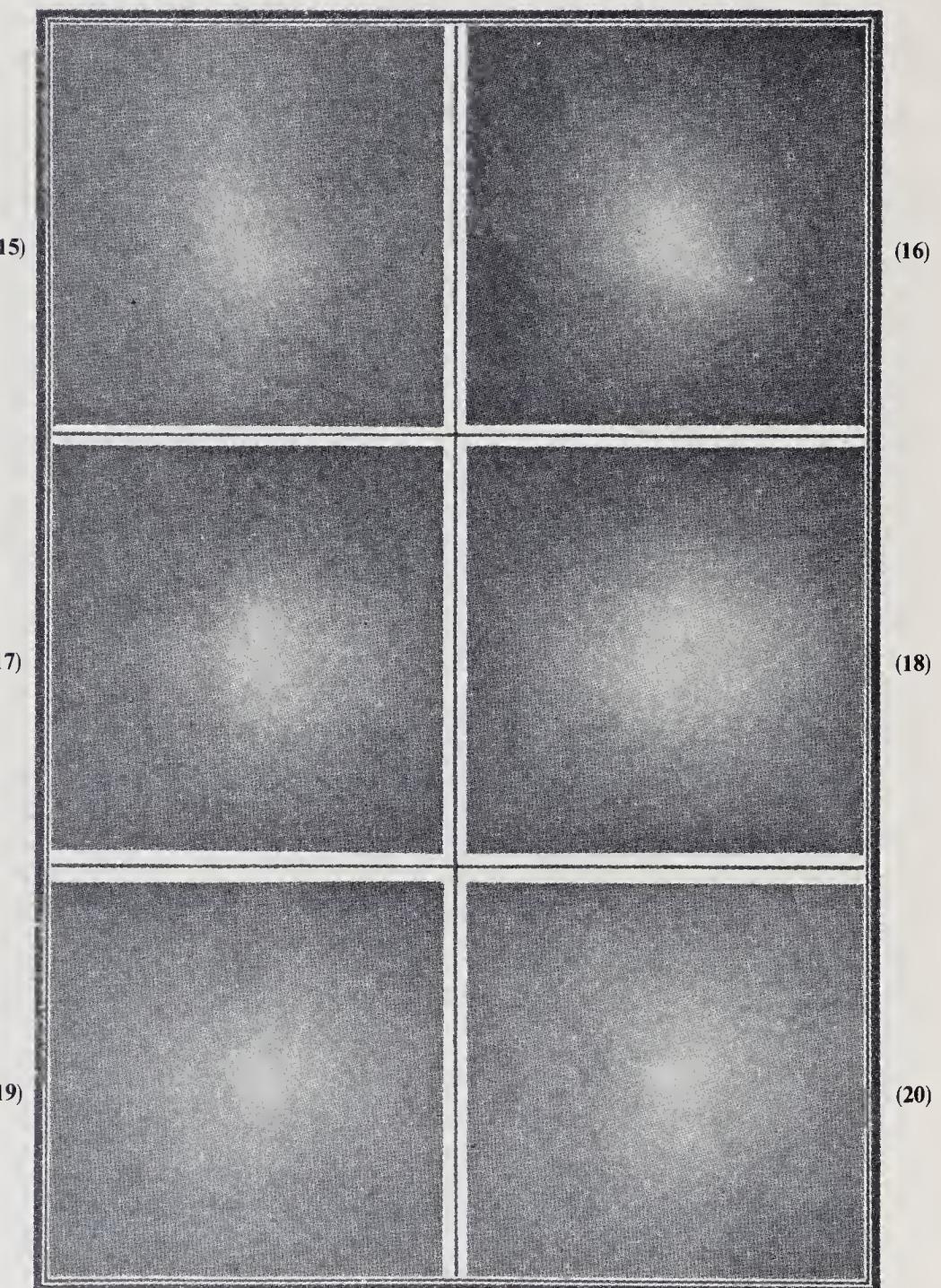


Figures 5-8. The lateral diffusion of light in a natural pearl.

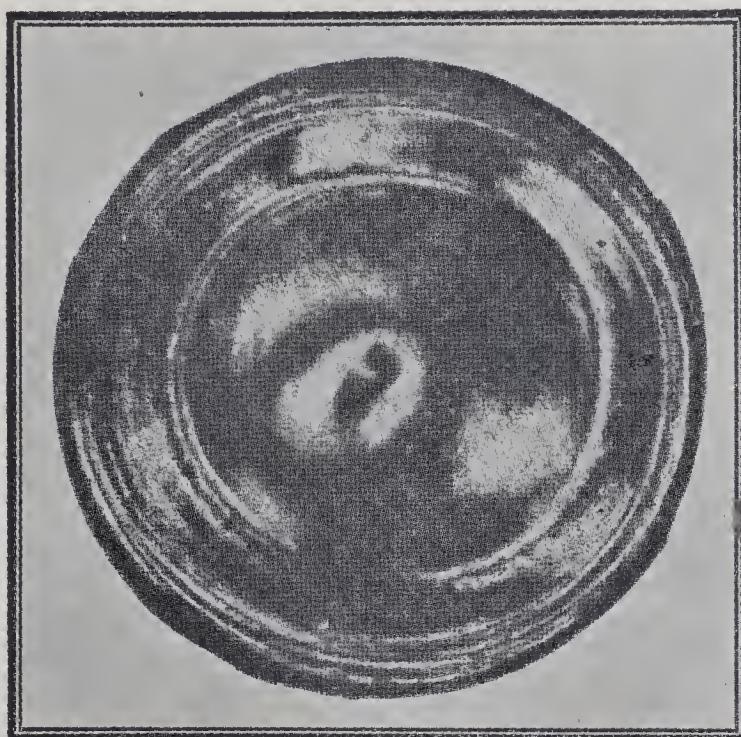
Plate II



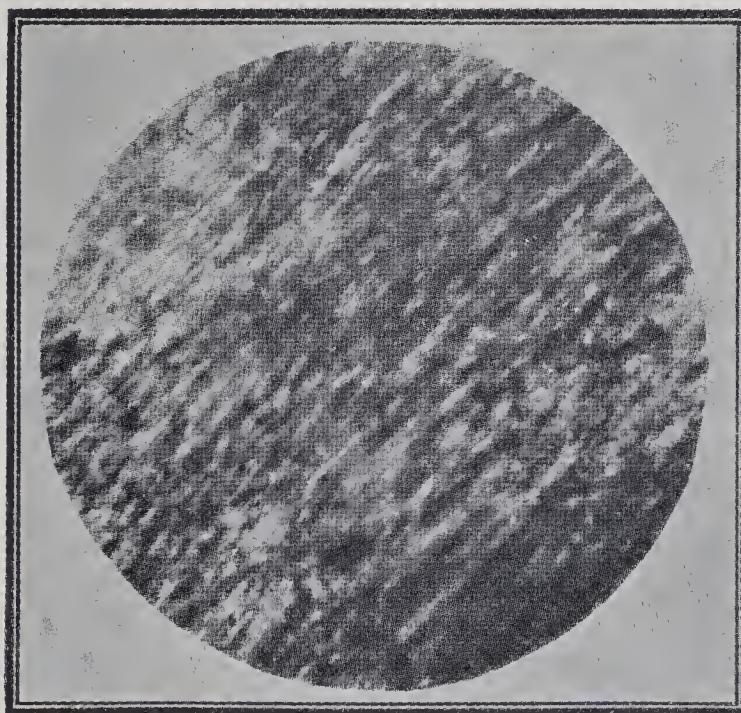
Figures 9-14. The chromatic diffusion halo in cultured pearls.



Figures 15–20. The chromatic diffusion halo in cultured pearls.



(21)



(22)

**Figures 21 and 22.** Illustrating the structure of the material in a cultured pearl.

## The structure and optical behaviour of iridescent agate

SIR C V RAMAN and A JAYARAMAN  
(Raman Research Institute, Bangalore)

Received September 9, 1953

### 1. Introduction

It is well known that agate exhibits a banded structure. One explanation of the banding which has been put forward is that the agate is the result of the deposition of silica in an intermittent manner from liquids containing the material in solution. The assumed manner of formation is, however, clearly hypothetical and it leaves the question of the physical nature of the banding resulting therefrom unanswered. A different explanation that has been suggested and received with some favour is the so-called silica-gel theory. This regards the banded structure of agate as analogous in its nature to the periodic precipitates formed in gelatinous substances in certain circumstances. We may remark, however, that the characteristic structure of agate is observed even in the absence of any material other than silica in its composition. Further, it is to be noted that the microscope shows agate to be a coarsely crystalline material and not a colloid. The explanation of its banded structure as a Liesegang phenomenon in a colloidal gel appears in the circumstances to be rather far-fetched.

The question of the nature of the banded structure of agate presents itself in a particularly interesting form when we consider the case of the specimens exhibiting iridescence. It has long been known that the stratifications in agate may be so close and so regularly spaced as to enable a polished plate of the material to function as a diffraction grating when traversed by a beam of light. It is natural to suppose that a structure exhibiting such a high degree of regularity with strata following each other some 10,000 times in a centimetre is a consequence of some special feature in the aggregation of the crystallites of quartz of which agate is composed. The fact that we had at our disposal two examples of iridescent agate encouraged us to undertake a careful study of this question by optical and X-ray methods. The investigation has revealed several interesting facts, and besides elucidating the particular problem under consideration has also thrown fresh light on the structure and optical behaviour of non-iridescent agate and chalcedony.

## 2. Some general observations

Enlarged photographs of our two specimens are reproduced as figures 1 and 2 respectively in plate I. They exhibit a banded structure over the entire area of the plates except in a region adjacent to the irregular upper edge of specimen I where it is definitely absent, while in the case of specimen II, the banding gradually fades off and becomes inconspicuous as we approach the triangular tip of the plate at its lower end. In both cases the banding meets the surface in a series of curved lines running parallel to each other and exhibiting several sharply defined changes of direction. The iridescent area in each case is a strip about a centimetre in width running parallel to the banding and traversing the entire specimen from one side to the other. In figure 2 it appears as a series of conspicuous bands running across the middle of the specimen, while in figure 1 the strip appears perfectly dark in its first segment on the right, faintly banded in the middle segment, and quite bright in the third segment towards the left.

Figures 3 and 4 in plate II are photographs of a small section of the iridescent area on specimen II greatly enlarged. The two photographs were recorded respectively by transmitted and by diffracted light, and it will be recognised at once that they are complementary, the areas appearing bright in one picture, appearing dark in the other and *vice versa*. The photographs exhibit other features of interest to which we shall revert later. It may be remarked here that the complementarity which they exhibit is a feature which is noticeable with both of our specimens over the entire area exhibiting a banded structure, those regions which appear bright by diffracted light appearing dark by transmitted light, and *vice versa*. Viewed obliquely to the direction of the illuminating beam, both specimens in the non-iridescent areas show a bluish-white opalescence.

## 3. Polarisation of the transmitted light

Our specimens I and II were respectively 3 and 2 millimetres thick. They are both noticeably transparent, but much more so in the case of the thinner specimen. In other words, a light-source such as an open window or the dome of an electric lamp could be seen through the agate with full definition in all its details, though overlaid by a field of diffuse radiation. As is to be expected, the areas exhibiting iridescence are much less transparent than the rest and they also impart a distinctly reddish tint to the light passing through them. *Per contra*, the non-banded areas near the upper edge of specimen I are distinctly more transparent than its banded areas, the yellowish-red tint of the transmitted light being however very conspicuous.

It is noteworthy that the intensity and colour of the light transmitted by our specimens are largely influenced by varying the inclination of the specimen with respect to the rays of light traversing it; the effect is very conspicuous when the

specimen is so tilted that the plane of incidence remains normal to the planes of banding of the material. The maximum transmission is observed when the light rays are parallel to the planes of banding; the light transmitted diminishes rapidly in intensity and at the same time becomes a deeper red in colour when the light rays make increasingly larger angles with the planes of banding, until finally it is lost altogether in a notably strengthened background of diffuse light. A tilt of the specimen in the same plane as the banding layers produces an effect of the same nature which however is much less conspicuous.

A remarkable observation made by us is that *the light transmitted by our specimens is completely polarised when observed through the areas exhibiting a banded structure*. This is the case even when the banding is inconspicuous. Further, a tilt of the specimen with respect to the light rays which notably alters the intensity and colour of the transmitted light does not affect the totality of its polarisation. The direction of electric vibration in the transmitted light lies in a plane normal to the planes of banding in the specimen. When the area of observation is moved to another adjacent position in which the planes of banding have taken a sudden turn, the direction of vibration in the transmitted light takes a similar sudden turn. Likewise, as we move along the curved areas which represent the banding planes, the direction of vibration in the transmitted light swings round in the same fashion. It should finally be remarked that for those areas of our specimen I where no banding is visible and which allow a transmitted light of an yellowish-red colour, a marked though incomplete polarisation of the same is observable, the direction of vibration being approximately the same as in the neighbouring banded areas.

#### 4. The diffusion of light accompanying transmission

When a small intense source of light is viewed through the banded non-iridescent areas of our specimens, we observe a phenomenon which is illustrated in figure 5 in plate III. On either side of the light source as seen through the specimen we notice a fairly intense but a narrow bundle of diffused light stretching out in a direction parallel to the planes of banding. Further away, this spreads out both longitudinally and transversely into a diffuse brush of light of rapidly diminishing intensity.

As mentioned above, the image of the light source seen through the banded areas of our specimens is completely polarised. This effect is demonstrated by figure 6 in plate III which represents the light source as viewed through a non-iridescent area of the agate coupled with a double-image prism of quartz. Of the two images produced by this combination seen side by side in the figure, the one on the right hand has the electric vibration normal to the banding planes while for the one on the left, the vibration direction is parallel to these planes. It will be noticed that the image of the source appears only in the former and is totally

absent in the latter. The vertical brush of light passing through the image is however seen in both images but is less intense in the latter, indicating that the brush is partially polarised in the same sense as the transmitted light. The farther away we move from the image of the light source in either direction, the less conspicuous becomes the difference in intensity between the two images. Owing to their overlap in the photograph, it is not possible to make a definite statement whether or not there is a reversal of the state of polarisation in the more distant parts of the brush.

### 5. The diffraction spectra

From figures 1 and 2 in plate I it is evident that the iridescent strips in our specimens do not form a single continuous diffraction grating over their entire width but consist of several distinct gratings with intervening gaps. The photographs reproduced as figures 3 and 4 in plate II show this very clearly; the strip contains six different gratings separated by intervals which are not iridescent and hence appear bright by transmitted light and dark by diffracted light. That the six gratings in the agate are dissimilar is apparent from the fact that the colours which they exhibit when it is viewed obliquely are not identical. That each individual grating is nearly perfect however is proved by the observation that when a source of monochromatic light is viewed through it, a series of well-defined and regularly spaced images formed by the diffracted light is seen; with a mercury arc lamp as source the two sets of images formed respectively by the green and yellow radiations are seen well separated. No images formed by the  $\lambda 4358 \text{ \AA}$  radiations are visible owing to the strong diffusion and lack of transparency of the agate in that region of the spectrum.

The spectra formed by the agate are not simply a series of images of the source. Actually, each spectrum including that of zero order is a diffusion pattern exhibiting the features already described and illustrated in figure 5 of plate III with their specific polarisation characters. The geometric images of the source appearing in the spectra are completely polarised with their vibration directions perpendicular to the lines of the diffraction grating, while the vertical bundle of diffused light accompanying each image exhibits a partial polarisation in the same sense. The diffuse brush appearing further out however exhibits a partial polarisation in the reverse sense, having its vibrations parallel to the lines of grating. These features are evident to inspection in figure 7 of plate III which was recorded with a mercury arc as source and a double-image prism of quartz superposed on the agate to exhibit the two components of polarised light in each spectrum separately.

It may be remarked that the diffraction phenomena described above are notably influenced by tilting the grating with respect to the incident light rays in

one plane or the other, as could have been anticipated from the observations of the same nature already reported for the non-iridescent areas. We may also make a brief reference to the diffraction phenomena which are observed when a light source is viewed through certain non-iridescent but conspicuously banded areas of the agate. They are of a much less striking character than those exhibited by the iridescent areas and will not here be described in detail.

## 6. Significance of the results

The optical phenomena described above enable us to derive the following conclusions regarding the structure of the agate in the areas exhibiting the diffraction spectra:

- I. The crystallites of quartz composing the agate arrange themselves in fibres along a direction normal to the planes of banding.
- II. The principal axis of the quartz in the individual crystallites lies in the planes of banding.
- III. Each fibre exhibits along its length a periodicity in the orientation of the principal axis of the quartz, such periodicity being the same for all the fibres.

The first proposition stated above follows directly from the nature of the diffusion patterns reproduced in plate III.

The second proposition finds its justification in the observed fact that the light regularly transmitted by the banded regions is completely polarised with its vibrations normal to the planes of banding. Had the optic axis of the quartz in the crystallites been orientated *at random*, the birefringence of the quartz would have resulted in the agate not transmitting any part of the incident light but merely diffusing it. On the other hand, had the optic axes all been *normal to the planes of banding*, the light regularly transmitted would have exhibited both components of polarisation. If, however, as indicated, the optic axes of all the crystallites lie *in the planes of banding*, the effective refractive index for a vibration normal to the planes of banding would be the same for all of them, while the index for a vibration in a transverse direction would vary from crystallite to crystallite. Hence the former component would be regularly transmitted, while the latter would be diffused and totally excluded from the transmitted light, in agreement with what is actually observed.

The third conclusion stated above follows inevitably if an aggregate of individual fibres is to function as a diffraction grating exhibiting the optical effects illustrated in figure 7 of plate III. In the circumstances of the case, the only type of periodicity in optical properties which could be admitted is that the optic axis lies in different directions along the length of the fibre, repeating themselves at corresponding points in the diffraction grating.

## 7. The X-ray diffraction patterns

As both of our specimens had sharply defined edges intersected by the banded structure, it was found easy to obtain X-ray diffraction patterns of the agate in selected regions. A narrow pencil of X-rays was allowed to graze the edge at the chosen region and the diffraction pattern was recorded with a flat-film camera. Figures 8, 9 and 10 in plate IV reproduce the patterns obtained in this manner using our specimen II and unfiltered X-radiation from a molybdenum target. Figure 8 is the record for the region exhibiting strong iridescence, figure 9 for a region further down which was non-iridescent but exhibited visible banding and figure 10 at the triangular tip where no banding was visible at all. We have obtained very similar records with our other specimen, but these have not been reproduced. The striking differences observed in the X-ray patterns of different regions in the same specimen are a clear demonstration that the structure of agate is a consequence of the grouping of the crystallites in specific orientations along the planes of banding. The X-ray pattern of the iridescent area reproduced as figure 8 in plate IV is readily identifiable as due to an aggregate of crystallites having one of the crystallographic *a*-axes as a common direction while the principal or *c*-axis assumes all possible orientations. This result is in full accord with the conclusions derived from the optical studies set forth earlier in the paper. The patterns reproduced in figures 9 and 10 show a less well-defined state of orientation of the crystallites. Indeed, in the latter, there is hardly any specificity of orientation indicated. This is not surprising since the banded structure of the agate is invisible near its extremity.

## 8. Some further observations

In the enlarged photographs of the iridescent agate (specimen II) reproduced in plate II, it is possible to recognize a good deal of visible structure in the material. Of particular interest are the curious wavy patterns seen in some of the strips, both in transmitted and by diffracted light. Similar patterns are seen over the entire iridescent area of our specimen I by merely holding it up against a window and viewing it through a magnifier of moderate power. These patterns are best examined by placing the agate on the stage of a low-power binocular microscope and viewing it either by direct or by oblique illumination from below the stage. Very interesting effects are observed if between the agate and the objectives of the microscope a polaroid sheet is interposed and turned round in its own plane. *The wavy patterns are vividly seen when the polaroid has its vibration direction parallel to the planes of banding of the agate. But they disappear completely when the polaroid is set with its vibration direction perpendicular to the planes of banding.*

The significance of the results stated above becomes evident when one recognises the patterns as being of the same nature as those seen when two similar diffraction gratings which are not perfectly in register are held together and viewed against a source of light. In the present case, we are dealing with a single grating which extends through a considerable depth of the material. Hence, unless the structure is of extraordinary perfection, superposition patterns of the nature observed would necessarily arise. In the light of these remarks, the disappearance of the patterns when the light vector is normal to the planes of banding is highly significant. Such disappearance is to be expected if the grating has its origin in a periodicity of the orientation of the principal axis of the quartz along the length of each fibre. For, such periodicity would influence the retardation of light waves having their vector parallel to the planes of banding, but would leave unaffected the propagation of light having its vector normal to those planes.

### 9. Concluding remarks

The ideas regarding the structure of iridescent agate set forth in section 6 are thus independently supported by the X-ray patterns and by the optical evidence. It remains now to find a reason why the principal axis of quartz exhibits a periodicity in its setting along the length of the fibres in the iridescent regions. We wish here tentatively to put forward a suggestion regarding this matter. It is known that quartz exhibits a type of twinning in which the principal axis in the two components of the twin are nearly at right angles to each other—more exactly make an angle of  $84^{\circ} 33'$  with each other. It seems to us that the fibres of quartz in iridescent agate may be described as polysynthetic twins in which the alternate elements are related to each other presumably in the same manner as in the twins of the kind referred to.

### 10. Summary

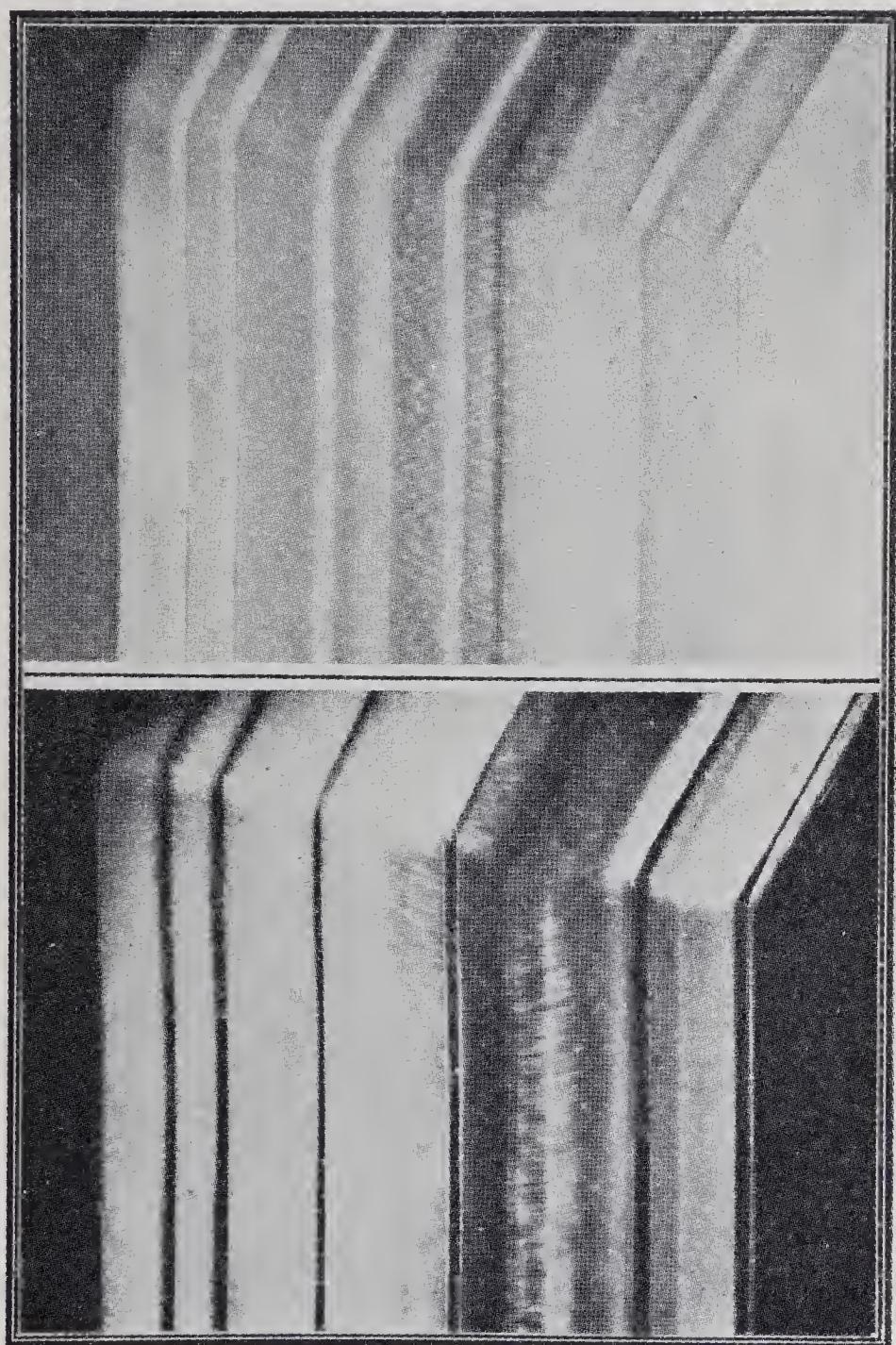
A detailed study has been made by optical and X-ray methods of two plates of banded agate which display iridescence over part of their area. The light transmitted by the banded areas is found to be completely polarised with the vector normal to the planes of banding. On the other hand, the wavy superposition patterns exhibited by the iridescent areas disappear for the same vibration direction. From these facts and the observed optical characters of the diffusion and diffraction phenomena it is deduced that the crystallites of quartz form fibres elongated in the direction of a crystallographic *a*-axis, while their principal or *c*-axes lie in the planes of banding but are orientated in a periodic

manner in these planes so as to build up a structure which functions as a diffraction grating. The X-ray results support these findings. More generally also, they indicate that the banding of agate is a consequence of the presence in it of groups of crystallites of quartz having common specific orientations.



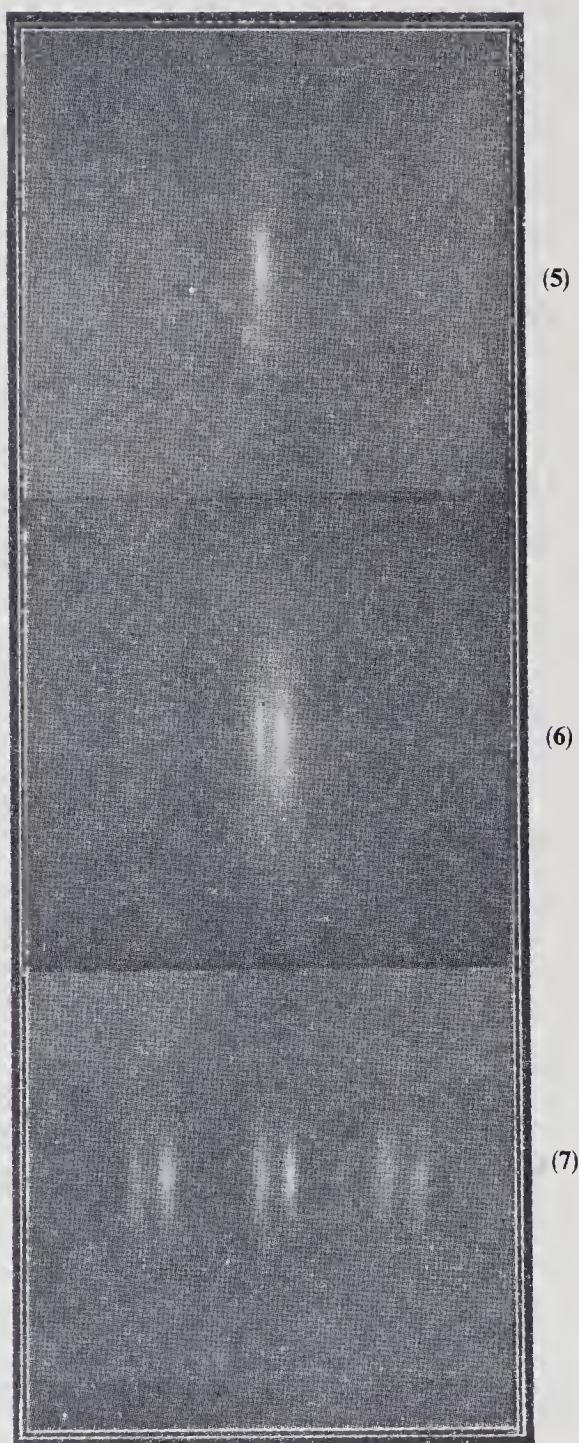
Figures 1 and 2

Plate I



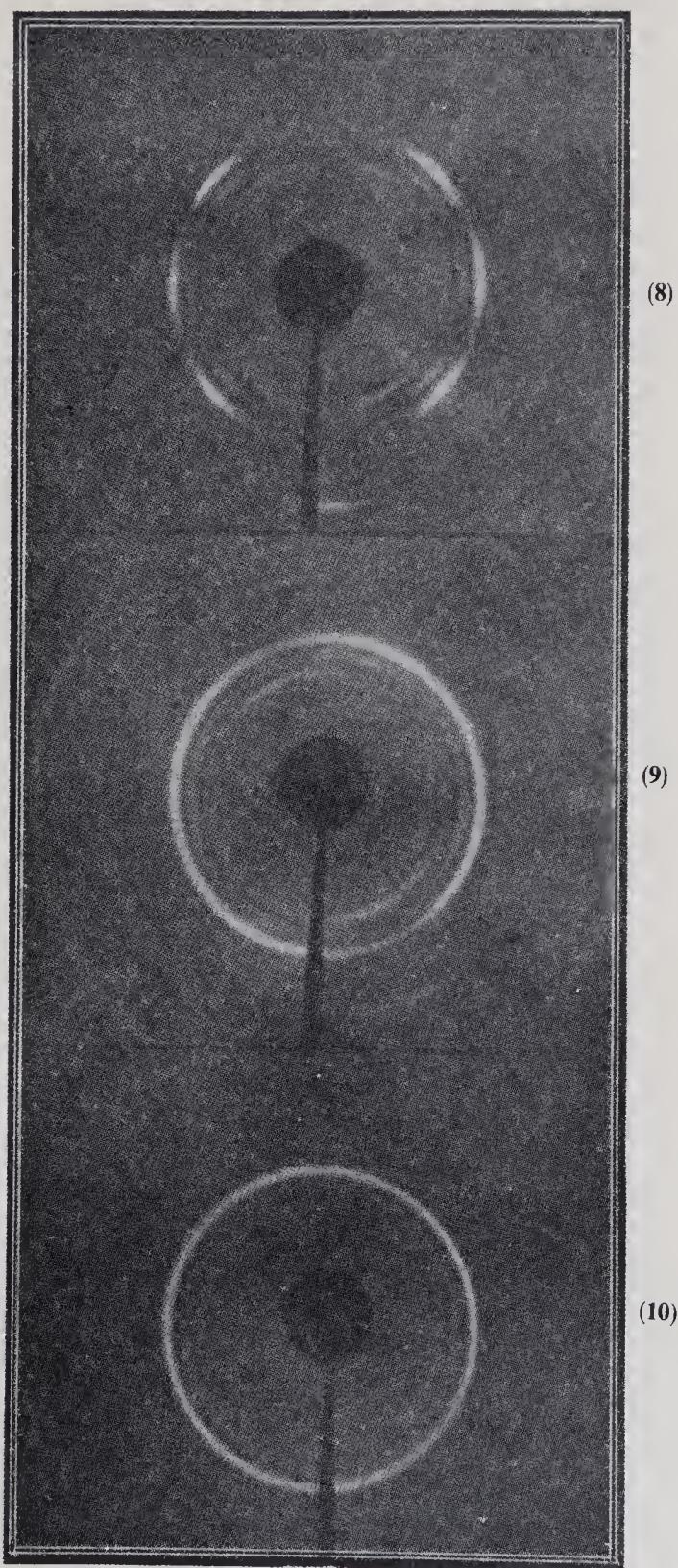
Figures 3 and 4

Plate II



Figures 5-7

Plate III



Figures 8-10

# The structure and optical behaviour of iridescent calcite

SIR C V RAMAN and A K RAMDAS

(Memoir No. 55, from the Raman Research Institute, Bangalore)

Received July 16, 1954

## 1. Introduction

Christiaan Huygens<sup>1</sup> noticed that one of his specimens of iceland spar contained an inner layer exhibiting iridescence and remarked that this was parallel to one edge of the rhombohedral cleavage and equally inclined to the two others. It is now recognised that such layers arise from internal twinning and that they may be artificially produced by subjecting a crystal of calcite to suitable stresses. It is also well-known that when a distant luminous object is viewed through a rhomb of iceland spar in which such twinning is present, three images of the object are seen instead of only one; the two outer images often exhibit vivid colour, while the central or undeviated image is usually colourless. The brightness of the images, their angular separation, and the colours which they exhibit vary greatly with the direction in the crystal along which the source of light is viewed. An explanation in general terms of the origin of the two outer images and of the colour and polarisation which they display appears in Mascart's treatise.<sup>2</sup> Grailich<sup>3</sup> and later Osthoff<sup>4</sup> investigated the reflection and refraction of light by the twinning planes in calcite. A summary of their results is given by Pockels.<sup>5</sup> A noteworthy observation regarding the optical behaviour of twinned calcite is also to be found recorded in a paper by Rayleigh<sup>6</sup>.

Numerous specimens of transparent calcite exhibiting internal twinning were available to us in the Museum of this Institute and this induced us to undertake the study of their optical behaviour. It was immediately noticed that specimens in which twinning layers traverse the crystal simultaneously in two or even three different directions exhibit gorgeous arrays of multi-coloured images arranged in geometric patterns when a source of light is viewed through them. Plates I and II accompanying this paper reproduce photographs obtained by us of a few of the many patterns observed with the material at our disposal. A detailed examination of the case of calcite containing only a single twinning layer also revealed many facts which had apparently been overlooked by the earlier investigators. We shall refer to these in the course of the paper, the purpose of which is to present the

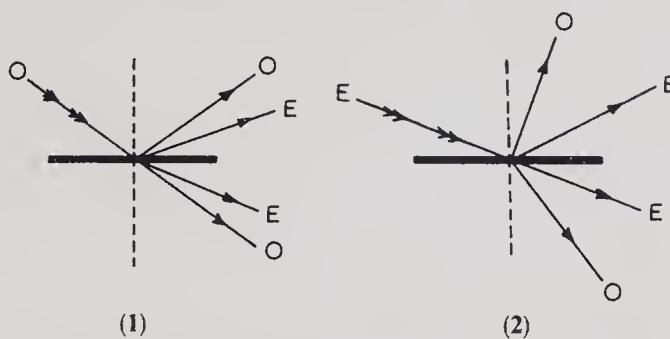
complete picture of the optical behaviour of iridescent calcite which has emerged from our studies.

## 2. Geometric theory

When a train of light-waves traverses a layer of calcite differing from the material on either side of it in crystallographic orientation, the waves would necessarily be reflected and refracted by the layer. Elementary considerations indicate that the angle of incidence  $\theta_i$  and the angle of reflection or refraction  $\theta_r$ , would be related to the corresponding refractive indices  $\mu_i$  and  $\mu_r$  by the general formula

$$\mu_i \sin \theta_i = \mu_r \sin \theta_r. \quad (1)$$

Since the medium is birefringent, it follows that for a given angle of incidence, a wave-train of either the ordinary or the extraordinary species would, in general, give rise to *two* reflected and *two* refracted wave-trains. Other inferences from the formula are: (1) One of the refracted wave-trains emerging from the layer in each case would travel in the same direction as the incident wave-train; (2) the angles of reflection and of refraction of the ordinary wave-train would necessarily be identical; and (3) the angles of reflection as also of refraction would, in general, be greater for the extraordinary than for the ordinary wave-trains (*see figure 1 and figure 2 below in which these results are embodied*).



**Figures 1 and 2.** Reflection and refraction by a twinning layer.

When a distant source of light is viewed through the opposing pair of faces of a cleavage rhomb of iceland spar, we observe only a single image of the source, though the wave-trains divide into the ordinary and extraordinary species and follow different paths within the crystal. It is readily seen from figures 1 and 2 that the same situation would subsist even when a twinning layer is present and is traversed by these waves. In such a case, however, the ordinary wave-train which emerges as an extraordinary one and the extraordinary wave-train which emerges as an ordinary one after passage through the layer, would both give rise to additional images, deviated respectively to one side and the other of the

principal image. The magnitude of their angular deviations may be deduced at once from the general formula and is the smaller, the more nearly the direction of observation through the crystal approaches the optic axis. It is important to remark that while the central or undeviated image would appear in the same direction for all wavelengths, such would not be the case for the deviated images. The dispersion of the refractive indices in calcite is very different for the ordinary and the extraordinary waves. Hence, the two lateral images would appear drawn out into spectra, and it may be remarked that such dispersion would be large when the wave-train under consideration emerges nearly parallel to the twinning layer.

The general formula indicates other results of interest. If  $\mu_i$  be the ordinary and  $\mu_r$  the extraordinary index,  $\theta_r$  would be real only if  $\theta_r \leq \sin^{-1} \mu_r / \mu_i$ . At the upper limit indicated, the reflected and refracted extraordinary waves would emerge parallel to the twinning layer, while for greater incidences they are non-existent. Likewise, when  $\mu_i$  is the extraordinary and  $\mu_r$  the ordinary index,  $\theta_r \leq \sin^{-1} \mu_i / \mu_e$ ; the limiting value is reached when the incident waves graze the twinning layer. In both cases, the limiting angle may be written as  $\sin^{-1} \mu_e / \mu_0$  where  $\mu_0$  is the ordinary index and  $\mu_e$  is the extraordinary index for the direction of propagation parallel to the twinning layer in the plane of incidence. Thus, if light be incident on a twinning layer simultaneously in all directions, a boundary line may be drawn in the field separating the directions of incidence of the ordinary wave-trains which give rise to extraordinary reflections and refractions and of those which do not. Likewise, the optical fields traversed by the reflected and refracted wave-trains are, each of them, divided by a boundary line on the two sides of which ordinary wave-trains resulting from incident extraordinary ones respectively appear and do not appear.

It is evident from the foregoing remarks that we cannot always expect to be able to observe the deviated images on both sides of the principal image when a distant light source is viewed through a calcite rhomb. As the angle of incidence on the twinning layer approaches and ultimately exceeds the limiting value, the extraordinary refraction resulting therefrom would emerge parallel to the twinning layer and ultimately disappear.

### 3. Intensity considerations

A factor which greatly influences the observed phenomena is the azimuth of the plane of incidence of the light on the twinning layer. It has already been remarked that the layer is parallel to one of the edges of the rhombohedral cleavage and equally inclined to the two others. It follows that a plane through the edge first mentioned which is perpendicular to the lamina would contain the optic axis of the calcite crystal and the optic axis of the twinning layer as well. The plane under reference would thus be a plane of symmetry for the entire crystal including the twinning layer. As in the case of potassium chlorate recently discussed in these

*Proceedings,*<sup>7</sup> it can be shown from elementary considerations that when the plane of incidence of the light coincides with this symmetry plane, reflections and refractions would disappear and the incident light-waves would emerge from the twinning layer with their direction of propagation as well as their intensity unaltered.

The foregoing conclusion is readily tested by viewing a distant source of light through the calcite rhomb held in front of the eye of the observer in such manner that the twinning layer is vertical while the plane of observation is horizontal; the source should be viewed through the faces of the rhomb which are bounded by edges of which none is parallel to the twinning layer. Only the undeviated image of the source can then be seen. But if the crystal is slightly tilted about a horizontal axis so that the plane of incidence of the light ceases to be horizontal, the deviated images make their appearance, and rapidly gain in intensity as the plane of incidence is turned away from the horizontal in either sense.

An interesting modification of this experiment is to view an extended area of illumination through the faces of the rhomb held in the manner indicated above and to rotate the rhomb about a vertical axis so that the plane of the twinning layer remains vertical but alters its orientation with respect to the direction of observation. A division of the field of observation into two parts differing in their intensity of illumination then comes into view. A dark and sharply defined boundary is seen to separate the two parts of the field except where it is cut by the horizontal symmetry plane. This dividing boundary becomes more and more conspicuously observable as we move away from the symmetry plane in either direction. Interposing a polaroid in front of the rhomb, it is found that the division of the field into two parts and the dark boundary separating them are most conspicuous when the vibration direction of the polaroid is vertical, but disappear when the same is horizontal. It is thereby made evident that the boundary is the one indicated by the geometric theory as the limit of the angle of incidence of the ordinary waves on the twinning layer beyond which the extraordinary reflections and refractions disappear. That the boundary vanishes in the symmetry plane and becomes more conspicuous as we move away from it is to be expected in the circumstances. The boundary is sharply defined evidently as a consequence of the weakening of the ordinary transmission by reason of the extraordinary reflections and refractions reaching their maximum intensity just prior to their disappearance at the limiting incidence.

A slight modification of the arrangements described above enables us to observe the boundaries at which the reflections and refractions of the extraordinary waves as ordinary waves terminate. For this purpose, the illuminated screen is held to one side so that the light reflected or refracted by the twinning layer comes into the field of view. The boundary is seen then as an arc of light bordered by coloured fringes and separating a bright from a dark part of the field of view. The bright arc is however interrupted at the symmetry plane, and gains in intensity as we move away from that plane in either direction. By inserting a

polaroid before and after the calcite rhomb respectively, it is readily demonstrated that the luminous arc has its origin in the trains of extraordinary waves which are transformed to ordinary ones by reflection or by refraction. The sharpness and brilliancy of the boundary are to be expected alike on geometrical and physical considerations.

#### 4. Interference phenomena

As has been already remarked, the deviated images of a distant light source seen through the twinning layer are spread out into spectra by reason of the difference in the dispersive powers of calcite for the ordinary and extraordinary waves. Using a narrow slit as the source of light, these spectra can be readily observed and are found to be channelled by interference bands crossing them. The position and number of the interferences vary with the specimen under observation and thus evidently depend on the thickness of the twinning layer in each particular case. Careful examination reveals that we have two sets of interferences simultaneously present in the spectra, one of which is on a finer scale than the other. The explanation of these effects is not far to seek. Returning to the text-figures 1 and 2, it will be evident that in the passage of the incident waves through the twinning layer, the birefringence of the latter would come into play. Hence, each of the wave-trains reflected or refracted by the layer would itself be the resultant of the wave-trains of the two different species possible within the layer, the optical paths of which would be different. Interferences of the same nature as those exhibited by crystalline plates in polarised light would therefore arise and would manifest themselves in the spectral character of the reflected and refracted wave-trains. Effects of the same nature as the ordinary interferences of thin plates would also simultaneously appear. The colours observed with extended light sources are a consequence of both species of interference.

Interference phenomena are also strikingly manifested at and near the boundaries of transmission, reflection and refraction considered in the preceding section. They take the form of alternate dark and bright bands of varying sharpness and intensity fringing the boundaries referred to. There again, we observe two species of interference, one of which is on a finer scale than the other. These boundary effects are best studied using a diffusing screen illuminated by a monochromatic source, though indeed they can be also observed with white light.

#### 5. Effects observed with multiply twinned calcite

We now turn to a consideration of the phenomena, typical examples of which are reproduced as figures 1, 2, 3 and 4 in plates I and II accompanying the paper. The photographs reproduced were obtained using a small aperture backed by a

tungsten filament lamp as the source of light. A photographic camera placed about three metres away was focussed on the source, the calcite rhomb being placed immediately in front of the lens. Panchromatic plates were employed for recording the patterns. The brilliant colour effects actually observed are, of course, not reproduced.

Figure 1 shows the three images observed with a calcite rhomb having a single twinning layer. In addition to the bright images, we observe a system of bright streaks, as also some diffuse light surrounding the images. The surfaces of the cleavage rhombs had not been specially polished and their unevenness was no doubt in part responsible for some of the unwanted effects. Nevertheless, our studies with numerous specimens left little doubt that the long bright streaks appearing in the photographs and also seen visually had their origin within the calcite rhombs. It appears reasonable to attribute them to a lack of perfect smoothness of the twinning layers within the crystal.

Another remark may usefully be made with regard to figure 1 in the plate. This was recorded through the faces of the calcite rhomb which had two of their edges parallel to the twinning layer. In these circumstances, the plane of incidence of the light on the twinning layer was, in general, far removed from the symmetry plane. By turning the crystal about one edge, the images could be made to approach towards or recede from each other. Simultaneously, there were large changes in the colour and intensity of the images. At particular settings which were nearly but not quite coincident, the two outer images vanished but on further rotation they reappeared in positions closer still to the principal image. The observations indicated that for the settings at which the images disappeared, the plane of incidence was nearly coincident with the symmetry plane.

Figure 2 in plate I shows the pattern of a type frequently observed by us and which arises from the simultaneous action of twinning layers parallel to two of the edges of the rhombohedral cleavage. A noteworthy feature in the photograph is that the middle spot in the outer rows has split into two components. These were found to be polarised in perpendicular directions. Figures 3 and 4 represent more complicated cases. It is to be noted that the spots appear in groups of threes, with the middle one in each row distinctly separated into two components. All the patterns exhibited special features of polarisation analogous to those observed in the simple case of a single twinning layer.

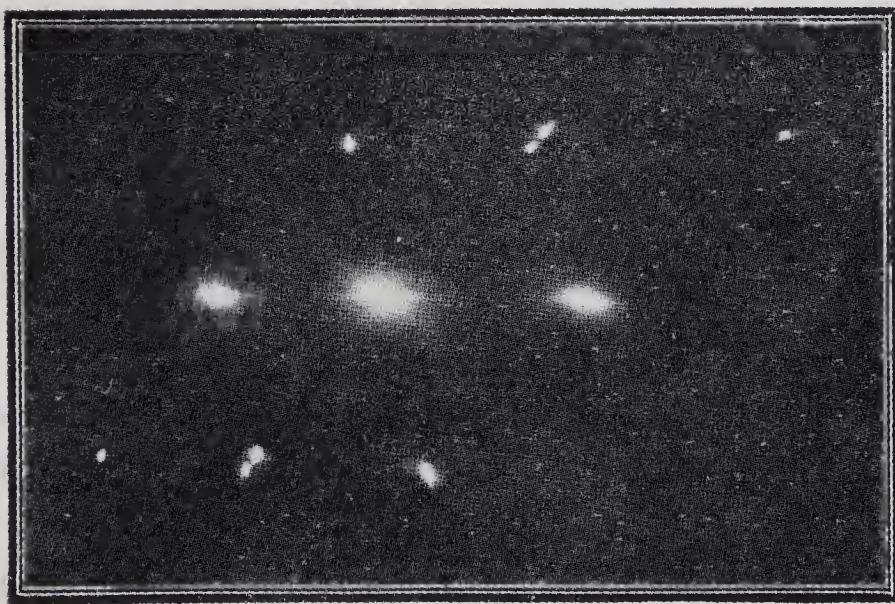
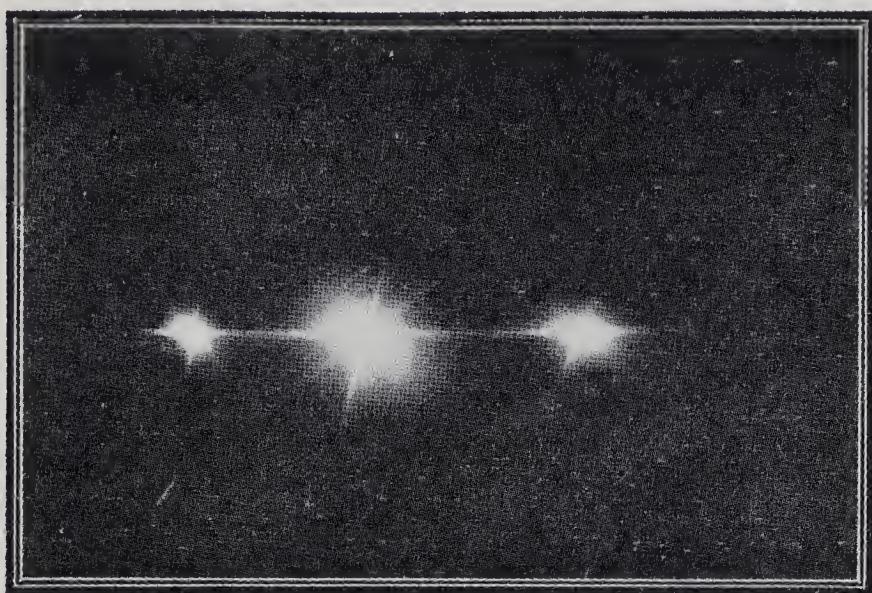
## 6. Summary

Arrays of multi-coloured images of a distant light-source arranged in geometric patterns are exhibited by calcite rhombs traversed by twinning layers in several directions simultaneously. The paper reproduces four photographs of such patterns and also discusses the theory of the reflection and refraction of light by twinning layers in calcite. The large difference between the ordinary and

extraordinary dispersive powers results in a linear source observed through such a layer appearing drawn out into spectra channelled by interferences. Interference bands also fringe the sharply defined boundaries seen separating the different parts of the optical field of reflection and refraction.

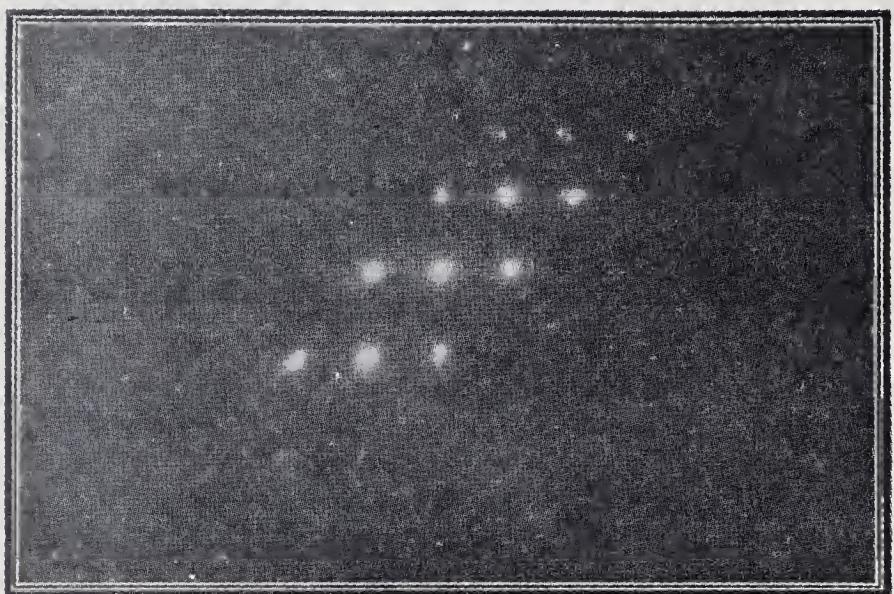
## 7. References

1. Christiaan Huygens, *Treatise on Light*, English Translation by Silvanus Thompson, University of Chicago Press, 98.
2. Mascart, *Traite' D'Optique*, 2.
3. Grailich, *Pogg. Ann.*, 1856 **98**, 205.
4. Osthoff, *Neues. Jahrb. Mineral. Beil-Bd.* **20**.
5. Pockels, *Lehrbuch Der Kristalloptik*, 203.
6. Rayleigh, *Scientific Papers*, 3, 212.
7. Raman and Krishnamurti, *Proc. Indian Acad. Sci.*, 1953 **A38**, 263.



Figures 1 and 2

Plate I



(3)



(4)

Figures 3 and 4

Plate II

# The structure and optical behaviour of jadeite

SIR C V RAMAN and A JAYARAMAN

(Memoir No. 70 of the Raman Research Institute, Bangalore)

Received March 16, 1955

## 1. Introduction

Jadeite is a mineral to which much interest attaches by reason of the use which has been made of it since ancient times—especially in China—for the fabrication of works of art which have been greatly admired. It is a much rarer material than nephrite which is another mineral product to which the name jade is also commonly given; happily, the two substances are readily distinguishable from each other. In its finest forms, jadeite is known as gem-jade or imperial jade and differs from the commoner varieties in its optical characters; it exhibits a beautiful green colour resembling that of emerald and is semi-transparent instead of being cloudy or opaque. There is an extensive literature which deals with jadeite from the mineralogical point of view; works on gemmology also naturally devote a good deal of space to it. We have not however found in the literature any explanation of the optical characters which jadeite exhibits in terms of its structure. Indeed, it does not appear to have been realised that there is a problem awaiting answer in that connection. The opportunity for examining the subject presented itself to us when a collection of specimens of Burmese jade which was acquired for the Museum of this Institute became available for our studies.

## 2. The structure of jadeite

The chemical composition of jadeite corresponds to the formula  $\text{NaAl}(\text{SiO}_3)_2$  and indicates that it belongs to the series of monoclinic pyroxenes of which diopside  $\text{CaMg}(\text{SiO}_3)_2$  is a typical example. X-ray studies<sup>1,2,3</sup> support the latter conclusion, the X-ray powder diagrams of jadeite and diopside showing a close resemblance to each other. The published chemical analyses<sup>4</sup> show the presence in jadeite of varying proportions of other oxides, notably the oxides of calcium and magnesium, thereby indicating that diopside is present as a minor constituent in the mineral. Physically, jadeite is a polycrystalline aggregate. Examination of thin sections under the polarising microscope reveals the

presence of individual crystals which are birefringent, their greatest and the least refractive indices being 1.667 and 1.654 respectively.

When light enters a polycrystalline aggregate in which the individual grains are birefringent, it would necessarily suffer reflection and refraction at the intercrystalline boundaries. The smaller the individual crystallites, the more numerous would be such reflections and refractions. Hence, on this view, none of the incident light would succeed in penetrating through the material, if it is fine-grained and also of sufficient thickness. In the absence of any absorption properly so-called, the incident light would mostly be sent back towards the source by repeated internal reflections. In other words, a fine-grained aggregate of birefringent crystals should present a high albedo by reflected light and appear opaque in transmission.

The foregoing inferences based on geometrical optics do not however represent what is actually observed in the case of jadeite. Indeed, the converse is much nearer the truth; in other words, the specimens exhibiting a coarse structure are those which are opaque to light and reflect it strongly, while the specimens which are most readily penetrated by light are those having a fine-grained structure. Why this is so is the problem considered in the present paper.

### 3. The X-ray diffraction patterns

To establish the relationship between structure and optical characters briefly indicated above, we have recorded the X-ray diffraction patterns of specimens exhibiting diverse optical behaviour. Three of these diagrams which are representative of the rest are reproduced in plate I. The film to specimen distance was in every case 5 cm and MOK $\alpha$  radiation was employed to record the patterns.

Figure 1 was recorded with a piece of jade about half a millimetre thick cut out from one of our specimens and polished flat on both sides. The X-ray pencil passed normally through the specimen. The plate exhibited a notable measure of translucency; when placed on a printed sheet of paper, the finest print could easily be read through it. The X-ray record shows clearly that the crystallites present in the specimen are of varying sizes and that crystallites of very small sizes are the most numerous; though individual bright-spots appear in the pattern, there are also numerous fainter ones which run into each other and appear as continuous rings.

Figure 2 is an X-ray diagram taken with similar arrangements, the X-ray pencil now grazing the edge of a flat ellipsoidal piece of green jade. It will be seen that the pattern is of the same general nature as that reproduced in figure 1 except that the continuity of the rings is less evident and the spottiness more conspicuous.

Figure 3 is the pattern recorded with a greenish-white specimen which was nearly opaque to light. It will be seen that the pattern consists of a number of

individual spots, some of which are very bright. But hardly anything in the nature of continuous rings can be discerned. In other words, the specimen consists of relatively large crystallites.

#### 4. Theoretical considerations

To understand the optical behaviour of jadeite, we have to put aside the considerations based on geometrical optics and deal with the matter from the standpoint of the wave theory of light. It is useful, in the first instance, to think of an extreme case in which the individuals in the polycrystalline aggregate are assumed to be of very small dimensions even in comparison with the wavelength of light and are also randomly orientated. Such an aggregate could obviously be regarded as equivalent to an optically isotropic medium with a refractive index which is the average of the principal refractive indices of the crystallites. A beam of light incident normally on a slab of such material would traverse it as a coherent wave-train, and emerge from the rear surface of the slab, but not the whole of the incident energy would succeed in so emerging. For, in consequence of the varying orientations of the crystallites and their birefringence, the medium would exhibit local variations in optical behaviour, and there would therefore be a diffusion of light both forwards and backwards. In the limiting case when the grains are very small, the diffusion would extend approximately with equal strength both forwards and backwards. More generally, however, there would be a concentration of the diffused radiation in the forward directions surrounding the path of the regularly transmitted light-beam. There would also be a diffusion of light backwards towards the light-source, but this would be less conspicuous.

The situation set forth above would be modified if the grains of the medium are of dimensions comparable with the wavelength of light. Nevertheless, provided the birefringence of the individual crystallites is small, we may continue to regard the aggregate as an isotropic medium which exhibits local variations in refractive index depending on the direction of vibration in the light beam traversing the material. These variations would result in the phase of light-waves passing through an individual grain being either accelerated or retarded as the case may be. The errors in phase thus resulting when summed up over the total path would tend to cancel each other out; the residual errors in phase would be the smaller relatively to the total path, the more numerous the particles are, in other words the smaller is their size. Thus, it follows that if the birefringence is not large and the material is very fine-grained, the waves of light would succeed in penetrating the medium. Nevertheless, the residual errors in phase would result in a reduction of the absolute intensity of the transmitted beam and ultimately also its total extinction. The missing energy would appear for the most part in a cone of diffuse radiation surrounding the direction of propagation of the incident light-beam.

Wave-theoretical considerations also indicate that the proportion of the

incident energy sent back towards the source as a diffuse reflection by a fine-grained aggregate would be far less than that indicated by considerations based on geometrical optics. For, the phase of a reflected wave relatively to the incident wave depends on whether the first or the second medium on the two sides of the reflecting boundary has the higher index. The boundaries encountered by a light-wave traversing a polycrystalline aggregate would obviously be of both kinds and in approximately equal numbers. The reflection in the two cases being in opposite phases, their effects would tend to cancel each other more or less completely in all directions.

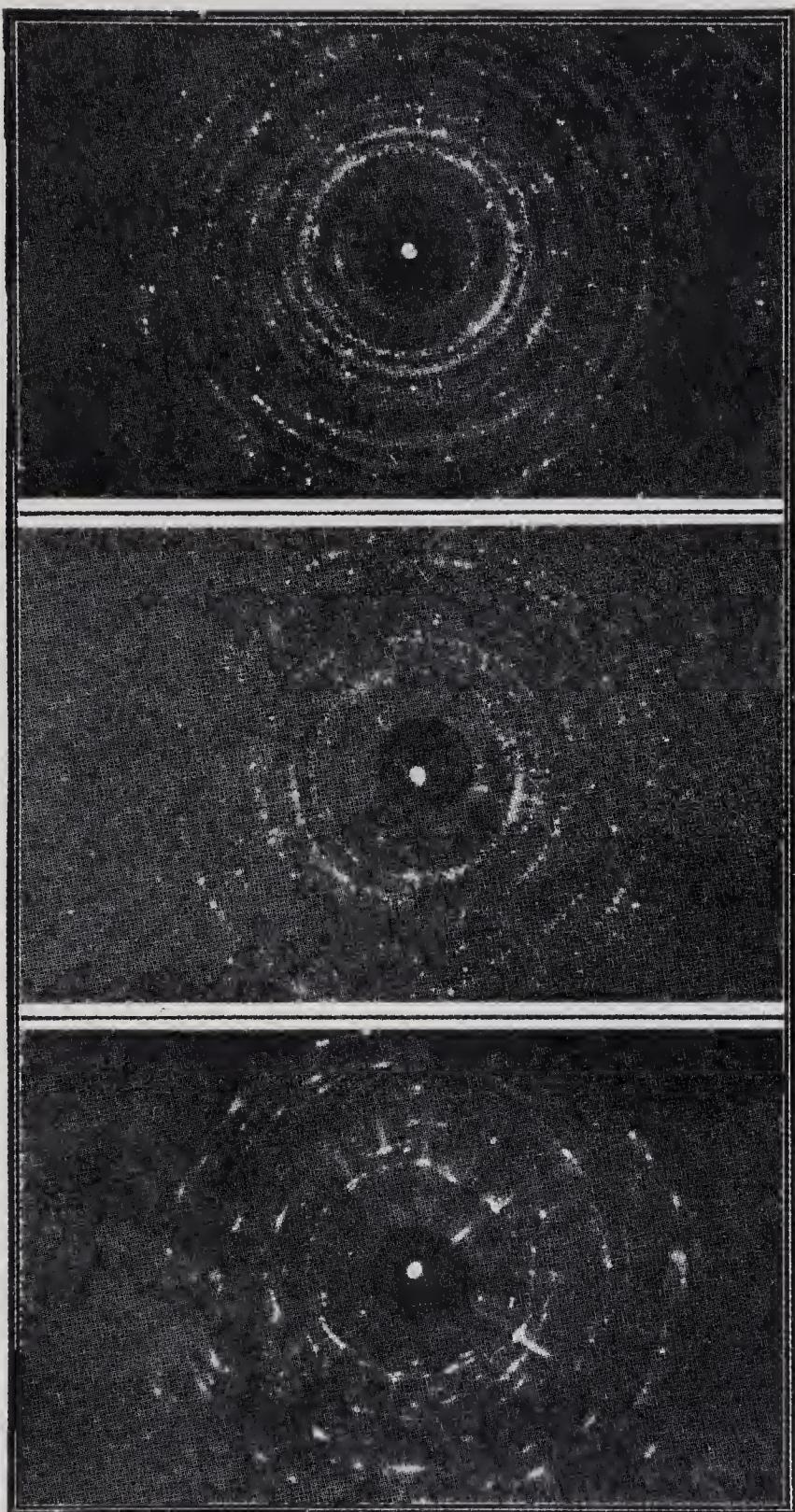
Thus we may sum up the situation by the statement that light would penetrate into a polycrystalline aggregate much more freely and would be reflected backwards much less freely than that might be anticipated in terms of geometrical optics, provided that the aggregate is sufficiently fine-grained. Thus, we have an explanation in general terms of the semi-transparency exhibited by the finest varieties of jadeite.

## 5. Summary

The phenomenon of semi-transparency exhibited by the finer varieties of jadeite is discussed. X-ray diffraction studies and theoretical considerations based on wave-optics alike indicate that this is a consequence of the very small particle size of the crystallites forming the aggregate.

## 6. References

1. Wyckoff R W G, Mervin H E and Washington H S, *Am. J. Sci.*, 5th Series, 1925, **10**, 383.
2. Warren B E and Biscoe J, *Z. Kristallogr.*, 1931, **80**, 391.
3. Yoder H S, *Am. J. Sci.*, 1950, **248**, 225.
4. Hintze Carl, *Handbuch Der Mineralogie*, Zweiter Band, 1897, p. 1175.



**Figures 1–3.** X-ray diffraction patterns of jadeite.

**Plate I**

## Crystals of quartz with iridescent faces

SIR C V RAMAN  
(Raman Research Institute, Bangalore)

Received May 10, 1950

### Introduction

The optical phenomena forming the subject of this paper are exhibited in a very striking manner by two small crystals of colourless transparent quartz which were obtained by the author some years ago from a jeweller in Bombay. An enlarged photograph of one of the crystals is reproduced as figure 1(a) in plate I accompanying the paper. As will be seen from the illustration, one of the pyramidal faces terminating the crystal exhibits a brilliant reflection. The colour of this at normal incidence is a bright green and changes to blue and then to bluish violet as the incidence is made more oblique. At the same time, the iridescence becomes distinctly weaker and much less saturated in hue. The coloured reflection is seen over the whole area of the face with fairly uniform colour and intensity. No trace of the phenomenon is exhibited by any of the other pyramidal faces of the crystal or by any other part of its surface. The second crystal similarly shows a brilliant iridescence on the largest of its pyramidal faces, its colour and intensity, remarkably enough, being practically indistinguishable from those of the first crystal. The second crystal shows, in addition, an iridescence of the same colour on two other pyramidal faces of smaller size, but not on a fourth which is adjacent to the largest iridescent face and of comparable area.

### 2. The nature of the iridescence

That the iridescence is not due to superficial films adhering to the crystals is obvious on an examination of its features. Had it had been of that nature, the area of colour would be that covered by the film and would not extend beyond it. Actually, when the crystal is held suitably with respect to the incident light, one observes a brilliant blue band of iridescence along the edge of the face but outside its area, while the face itself remains dark. This effect which is illustrated in figure 1(d) in plate I is due to light which enters the crystal face near its edge and after suffering a reflection *within* the crystal, emerges through the *contiguous* face.

When the crystal is held appropriately, it is possible also to observe the converse effect, viz., light enters the crystal through the contiguous face, and after reflection within the crystal manifests itself as a bright blue band parallel to the edge of the face but *inside* it, the face itself not displaying the usual iridescence. In suitable circumstances, also, both effects may be simultaneously observed, bright blue bands being seen alongside the edge on either side, the latter itself appearing as a dark line of separation. That the iridescence arises from reflection inside the crystal and not at the external surface is further evident from the fact that the outer margin of the coloured area is, in general, not exactly coincident with the edge of the face; between them appears a strip without colour and of width varying with the obliquity of incidence of the light and with the setting of the edge with respect to the direction of observation. This effect is illustrated in figure 1(c) of plate I in which the lower edge of the face is seen distinctly doubled.

It is thus evident that the iridescence is due to a layer of material which lies below the surface of the crystal and forms an integral part of its structure. The observations indicate the thickness of the layer to be of the order of a quarter of a millimetre. It follows that the coloured reflection from within the crystal would be diluted by the reflection of white light from its exterior surface in an increasing measure as the incidence is made more oblique. This is actually observed, as has already been indicated, and the explanation given is confirmed by the effect of immersing the crystal in a beaker of water, or better still, xylene. By such immersion, we weaken or suppress the white-light reflection, and the iridescence is thereby notably improved in intensity as well as in respect of the saturation of its hue. The polarisation of the white-light reflection at oblique incidences may also be utilized to reduce its intensity by viewing the crystal face through a suitably orientated polaroid. At the polarising angle for quartz, the external reflection is completely suppressed, and the internal reflection which is then of a violet colour appears of a saturated hue, though to some extent it is enfeebled in intensity by its own partial polarisation.

As is to be expected from the intensity of the iridescent reflection, the crystal faces which show the phenomenon exhibit the complementary tint by transmitted light in a conspicuous manner. The transmission colour for normal incidence is a lively rose-pink; this fades away to pale yellow and finally to white as the incidence becomes more oblique.

### 3. Its spectral character

Spectroscopic examination of the iridescence exhibited by the crystal faces shows it to be essentially a *monochromatic reflection*. The reflected light at normal incidence exhibits a few narrow streaks close to each other in the green region; as the incidence is made more oblique, these streaks move towards the violet end of the spectrum. Examination of white light transmitted normally through the

crystal face reveals a set of narrow bands of extinction in the same position in the spectrum as the bright streaks observed by reflected light. These effects are illustrated in figure 2(a), (b) and (c) in plate I, the reflection and extinction bands being indicated by arrows. The photographs were taken with sunlight as the source. The diffuse background seen in the reflected spectra reproduced as figure 2(a) and (b) is due to the reflection of white light from the surface and some parasitic illumination returning from the rear of the crystal. The former effect becomes more important at oblique incidences. In figure 2(c), the extinction bands due to the crystal are those marked, the rest being the Fraunhofer lines in the solar spectrum.

From the facts stated, it is clear that the iridescent material is essentially a stratified medium consisting of a great many parallel layers of extreme thinness which is more or less exactly the same for all the layers. If we assume the iridescence observed at normal incidence to be a second-order reflection, it would follow that the individual laminae would be  $0.34 \mu$  thick, and as the thickness of the entire iridescent layer is about  $250 \mu$ , there would be room in it for about 700 layers. If these were all of exactly the same thickness, they would result in extremely sharp monochromatic reflections and extinctions.

#### 4. The nature of the stratifications

As is well known, quartz exhibits two principal kinds of twinning, viz., the electrical and the optical, which may also be described as the orientational and chiral types of twinning respectively. We may evidently dismiss the electrical type of twinning without further consideration in relation to our present problem. Chiral twinning is very common in quartz and frequently exhibits itself as a polysynthetic or lamellar twinning in which the right-handed and left-handed layers are parallel to each other and to the rhombohedral planes of the crystal structure. Such polysynthetic twinning is indeed characteristic of "amethystine" quartz and exhibits itself prominently when a section cut normally to the optic axis of the crystal is viewed through a polarising microscope. The thickness of the twinning layers is known to be highly variable; it may be sufficiently large to be seen without optical aid, or so small as to be invisible even under the polarising microscope. Large variations have been observed even within a single section plate.

The two crystals now under study do not exhibit the slightest hint of amethystine colour. Nevertheless, in their external form, they show the same features as amethystine quartz, and indeed reproduce perfectly the features observed in a great number of crystals of that material collected by the author from the campus of the Osmania University at Hyderabad and deposited in the Museum of this Institute. The prismatic faces are completely missing, and their place is, for the greater part, taken by an array of terraces running in zig-zag

fashion parallel to the rhombohedral faces of the crystal. One such set of terraces, lying below a pyramidal face which does not exhibit iridescence is visible in figure 1(a) in plate I. Though the matter has not been tested by section-cutting, since this would have involved destruction of the specimens, it may be taken for granted that the crystals displaying iridescence consist of polysynthetically twinned quartz in which the right-handed and left-handed forms lie in layers parallel to the rhombohedral faces.

Chiral polysynthetic twinning in quartz would not, however, necessarily give rise to iridescence. Had this been the case, the phenomenon would have been noticed and reported long ago by many observers. It is obvious that a crystal face would not exhibit any visible colour by reflection unless the laminations contiguous to it have a sufficient reflecting power and are sufficiently fine and sufficiently numerous to build up a coherent monochromatic iridescence. Even in the two crystals forming the subject of the present study, the conditions necessary for iridescence evidently exist only for some of the crystal faces and not for the others. It may be remarked in this connection that an examination of their external forms reveals some striking differences between the pyramidal faces which display iridescence and those which do not. The latter are terminated by zig-zag lines below which lie a succession of terraces well separated from each other. On the other hand, in all the four cases in which iridescence is observed, we notice immediately below the iridescent face, an area having the correct crystallographic orientation for a prismatic face but presenting a peculiar grooved and eroded appearance; where this meets the iridescent face, we notice a step-like configuration, indicative of a laminated structure of the material parallel to the face. These features can be made out by a study of figures 1(a), (b), (c) and (d) in plate I.

## 5. Some further considerations

The suggestion made above that the stratifications giving rise to the iridescence in quartz are of the polysynthetic chiral type raises some further questions. The iridescence exhibited by some specimens of potassium chlorate was explained long ago by Rayleigh as due to polysynthetic twinning in the monoclinic crystals of that substance. The special features observed in the case of potassium chlorate, viz., the disappearance of the iridescence at normal incidence and its periodic appearance and disappearance at all incidences when the crystal is rotated in its own plane, are consequences of an orientational type of twinning. It is not surprising that these features are not met with in the case of quartz. The orientational twinning in the case of potassium chlorate also results in some peculiar polarisation effects. No such effects are observed in the case of the iridescence of quartz. Provided that the depolarisation due to the passage of the light through the quartz is avoided or duly taken account of, the iridescent

reflections are found to exhibit a normal behaviour, in other words, they show, at least qualitatively, the degree and kind of polarisation to be expected for reflection at the boundary between two media of nearly equal refractive index.

Finally, we are faced with the question whether the optical difference between layers of right-handed and left-handed quartz is sufficient to give an appreciable reflection of light at the boundary of separation between them. If the answer to this question be in the negative, we would be faced with a dilemma, since it would be difficult to explain otherwise the iridescence which is actually observed and which is so clearly related to the architecture of the quartz crystal. It seems, however, just possible that the polysynthetic twinning may be accompanied by a segregation at the boundaries between the right-handed and left-handed quartz of extremely thin layers of impurity material. Such layers when regularly disposed could give rise to coherent reflections of sufficient intensity to explain the observed iridescence.

The photographs illustrating this paper (plate I) were obtained by Mr A Jayaraman, whose highly competent assistance has also otherwise been of value in the work described.

### Summary

The paper is a study of the iridescence exhibited by some of the pyramidal faces of two crystals of transparent quartz in the possession of the author. Spectroscopic examination shows the reflections and the corresponding extinctions to be monochromatic. The thickness of the iridescent layer may be directly observed, and the number of laminations inferred to be present is sufficient to explain the observed characters of the iridescence. The nature of the stratifications in the crystal giving rise to the iridescence is discussed. Photographs of one of the crystals and of the spectral character of the reflections and extinctions illustrate the paper.

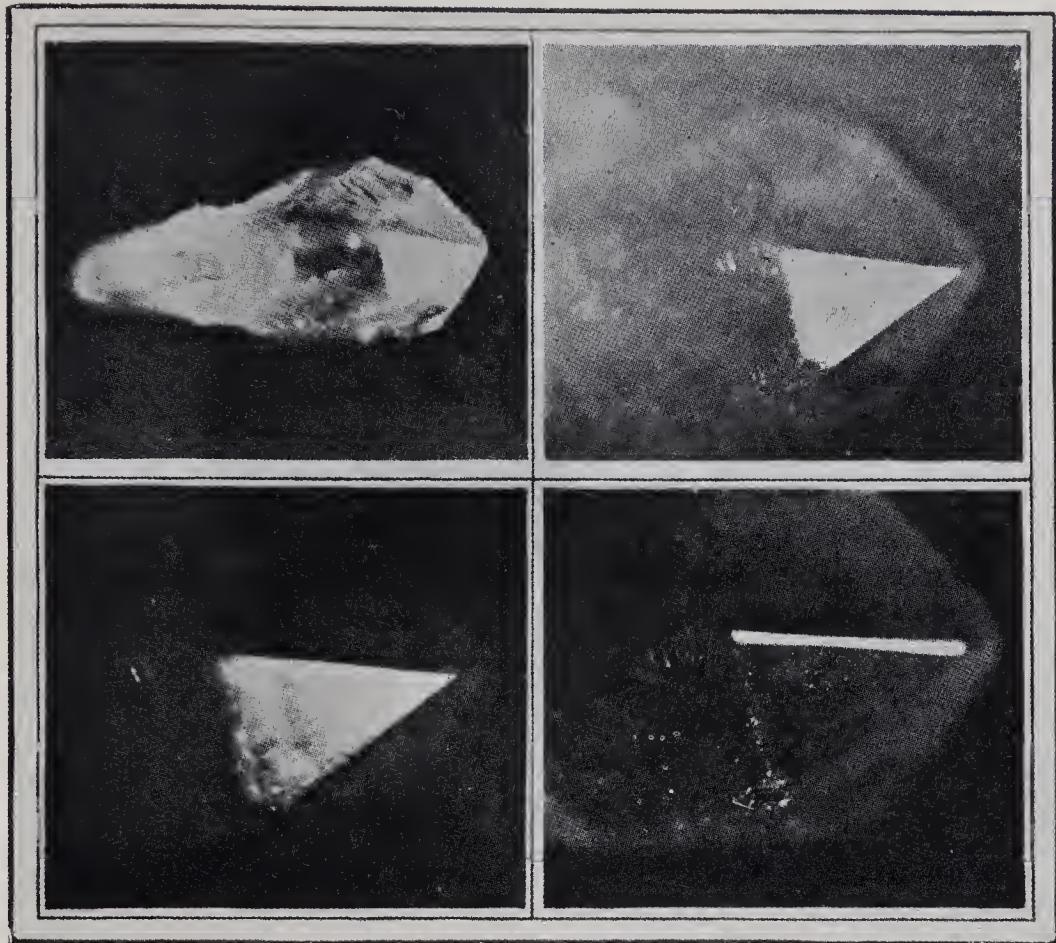


Figure 1

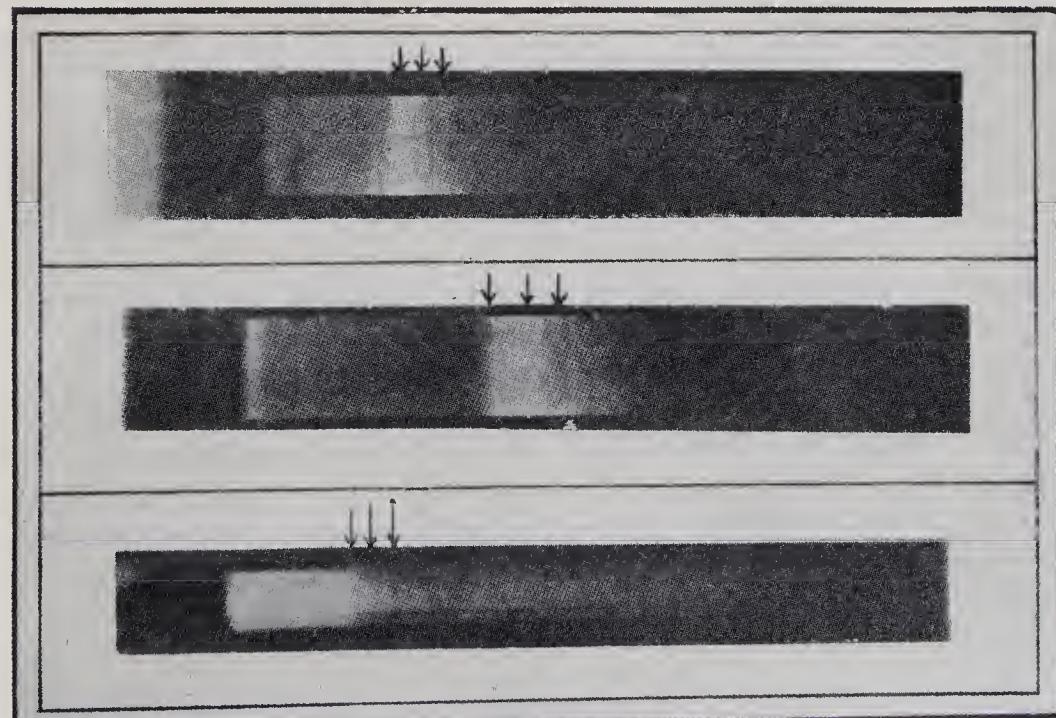


Figure 2

Plate I

# The optical anisotropy and heterogeneity of vitreous silica

SIR C V RAMAN  
(Raman Research Institute, Bangalore)

Received March 13, 1950

## 1. Introduction

Vitreous silica is a remarkable and most useful material and the investigation of its structure and properties is therefore of much interest. As it is an amorphous solid, one would naturally expect its optical behaviour to be that of an isotropic medium. Actually, however, a polished plate of vitreous silica when interposed in the path of a beam of light between a polariser and an analyser set in the position for extinction always gives rise to an observable restoration of light, as was remarked long ago by Rayleigh (1920). A characteristic feature of the phenomenon is that the restoration of light is not uniform over the surface of the plate. This effect is particularly striking in the case of the disks of the so-called optical silica which are built up by a special process. These exhibit a birefringence pattern of concentric circles, evidently connected with the way in which the material had been fabricated (figure 10 in plate II).

The present paper describes the results of a re-examination of the behaviour of vitreous silica referred to above, undertaken with a view to elucidate the nature and origin of the phenomenon. The material available for the study included several specimens of the silica glass collected by Dr L J Spencer in the Sand Sea of the Libyan desert in December 1934 and very generously presented to the author during a visit to his London home in 1948. The examination of the specimens of this naturally occurring substance has yielded highly significant results. Numerous examples of the commercially available material have also been examined. These included circular discs of different thicknesses and diameters, two belonging to this Institute and several others very kindly loaned for the study by Prof. R S Krishnan. Two silica rods with different forms of cross-section which were presented to the author by Messrs. Adair Dutt of Madras have also been studied.

Large Nicols, such as those used by Rayleigh in his investigation, were not available. But polaroids three inches square in area serve the same purpose admirably. Except in the case of disks having polished faces, it is useful and indeed

generally necessary to immerse the specimen under study in a flat-sided trough filled with xylene or carbon tetrachloride. The use of a light source of adequate intensity is essential. Indeed, the most satisfactory way of examining any specimen is to view it when traversed by a direct beam of sunlight with the arrangements described above.

Since the optical anisotropy exhibited by vitreous silica exhibits local variations, it follows that the material is optically heterogeneous. This may be readily demonstrated without the use of polarised light by merely holding a polished disk of vitreous silica in the path of a beam of light diverging from a brilliant source of light of small area. The light which has traversed the disk when received on a screen placed at a suitable distance is found to exhibit a pattern of light and shade bearing a recognisable relationship to the features exhibited by the same specimen between crossed polaroids.

## 2. Observations with natural silica glass

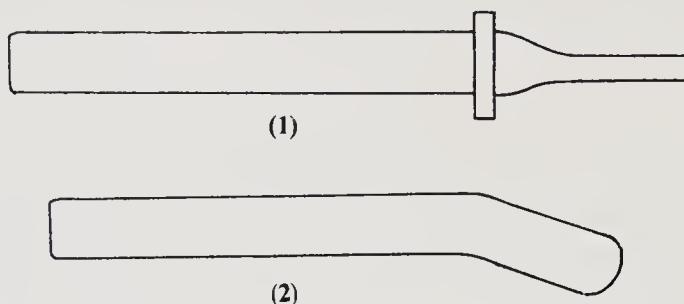
A remarkable occurrence of vitreous silica scattered over an extensive area in the Libyan desert was reported in a paper by Clayton and Spencer (1934). Further details appeared in a later memoir by Spencer (1939). The material has a pale greenish-yellow colour and some of the specimens are clear and transparent. Chemical analysis shows the mineral to be nearly pure silica,  $\text{SiO}_2$  making up  $97\frac{1}{2}\%$  while the rest consists of various metallic oxides. The five specimens gifted to the author by Dr Spencer from his collection are fully representative of the Libyan occurrence and show the various characters described and illustrated in the paper by Clayton and Spencer. Two of them, though interesting in themselves, contain numerous inclusions and are therefore not suited for the present investigation. The three others when immersed in a trough containing xylene or carbon tetrachloride and placed between crossed polaroids exhibit some striking effects which are illustrated in figures 1, 2 and 5 of plate I. Streaks or sheets of luminosity are observed traversing the interior of the glass: there are several such in each specimen, and they run parallel to each other in a direction coinciding more or less exactly with that of the longest dimension of the piece. The luminosity attains its maximum intensity when the specimen is so set that the bright streaks or sheets bisect the angle between the principal planes of the two polaroids. As is to be expected in these circumstances, they disappear when set so as to lie in either of these two planes, the whole of the specimen then appearing more or less perfectly dark.

The photographs reproduced as figures 1, 2 and 5 in plate I were recorded with the specimen in each case set so that the luminous streaks or sheets are of maximum intensity: they are seen in the figures running diagonally. The effect was particularly conspicuous with the specimen represented in figure 5 which was very clear and transparent: the trough used was unfortunately not large enough

to hold the entire piece, otherwise the effects would have shown up much better in the photograph. The specimens illustrated in figures 1 and 2 in plate I are distinctly cloudy but nevertheless show the phenomenon clearly enough.

### 3. Observations with transparent silica rods

The two rods studied are shown diagrammatically as figures 1 and 2 below in the text. The rod illustrated in figure 1 has a cylindrical cross-section with a flange added at one end as shown. The second rod has a flattened cross-section and is bent in its own plane into a curve towards the end as shown in figure 2.



Figures 1 and 2

Examination of the cylindrical rod when immersed in carbon tetrachloride and placed between crossed polaroids shows a birefringence pattern exhibiting a great number of lines or fibres running more or less exactly parallel to the axis of the rod (figure 8 in plate II). This effect is most conspicuous when the axis of the rod is inclined at  $45^\circ$  to the planes of vibration of the two polaroids and vanishes completely when it is set parallel to either of these planes. In the vicinity of the flange and up to some distance on either side of it, however, a different effect is simultaneously observed. This is of much greater intensity and may be isolated by setting the rod either vertical or horizontal; the fibrous structure then ceases to be visible and the restoration of light shows the continuous variation of intensity characteristic of a photoelastic pattern. The second effect thus evidently arises from a distribution of permanent stresses existing in the vicinity of the flange. When, however, the rod is set in an inclined position, both types of birefringence—structural as well as stress-optical—appear simultaneously, and they are superposed on each other. Some very curious features are observed when a fibre-line crosses a dark band of the stress-optical pattern.

The bent rod illustrated in figure 2 also exhibits a structural birefringence pattern, consisting of fine fibres running parallel to the axis of the rod and bending round towards the end so as to follow its curvature. There are indications that there exists simultaneously a stress-optical birefringence, as the result of the

superposition of which the structural birefringence is seen more weakly at some parts of the cross-section than at others. A similar effect is also apparent in the case of the cylindrical rod (figure 8 in plate II).

#### 4. Observations with transparent silica disks

Reference has already been made above to the behaviour of disks of the so-called "optical silica" built up in a particular manner which show a birefringence pattern consisting of concentric circles. The behaviour of one such disk, 4 centimetres in diameter and 8 millimetres thick, when viewed normally to itself between crossed polaroids, is illustrated in figure 10, plate II. It will be noticed that the black cross seen in the pattern cutting across the circular rings is somewhat distorted in the vicinity of the centre; when the disk is rotated in its own plane, the cross shifts about a little, showing that the structure giving rise to the observed pattern is not perfectly centro-symmetric. The disk may also be viewed *edgewise* along a diameter, its plane making any desired angle with the principal planes of the polaroids: the restoration of light then observed is very feeble if the plane of the disk is set parallel to either of them, and quite strong if set at an angle of  $45^\circ$  with either of them. We shall return later to the question of the interpretation of the effects observed with this disk, but will here draw attention to a remarkable feature observed in figure 10 in plate II, namely the sharp definition of the boundaries between the dark and bright areas in the pattern.

Two other disks included in the present study also show a black cross when viewed normally between crossed polaroids, but they are of the so-called "ordinary" silica, and the observed characters of the birefringence are quite different (see figure 6 in plate I, and figure 12 in plate II). In both of these cases, the field of light in the space between the arms of the black cross consists of a criss-cross pattern of streaks intersecting each other: the general directions of the two sets of streaks are respectively along the two diagonals making an angle of  $45^\circ$  with the arms of the black cross, as is particularly clear in figure 6, plate I, but not so clear in figure 12 in plate II, the black cross being also a little hazy in that figure.

Figures 7, 9 and 11 in plate II reproduce photographs of still another disk viewed normally to itself between crossed polaroids, the three figures representing three different settings of the disk *in its own plane*. It will be noticed that this disk does not exhibit a black cross, and that its appearance is altogether different in the three settings. In figure 7, we see that the streaks seen on the disk run only along one diagonal, in figure 9 they run only along the other diagonal, while in figure 11 a few patches appear exhibiting a criss-cross pattern with streaks running along both diagonals and intersecting each other. The remarkable difference between the behaviour of this disk and those of the two others—which show a black cross and a criss-cross pattern of streaks all over in every setting—is evidently related to the fact that it is a thin disk, being only 2 millimetres thick,

while the other two disks are 13 millimetres and 4 millimetres thick respectively. This explanation is supported by the results of an examination of the thickest of the three disks *viewed edgewise along a diameter*. Such examination immediately reveals in it the presence of a great many birefringent streaks parallel to the surface of the disk (figure 4 in plate I): these are equally conspicuous in all settings of the disk in its own plane, and thus effectively form birefringent layers or sheets within the disk parallel to its faces. They appear most brilliantly when the plane of the disk is set at  $45^\circ$  to the principal planes of the polaroids, but continue to be visible over a very considerable range of settings of the disk on either side of this position and disappear only when the disk is parallel to one or other of the two planes. In the latter position, streaks may be seen running in directions inclined to the surface of the disk, but they are much fainter (see figure 3 in plate I).

In figure 6, plate I, one notices that towards the edge of this disk, the criss-cross structure of the birefringence is apparently replaced by a somewhat brighter continuum. The explanation of this effect has been investigated by immersing the disk in a trough of liquid and viewing it *edgewise* between crossed polaroids. Such an examination revealed that the structure of the disk is effectively modified near the cylindrical edge by the firepolishing to which the latter had apparently been submitted. A feeble photo-elastic birefringence is also visible near the edges by reason of the disk having been sawn through to form its faces. The other two disks do not show this effect: they have polished faces and ground edges.

## 5. Interpretation of the facts

Before we proceed to consider the explanation of the facts brought to light by the present investigation, it may be useful briefly to comment on the opinions expressed by Rayleigh regarding the nature of the effects noticed by him. From certain evidence detailed in his paper, he came to the conclusion that the birefringence pattern of concentric circles shown by the built-up silica disks was a stress-optical phenomenon. On the other hand, the birefringence exhibited by the silica disks of the ordinary variety was ascribed by him to a crystalline granular structure of the vitreous silica which he thought might have been derived from the quartz from which it is obtained by fusion. He believed also that when the silica is fused and drawn out into rods, these same crystalline granules persist but are elongated into fibres.

With regard to the above-mentioned suggestions of Rayleigh, we may remark that theoretical considerations make it extremely difficult to accept them as probable or even possible. As is well known, the formation of vitreous silica from crystalline quartz is attended by a notable diminution in density from 2.65 to 2.20, and is accompanied by a sharp drop of the refractive index to 1.458 for vitreous silica from the much higher values 1.544–1.553 characteristic of quartz. There is

simultaneously a fundamental change in structure, as is shown directly by X-ray studies, and is indicated also by the remarkable changes in physical properties, notably the drop in the thermal expansion coefficient from  $34 \times 10^{-6}$  to  $1.3 \times 10^{-6}$ . Moreover, in the range of temperature  $1470^\circ\text{--}1710^\circ$  immediately preceding that of fusion, the stable crystalline form of silica is not quartz but high-cristobalite, which is an optically isotropic material. It is also known that when vitreous silica devitrifies, the product is not quartz but cristobalite. In view of all these facts, one could scarcely suppose that any trace either of the crystalline structure or of the birefringence of quartz could survive in the molten liquid obtained by its fusion and be carried over to the glass formed on solidification.

We may also remark that it was the criss-cross structure of the birefringence patterns exhibited by fairly thick disks of the ordinary silica which led Rayleigh to his hypothesis of a granular structure for vitreous silica in the mass. Actually, however, as shown by the present investigation, patterns of this type represent merely the integrated optical effect of the passage of the light through the many birefringent layers present in a thick disk. Figures 7 and 9 in plate II show that even in a disk 2 millimeters thick, the birefringence pattern takes the form of elongated streaks and *not* of a criss-cross pattern. The facts of observation thus lend no support to the postulated existence of crystalline granules having an average dimension of half millimetre in vitreous silica.

We are thus forced to seek for an alternative explanation of the observed phenomena. It is useful to consider the problem in two stages. The first is the purely phenomenological approach to the facts. The various observations described in the present paper make it perfectly clear that in vitreous silica, two kinds of "accidental birefringence" are possible. The first kind is the well known type of birefringence which is observed in a stressed isotropic solid. If such birefringence is observed in a specimen not subjected externally to any stress, we have necessarily to assume that it arises from an internally compensated system of stresses. How such stresses are set up and persist is a question the answer to which depends on the previous thermal and mechanical history of the specimen. It may be remarked that the thermal expansion coefficient of vitreous silica is extremely small even at high temperatures. From this, it follows, and indeed is actually the case, that the photo-elastic effects arising from an unequal heating of a specimen would be small. One may therefore reasonably assume that though stresses arising from "imperfect annealing" may arise in vitreous silica, as in other types of glass, they would not be so large as to overshadow any other possible kind of effect. This leads us naturally to the recognition of a second kind of "accidental birefringence" in vitreous silica—and presumably therefore also in other amorphous solids—of a "structural birefringence" also arising from the previous thermal and mechanical history of the specimen. The distinction between this and the other is indicated by its name, viz., that we are concerned *not* with the elastic deformations of an isotropic medium and the optical consequences thereof, but with changes of the ultimate structure of the substance itself.

resulting in its becoming birefringent. Accepting such a possibility, we see at once that the phenomena brought to light by the present investigation, both in natural silica glass and in the material prepared artificially, find a natural explanation. Indeed it would be difficult to find any other explanation, since their general character definitely excludes an interpretation of them as stress-optical birefringence of the familiar variety.

## 6. Origin of the structural birefringence in vitreous silica

As is well known, viscous liquids when stirred exhibit a temporary birefringence which disappears more or less quickly with time. A theory of this phenomena connecting it with the linear dimensions and optical characters of the molecules of the fluid and with its viscosity was given long ago by the present writer and K S Krishnan (1928). The case of vitreous silica is rather different from that of the organic compounds with discrete molecules considered in that paper. We may indeed recognize the presence in vitreous silica of a fundamental building unit, viz., a silicon atom surrounded tetrahedrally by four oxygen atoms. But such a unit cannot be regarded as capable of moving or rotating independently of the neighbouring units of the same kind. Indeed, in the solid, the units would be firmly bound to each other at the corners by the sharing of the oxygen atoms. Free mobility of the units in the molten or liquid state would require the breaking and reforming of vast arrays of such bonds. It is this circumstance which distinguishes the behaviour of vitreous silica in the fluid state from that of ordinary liquids composed of discrete molecules bound to each other by comparatively weak forces. Given sufficient time and favourable circumstances, one may expect to find that in the molten silica the building units link themselves in such manner as to become effectively an optically isotropic structure. Such a liquid on solidification would be optically non-birefringent. But that in any actual set of circumstances, and especially when the molten liquid is subject to any type of mechanical disturbance, it is unlikely that such an ideal state would be actually reached or that it would be exhibited in the finally resulting glass. The fashioning of a glass necessarily involves the manipulation of the material in a semi-molten state into the particular form desired. Any such operation would necessarily bring into action the tendency of the bonds connecting the silicon atoms with the oxygen atoms to resist disruption, and for the units to take up new positions by shifting the directions of the bonds rather than by their disruption and reformation. The formation of optically birefringent streaks or sheets in the medium would be a natural consequence.

The foregoing is of course only a general and qualitative picture. But it appears to afford a reasonable explanation of the special type of irregular or accidental birefringence of an obviously structural character exhibited by vitreous silica, and especially of the relationship between the optical characters of the birefringence

and the geometric form of the specimen under examination which emerges from the actual facts of observation.

The photographs accompanying this paper were obtained by Mr J Padmanabhan, whose efficient assistance I have much pleasure in acknowledging.

### Summary

The paper describes the birefringence exhibited by vitreous silica, both in the naturally occurring material found in the Libyan desert and in the commercially available material in the forms of rods and disks. The facts revealed by the investigation are discussed. It is shown that Rayleigh's belief that vitreous silica in the mass has a crystalline granular structure cannot be sustained. It is shown further that, besides the familiar stress-optical birefringence, a second kind of effect, viz., "structural birefringence" is also possible in amorphous solids and that this is particularly prominent in vitreous silica for reasons which are discussed.

12 photographs illustrate the paper.

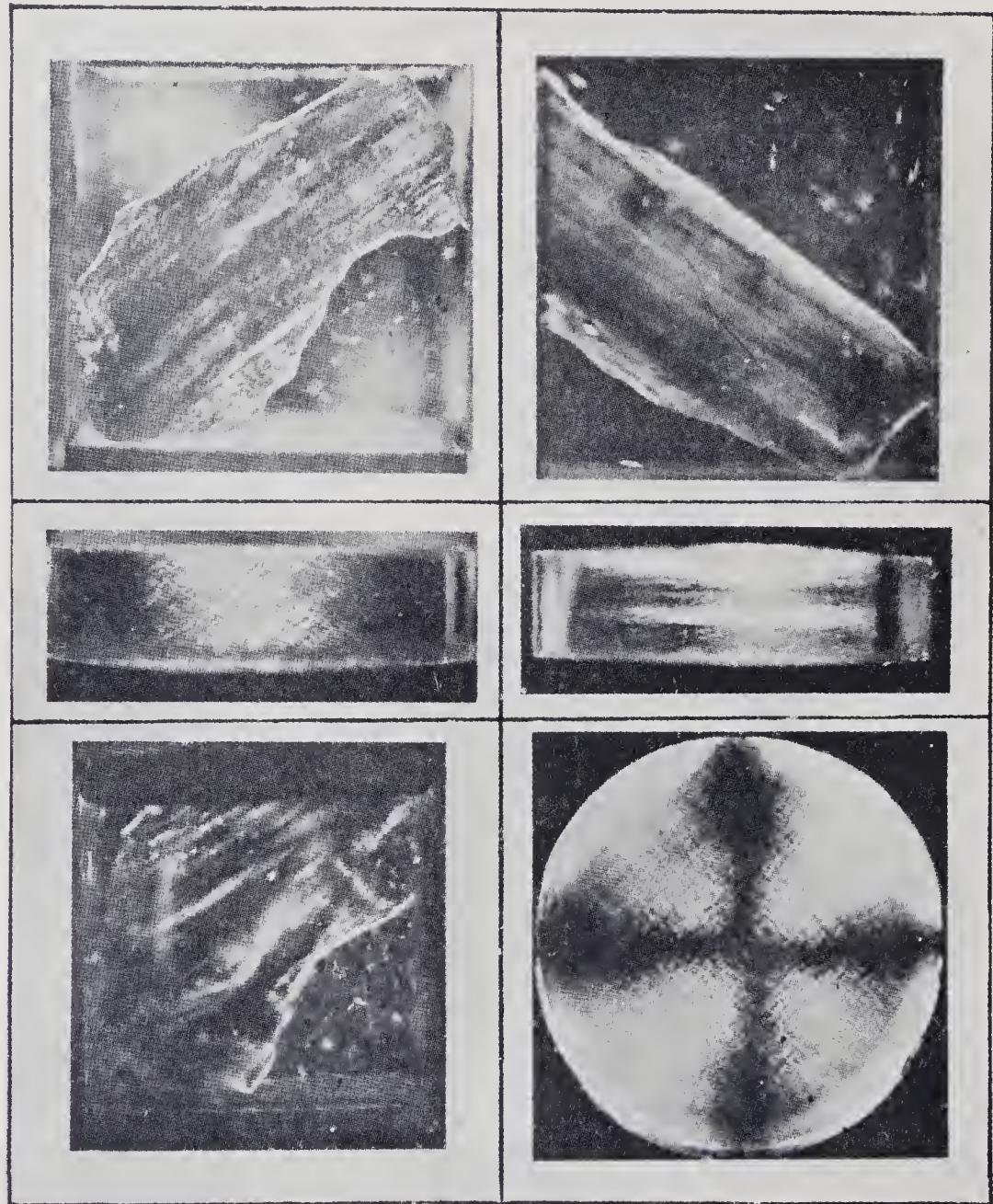
### References (In chronological order)

Rayleigh *Proc. R. Soc. London*, 1920, **A98**, 284.

Raman and Krishnan *Philos. Mag.*, 1928, **5**, 769.

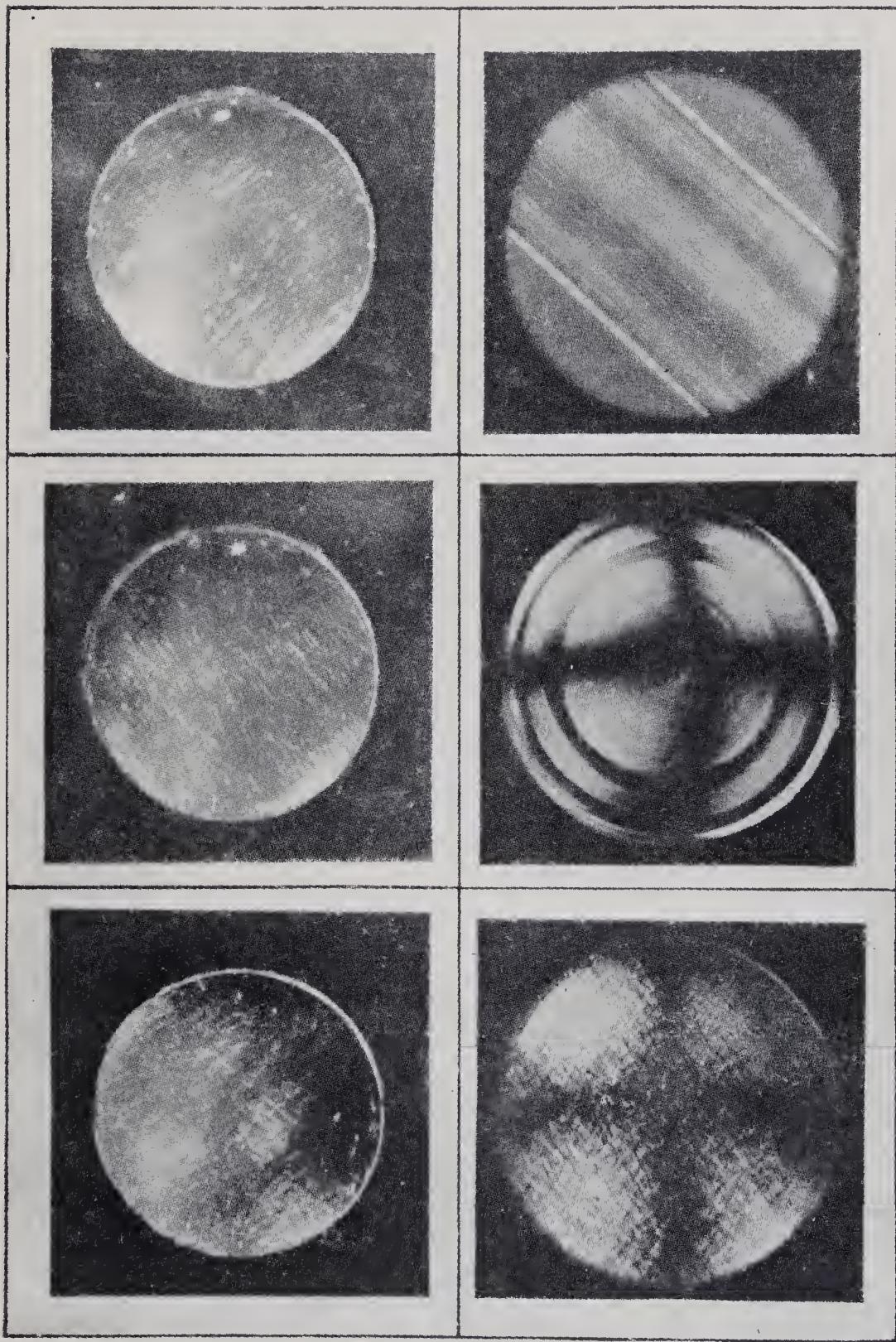
Clayton and Spencer *Mineral. Mag.*, 1934, **23**, 501.

Spencer *Mineral. Mag.* 1939, **25**, 432.



Figures 1-6

Plate I



Figures 7-12

## Structural birefringence in amorphous solids

SIR C V RAMAN  
(Raman Research Institute, Bangalore)

Received April 18, 1950

### 1. Introduction

The birefringence exhibited by optically isotropic solids when deformed by stress is familiar knowledge and forms the theme of the subject of photo-elasticity. There exists, however, a second kind of birefringence which may also be exhibited by amorphous solids and which differs both in its origins and in its observable characters from the photo-elastic effect. To distinguish it from the latter phenomenon, it has been designated as structural birefringence (Raman 1950). The name is intended to convey the idea that such birefringence owes its origin to anisotropy of structure existing even when the material is free from stress. Such anisotropy is, of course, not a normal property of the material as in the case of crystals, but is “accidental” in the sense that it is a consequence of special circumstances existing during the formation of the solid. The recognition of such birefringence as a distinct phenomenon is compelled by a study of the facts observed with vitreous silica and described in the paper cited. Structural birefringence in the case of this substance manifests itself as streaks or sheets of luminosity—inexplicable on the basis of photo-elastic theory—which are clearly the result of flow in the material while in a plastic state before its final solidification.

The present paper describes similar studies made with other materials and especially with the inorganic glasses. The results show unequivocally that structural birefringence is also exhibited by such glasses, either by itself or in conjunction with the photo-elastic effect. As is well known, the process known as “annealing” is an essential part of the technique of glass manufacture. Its purpose is to remove the internal stresses set up in the fabricated material by differential rates of cooling of its parts, and the test applied to determine whether this has been accomplished is the disappearance of birefringence. Except, however, in the case of high-grade optical glass where special techniques are employed to obtain a perfectly homogeneous and isotropic product, the process of annealing never actually succeeds in removing all observable birefringence. Indeed, the commoner commercial varieties of glass exhibit, when critically examined, an easily noticeable birefringence. It is with this phenomenon that we are concerned in the present paper.

As already noted in the paper on vitreous silica, the detection and study of a feeble birefringence needs the use of a light source of adequate intensity. The most satisfactory method is to place the object under examination between two crossed polaroid sheets, and send a beam of sunlight through it. For observation or photography of a large area of the object at one time, it will be necessary to diffuse the incident light beam by a sheet of ground glass. As polaroid sheets are available up to twelve inches square in area, quite large objects can be examined in this way. It is necessary that the surfaces of the object through which the light enters and emerges are flat and parallel. This requirement may be avoided by immersing the object in a flat-sided cell containing a liquid of suitable refractive index. But this naturally restricts the size of the objects which can be examined.

## 2. The birefringence of plate glass

Common glass is produced commercially on a large scale in the form of sheets or plates of any desired thickness. The process of the manufacture and the annealing of the product are both so highly perfected that a sheet of quarter-inch plate glass when held normally between crossed polaroids usually shows no noticeable restoration of light. One might be tempted to infer from such an observation that the material is optically isotropic. Actually however, this is not the case, as becomes apparent when the plate is set and viewed edgewise between crossed polaroids, the light traversing the material in a direction parallel to its surfaces. A strong restoration of light is then noticed; this is a maximum when the plate is inclined at an angle of  $45^\circ$  to the principal planes of the polariser and analyser but, as is to be expected, vanishes when the plate is set parallel to either of these planes. The origin of the birefringence becomes evident when the edge of the plate is viewed through a magnifying lens in the circumstances stated. It is then seen that the entire thickness is made up of a great many laminae parallel to the surfaces of the plate overlying each other (see plate III). To see the laminae clearly, it is necessary that they should be viewed in a direction accurately parallel to the surfaces of the plate; further, as already remarked, the edges through which the light enters and emerges should be flat and parallel. (Alternatively, the observations may be made with the plate immersed in a flat-sided cell containing xylene). The fact that the individual laminae are birefringent and in varying degrees is evident from the varying intensity of the restoration of light that they produce. The same may also be very elegantly exhibited by superimposing a quartz wedge on the edge of the plate; the straight fringes due to the wedge run at right angles to the plate and appear above and below it, while the fringes due to the combination of the wedge and the plate appear in the central strip. The course of the latter fringes then displays the birefringence of the individual laminae very clearly (see plate III).

The foregoing descriptions refer to the phenomena exhibited by a strip of plate

glass at a sufficient distance from its free edges. At and near these free edges, however, we observe a restoration of light which is a distinct phenomenon, as is shown by its being most conspicuous when the strip is held in such a position (parallel to the principal plane of either the polariser or the analyser) in which the structural birefringence vanishes; it is evidently a photo-elastic birefringence produced by the stresses set up in the vicinity of the edges of the strip when it is cut. If the strip be inclined so as to restore the visibility of the structural birefringence, we notice a superposition of the two effects in the vicinity of the edges. Such superposition and the special features arising from it are particularly conspicuous when the plate under observation is thick, and its length is also not much greater than its thickness. A characteristic effect noticed is that a lamina which appears as a bright streak on one side of the plate changes over to a dark streak on the other side as it crosses a dark band of the photo-elastic pattern, and *vice versa*. Several examples of this effect are to be seen in the figures reproduced in plate IV.

It should be mentioned here that if the edges of a thick plate of glass are smoothed and polished, its laminated structure may be observed even without the aid of polarised light, by merely viewing the plate in a direction accurately parallel to its surfaces. The individual laminae are then clearly visible, but they disappear if the plate be slightly tilted. If a narrow illuminated slit is observed through the edge of the plate, the laminated structure gives rise to various interesting optical effects ascribable to reflection and diffraction. These vary rapidly when the direction of the light rays traversing the plate is altered with reference to the plane of the laminations. To describe or discuss these effects in any detail would take us far beyond the scope of the present paper.

It seems fairly obvious that the laminated anisotropic structure of plate glass revealed by its optical behaviour is a consequence of the process employed in its manufacture. The molten glass emerges from the container in the furnace and passes between the forming rollers while it is still in a plastic condition and becomes a sheet which moves on continuously until it finally sets and becomes solid. It is scarcely to be supposed that a sheet of glass formed under these dynamic conditions would possess the isotropic structure which is the ideal state of an amorphous solid. It appears much more probable that the movement of the layers of the material with respect to each other would result in the final product having a laminated structure, as is actually observed. The thickness of the laminae would presumably be determined by the plasticity of the material and the speed of its passage through the rollers, as well as by their distance apart.

### 3. The birefringence of moulded glass

The process employed for the mass production of objects of glass having a desired form is to use moulds. The glass is poured into the mould while in the fluid state

and removed from it when it has solidified. Examination in polarised light of glass formed in this manner shows that the birefringence pattern which it exhibits bears a readily recognisable relationship to the geometric shape of the object. For instance, a circular disk of glass when viewed normally between crossed polaroids shows a dark cross which remains fixed when the disk is rotated in its own plane, the arms of the cross lying in the principal planes of the polariser and the analyser; the disk also exhibits a strong birefringence when held at an angle of 45° to these planes and viewed edgewise. A cube of moulded glass exhibits cubic symmetry in its birefringence, the pattern observed being the same whichever be the pair of faces through which it is viewed: the black cross seen is parallel to the edges of the cube in one symmetrical setting and to the face-diameters in another symmetrical setting, while in intermediate positions, the dark band seen takes the form of a swastika, the arms of which start at the face-centres and end at the face-corners. An equilateral prism of glass viewed through its end-faces shows trigonal symmetry in its optical behaviour; the birefringence pattern varies with the setting of the prism but repeats itself at regular intervals when the prism is rotated as required by such symmetry. Spheres and spheroids of moulded glass likewise exhibit the symmetry of their respective forms in their behaviour in respect of birefringence.

The foregoing statements, however, require to be qualified in an important respect. In every case, the geometric patterns implied by these descriptions are modified by the superimposition of a "structural birefringence" pattern. This consists of bright streaks traversing the glass block, their form and distribution bearing a recognizable relation to the shape of the block and being strongly suggestive of the shape of the flow lines of a viscous liquid enclosed within the walls of a mould of the concerned geometric shape (see plate I). The structural birefringence in common glass has thus evidently a similar origin to that observed in the case of vitreous silica. The similarity of behaviour is even more vividly indicated by the photograph reproduced as plate II, which shows one of the flat walls of a large glass trough as viewed through a crossed pair of 6" polaroids placed on either side of it.

The photographs reproduced in plates I, II and III accompanying this paper were obtained by Mr J Padmanabhan, whose excellent assistance in the investigation, I have much pleasure in acknowledging. Plate IV is reproduced from material obtained during an unpublished research by Mr Bawa Kanwal Singh, made at the author's suggestion.

### Summary

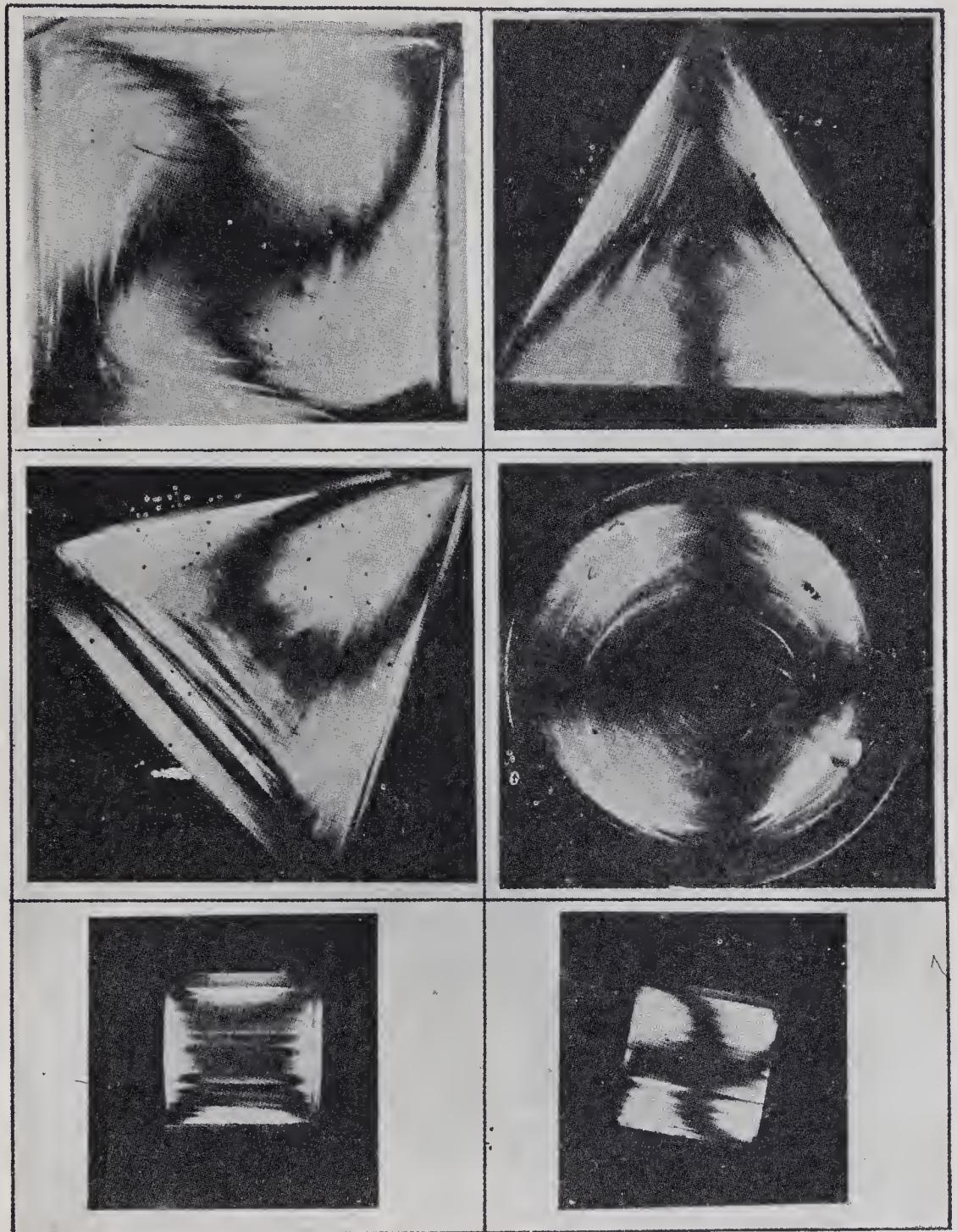
The result reported in an earlier investigation with vitreous silica is now shown to be true also for other amorphous solids, including especially inorganic glasses; besides the well known photo-elastic effect, another kind of birefringence may be

observed differing from the former both in its origins and in its observable characters. This "structural birefringence" arises from anisotropy of structure present in the solid by reason of the circumstances of its formation. It is conspicuously seen with plate glass whose optical behaviour shows it to have a highly laminated structure, while in moulded glass, it exhibits itself as luminous streaks or sheets of variously curved forms.

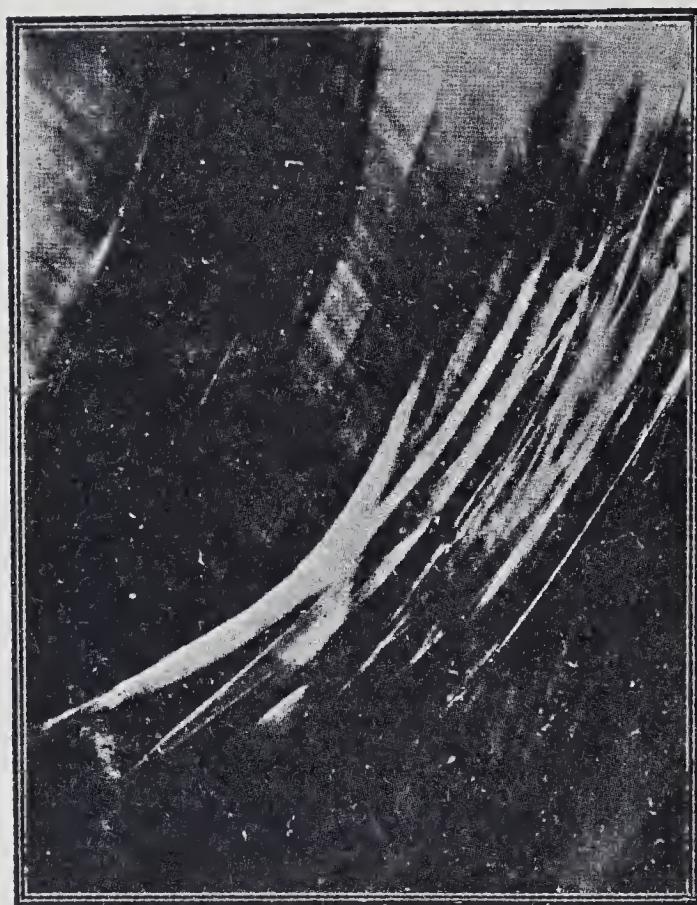
Numerous photographs illustrate the paper.

### Reference

Raman, C V *Proc. Indian Acad. Sci.* 1950, A31, 141.

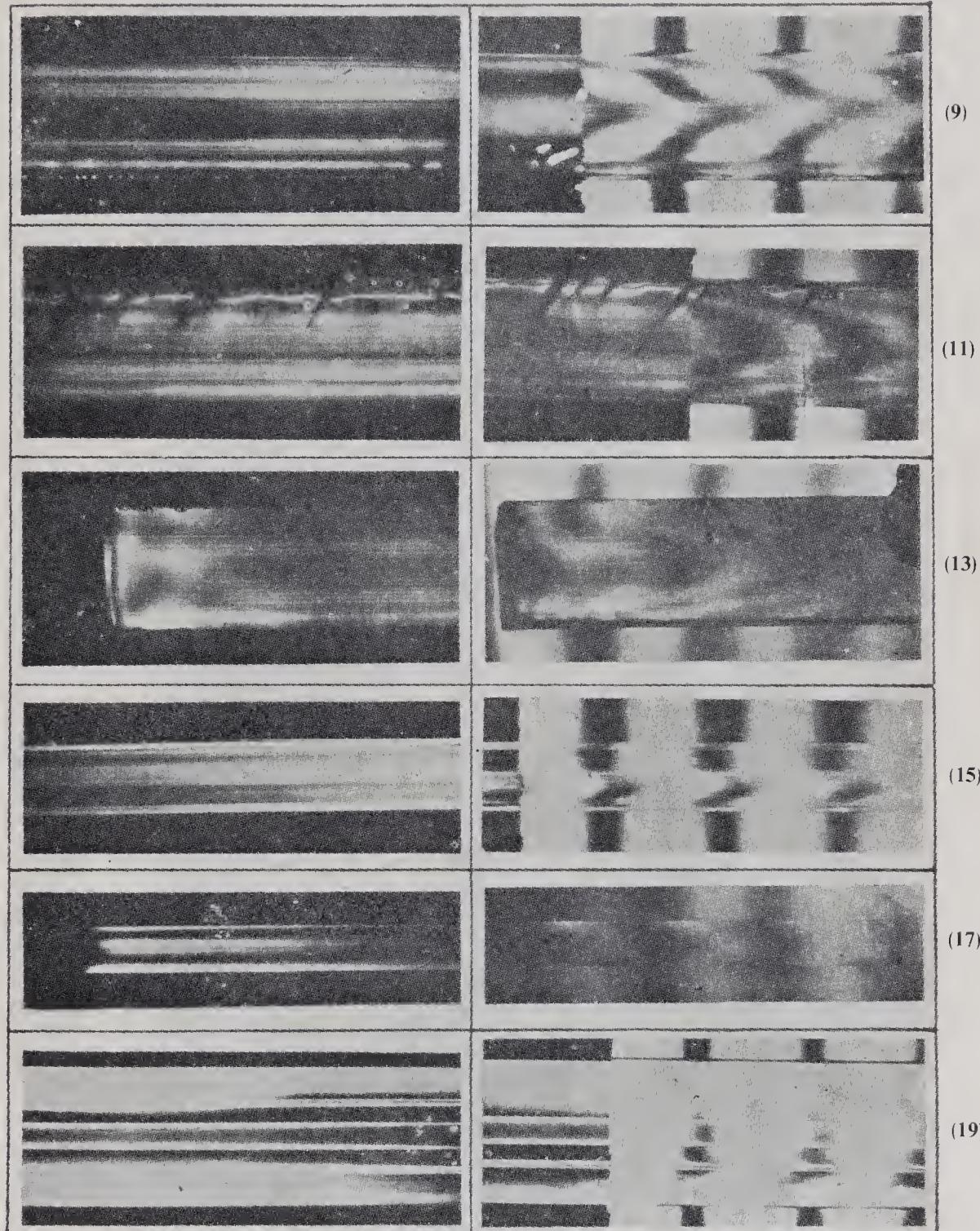


**Figures 1–6.** Birefringence patterns seen between crossed polaroids. 1. Cube of canary-yellow glass. 2 and 3. Equilateral prism of glass in two different settings. 4. Sphere of canary-yellow glass. 5 and 6. Cube of glass cut from thick plate in two different settings.

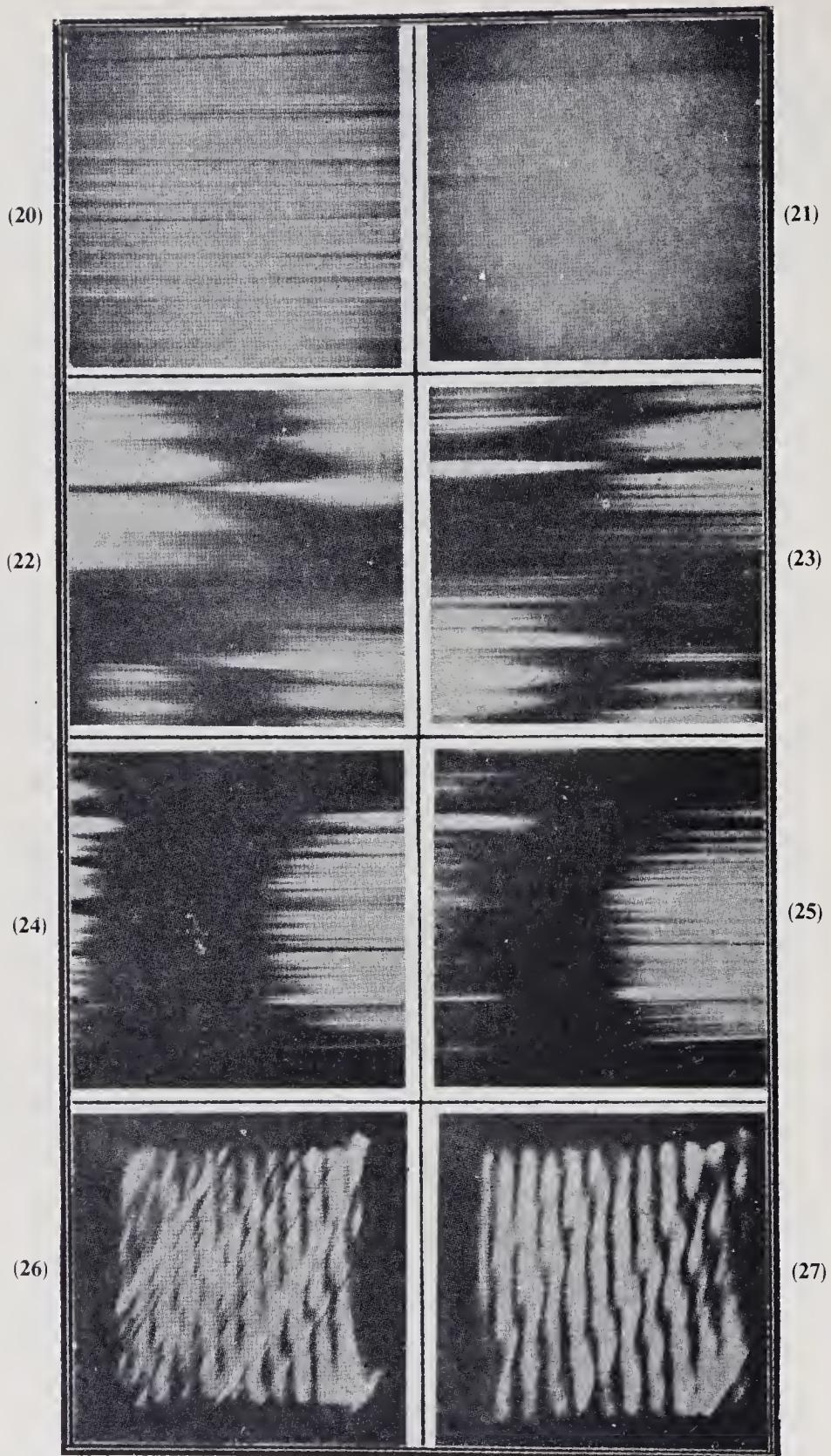


**Figure 7.** Part of one face of a large glass trough, seen through six-inch polaroids sheets crossed, set on either side of it.

**Plate II**



**Figures 8–19.** Plates viewed edgewise, between crossed polaroids. 8. Quarter-inch thick glass plate, three inches wide. 9. Same as figure 8 but with the quartz wedge superposed. 10. Quarter-inch glass plate,  $1\frac{1}{4}$ " wide. 11. Same as figure 10 with quartz wedge superposed. 12 and 13. Same as figures 8 and 9, but showing free edge. 14. One-eighth inch glass plate two inches wide. 15. Same as figure 14 with quartz wedge superposed. 16. One-sixteenth inch glass plate,  $\frac{1}{2}$ " wide. 17. Same as figure 16 with quartz wedge superposed. 18. Quarter-inch plastic sheet,  $3\frac{1}{2}$ " depth. 19. Same as figure 18 with quartz wedge superposed.



**Figures 20–27.** Photographs of glass block cut from thick plate. **20.** Showing the laminated structure of the block viewed in its plane. **21.** Same as figure 20, but with the block tilted slightly. **22–25.** Glass block seen between crossed polaroids, in various settings, showing laminations. **26** and **27.** Glass block with Babinet compensator fringes superposed obliquely, showing effect of the laminations.

# The lamellar structure and birefringence of plate glass

SIR C V RAMAN  
(Raman Research Institute, Bangalore)

Received June 12, 1950

## 1. Introduction

Common sheet or plate glass is manufactured by passing molten glass while in a plastic state between moving rollers and possesses a lamellar structure which owes its origin to this dynamic procedure of shaping the material. The structure becomes visible when a strip of the plate glass is viewed edgewise through a magnifier, using light which has traversed the strip in a direction parallel to its surfaces. The entire thickness of the strip is seen to be made up of a great number of distinct laminae parallel to each other and to the surfaces of the strip. That the lamellar structure is associated with a characteristic type of birefringence becomes evident when the plate is viewed in the same manner when held between crossed polaroids. A strong restoration of light is then observed except when the surfaces of the strip are parallel to the vibration direction of either the polariser or the analyser. The individual laminae differ in the strength of their birefringence as indicated by the intensity and colour of the restoration of light which they produce in these circumstances. The variation in birefringence in the successive laminae may be exhibited by superposing a quartz wedge lengthwise over the edge of the strip. Photographs of these effects were reproduced with a recent paper in these *Proceedings* to illustrate the thesis that amorphous solids may exhibit an intrinsic or structural birefringence arising from the circumstances of their formation and distinct in its nature from the well known double refraction produced by stress (Raman 1950).

We return to the subject in the present communication mainly because better technique has since made it possible to portray the lamellar structure of plate glass and the birefringence associated with it in a more satisfactory manner. By using glass strips with edges ground flat and polished, and employing a higher magnification with the illumination so adjusted as to secure optimum visibility of the structure, the earlier photographs have been greatly improved upon. This will be evident on a comparison of figures 12 and 13, 14 and 15, 16 and 17, in plate III of the previous paper with the corresponding figures 1 and 2, 3 and 4, 5 and 6 in plate I accompanying the present communication. The number of distinct

laminae visible is now much larger; for instance, some thirty laminae are visible in a  $\frac{1}{16}$ " glass plate (figure 5), while in a  $\frac{1}{4}$ " glass plate (figure 1) at least a hundred may be counted. Figure 2 exhibits at its extreme left a small part of the edge of a strip of a  $\frac{1}{4}$ " plate not covered by the quartz wedge; its continuation towards the right on which the wedge fringes appear superposed exhibits the variation of the birefringence over the entire thickness. The photograph shows that the birefringence is noticeably discontinuous as between the successive laminae. Figures 4 and 6 in plate I similarly illustrate the effect of superposing a quartz wedge on the birefringence patterns of  $\frac{1}{8}$ " and  $\frac{1}{16}$ " plate glass. The same without such superposition are reproduced as figures 3 and 5 respectively in the plate.

Careful examination of a six-inch strip of  $\frac{1}{4}$ " plate glass one inch wide showed no noticeable change even in respect of the finer details of its lamellar structure over its entire length or as between the two sides of the strip. Considering the observed facts in their entirety, viz., the great number of the individual laminae, their sharpness, their remarkable parallelism and uniformity, as well as their association with a birefringence which varies in a discontinuous manner as between adjacent laminae, we are led to the conclusion that they represent essentially a stratification in the physical structure of the medium resulting from the circumstances of its formation, as already indicated. We may, in fact, not inaptly compare the lamellar structure of plate glass with the sets of parallel slip-planes well known to be present in crystalline solids which have been subjected to plastic deformation.

## 2. The visibility of the stratifications

The conditions under which the lamellar structure and the associated birefringence are most clearly visible are related to the optical effects produced by the stratifications in the medium when light traverses it. As already indicated, the observation of the laminae requires that the plate should be viewed edgewise and that the incident light beam should traverse it in a direction parallel to its surfaces. To secure this condition, it is obviously necessary to restrict the angular extension of the source of light. Indeed, the structure is completely invisible when the plate is viewed edgewise against an extended source of light, e.g., an open window. It is also invisible when light arising from a source of restricted area traverses the plate in a direction inclined at more than a few degrees of arc to the plane of the laminations. The reason for these facts becomes apparent when a narrow illuminated slit is viewed from a distance through the edge of the plate held parallel to it. The slit is then seen spread out into a diffraction pattern. This is most conspicuous when the direction of observation is exactly parallel to the surfaces of the plate. It undergoes various changes and ultimately disappears, leaving only the undeviated image of the slit, as the plate is tilted and the light

traverses it in a direction inclined to its surfaces when such inclination exceeds a few degrees of arc. We conclude from these observations that the lamellar structure is visible when it is capable of producing observable diffraction effects and that ceases to be visible when such effects do not arise.

It is not to be understood from the foregoing that a narrow slit is the most suitable source of illumination for observing the lamellar structure. Indeed, with such a source, the structure appears overlaid by numerous fine streaks displaying colours, evidently due to interference. To suppress these, the angular width of the source should be increased, but not to such an extent as to obliterate the details of the structure. Actually, there is an optimum value for the angular extension of the light-source in a direction transverse to the stratifications which enables them to be seen most clearly. In these circumstances, the structure reveals itself as a series of dark lines of varying width and intensity traversing a bright field, provided the plate is held symmetrically with respect to the angular extension of the source.

It is worthy of remark that the birefringence may be observed even when the lamellar structure is invisible by reason of too great an angular extension of the light-source. It then manifests itself as a restoration of light in which the differences between adjacent laminae are obliterated. Even so, the birefringence is seen to vary over the thickness of the plate. Two dark lines running parallel to each other with bright strips on either side are seen on the edge of the plate, except near its free ends where they curve round to join the corners. These dark lines evidently represent the neutral lines where there is no birefringence separating regions in which the birefringence is of opposite signs. In general, they appear symmetrically placed with reference to the edges of the strip and divide its area approximately in the ratio 1:3:1, but there are also exceptions, as for instance, the  $\frac{1}{8}$ " plate whose structure is represented in figures 3 and 4 in plate I.

### 3. The diffraction phenomena

We proceed to consider the diffraction effects alluded to above which are observed when a fine illuminated slit is viewed edgewise through a plate held parallel to it. These effects depend on the intrinsic character of the stratifications, but they are also influenced by the circumstances of observation, viz., the depth of the medium through which the slit is viewed, the inclination of the incident light rays to the plane of the stratifications and also by the width of the aperture of observation which determines the number of stratified layers effectively taking part. A study of the influence of these factors reveals various similarities between the present case and the diffraction effects arising when light traverses a medium containing a stationary pattern of ultrasonic waves. The explanation of the latter effects (Raman and Nath, 1935 and 1936) enables us more readily to understand

the phenomena observed in the present case, though there are also important differences to be noted.

The depth of the stratified medium which the light has to traverse can be varied within wide limits by altering the width of the strip of glass cut and prepared for the observations. When a narrow illuminated slit is viewed in a direction parallel to the surfaces of the strip, it is found that the greater the depth of the medium, the larger is the fraction of the incident energy which is thrown into the diffraction pattern. This appears extending symmetrically on either side of the slit. When the depth of the medium is sufficiently large, the whole of the incident light is diffracted and the slit itself ceases to be visible. Simultaneously, the diffraction pattern widens out on either side, the direction of maximum intensity remaining at its centre.

The character of the effects observed is notably altered when the surfaces of the plate are inclined to the direction of the illuminated slit. If the depth of the medium is not altogether too small, the effect of such inclination is to divide the pattern into two distinct parts, one of which remains at the centre and the other moves away to one side of it. We may describe these as the *transmission* and *reflection* patterns respectively, these words being indicative of their origins as well as of their geometric positions. As their separation increases, the reflection pattern diminishes in intensity and ultimately disappears, while the transmission pattern contracts by gaining intensity at the centre and losing it at the margins, until finally only the undeviated image of the slit is seen. The separation of the diffraction pattern into two distinct parts as described above is not so evident if the depth of the medium is small. The effect of inclining the plate in such a case is to cause the diffraction pattern at first to expand laterally in an unsymmetrical fashion and then to contract once again and finally to disappear.

Even when the source is of white light, the diffraction pattern exhibits a visible structure; with monochromatic light, it appears resolved into a crowd of discrete lines. The latter observation may, at first sight, seem to be surprising in view of the fact that the stratifications in the medium are very far indeed from constituting a regular diffraction grating. Actually, however, the result observed is that which is theoretically to be expected. For, while the diffraction of light by the individual stratifications determines the angular *extension* of the pattern, its *structure* is determined by the interference of the effects of all the stratifications falling within the aperture of observation. A regular stratification would give rise to a relatively small number of intense maxima of illumination appearing as lines in the diffraction pattern. On the other hand, an irregular stratification would give rise to a much larger number of maxima but of correspondingly diminished intensity. But their sharpness would, in either case, be determined by the total aperture of observation and hence would be the same in both cases. The case is analogous to the diffraction of light by a cloud of small particles distributed irregularly over the area of an aperture; these are observed to give rise to a great many *sharply defined* images of the light-source in the field of view (Ramachandran, 1943).

#### 4. Observations with polarised light

As we are here concerned with the optical behaviour of a stratified *birefringent* medium, the question naturally arises whether the diffraction effects arising when it is traversed by light would depend on the state of polarisation of the latter at entry. It is evident from the observed facts that the retardation of phase produced by the plate differs for vibrations respectively parallel and perpendicular to the stratifications and that such difference is not the same for all of them. Hence the rays emerging from the glass would differ from each other in phase to an extent depending on the state of polarisation of the incident light. In these circumstances, we may expect the diffraction pattern to be noticeably different for the two components of the light vector.

That the stratifications are far from being perfectly periodic and that in consequence the diffraction pattern does not possess a simple structure makes an experimental test of the theoretical conclusion stated above not so easy as may seem at first sight. Careful studies using a monochromatic light-source would be needed to reveal the expected effect in all its detail. Some preliminary observations which have been made with a white light-source however indicate that an effect of the nature indicated does exist. For this purpose, a slip of glass one millimetre thick was prepared and polished so as to have reasonably flat and parallel faces. It was placed between a pair of polaroids and an illuminated slit was viewed through the combination. When the polaroids were in the crossed position and the stratifications in the glass were inclined at  $45^\circ$  to their vibration directions, the diffraction pattern continued to be visible as the result of the birefringence of the glass, though rather faintly. One of the polaroids was then rotated a little with respect to the other. It was then observed that the pattern became brighter but with a very noticeable change in its structure, some parts gaining intensity much more than others.

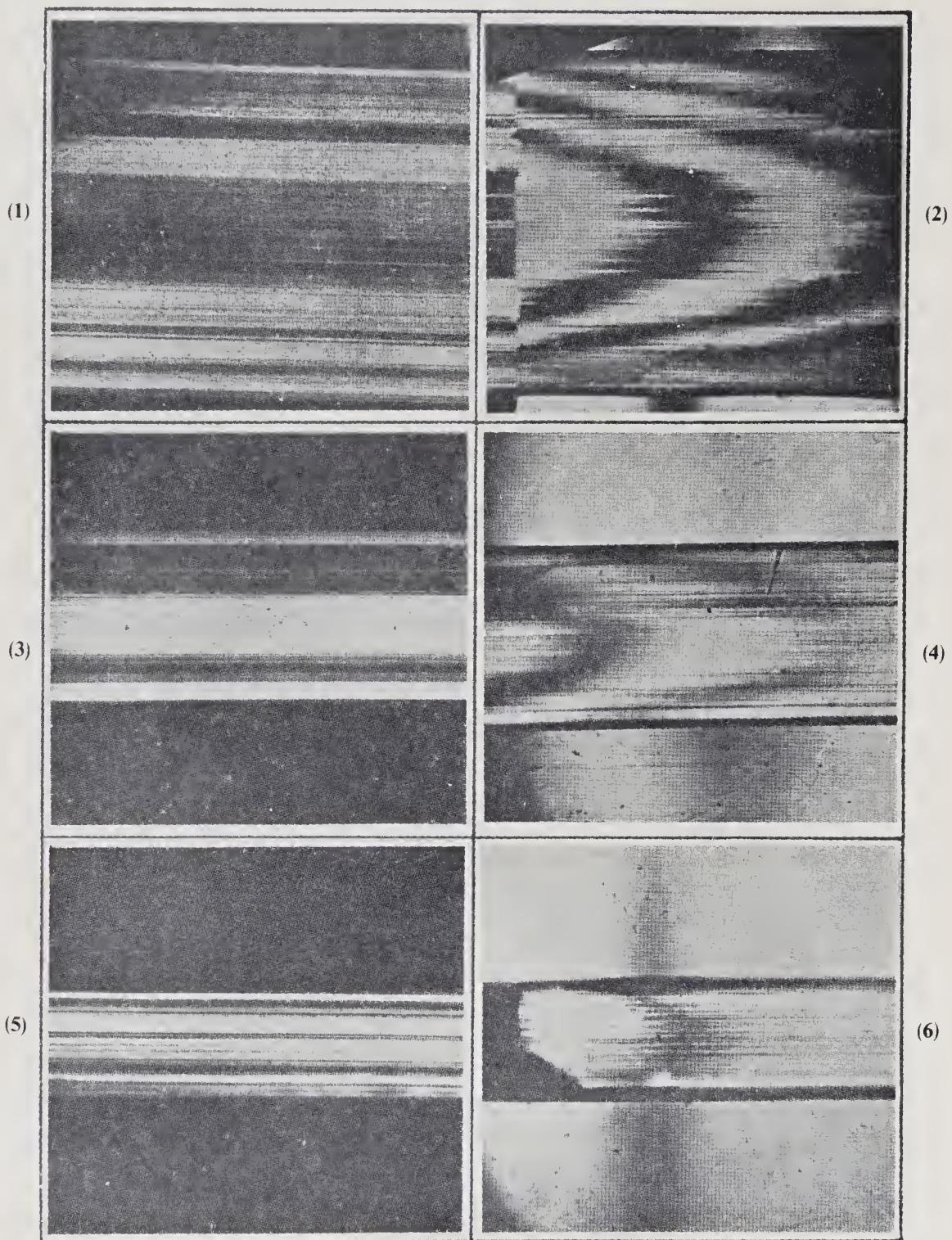
I have much pleasure in acknowledging the valuable assistance of Mr J Padmanabhan in this investigation.

#### Summary

Using carefully prepared material with adequate magnification under conditions securing the optimum visibility, photographs exhibiting the lamellar structure of plate glass and the associated birefringence have been secured which exhibit far more detail than previously. The visibility of the structure is closely related to the diffraction phenomena to which it gives rise. The latter are described and discussed in detail.

#### References

- Ramachandran, G N *Proc. Indian Acad. Sci.*, 1943, A18, 190.
- Raman, C V *Proc. Indian Acad. Sci.*, A31, 141 and 207.
- Raman, C V and Nath, N S *Proc. Indian Acad. Sci.*, 1935, A2, 406 and 413; 1936, A3, 75, 119 and 459.



Figures 1-6

Plate I

## “Smoky” quartz

The deeply tinted varieties of quartz, such as “smoky” quartz and the yellow or Madagascar variety, are generally transparent in the infra-red region of the spectrum to the same extent as clear rock-crystal, as may easily be demonstrated with the aid of a thermopile and galvanometer. I wish to suggest that a very simple physical explanation of this property may be offered. As has been emphasised in a paper by Prof. R J Strutt (now Lord Rayleigh) in the *Proceedings of the Royal Society* for 1919, these varieties of quartz are really optically turbid media, the opacity arising from the scattering of the radiations in their passage through the crystal by a cloud of small particles present as inclusions. Since scattering of this kind is effective in inverse proportion to the fourth power of the wavelength, it can easily be seen why the longer heat-waves can traverse the crystal without appreciable loss. Some photometric observations which I have made of the relative transparency of the yellow and colourless varieties in different parts of the spectrum support this explanation.

In the paper just quoted Rayleigh has described the very beautiful and striking effects that arise owing to optical rotatory dispersion when a strong beam of *polarised* light is sent through a block of smoky or yellow quartz in the direction of the optic axis; the track of the beam, as made visible by the scattering particles and observed in a transverse direction, shows bright and dark bands if monochromatic light be used, and alternations of colour if the incident beam is of white light, the effect being due to the fact that the scattering particles themselves act as *analysers* of the light incident on them. I find that the phenomenon discovered by Lord Rayleigh can be very prettily shown in another way which is also instructive. A thin, flat sheet of *unpolarised* white light may be sent through the crystal in a direction *transverse* to the optic axis, and the track of the beam observed in a direction parallel to the optic axis through a Nicol. In this case the scattering particles act as *polarisers*, and the scattered light suffers a rotatory dispersion of its plane of polarisation in traversing the quartz along the optic axis before reaching the observer's eye. Hence the whole track of the beam as seen through the observing nicol appears coloured, the tint fluctuating periodically with the thickness traversed as the block is moved to and fro in the line of sight or when the analysing nicol is rotated.

Rayleigh has shown in his paper that the track of a beam of light traversing a beam of *transparent* colourless quartz can be successfully photographed. I find that by using a concentrated beam of sunlight it is possible *visually* to detect the Tyndall blue cone even in this case. Its intensity, however, is exceedingly small.

# The structure of amethyst quartz and the origin of its pleochroism

SIR C V RAMAN and A JAYARAMAN

(Meomoir No. 58 from the Raman Research Institute, Bangalore)

Received November 6, 1954

## 1. Introduction

By reason of the very beautiful colour which amethyst exhibits, this material has been used as a gem-stone since ancient times. Much interest therefore attaches to the problem of the origin of its colour, for a solution of which we need to know how amethyst and colourless quartz differ in respect of their structure. In the present investigation we have sought to elucidate the nature of this difference by a fact-finding study of those properties of amethyst which are calculated to throw light on its physico-chemical make-up. The results have led us to a view of the nature of amethyst which is altogether different from those which have found expression in the extensive literature of the subject, but which nevertheless appears to be both simple and natural.

## 2. The density of amethyst quartz

If the colour of amethyst were due to the presence of appreciable quantities of the oxides of heavy metals such as manganese or iron, as has sometimes been suggested, we may expect this to come into evidence in precise determinations of the density of the material. For such a test, it is clearly necessary to use specimens which do not exhibit visible cracks, inclusions or surface impurities. We have therefore chosen to work with selected material in the form of cut and polished gem-stones. A Sartorius analytical balance was employed and the density of each specimen was measured in the usual manner by transferring it from a cup in air to a second cup held suspended by a fine wire under water. Table 1 shows the densities thus determined of six pieces of colourless quartz, while table 2 shows the corresponding results obtained with thirteen different specimens of amethyst. Necessary corrections were made in each case for the temperature of the water and the buoyancy of air. The remarks made against each specimen in the tables indicate its optical behaviour.

**Table 1.** Density determinations with quartz

Description	Mass in grams	Density in grams per c.c.	Remarks
Quartz crystal with natural faces	3.9264	2.651	Very transparent and free from inclusions
—	0.595	2.650	—
Polished quartz sphere I	4.7197	2.652	A few needles inside but quite transparent
Polished quartz sphere II	3.7886	2.651	Very transparent and free from inclusions
Polished quartz sphere III	2.5042	2.653	Exhibits a weak star due to inclusions
Polished quartz sphere IV	2.4194	2.667	Exhibits a markedly diminished transparency and a bright star due to inclusions

**Table 2.** Density determinations with amethyst

Description	Mass in grams	Density in grams per c.c.	Remarks
Intensely coloured	2.3394	2.651	
—	1.8521	2.652	
—	1.3466	2.651	
—	1.0846	2.652	
—	0.7137	2.650	
Moderately coloured	2.2276	2.651	
—	1.4184	2.650	
—	1.2545	2.650	
Lightly coloured	3.1782	2.650	
—	1.1595	2.653	
—	1.1937	2.651	
—	1.0351	2.650	
—	0.7481	2.654	Visible inclusions

It will be evident from a comparison of the figures in the two tables that in the case of colourless quartz of the best quality, the density comes out consistently as 2.651, the uncertainty not exceeding one unit in the last decimal place. On the other hand, colourless quartz containing inclusions gives definitely higher values. The determinations for amethyst do indeed show variations in the third decimal place, but these deviations are in no way correlated with the depth of the colour exhibited by the specimen. The differences are therefore either purely experi-

mental or else arise from residual defects in the specimens which are indeed noticeable when they are critically examined under immersion in a liquid cell.

The data appearing in the two tables give no support to any explanation of the origin of the colour of amethyst as due to metallic impurities. On the other hand, *they show quite definitely that the density of amethyst quartz does not differ measurably from that of colourless quartz of optical quality.*

### 3. The scattering of light in amethyst

Colourless transparent quartz free from internal inclusions gives an observable scattering of a blue colour and of uniform intensity when traversed by a concentrated pencil of sunlight. But the effect is extremely weak and is observable only in favourable circumstances. Figure 1 in plate II shows a transparent crystal of quartz of optical quality immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. The track of the beam in the liquid appears in the photograph, but the track within the crystal is hardly to be seen by reason of its extreme weakness.

Figure 2 in the same plate shows a similar experiment with a crystal of smoky quartz immersed in a cell containing distilled water. It will be noticed that the Tyndall track within the crystal is conspicuously observable.

Figure 3 in the same plate is a photograph of a crystal of amethyst quartz immersed in carbon tetrachloride. The track of the beam in the liquid both before entry into the crystal and after emergence from it is very conspicuous. Within the crystal itself, there are two regions adjoining its rhombohedral faces in which no track is visible. These regions are precisely those which exhibit the amethystine colour, while the region midway between them exhibits a conspicuous Tyndall effect which is due to inclusions present in this colourless part of the quartz. The crystal had a density of 2.563, which is slightly higher than that of pure quartz, thus indicating the presence of such inclusions.

Figure 4 in the same plate is a photograph of a cut gem of amethyst immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. Here again, the track of the beam is totally invisible within the crystal.

Visual observations with all the specimens of amethyst listed in table 2 yielded the same result. Hence we conclude as follows: *amethyst quartz does not exhibit the Tyndall scattering so conspicuously observable in the case of smoky quartz; its behaviour in this respect is comparable with that of colourless transparent quartz.*

### 4. X-ray diffraction studies

The experimental facts set forth in the two preceding sections appear very significant. It seems difficult to reconcile them with any explanation of the colour

of amethyst as due to impurity material present in a colloidal or even in a molecularly dispersed form. Nor does it appear easy to reconcile them with an attribution of the colour to defects or imperfections of crystal structure or to a stoichiometric deficiency or excess of either silicon or oxygen in the lattice. On the other hand, they fit in perfectly with the hypothesis that amethyst is a crystalline material very similar to colourless quartz but with a different electronic configuration. Such configuration might well belong to a lower symmetry class than that of  $\alpha$ -quartz, and this would immediately account for the fact that amethyst is optically biaxial whereas colourless quartz is uniaxial. A different electronic configuration belonging to a lower symmetry type would necessarily involve an alteration in the electronic energy levels and hence also to an altered absorption spectrum. The pleochroism and the optical characters of amethyst would thus both find a natural explanation on the present view of its structure.

It is evident from the foregoing that a thorough study of the pleochroism of amethyst and of its absorption spectra should prove useful in dealing with the problem of its structure. Such a study has been carried out at this Institute by Mr S Pancharatnam and his results are reported in the paper following the present one in the same issue of the *Proceedings*. We shall not traverse the same field here but will proceed to describe the results of an entirely different technique for investigating the problem under issue.

If colourless quartz and amethyst differ in their electronic configurations, comparative X-ray diffraction studies may be expected to reveal the existence of such differences and even to indicate their nature and magnitude. In view of the near resemblance between the two structures, it appeared unlikely that the usual methods of X-ray structure determination would prove useful in this connection. We have therefore chosen to adopt a different technique which we shall now proceed to describe and which is based upon certain well-known facts regarding amethystine quartz.

A section plate of amethyst cut in any arbitrary direction often exhibits a variety of features. Commonly noticeable is the appearance of bands of colour alternating with clear quartz running parallel to the intersection of a rhombohedral face of the crystal with the surface of the section plate. Sectors exhibiting different colours are also noticeable on section plates cut obliquely to the trigonal axis of quartz. Thus, if a pencil of X-rays traverses such a section plate, the material over different parts of the area should exhibit differences in the X-ray reflection intensities corresponding to the optically observable features on the plate. In this connection, however, some important remarks are necessary. As is well known, any mosaicity or imperfection in crystal structure would reveal itself in a general increase in the intensity of X-ray reflection. Hence, what we have to look for in the present case is not an enhancement of reflection intensity corresponding to the areas of colour on the plate, but differences in X-ray reflection intensity which vary with the particular crystal planes giving the

reflections and hence connote real differences in crystal structure in the different areas on the plate.

It has also to be remarked that quartz often exhibits internal twinning. If such twinning be of the electrical type, areas on the plate in which the electric axis is oppositely orientated would, in general, give different X-ray reflection intensities. Hence it is essential to work with section plates in which electrical twinning is absent.

## 5. Technique and results of study

A plate about 1 millimetre thick and about 2 cm by 1.5 cm in areas was cut out from a large clear crystal of amethyst. The plate exhibited both the bands and sectors of colour described earlier. By fine grinding the surfaces of the plate and then etching with dilute hydrofluoric acid and examining them under a spot-light, it was verified that the area on the plate chosen for the study and which exhibited the bands and sectors of colour was completely free from both optical and electrical twinning. The absence of optical twinning was also independently verified by an examination of the plate between crossed polaroids when immersed in a cell containing benzyl alcohol which has very nearly the same refractive index as quartz.

The X-radiation from a rotating target tube run at 50 mA and 60 kV emerged through a 1 millimetre hole and was allowed to diverge until the area of the crystal plate was completely bathed by the beam at a distance of about 40 cm. A photographic film was placed at a distance of about 10 cm behind the crystal plate. This distance was found to be sufficient to avoid overlapping of the Laue reflections which in these circumstances are necessarily of rather large size. In effect, each Laue spot recorded on the photographic film presents a picture of the irradiated area of the crystal.

Figure 1 in plate I is a reproduction of the larger part of a Laue diagram obtained in the manner described above. At the centre of the picture has been placed in its correct orientation a photograph taken by transmitted sodium light of the area of the crystal plate actually employed in X-ray diffraction. It will be seen that the plate exhibits a set of parallel bands towards the left, while at its centre and towards the right appear a pattern of sectors which by ordinary daylight exhibit the different colours indicative of their pleochroism. Fainter bands are also visible towards the upper right-hand corner.

On a scrutiny of the pictures of the crystal appearing in the figure as Laue reflections, the following features emerge. All the pictures exhibit varying degrees of distortion, but this does not prevent us from comparing them with the optical picture of the crystal appearing at the centre of the figure. The latter, it should be mentioned, has been slightly enlarged to make the comparisons easier. Two irregular bright streaks appear in all the pictures; these arise from defects in the

crystal which were readily visible on a direct examination and are irrelevant for our present purpose. Some of the stronger Laue reflections exhibiting significant features have been numbered as a series from 1 to 9 for convenience of reference. Number 1 shows prominently the set of parallel bands appearing on the left of the crystal plate. The same bands can be seen faintly in some others of the numbered spots but are invisible in no. 6. The large sector appearing at the centre of the plate presents very different aspects in the different spots. Compare, for example, nos. 2, 3, 6, 8 and 9. The complex pattern of sectors on the lower right of the specimen can be made out in several of the pictures but presents altogether different aspects in them. Compare for example, nos. 3 and 8. The bands seen in the upper right-hand corner of the crystal are very conspicuous in nos. 2 and 3 but are weak in nos. 6 and 9. The record thus clearly establishes that amethyst is a crystalline solid which gives coherent X-ray reflections, the intensities of which differ from those of colourless quartz and are also different for areas exhibiting different colours by transmitted light. A correlation is thus established between the pleochroism of amethyst on one hand and its crystal structure on the other hand.

## 6. Acknowledgement

We wish to take the opportunity of expressing our gratitude to Sir Purshotamdas Thakurdas for his generous gift of the rotating-target X-ray set manufactured by Messrs. Newton-Victor which has been used in the present investigation.

## 7. Summary

Comparative measurements with clear quartz and amethyst show conclusively that these two materials do not differ measurably in their density. Amethyst and clear quartz also resemble each other in not giving any Tyndall effect of the kind so conspicuously observable with smoky quartz. These facts indicate that amethyst is a crystalline material very similar to colourless quartz in its make-up, but with a different electronic configuration belonging to a lower symmetry class. The optical biaxiality and the pleochroism of amethyst then follow as natural consequences. This view of the nature of amethyst is confirmed by X-ray diffraction studies made with a section plate of amethyst free from internal twinning but exhibiting colour bands and colour sectors over its area.

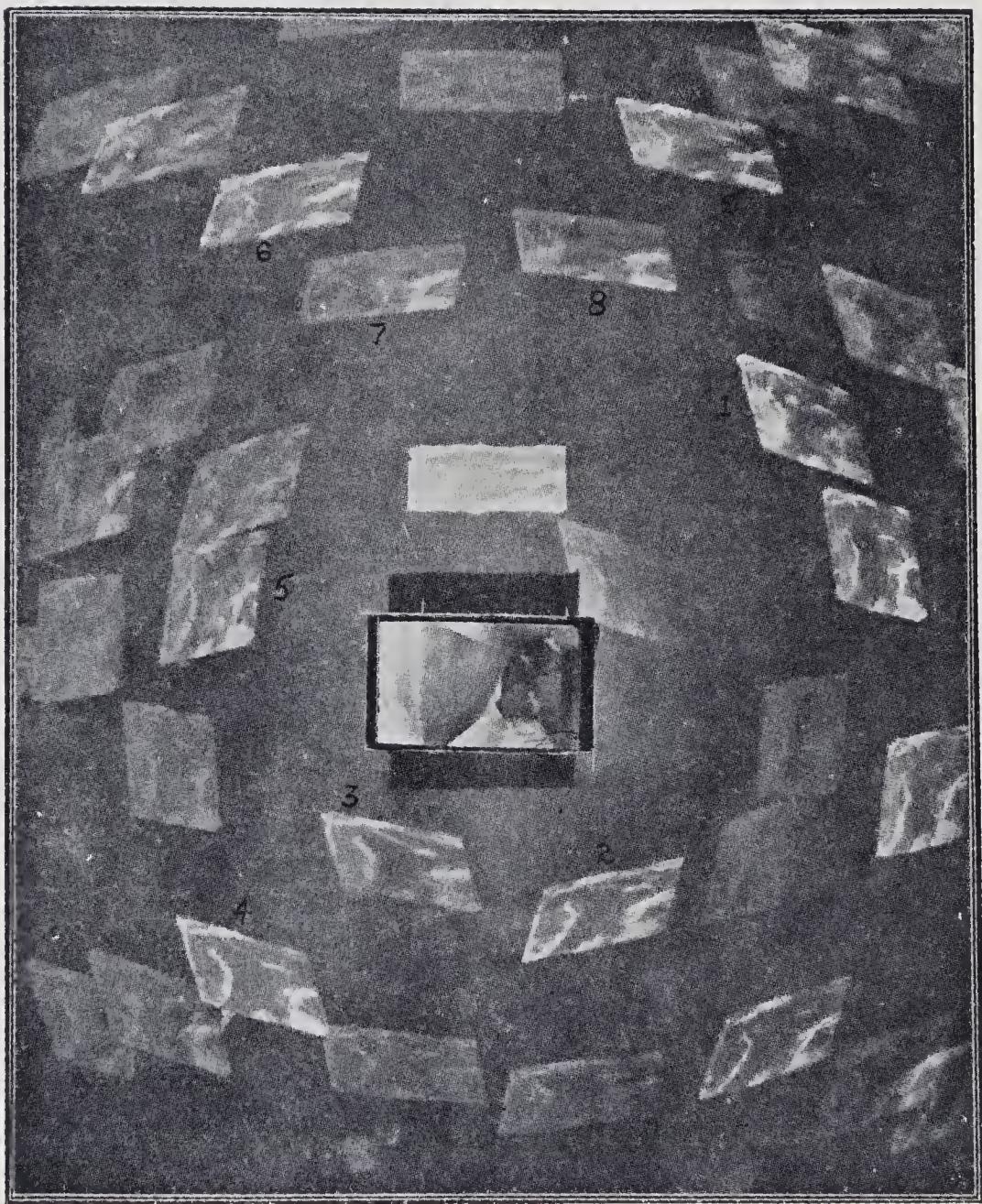
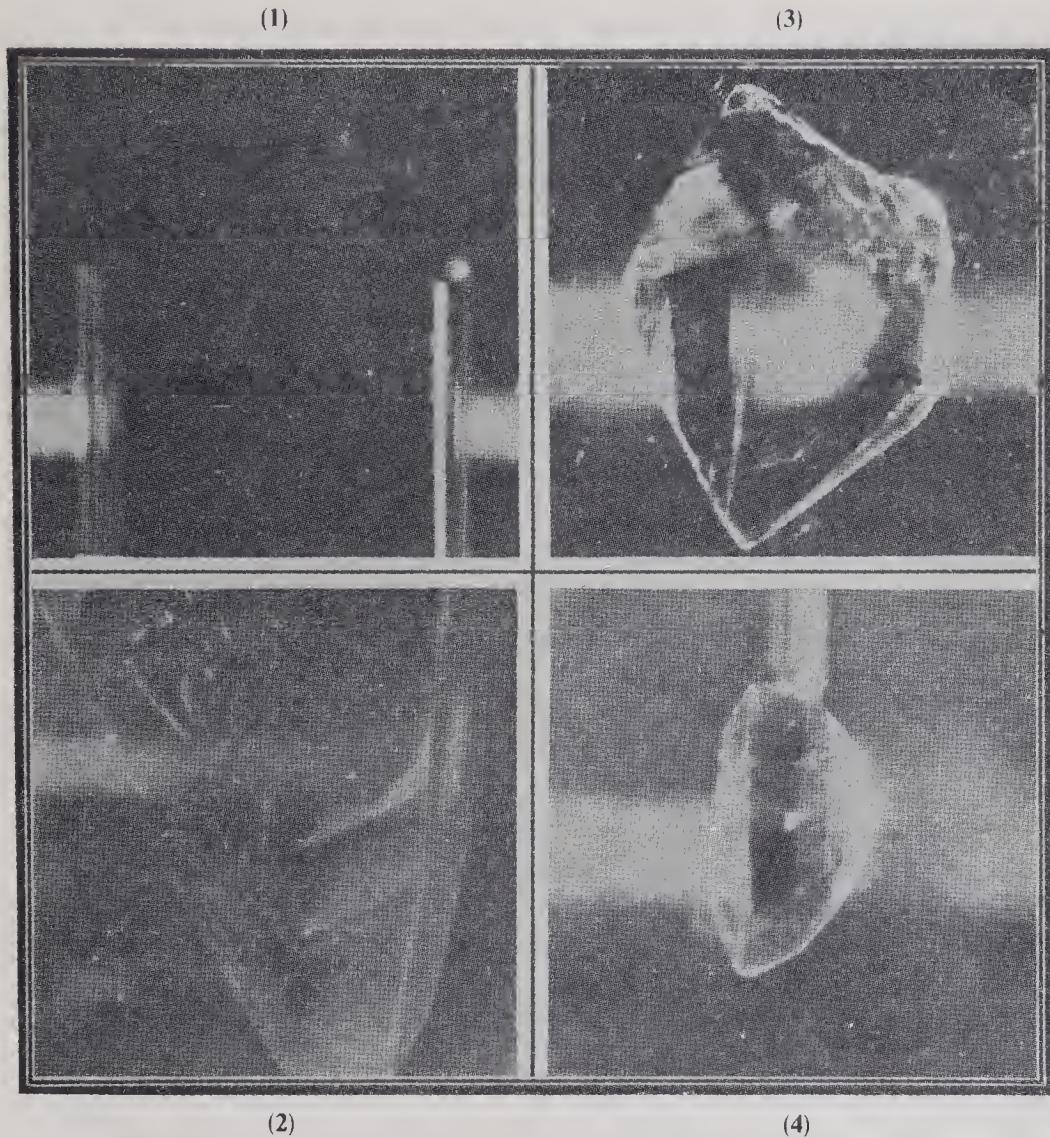


Figure 1. Laue pattern of amethyst section plate.

Plate I



Figures 1-4. Scattering of light in clear quartz, amethyst and smoky quartz.

Plate II

## The birefringence patterns of crystal spheres

SIR C V RAMAN

(Memoir No. 82 of the Raman Research Institute, Bangalore)

Received 7 January 1956

The preparation of polished spheres of crystalline solids is an ancient art, and indeed it is not uncommon to find large spheres of quartz as exhibits in natural history museums. Using appropriate techniques, it is possible to prepare spheres with different materials and of any desired size, even as small as half a centimetre in diameter. A spherical shape is evidently the most appropriate for a crystal to possess if we wish to observe or exhibit the variation of its optical properties with the direction of propagation of light over the entire possible range. Hence, a collection of such spheres is a useful acquisition for a crystallographic museum.

We may mention here as an example the case of the well known pleochroic mineral iolite. Holding a polished sphere of this crystal so that it can be turned round and viewed against an extended source of light with a magnifier, Brewster's brushes can be seen around each of the two optic axes in the rear of the sphere. More generally, we place a crystal between a polariser and an analyser, viz., two sheets of polaroid, and view it against an extended source of light. An arrangement should be provided for holding the sphere and altering its setting as desired. The birefringent pattern then seen in various settings shows at once whether the crystal is uniaxial or biaxial, whether the birefringence is weak or strong, whether the material is or is not optically active, and in the case of a biaxial crystal, what the angle between the optic axes is and how their positions vary with the wavelength of the light.

The plates accompanying the present paper illustrate some typical examples of such birefringent patterns. Plates I and II refer to the case of quartz in different settings, plate III to beryl, plate IV to calcite, plate V to topaz, and plate VI to the case of iolite already mentioned. The spheres used in this study were prepared at this Institute by Mr J Padmanabhan who also photographed the birefringence patterns, using for this purpose the monochromatic illumination furnished by a sodium vapour lamp. The principal difficulty encountered in the work was that of obtaining material for preparing the spheres which besides being of adequate size had also the requisite degree of optical perfection. Any imperfections inevitably show up in the birefringence patterns. This is evident, for example, from the slight

irregularities noticeable in the figures recorded for beryl and topaz in plates III and V respectively.

By way of explanation of the observed effects, we may remark that a beam of light incident on a sphere and traversing it along a diameter would be brought to a focus at a point outside the sphere and at a distance from it depending upon the refractive index. Since there are two refractive indices for any given direction of propagation within a crystal, the positions of the two foci would be different except in the special cases when the direction of propagation within the crystal coincides with an axis of single-wave velocity. Hence, in all directions other than these axes the optical paths would be different for the two indices and interferences can therefore arise. The convergence of the light beams produced by the sphere would result in these interferences appearing in good focus on the surface of a sphere concentric with the crystal sphere but of larger diameter. Hence, when the sphere is rotated, the pattern would rotate with it, and its appearance as seen in any given direction would alter progressively.

With white light, the interferences in the vicinity of the axes of single wave-velocity exhibit colours. They are very fine in the case of calcite (plate IV) but can be readily seen through a magnifier. These rings can also be seen with a magnifier in the case of topaz but not visible in the photographs of low magnification reproduced in plate V. As seen through a magnifier, they appear unsymmetrically located with respect to the optic axes, evidently as the result of the dispersion of these axes.

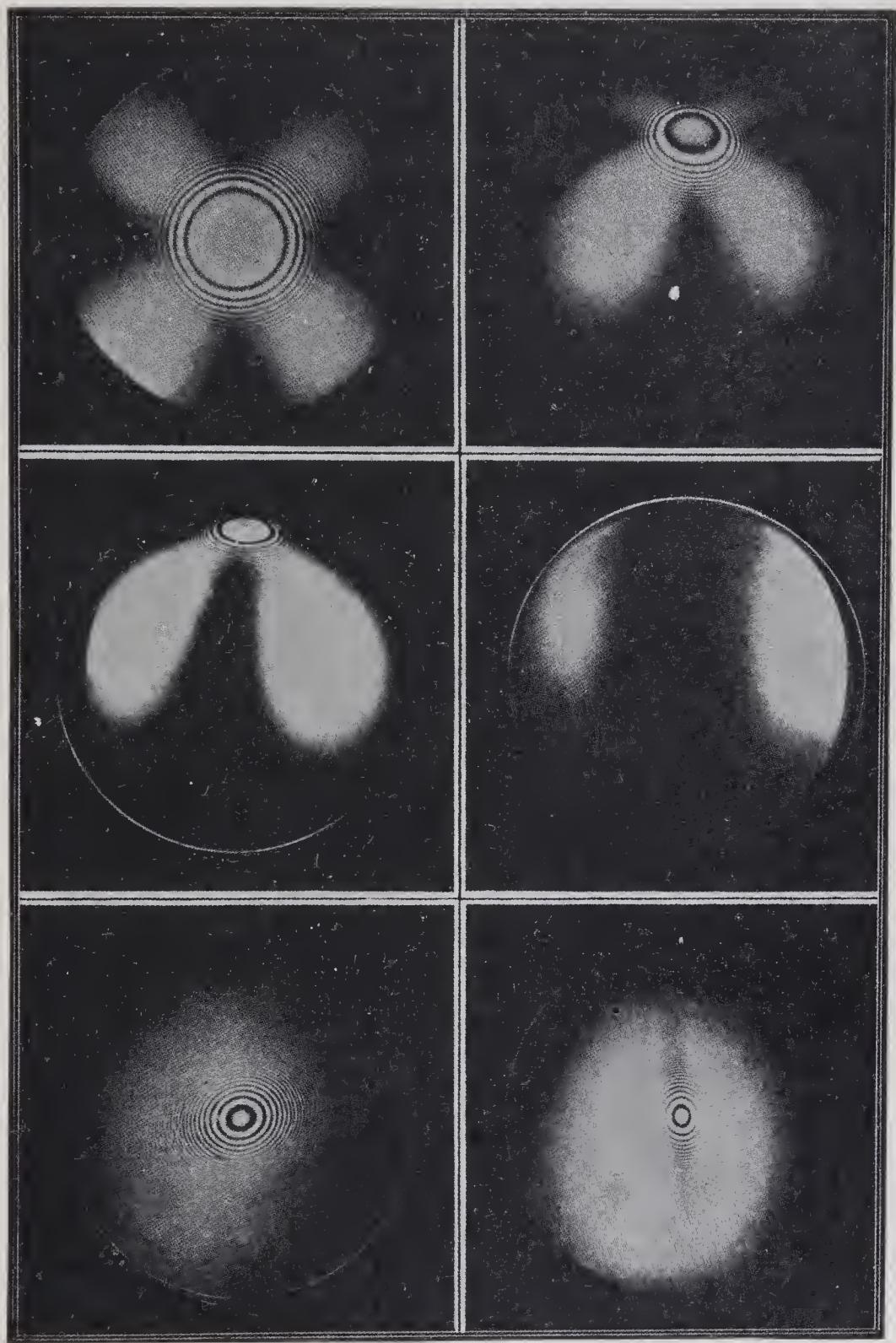
Of a different nature are the circular or elliptic interference rings observed with the various crystals in directions very remote from the axes of single-wave velocity (see figures 5 and 6 in plate I, figures 3, 4, 5 and 6 in plate II, figures 5 and 6 in plate III and figures 7 and 8 in plate V). These interferences are only seen in monochromatic light and hence correspond to large differences of path between the two sets of waves which overlap.

Figure 4 in plate II is of special interest. It was recorded when the optic axis of the quartz sphere was set accurately parallel to the vibration direction of the polariser, the analyser also being accurately crossed with respect to it. It will be seen that the rings have not vanished even in this critical setting, but are faintly visible. Their visibility may be ascribed to the non-extinction of the transmitted light consequent on the optical activity of quartz in a direction transverse to the optic axis.

Figure 1 in plate VI represents Brewster's brushes as exhibited by iolite without any polariser or analyser. Similar brushes running parallel to them are also seen in the vicinity of the other axis of single-wave velocity. The other figures in plate VI exhibit the effects of introducing either a polariser or an analyser, or both between the source of light and the eye of the observer.

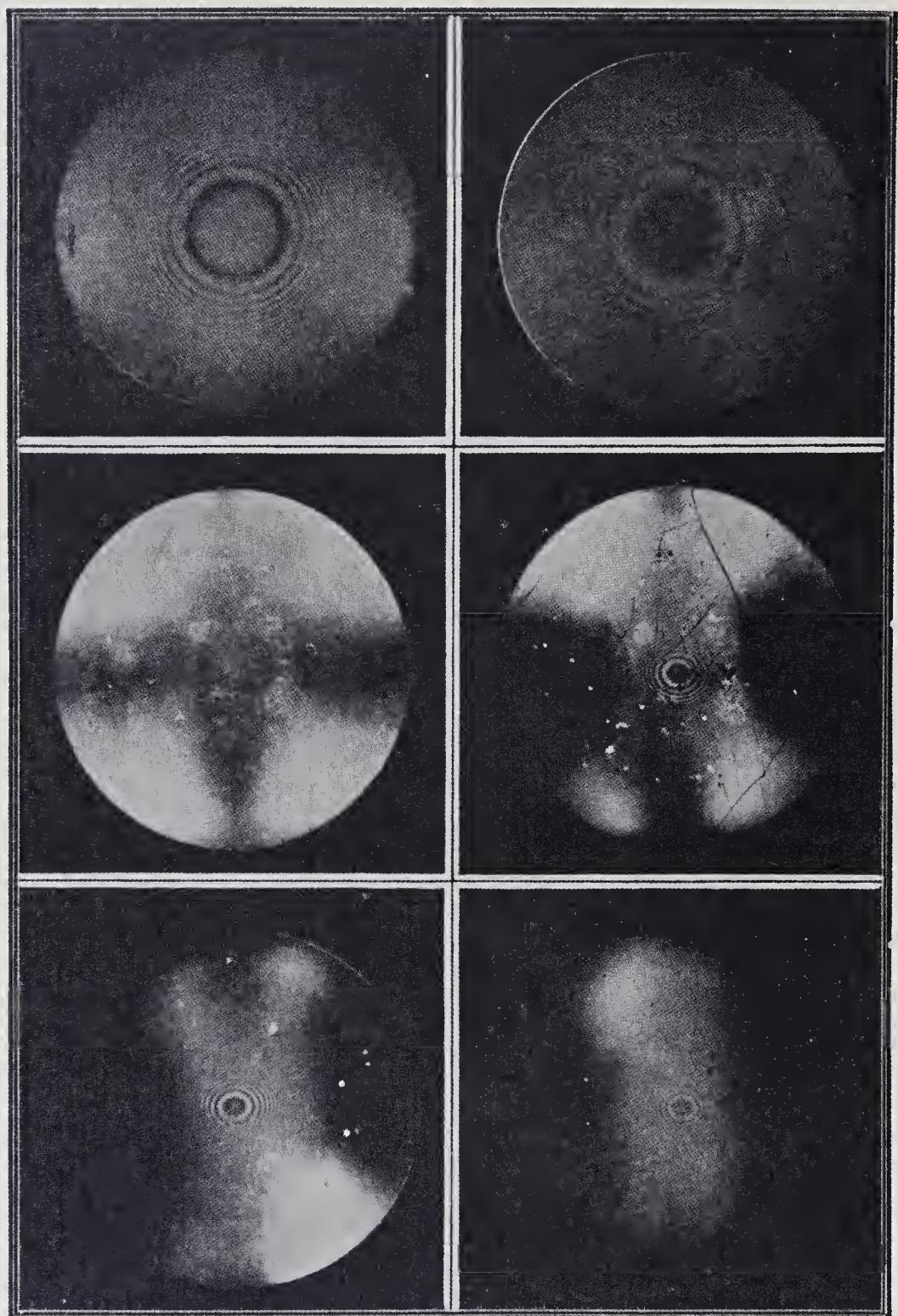
### Summary

Light from an extended source traversing a sphere reaches foci lying on a concentric spherical surface of a larger radius determined by the refractive index. Hence, if the incident light be polarised and the sphere is viewed through an analyser, the interferences arising from the birefringence of the material are focussed by the sphere itself on such concentric surface and rotate with the sphere when the latter is rotated. Photographs of such patterns in typical cases are reproduced.



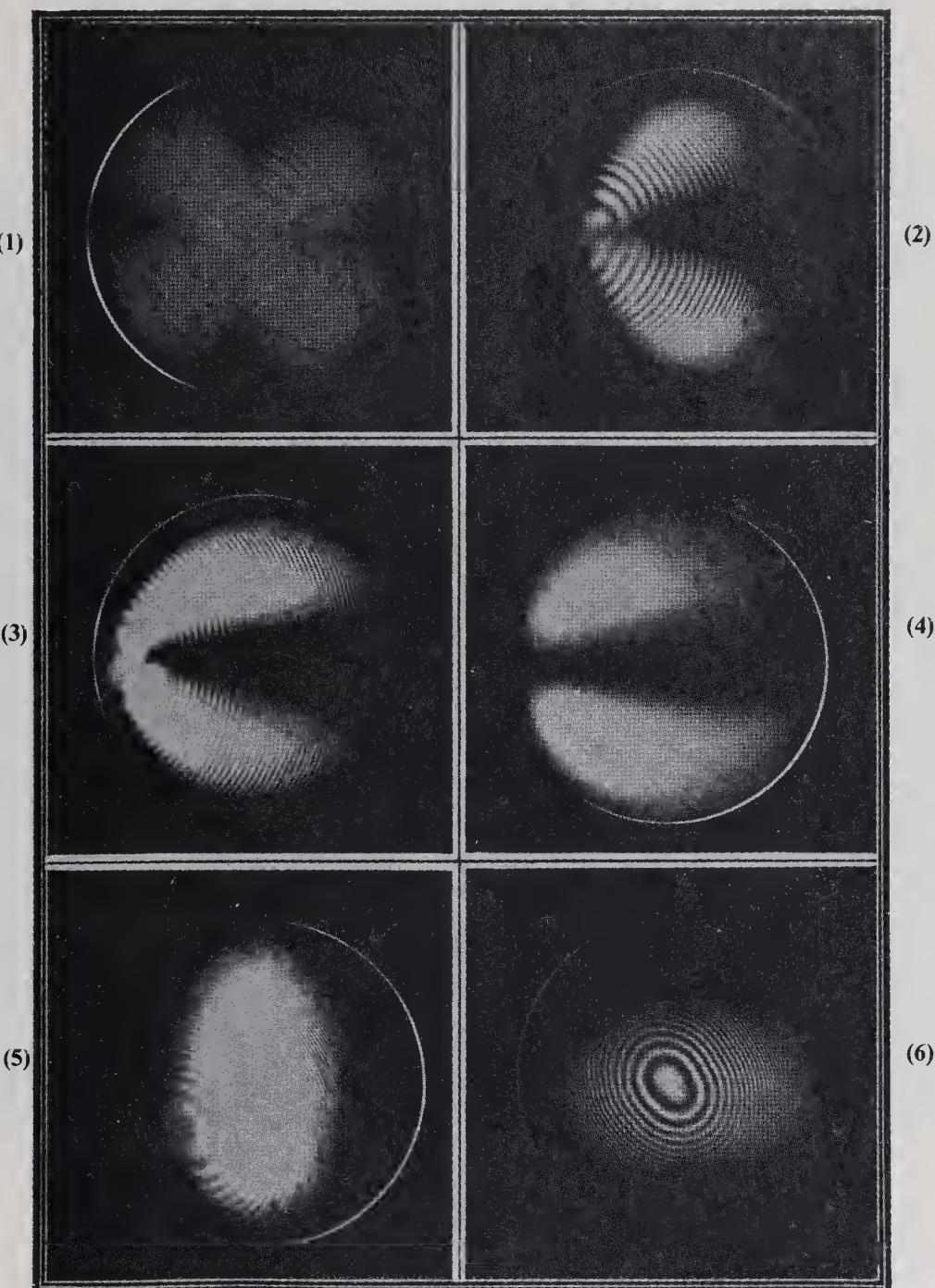
Figures 1–6. Birefringence patterns of quartz sphere.

Plate I

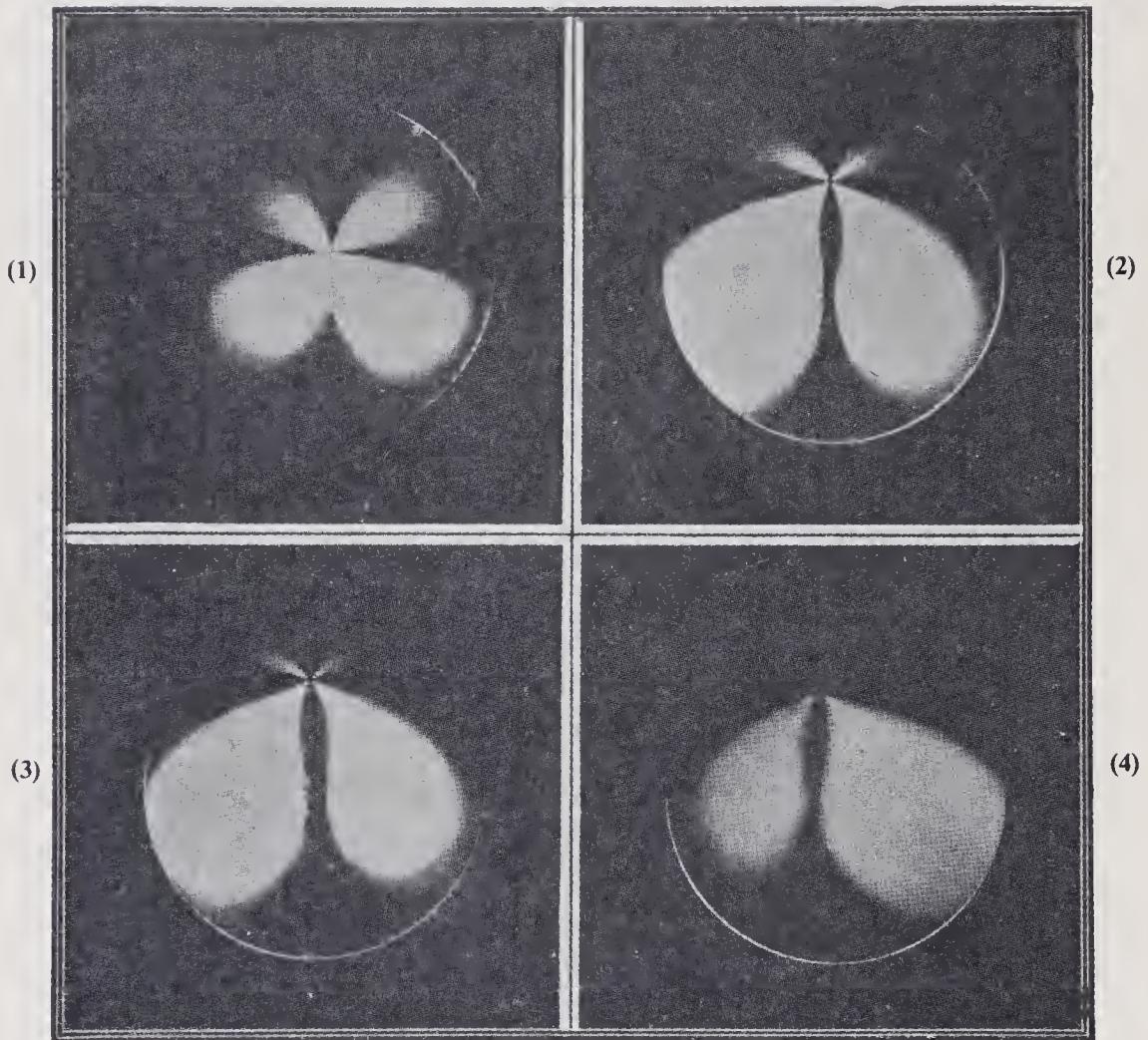


**Figures 1–6.** Birefringence patterns of quartz sphere.

**Plate II**

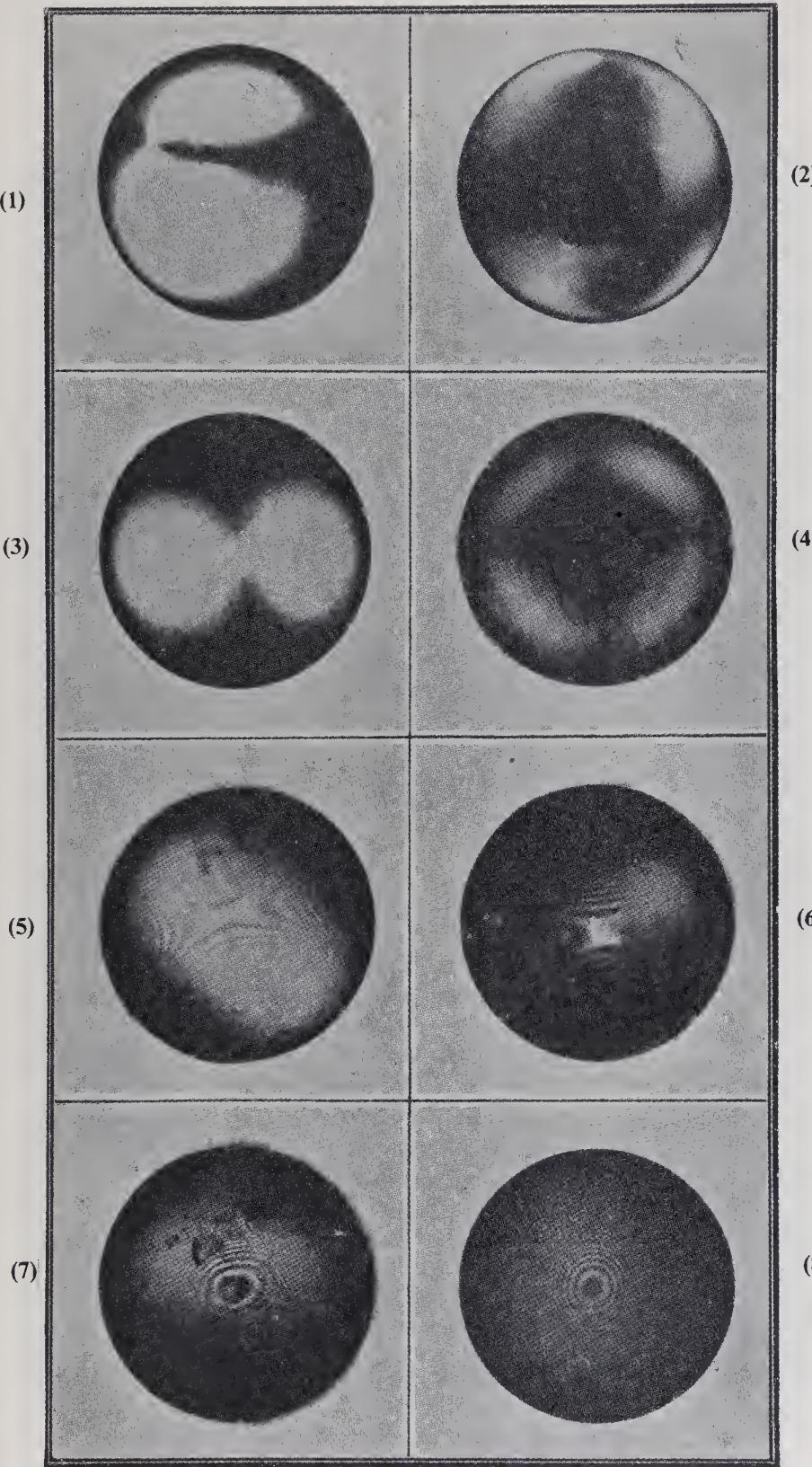


Figures 1–6. Birefringence patterns of beryl sphere.

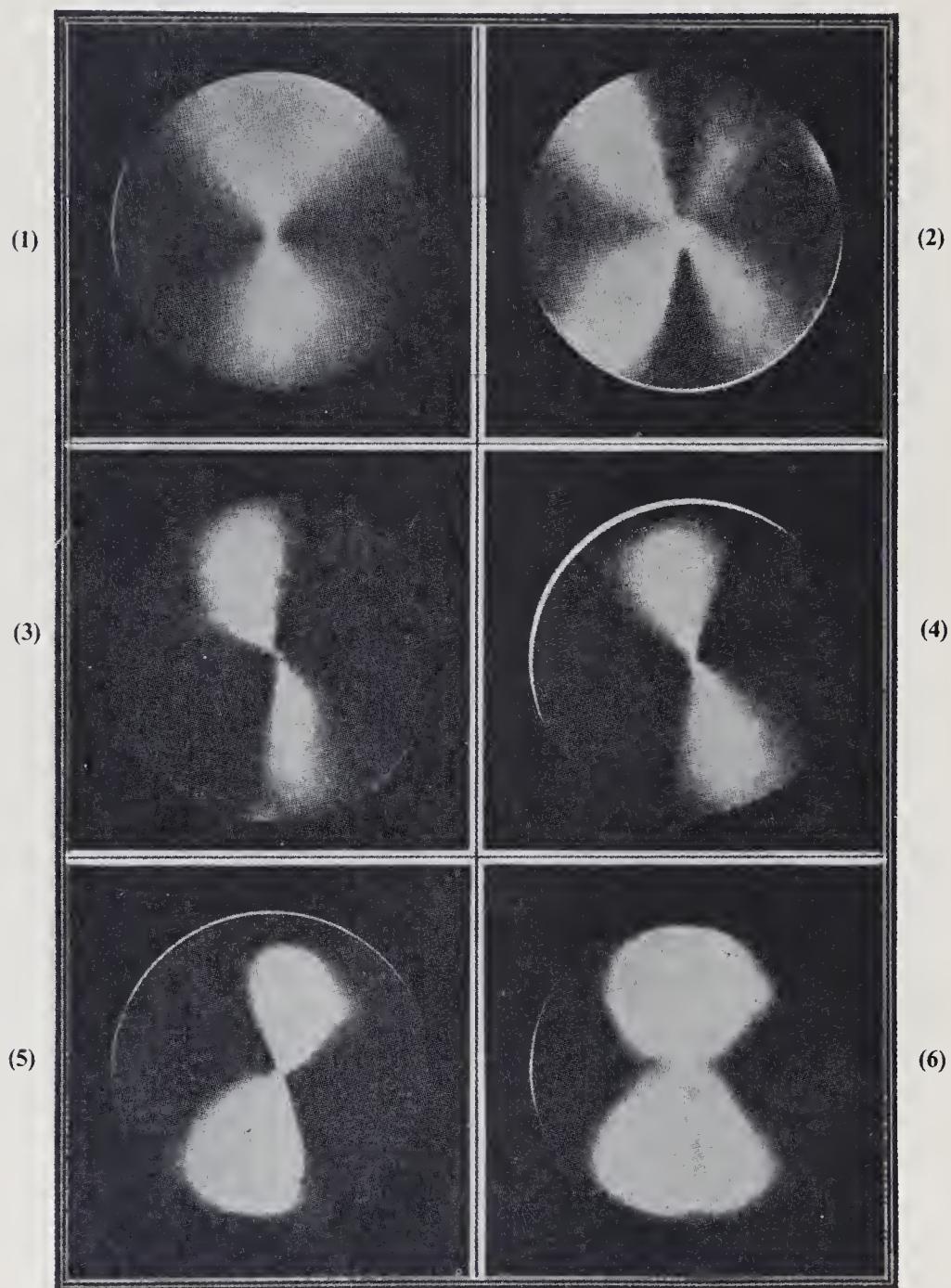


Figures 1–6. Birefringence patterns of calcite sphere.

Plate IV



**Figures 1–8.** Birefringence patterns of topaz sphere.



Figures 1–6. Birefringence patterns of iolite sphere.

Plate VI

## Amethyst—its nature and origin\*

Amethyst is a variety of crystalline quartz which, instead of being colourless and transparent like the ordinary form of rockcrystal, exhibits a beautiful purple colour, in consequence of which it has been esteemed as a gem-stone since ancient times. Mineralogists have naturally been much interested in the question of the origin of this colour. Problems of the same nature arise in regard to numerous other minerals and it was customary in the past to explain the colour in such cases as due to impurities assumed to be present in the material and diffused through it in an atomic or a colloidal form. A different view regarding the origin of colour in many minerals has latterly been gaining favour, namely, that it is a consequence of defects in the regularity of structure such as would be caused, for example, by the crystal having been subject over long periods of time to radiations traversing its substance. Explanations along one or the other of these two lines are to be found in the extensive literature concerning amethyst, but it can scarcely be claimed that they are based on evidence of a convincing nature. Still another view regarding amethyst which for a long time held the field is that it consists of quartz in which layers of the right-handed and left-handed varieties alternate. Why such alternation should result in colour is a question which was left unanswered.

The problem of amethyst has been under investigation at my Institute in Bangalore during the past year and conclusions regarding the nature of this material have been reached which are different from anything which has been so far suggested. They are based on the results of fact-finding research on those properties of amethyst which appeared to us most likely to throw light on its physico-chemical constitution.

The first series of studies undertaken by Mr A Jayaraman and myself were precise measurements of the density of amethyst quartz. For such measurements to have scientific value, it is necessary to work with selected material free from cracks, inclusions and visible impurities. Accordingly, cut and polished gemstones believed to be of Ceylonese origin were used for the determinations. The specimens employed varied notably in their depth of colour. Differences of the order of one or two units in the third decimal place were indeed noticed in their densities, but such differences exhibited no correlation with the depth of the colour of the specimen; neither did the values differ significantly from that of colourless quartz.

\*Presidential address delivered at the annual meeting of the Indian Academy of Sciences held at Belgaum on the 26th of December 1954.

Careful studies have also been made regarding the behaviour of amethyst in magnetic fields. Quartz is diamagnetic, and exhibits a very feeble diamagnetic anisotropy. Metallic oxides such as those of manganese or iron to which the colour of amethyst has been attributed in the past are highly paramagnetic and hence, if present, might be expected to reveal themselves by an altered magnetic susceptibility. Here again our results were entirely negative. All our amethyst specimens were diamagnetic and their susceptibility showed no significant variations from that of colourless quartz.

The next property investigated was the scattering of light in its passage through the solid. As is well known, this is a severe test of the regularity of the structure of the material and of the absence of inclusions, the latter, if present, revealing themselves immediately by a largely enhanced intensity of light-scattering. Clear quartz of the best quality does indeed exhibit light-scattering, but this is extremely feeble. In smoky quartz, on the other hand, a Tyndall effect is very conspicuous. But in amethyst no such phenomenon is observable. The difference is illustrated in figure 1 in which the tracks of a beam of sunlight in smoky quartz

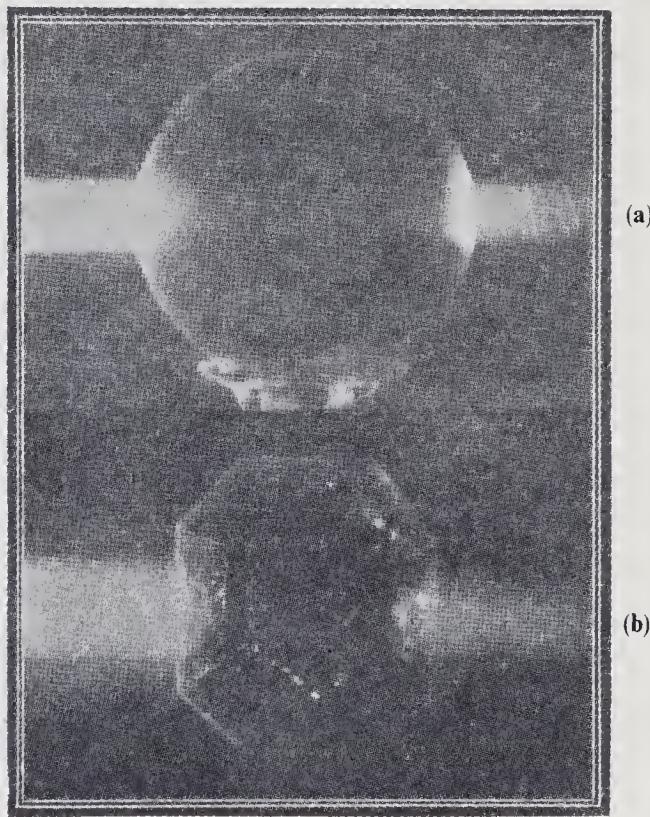


Figure 1. a. Smoky quartz. b. Amethyst.

and in amethyst are exhibited side by side, the specimen in each case being immersed in a cell containing benzyl alcohol to avoid refraction effects.

Thus we are led to the view that amethyst is a crystal with a regular structure and that the cause of the colour is to be looked for in the ultimate constitution of the crystal itself. This view is independently confirmed by the results of research in two other and quite different directions. The first is a study of the X-ray diffraction by amethyst carried out by Mr Jayaraman and myself, and the other, a detailed investigation of its optical properties by Mr S Pancharatnam. I shall now proceed to summarise the findings reached.

In view of the close association of colourless quartz and amethyst as found in nature, one could scarcely expect to find any readily measurable differences in the spacings of their three-dimensional crystal lattices. What we have to look for are differences in the electronic distribution and therefore also the reflecting powers for X-rays of the lattice planes in the two crystals. To establish the existence of such differences by the usual methods followed in X-ray structure determination would obviously be laborious and might even be infructuous. We have therefore employed a method which has proved itself to be both simple and effective. The section-plate of amethyst finally chosen for the study was cut obliquely to the optic axis of the quartz and by etching tests was ascertained to be free from either optical or electrical twinning over its effective area. It however exhibited a pattern of colour bands and colour sectors of the kind almost invariably to be seen in amethyst. The section-plate was irradiated by an X-ray pencil over its whole area and gave a Laue pattern in which each Laue spot was itself an extended picture of the crystal. It was found that the Laue spots also exhibited the features optically observable in the section-plate but in a very different way in the different spots, thus clearly showing that the variations in the colour observed over the area of the plate correspond to variations in the X-ray reflecting power which are different for the different lattice planes, as is to be expected on the foregoing view regarding the nature of amethyst.

The optical investigation by Mr Pancharatnam has also yielded highly significant results. They may be summarised by the statement that amethyst is optically biaxial, that it exhibits trichroism and that these two properties taken together show amethyst to possess only monoclinic symmetry instead of trigonal symmetry as in the case of colourless quartz. The studies have also revealed that the diad axis of monoclinic symmetry coincides with one of the three electrical axes of the associated quartz. The latter is different for the three colour-sectors usually observed in a section-plate of amethyst, their diad axes being inclined to each other at an angle of  $120^\circ$ .

Whereas it has hitherto been supposed that amethyst exhibits a single absorption band in the green region of the spectrum, Pancharatnam has found that there are three different absorption spectra differing enormously in the strength as well as in the position of the absorption band, corresponding to the vibrations along the three colour axes within the crystal. The weakest of the three absorptions is for vibrations along the diad axis; the absorption maximum for it is near  $5000\text{ \AA}$  and the transmitted light is light orange in colour. The two other

colour axes lie in a perpendicular plane and make angles of about  $45^\circ$  on either side of the trigonal axis of quartz. For one of them the absorption is particularly intense and is centred round  $5250\text{ \AA}$ , the transmitted light being a deep reddish purple. For the third axis, the absorption maximum is near  $5750\text{ \AA}$  and the transmitted light is blue in colour.

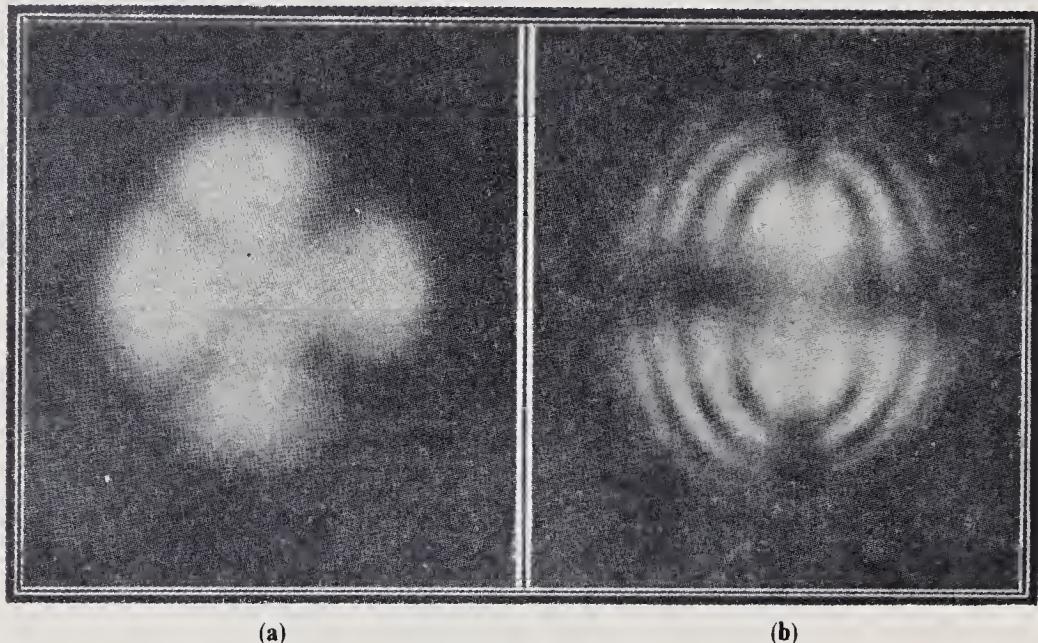


Figure 2. a. Idiophanous figure. b. Biaxial figure.

Figures 2 (a) and (b) respectively are photographs of the so-called idiophanous figure of absorption exhibited by amethyst in convergent unpolarised light and of its biaxial figure as seen between crossed polaroids. The former figure was photographed in the green monochromatic light of a mercury lamp and the latter in deep red light, the crystal in both cases being viewed along the trigonal axis of the quartz.

Very small and not improbable displacements of the silicon atoms along the electric axes on which they lie would suffice to alter the trigonal symmetry of colourless quartz to the monoclinic symmetry of amethyst. The accompanying deformation of the oxygen tetrahedra surrounding each silicon atom would offer a pathway to the explanation of the pleochroism exhibited by amethyst. We shall not pause here to discuss these points in further detail, but will pass on to consider the very interesting question as to the circumstances in which silica crystallises as amethyst instead of as colourless quartz. The study of a great number of specimens collected from near Hyderabad City in South India points to certain conclusions regarding this matter. A feature very commonly observed in the individual specimens is that a region of intense colouration is observed separated from another which is comparatively free from colour by internal planes parallel

to the external rhombohedral faces of the crystal. X-ray shadowgraphs of the specimens disclose that along the boundary between these two portions of the material, there is invariably a deposit of fine particles which chemical examination reveals to be ferric oxide. The conclusion is thus almost irresistibly suggested that amethyst is formed from silicious material containing ferric impurities and is consequent on the progressive elimination of these impurities during the growth of the crystal. At some stage in the process, the impurities separate out into distinct particles, and then cease to play any further role in the crystallisation, which accordingly continues as clear quartz. Figures 3 (a) and (b) illustrate the foregoing remarks. The former is a section-plate cut perpendicular to the trigonal axis; the hexagonal ring containing the ferric oxide particles is very

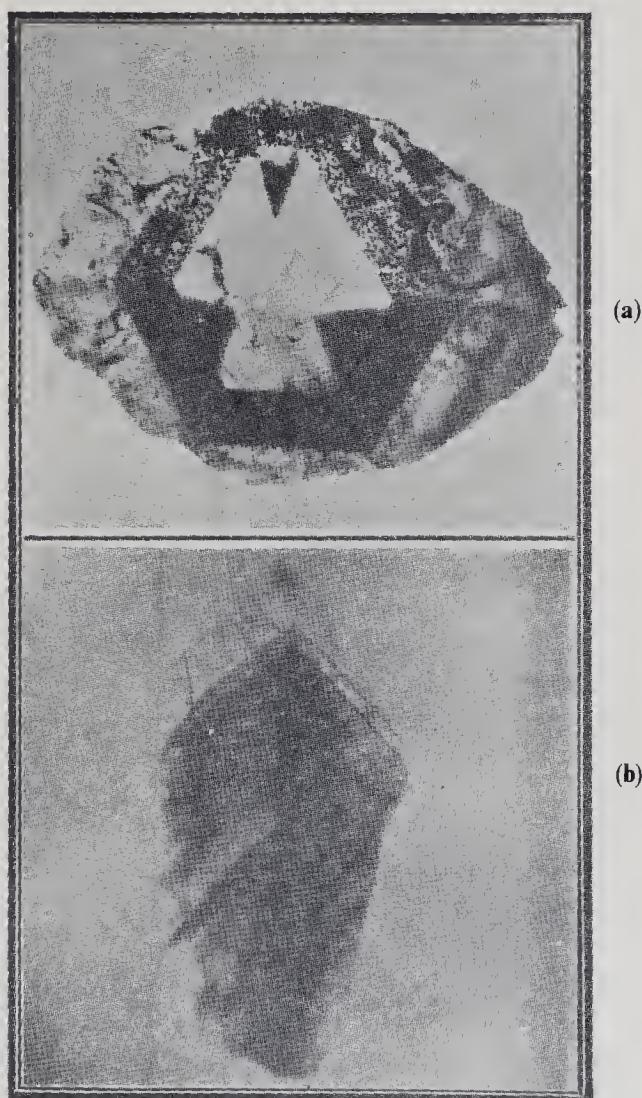


Figure 3. a. Transverse section. b. Complete crystal.

conspicuous and surrounds the inner region of quartz in which the three colour sectors adjacent to the three of the rhombohedral faces are clearly seen. Figure 3(b) is a picture of an entire small crystal of amethyst immersed in benzyl alcohol and viewed transversely by sodium light. Regions of colourless and coloured quartz are clearly seen in the picture, separated from one another by a sharply defined boundary which carries a dark deposit of ferric oxide.

C V RAMAN

# On the structure of amethyst and its genesis in nature

SIR C V RAMAN and A JAYARAMAN  
(Memoir No. 62 of Raman Research Institute, Bangalore)

Received December 14, 1954

## 1. Introduction

In a recent issue of these *Proceedings*,<sup>1</sup> evidence was presented showing that amethyst is a crystalline solid akin to colourless quartz in its structure but with a different electronic configuration which is assignable to a lower symmetry class and giving X-ray reflection intensities differing from those of quartz. These findings are supported and illumined by the results reported in a paper by S Pancharatnam<sup>2</sup> published simultaneously with ours. It was shown by him that amethyst is optically biaxial and exhibits trichroism, and that when these two properties are considered together, they indicate only monoclinic symmetry for amethyst, whereas colourless quartz has trigonal symmetry. Interesting relationships however exist between amethyst and the associated quartz in their crystallographic orientations. The monoclinic symmetry axis of amethyst coincides with one of the electrical axes of quartz; the latter is different for the three colour sectors usually appearing in a crystal of amethystine quartz. The right or left-handedness of the crystal determines which of the two axes meeting a particular rhombohedral face is the symmetry axis of the amethyst in the colour-sector contiguous to that face. For vibrations along the monoclinic symmetry axis, the colour of the transmitted light is a light orange with a maximum of absorption in the spectrum near 5000 Å. For vibrations along the two other colour axes, the colour of the transmitted light is respectively blue with an absorption maximum near 5750 Å and a deep reddish-purple with an absorption maximum near 5250 Å. These two axes lie in a plane perpendicular to the symmetry axis and make angles of approximately 45° on either side with the *c*-axis of quartz. The latter coincides approximately with the acute bisectrix in the biaxial figure.

In the present paper, we shall report some further experimental results and proceed to make some suggestions regarding the structure of amethyst which offer a pathway to the explanation of its optical behaviour. Some evidence is also presented which throws light on the very interesting question of the genesis of amethyst in nature.

## 2. Amethyst and smoky quartz

With our earlier paper, photographs were reproduced to illustrate the very significant difference between amethyst and smoky quartz in their optical behaviour, viz., that the former does not exhibit the diffusion so conspicuously evident in the case of the latter when traversed by a pencil of light. We have since obtained somewhat better pictures exhibiting this difference, which are reproduced as figures 1, 2, 3 and 4 in plate I accompanying the present paper. For recording these photographs, the specimen under study was immersed in a flat-sided cell containing freshly distilled benzyl alcohol which has a refractive index nearly the same as that of quartz. A narrow beam of sunlight traversed the specimen thus immersed and the cell was viewed transversely and photographed with approximately the same exposure time in each case.

Figure 1 is a record obtained with a polished cylinder of optically clear Brazilian quartz. Visually, a faint blue track could be seen, but a much longer exposure time than that actually employed would have been necessary to record the same. The track of the beam in the benzyl alcohol however appears with great intensity.

Figure 2 is a similar record obtained with a polished sphere of smoky quartz which had been specially prepared from a rounded pebble from Ceylon presented to us by Dr C S Pichamuthu to whom our thanks are due. The specimen was only faintly smoky, but nevertheless, as can be seen from figure 2, the track of the beam was conspicuously visible, and was many times brighter than the track in

**Table 1.** Comparison of diamagnetic susceptibilities

Description	Mass in grams	Density in gm. per c.c.	Deflection in the magnetic field: scale divisions
<i>Amethyst</i>			
Intensely coloured	2.3394	2.651	9.1
—	1.8521	2.652	9.2
—	1.3466	2.651	9.0
—	1.0846	2.652	9.0
—	0.7137	2.650	7.0
Moderately coloured	2.2276	2.651	9.3
—	1.4184	2.650	8.0
—	1.2545	2.650	9.0
Lightly coloured	1.1595	2.653	8.7
—	1.1937	2.651	8.8
—	1.0351	2.650	9.0
—	0.7481	2.654	9.0
Colourless quartz	0.7481	2.650	9.1
—	0.334		9.1

colourless quartz as seen visually. The progressive extinction of the incident beam in traversing the smoky quartz is very evident in figure 2. The scattered light is, of course, also enfeebled by absorption before its emergence.

Figures 3 and 4 are slightly enlarged reproductions of photographs obtained with two strongly coloured amethyst gem-stones in our possession. In neither case does the interior of the crystal exhibit any visible evidence of the passage of the light through it. The track of the beam in the benzyl alcohol is weaker after its passage through the amethyst than before it. This is to be expected in view of the absorption of light in the crystal which is strongest in the green, yellow and orange regions of the spectrum. A similar absorption would necessarily also operate on the scattered light, if any, before it emerges in a transverse direction. But since the shorter wavelengths in the visible spectrum are the least absorbed in amethyst and would also be the strongest in the light-scattered by it and since also, the thickness needing to be traversed is relatively small owing to the particular shape of our specimens, such absorption would in no way have prevented the observation of a Tyndall effect, had this been actually present.

### 3. The diamagnetic behaviour of amethyst

In view of a recent report which appeared in the columns of *Nature*<sup>3</sup> claiming that strongly coloured specimens of amethyst are paramagnetic and that the colour of amethyst is accordingly to be ascribed to the presence of ferric iron in it, we thought it worthwhile even before our first paper was published to make some qualitative tests to ascertain the true position regarding this matter. In view of the very high paramagnetism exhibited by oxides of iron, very small percentages of the same present as included material would suffice to give wholly misleading results regarding the magnetic behaviour of amethyst. It is accordingly of the highest importance to use selected specimens shown by rigorous optical test to be free from such inclusions. In our preliminary observations, we used the same cut and polished gemstones as those for which the densities had been determined and reported in our first paper. Each specimen was tested in turn by attaching it to the end of a long vertical fibre and placing it in a powerful non-homogeneous magnetic field. When the electromagnet producing the field was excited, the specimen moved to a different position at which the restoring force due to its weight was balanced by the force of magnetic repulsion. The displacement produced would, in these circumstances, be determined by the mass-susceptibility of the specimen and independent of its size. Tested in this way, all the specimens listed in our earlier paper were found to be diamagnetic, and there were no noticeable differences in their behaviour in this respect.

To place the matter beyond all doubt, we have repeated these preliminary studies with improved technique. Each of the specimens under study was hung by a single rayon fibre about a metre long enclosed in a glass tube to protect it from

disturbing air currents. A permanent magnet fitted with wedge-shaped pole pieces was employed to produce a non-homogeneous field. The magnet itself could be moved in such a manner that the specimen originally hanging in field-free space was transferred to a pre-determined position in a suitably chosen part of the field. The resulting displacement of the specimen was read off from the movement of the suspending fibre seen optically projected on a distant scale. Table 1 gives the results of measurements made with our specimens of amethyst, as also with pieces of colourless quartz. The data leave no room for doubt that, *to a first approximation, amethyst and quartz have the same magnetic susceptibility*. It is thus clear that the results reported in *Nature* and referred to above were based on observations made with impure and therefore unsuitable material. Incidentally, it should be mentioned that the difference between the diamagnetic susceptibility of colourless quartz along directions parallel and perpendicular to the trigonal axis as reported in the same communication is some twenty to thirty times larger than the actual difference. The latter is quite small, being indeed a little less than one half of one per cent of the susceptibility in either direction.

#### 4. Crystal structure of amethyst

As is well known, quartz in its low and high temperature forms possesses structures which are very similar to each other, though differing in detail. In either case, the unit cell contains three  $\text{SiO}_2$  groups, the silicon atoms being disposed in planes perpendicular to the trigonal axis of symmetry which divide the cell length into three equal parts. The oxygen atoms in high quartz are situated in three planes half-way between those containing the silicones, while in low-quartz they appear in six planes which are nearly but (according to a recent report) not quite those of aliquot subdivision of the *c*-axis into nine equal parts. While the silicon atoms are situated in the special or symmetric positions in high-quartz, they are displaced from those positions in low-quartz and located on the three digonal axes of symmetry of the structure. The *c*-axis in either case is a screw axis, six-fold and three-fold respectively in the two cases.

If in the low-temperature form of quartz we imagine *one* of the three silicon atoms in the cell to be displaced along the digonal axis on which it lies, either towards or away from the position it would occupy in high-quartz, all the symmetry elements of the low-quartz structure would disappear, except the digonal axis in question. The modified structure would then possess only monoclinic symmetry. The same would continue to be the case if the two other silicon atoms in the cell are also displaced along their respective digonal axes, the magnitude of such displacement being the same for both but differing either in sense or magnitude or both from that of the first silicon atom. Any movement of the silicon atoms would necessarily involve movements of the oxygen atoms linked to them, as also a deformation of the oxygen tetrahedra surrounding the

silicons. It would be easy however to picture such displacements of the oxygen atoms as would preserve the monoclinic symmetry contemplated above.

Thus, by a relatively simple and not improbable alteration in the structure of low-quartz, we arrive at a modification thereof possessing only monoclinic symmetry, the diad axis characteristic of such symmetry coinciding with one of the electrical axes of quartz in the undisturbed state. This is the situation which actually exists in amethyst as is shown by the study of its birefringence and pleochroism. We are therefore justified in pursuing the hypothesis and developing its consequences further. Since the surviving diad axis of symmetry may be any one of the three electrical axes of low-quartz, it follows immediately that there are three possible species of amethyst which are however different only in respect of their orientation within the colourless quartz. We thus arrive at an immediate explanation of the fact that the amethystine colour in quartz usually appears in three sectors, the orientation of its monoclinic axis altering by  $120^\circ$  when we pass from one sector to the next.

Figures 1 and 2 in plate II accompanying the present paper illustrate the feature referred to. These photographs were obtained of two crystals of amethyst immersed in a cell of benzyl alcohol by the light of a sodium vapour lamp transmitted through it. Figure 1 shows only two colour sectors, the absence of a third sector being readily understood as the corresponding rhombohedral face was absent in the external form of the crystal. In figure 2 the three colour sectors are seen but are of very different sizes, such difference also being manifest in the external development of the corresponding rhombohedral faces. Figures 3 and 4 in plate II illustrate another feature very commonly observed in amethystine quartz. They are photographs of cut gem-stones viewed by transmitted light under immersion. Figure 3 exhibits one set of internal lamellae consisting of alternate layers of colourless quartz and of amethyst, while in figure 4, two such sets are seen. In each case, the lamellae are parallel to the rhombohedral planes in the quartz structure.

## 5. The optical properties of amethyst

The change from trigonal to monoclinic symmetry would necessarily involve an alteration in the optical behaviour of amethyst as compared with that of colourless quartz. The low birefringence of quartz is explicable as arising from the approximately tetrahedral grouping of the oxygen atoms around each silicon atom, while its optical activity is a consequence of the presence of a screw axis in the structure. Since amethyst possesses only monoclinic symmetry, it should be optically biaxial, the symmetry axis being one of the optic vibration directions; the other two would lie in a plane perpendicular to it. The trigonal axis is the direction of maximum polarisability in quartz, and if the changes of polarisability produced by the change of structure are small, the same direction would continue

to be the direction of maximum polarisability also in amethyst. The *c*-axis of quartz would then appear as the acute bisectrix in the biaxial figure exhibited by amethyst between crossed polaroids. It may be presumed that there would also be noticeable changes in optical activity, but these would probably not be large.

Colourless quartz is quite transparent in the visible and ultraviolet regions of the spectrum but exhibits complete opacity even in thin layers beyond 1436 A.U. Chandrasekhar<sup>4</sup> has shown that the optical rotatory dispersion of quartz is represented accurately by a single-term formula containing a characteristic wavelength at 926 A.U. and that the refractive dispersion is also tolerably well represented by a single-term formula of the Drude-Sellmier type containing the same wavelength, both in respect of the ordinary and extraordinary indices with only a change in the oscillator strength as between these two. It would seem therefore that the absorptions present at wavelengths greater than 926 A.U. influence the refraction and dispersion only to a minor extent. The high transparency of quartz in the visible and ultraviolet is undoubtedly a consequence of the saturated character of the silicon-oxygen bonds and their tetrahedral grouping in the crystal. As already remarked, the change in structure from quartz to amethyst would necessarily involve a distortion of the oxygen tetrahedra surrounding each silicon. It is not unreasonable to assume that it is this distortion which is responsible for the appearance of the absorption bands in the visible and near ultraviolet characteristic of amethyst. In view of its monoclinic symmetry; the diad axis is necessarily one of the axes of the absorption ellipsoid, the other two lying in a plane perpendicular to it. Since the edges of the oxygen tetrahedra are variously inclined to the *c*-axis of quartz, there is no reason to assume that the latter would itself be one of the colour axes, and indeed actually it is not.

## 6. The genesis of amethyst

A great collection of amethystine quartz collected by one of us some years ago from the University area near Hyderabad City in South India was available to us for examination. Certain general features observed with this material will now be described, as they are very illuminating in relation to the problem of the genesis of amethyst in nature.

An exceedingly common feature in our specimens is the appearance of an intense amethystine colour in the lower part of the crystal, the same being sharply terminated by one or more rhombohedral planes, while the upper part of the crystal is either completely colourless or exhibits a very light colour arranged in layers parallel to the same rhombohedral faces. A convenient way of exhibiting this feature is to immerse the crystal in a flat-sided cell containing benzyl alcohol and to photograph the same by the transmitted light of a sodium vapour lamp. The coloured regions appear quite dark in the resulting photograph, while the

outer regions are almost completely transparent except for faint shadows due to defects in the material or the light colouration existing therein. Figures 3, 5 and 6 in plate IV represent typical examples of this kind, the two former pictures representing the same crystal as viewed in perpendicular directions transverse to the *c*-axis.

A different and very illuminating procedure is to obtain a radiogram of the entire crystal or of a suitable section of it. Figures 1 and 2 in plate III represent optical photographs of two such sections which were each about 5 mm thick parallel to the *c*-axis, while figures 3 and 4 are radiograms respectively of the same specimens taken with the X-ray film quite close to the crystal. In the two former pictures, the transparent and coloured regions of quartz exhibit an intense contrast. *No such contrast appears in the radiogram, and indeed after many trials we have been unable to observe the smallest difference between the X-ray transmissions of colourless and amethystine quartz.* A very interesting feature is however noticeable in figures 3 and 4. This is the appearance of a dome or a layer, as the case may be, of material quite opaque to X-rays. This layer is viewed edgewise in the radiogram in figure 4 and hence appears as a single dark streak, while in figure 3 it is viewed sideways and appears resolved into a large number of small specks lying on the boundary between the coloured and uncoloured quartz and forming a pyramidal dome having the same shape as that boundary. This material can easily be taken out and subjected to chemical analysis and discloses itself to be ferric oxide.

The same phenomenon as seen in a thick transverse section is represented in figures 1 and 4 of plate IV, the former being the optical photograph and the latter an X-radiogram. The pattern of sectors of coloured and colourless quartz which is so conspicuous in the central region of figure 1 is completely absent in figure 4, but the encompassing hexagonal ring of particles of ferric oxide shows up clearly in both the pictures. Figure 2 in plate IV is an optical photograph of a thin transverse section cut through a part of another crystal so chosen that the dome of ferric oxide is seen in its entirety. The dark area at the centre is in fact a dense aggregate of particles of that material. To the left of it is seen a thin layer of coloured amethyst stretching out from one of the edges of the same area.

The features described and illustrated above are equally well exhibited by thousands of other specimens in our collection. The inference suggested thereby seems irresistible, namely that the transformation from colourless quartz to amethyst occurs during the growth of the crystal and that the change of structure from trigonal to monoclinic symmetry is brought about by the presence of the ferric impurities in the crystallising material and during their progressive expulsion from the growing crystal. At some stage during this process, the ferric oxide separates completely, forming aggregates and thereafter ceases to play any role, the further crystallisation appearing in the form of colourless quartz. This hypothesis completely accounts for the very close relationship between the form and extension of the colour sectors of the amethyst and the form of the

encompassing dome of ferric oxide particles, as also of their very obvious relationship to the external form of the crystal.

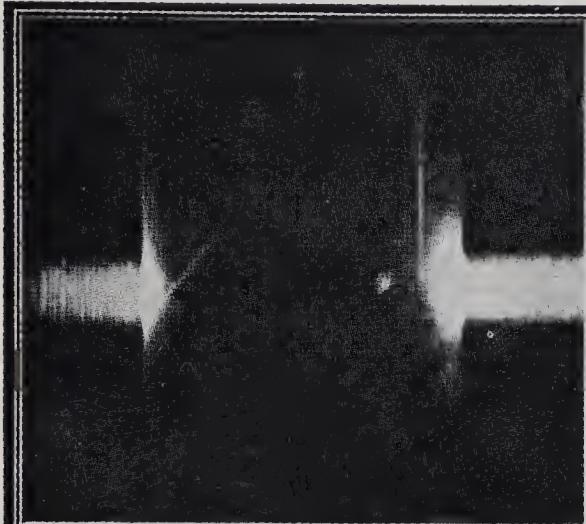
### 7. Summary

Amethyst is diamagnetic, its susceptibility being not measurably different from that of colourless quartz. The optical characters indicate only monoclinic symmetry, of which the diad axis coincides with one of the three electric axes of the associated quartz. An immediate explanation of why three colour sectors usually appear in amethystine quartz is thus forthcoming. The nature of the modifications in structure which alter trigonal to monoclinic symmetry is indicated. A study of an extensive collection of material indicates that the change of structure occurs during the growth of the crystal from material containing ferric impurities and is consequential on the progressive elimination of these impurities which are finally deposited as a dome of discrete particles on the boundary between the amethyst and the colourless quartz.

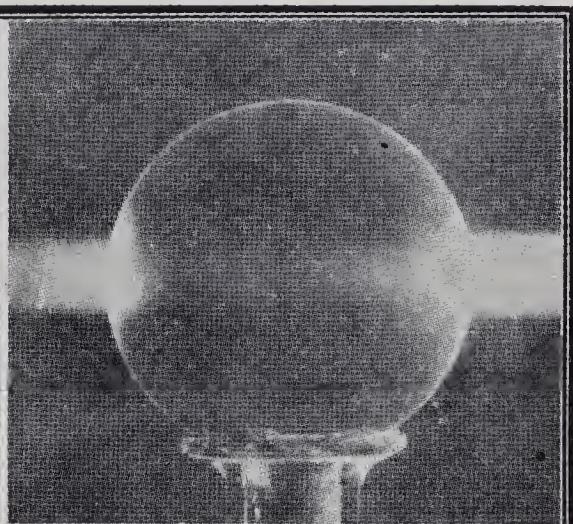
### References

1. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1954, **40A**, 189.
2. S Pancharatnam, *Ibid.*, 1954, **40A**, 196.
3. M Leela, *Nature*, 1953, **172**, 464.
4. S Chandrasekhar, *Proc. Indian Acad. Sci.*, 1953, **37A**, 468.

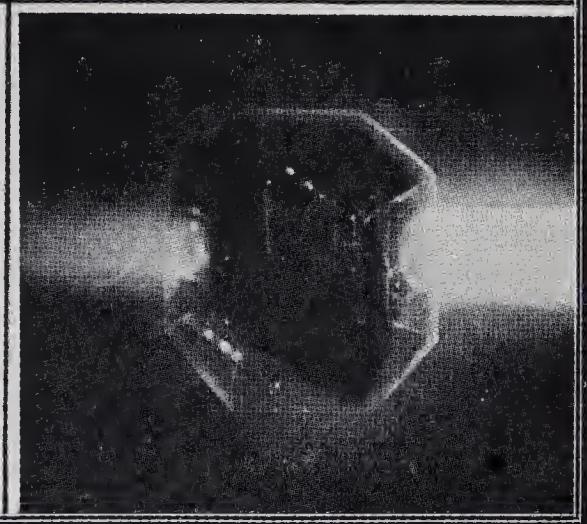
(1)



(2)



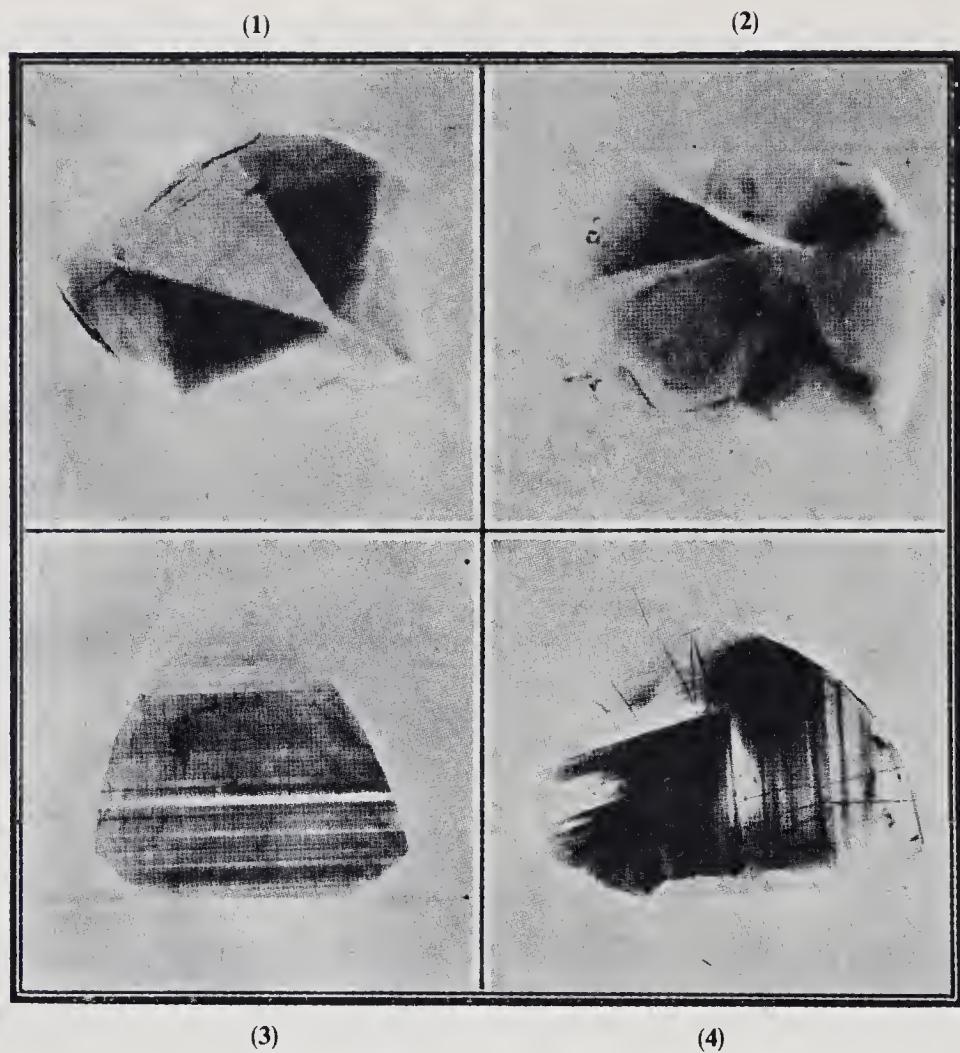
(3)



(4)

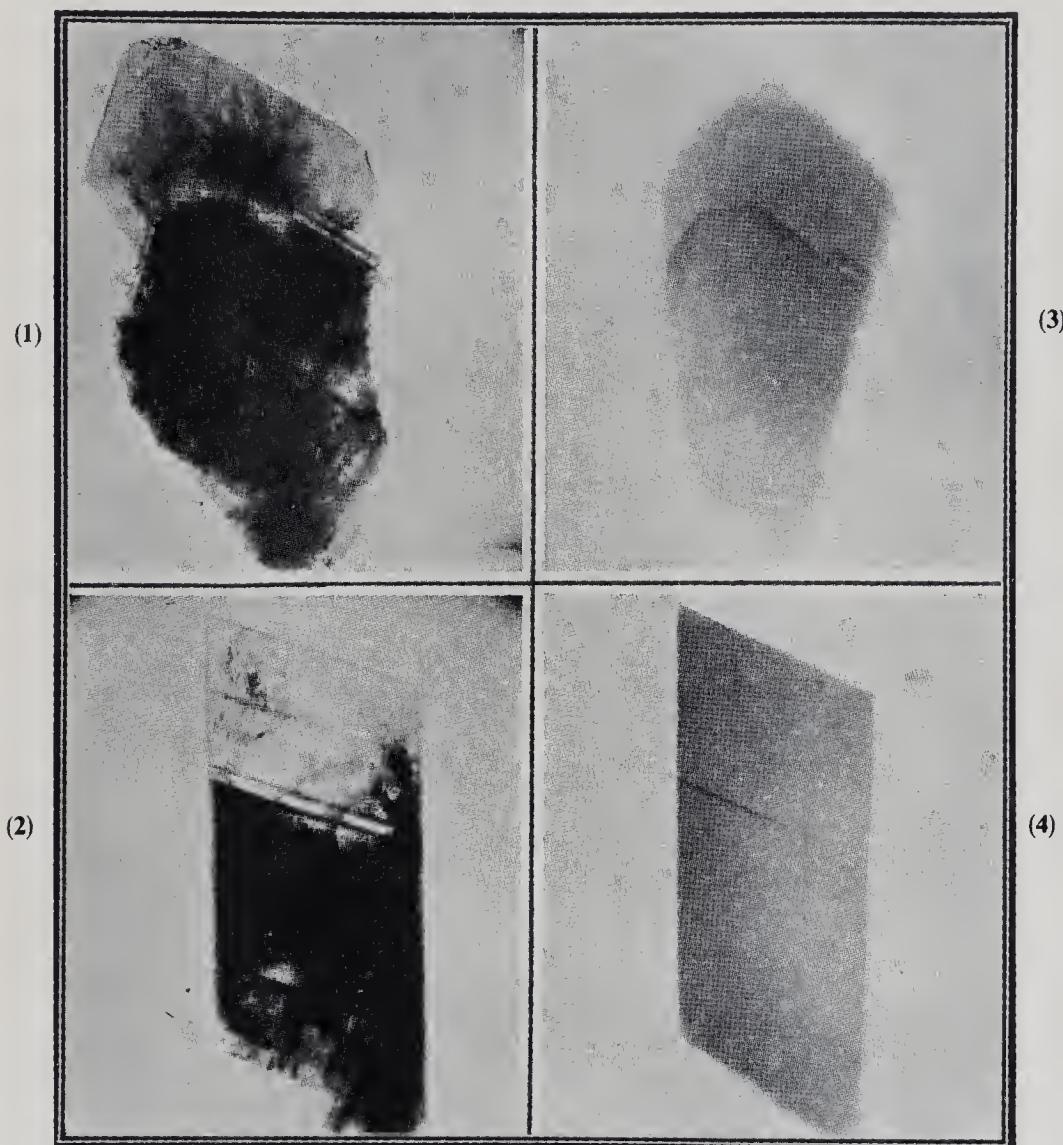
**Figures 1–4.** Scattering of light in smoky quartz and amethyst.

**Plate I**



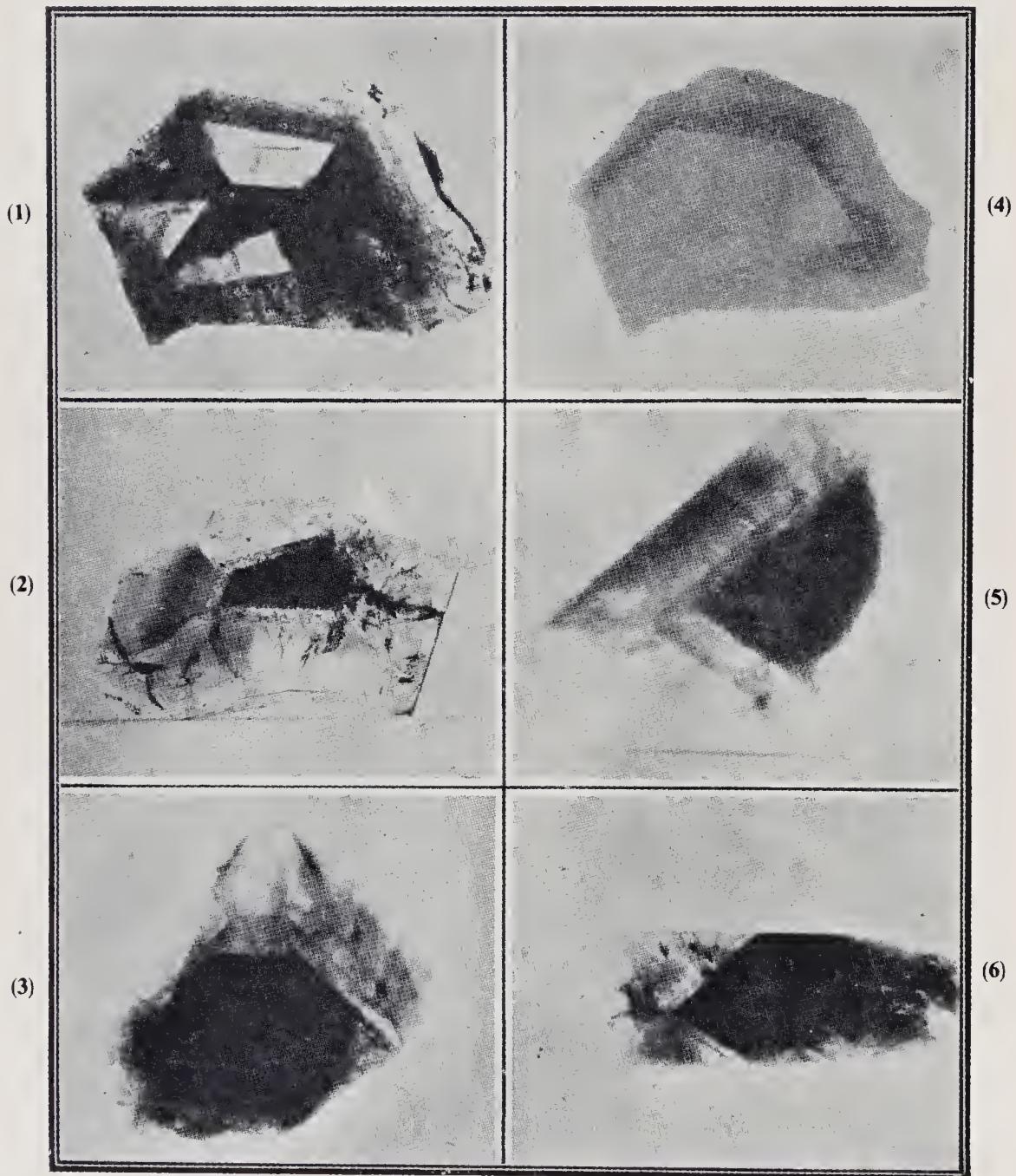
**Figures 1–4.** Colour-sectors and colour-layers in amethyst.

**Plate II**



**Figures 1–4.** Photographs and radiograms of amethyst.

**Plate III**



Figures 1–6. Photographs and radiogram of amethyst.

Plate IV

## On the optical behaviour of crypto-crystalline quartz

SIR C V RAMAN and A JAYARAMAN  
(Memoir No. 64 of the Raman Research Institute, Bangalore)

### 1. Introduction

The present paper may be regarded as a sequel to two earlier communications<sup>1, 2</sup> by the present authors in these *Proceedings* which dealt with the structure and optical behaviour of iridescent agate and of the commoner forms of chalcedony. We have felt it desirable to supplement those two papers by a somewhat fuller description and discussion of the optical phenomena presented by these materials. Of particular interest is the property exhibited by the relatively more transparent specimens of chalcedony of polarising the light transmitted by them perfectly. This phenomenon is illustrated in a striking manner by figures 1 and 2 reproduced in plate I; these are photographs of the entrance to the building of this Institute and of the landscape beyond as viewed through a plate of chalcedony about a millimetre thick on which was superposed a polaroid sheet. In figure 1, the building and landscape are seen clearly, while in figure 2 they are completely smudged out. In the former case, the polaroid had its vibration direction parallel to the fibres of quartz composing the chalcedony, while in the latter the vibration direction of the polaroid was transverse to the fibres. Similar effects are exhibited by figures 3 and 4 which are photographs of a sodium vapour lamp recorded in analogous circumstances. Polarisation effects of the same nature are also observed in the transmitted light which appears along with the diffraction spectra exhibited by iridescent agate. We shall return to these phenomena later in the paper.

An interesting and important aspect of the present subject is the close correlation which exists between the optical phenomena and the structure of the materials as revealed by X-ray diffraction studies. Large variations in structure are evident from the series of twelve X-ray diagrams reproduced in plate III and plate IV, and they correspond to striking differences in optical behaviour.

### 2. Some theoretical considerations

The phenomena exhibited by chalcedony and agate in varied circumstances are best elucidated by first considering a few idealised cases in the light of a simplified

geometric theory. We may assume the material to be composed of crystallites of quartz completely filling its volume. Had the material been optically isotropic, light would freely pass through the polycrystalline aggregate. Actually, the birefringence of the quartz is sufficient to ensure the total diffusion of the light in its passage through a plate of the material as a result of the refractions at the inter-crystalline boundaries, provided that the optic orientation of the crystallites is assumed to be entirely at random. A distant source of light viewed through such a plate would be invisible; a diffuse halo of light would be observed in the same general direction which would exhibit no observable polarisation even if the incident light be fully polarised.

It is evident from the foregoing that a preferred orientation of the crystallites is a *sine qua non* in order that any observable fraction of the light be regularly transmitted through the material. Indeed, the geometric theory demands a perfectly ordered orientation of the crystallites for an optical image of a light source to be visible through a plate of the substance. The maximum transmission would occur if the crystallites were so arranged that the principal optical axis of quartz, viz., the *c*-axis were aligned in perfect parallelism for all of them. Actually, we have not encountered a case of this kind in our studies, though an approximation to it has been noticed in some specimens of fibrous quartz.<sup>3</sup> On the other hand, chalcedony consisting of crystallites of quartz with some direction perpendicular to the *c*-axis such as [1100] or [1120] set more or less perfectly parallel for all of them appears to be fairly common. In such an arrangement, the orientation of the *c*-axis would vary from one crystallite to another.

### 3. The X-ray diffraction patterns

The foregoing remarks are illustrated by figures 1 to 6 in plate III and figures 1 to 6 in plate IV. Figure 1 in plate III is the X-ray diffraction pattern of agate recorded for a region exhibiting brilliant iridescence and using unfiltered MO radiation. It is seen that the pattern is a fibre diagram in which the crystallites are orientated with fair precision in a direction parallel to the *a*-axis of quartz, while their *c*-axes are orientated in all possible directions perpendicular thereto. Figure 2 in the same plate was also recorded with another piece of agate exhibiting iridescence; it shows a lesser precision in the orientation of the crystallites but which is of the same kind. Still less well defined is the orientation of the crystallites of the same nature seen in figure 3. This was obtained with a polished plate of chalcedony exhibiting a fair measure of transparency.

Figure 4 in plate III was obtained with a polished plate of chalcedony which was remarkably transparent, being in fact the one with which the photographs reproduced in plate I were obtained. It can be interpreted as a fibre diagram in which the fibres are parallel to the [1100] direction, while the *c*-axis takes all possible orientations perpendicular thereto. A clear indication of the same type of

fibering is illustrated in figure 5 which was recorded with a translucent specimen of coloured agate. Figure 6 in plate III was recorded with the same iridescent agate as figure 1 but in a region exhibiting no conspicuous banding or iridescence. The figure does exhibit preferred orientation of the crystallites but not of a sharply defined character, which appears to be intermediate between the types illustrated in figure 1 and figure 5 in plate III.

Figure 1 in plate IV is an X-ray diagram of powdered quartz. The remaining five figures in the plate are diagrams of chalcedony and agate in which hardly any preferred orientation is to be noticed. Figure 6 in plate IV which almost resembles figure 1 in the same plate was recorded with a chip of chalcedony exhibiting little transparency.

#### 4. Polarisation of the transmitted light

We may now consider the case of a plate of chalcedony assumed to be cut in such a manner that the *a*-axes of the crystallites are all parallel to each other and to the surface of the plate. If light be normally incident on such a plate with its vibration direction parallel to the common direction of the *a*-axes of the crystallites, it is evident that it would be freely transmitted by the plate. If, on the other hand, the vibration direction of the incident light be transverse to the same common direction, the variation of the direction of the *c*-axis from crystallite to crystallite would result in the light being refracted at the inter-crystalline boundaries and hence none of the incident light would be transmitted. The directions in which the light diffused would emerge and the state of its polarisation would both depend upon the orientation of the inter-crystalline boundaries, in other words on the shape of the crystallites. If the latter are elongated cylinders or fibres with their length parallel to their *a*-axes, the light diffused would appear as a fan of refracted rays lying in a plane perpendicular to the direction of the fibres: it would also be completely polarised with the vibration direction transverse to the fibres.

#### 5. Diffraction phenomena

Though geometric considerations of the kind set forth above suffice to give a qualitative picture of the phenomena, they would not describe completely what is actually observed. The light rays deviated by the individual fibres would evidently be in a position to interfere with each other. Hence the fan of rays diffused by the plate should properly be regarded as due to the passage of light through an irregular phase-change grating. This would diffract the light in various directions transverse to the fibres. Further, if the length of the individual fibre were not great enough, light would also be spread out by diffraction to some extent in other directions.

The importance of the part which diffraction plays in the optical phenomena is most strikingly evident in the case of iridescent agate. As has been already remarked and illustrated in our earlier paper on the subject, the light *regularly* transmitted by iridescent agate is perfectly polarised, the only difference between the iridescent and non-iridescent regions being that the intensity of transmission is greatly enfeebled in the former by reason of the radiation energy being copiously diffracted in other directions. It is highly significant that these diffracted radiations are neither wholly nor even partly concentrated in specific directions as would be the case with ordinary gratings. The diffracted radiations in fact appear as elongated streaks, and that they are well-defined streaks is made evident by using a monochromatic light source and selected regions on the agate where the spacings are most regular. No image of the source is however seen except at the centre of the spectrum of zero order. The diffraction streaks exhibit a partial polarisation which is in the same sense as the polarisation of the regularly transmitted light near their central regions but in the opposite sense further out in the streaks on either side. This situation will be evident from the photographs reproduced as figures 3 and 4 in plate II exhibiting respectively the two components of polarisation of the diffraction pattern observed with sodium light.

The explanation of the facts stated above leads us directly to the solution of the problem of the nature of the laminations in iridescent agate which we shall now proceed to consider.

## 6. The structure of iridescent agate

We shall assume that the fibres of quartz in the iridescent layers of agate have all a common direction and also a common optic orientation. That this assumption is substantially correct is evident from the complete polarisation of the light regularly transmitted through the iridescent layers and is further confirmed by the X-ray diffraction studies to which we have already referred. What then is the nature of the periodicity that gives rise to the diffraction spectra? We have already remarked that the diffraction streaks observed with fibrous chalcedony are a consequence of the varying orientation of the *c*-axis from fibre to fibre. Hence, the natural interpretation of the observed optical behaviour of the iridescent regions is that the orientation of the *c*-axis is periodic along the length of each individual fibre. In fact, one is led to that interpretation by a simple process of exclusion. What is actually observed is a diffraction of light by a phase-change grating which is irregular along the plane of the laminations but is regular and periodic in the perpendicular direction, in other words, *along* the length of the fibres. A periodicity in the orientation of the *c*-axis along the length of each fibre is just what is required to give rise to such a situation. We remark that since the change

of phase affects only the vibration transverse to the fibres, it would give rise to diffracted beams polarised in that sense. But, as we have already seen, such beams are not regularly transmitted but are diffused into a fan of rays. The non-appearance of any optical images of the source in the spectra is thus explained. We do indeed observe in the spectra a region of enhanced intensity near their centres which is partially polarised in the same sense as the regularly transmitted light. But this is evidently a secondary effect arising by reason of our assumption of a perfectly orientated fibre structure being an idealisation which differs noticeably from the actual situation.

## 7. The moiré patterns of iridescent agate

A striking confirmation of the conclusions set forth above is furnished by a study of the moiré patterns exhibited by the iridescent regions. These patterns are readily observed by merely holding up the plate against a source of light and viewing it through a magnifier. They are only seen in the regions displaying iridescence. Small tilts of the plate produce large changes in the configuration of the patterns, thereby indicating their origin, which is that the laminations in the material at different depths are not in perfect register. The introduction of a polaroid between the iridescent agate and the observer's eye produces a remarkable change in the moiré pattern. When the vibration direction of the polaroid is transverse to the laminations, in other words parallel to the fibre direction, the moiré pattern disappears practically completely. If, on the other hand, the polaroid is set with its vibration direction parallel to the laminations and hence transverse to the fibres, the moiré pattern becomes extremely conspicuous. These effects are shown in figures 1 and 2 in plate II.

The interpretation of the facts is obvious viz., that the periodic changes of phase produced by the grating which progressively transform themselves to periodic variations of amplitude are operative only in respect of the optical vibrations transverse to the fibre length. This is precisely the result which would ensue as a consequence of a periodic change in the orientation of the *c*-axis along the length of each individual fibre.

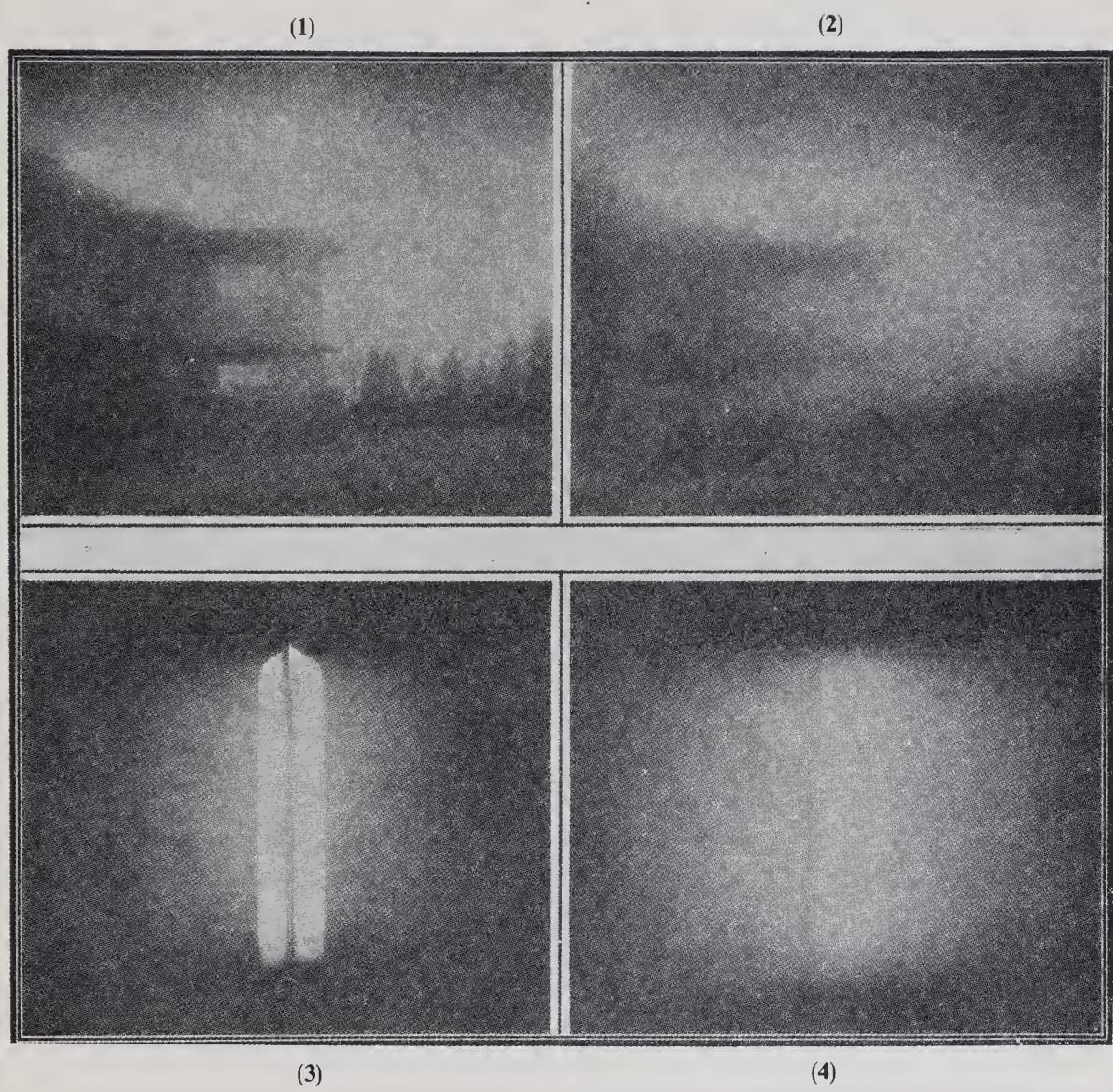
Neither the observed diffraction effects nor the behaviour of the moiré patterns could be reconciled with a periodicity of structure due to a rhythmic segregation of opal as has been suggested in recent paper<sup>4</sup> on iridescent agate which has been brought to our notice. Further, as has been shown elsewhere<sup>5</sup> by us, the opal that is actually found associated with agate is identifiable with  $\alpha$ -cristobalite. This exhibits a very intense X-ray diffraction ring with a spacing of 4.03 A.U. Not even a trace of a ring with such a spacing is to be observed in the X-ray diagram recorded by us in the strongly iridescent regions of our agate specimens.

## Summary

The polarisation of the light regularly transmitted by fibrous chalcedony and the character of the diffraction spectra exhibited by iridescent agate are described and discussed. It is shown that the phenomena point conclusively to the laminations in iridescent agate responsible for the diffraction effects being a consequence of the periodic orientation of the *c*-axis of quartz along the length of the fibres. Photographs illustrative of the optical effects and of the X-ray diffraction patterns of the materials are reproduced.

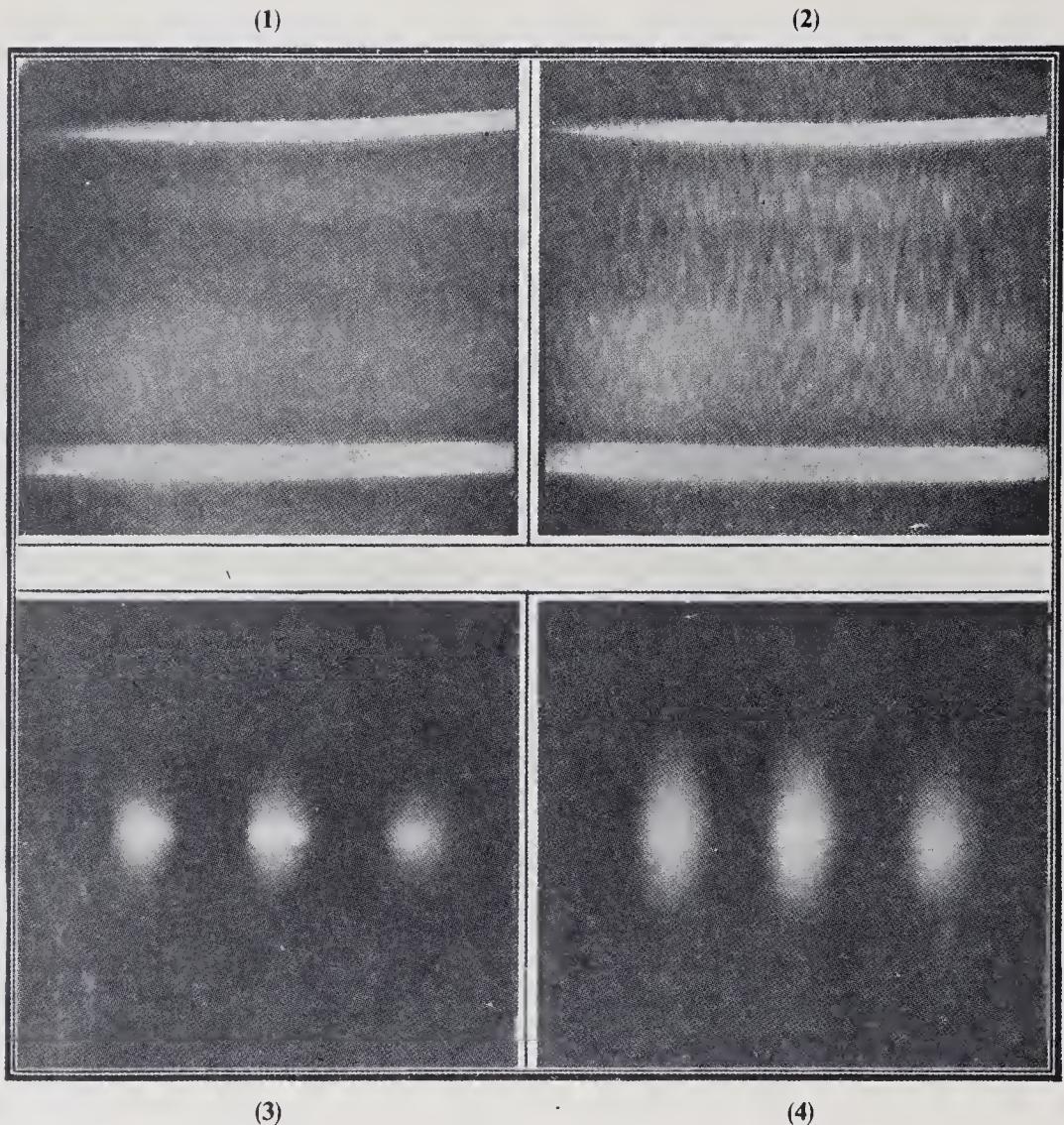
## References

1. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1953, **38A**, 199.
2. A Jayaraman, *Ibid.*, 1953, **38A**, 441.
3. C V Raman and A Jayaraman, *Ibid.*, 1954, **40A**, 107.
4. F T Jones, *Am. Mineral.*, 1952, **37**, 578.
5. C V Raman and A Jayaraman, *Proc. Indian Acad. Sci.*, 1953, **38A**, 343.



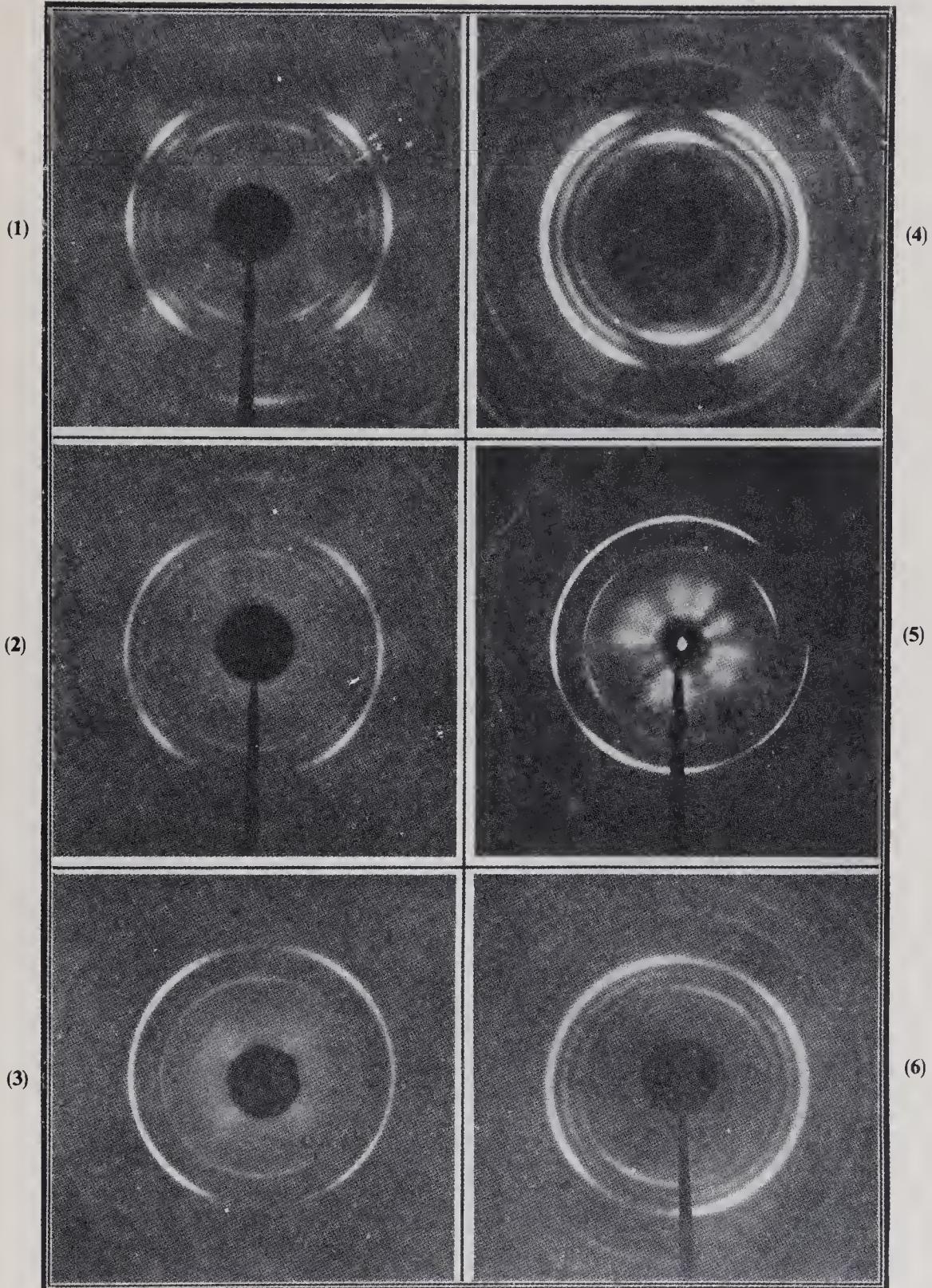
Figures 1–4. Polarisation of light by chalcedony.

Plate I



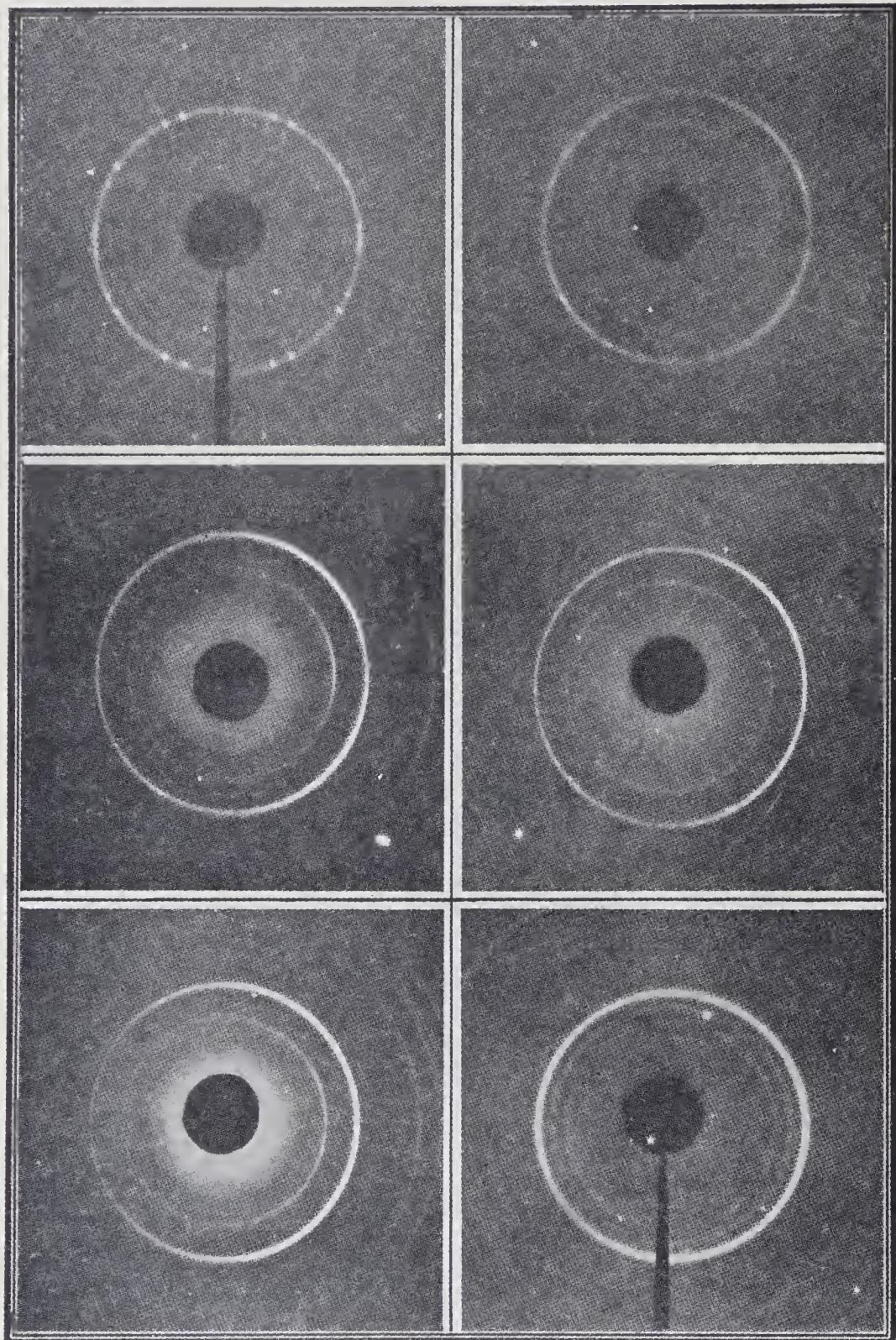
Figures 1–4. Polarisation of light by iridescent agate.

Plate II



**Figures 1–6.** X-ray diffraction patterns.

**Plate III**



**Figures 1–6.** X-ray diffraction patterns.

**Plate IV**

## X-ray study of fibrous quartz

SIR C V RAMAN and A JAYARAMAN

(Memoir No. 57 from the Raman Research Institute, Bangalore)

Received September 16, 1954

### 1. Introduction

Mineralogists designate a mineral as fibrous when it consists of visibly distinct rods or threads, irrespective of whether these are separable or not from each other. Many gradations between a coarsely columnar and a finely fibrous structure are to be observed, the finely fibrous materials often exhibiting a silky lustre. In his *Handbuch der Mineralogie*, Hintze<sup>1</sup> reports the secondary quartz often appears as pseudomorphs of the original minerals which it has replaced, and that when such minerals had a fibrous structure, the secondary quartz formed therefrom is also fibrous.

The material examined in the present investigation was very kindly placed at our disposal by the Director of the Geological Survey of Mysore. It had been collected by Dr Pichamuthu many years ago and the following description of the circumstances in which it had been found is quoted from his monograph<sup>2</sup> on the iron formations of the Eastern Bababudan Hills in Mysore.

"The writer has collected from various parts of the Bababudans specimens of fibrous quartz. In some of the siliceous layers which are formed of fibrous aggregates of quartz crystals, the fibres are disposed at right angles to the plane of bedding and are separable in some cases. The fibres are not always straight, but often bent. These layers frequently exhibit a chatoyant lustre. In micro-sections, these quartz layers are seen to contain fibrous amphiboles. Though in no one place it was possible to trace a layer of fibrous amphibole passing into a layer of quartz, the collections made by the writer show that the quartz has replaced amphibole. Similar fibrous quartz has long been known to occur associated with the banded ironstones of South Africa. The prevalent view in South Africa is that fibrous asbestos has been pseudomorphosed by silica."

### 2. Optical behaviour

The material consisted of small rods each a few millimetres long and less than a millimetre thick. They were practically colourless. On the stage of the polarising

microscope and immersed in a liquid of suitable index, the material appears transparent. When the vibration direction of the polariser is parallel to the length of the specimen, the refractive index is nearly equal to the extraordinary index of quartz as judged by the Becke line test. Between crossed Nicols, the extinction is almost perfect when the longer dimension of the specimen is either parallel or perpendicular to their vibration directions. When a quartz wedge is introduced parallel to the length of the specimen, the interference colour rises in the Newtonian scale, thereby revealing that the *c*-axis of the quartz is parallel to the length of the specimen.

### 3. X-ray examination

The foregoing inference from the optical observations is generally confirmed by the results of the X-ray diffraction studies. Two typical examples of X-ray diffraction patterns taken with the specimens set *at right angles* to the direction of the X-ray beam are reproduced as figures 1 and 2 in plate I, CuK<sub>α</sub> radiation being employed. It will be recognised from the figures that the pattern is approximately a fibre diagram with the axis of the fibre nearly parallel to the *c*-axis of quartz which is set horizontal in the figures. There is however a certain lack of symmetry, indicating that the fibering is far from being as perfect as that shown by asbestos or by satin-spar. Figures 3 and 4 are photographs taken with the same specimen as in figure 1 and with unfiltered Mo radiation, but with the specimen set *longitudinally* to the direction of the X-ray beam. The two figures represent slightly different settings of the rod. Had the quartz been truly fibrous, we should have expected to obtain a diagram consisting of complete circles. This is far from being actually the case and hence it would seem correct to describe the material as polycrystalline quartz with a preferred orientation for the *c*-axis rather than as truly fibrous quartz. Micro-sections of the original formation prepared by Dr Pichamuthu and seen by us showed no break in continuity of the individual fibres along their length under the polarising microscope, thereby supporting the view of the structure indicated by the X-ray diagrams.

### 4. Comparison with chalcedony

The principal reason why we have felt it desirable to place the results of the present study on record is in view of the earlier publications<sup>3,4</sup> from this Institute on the structure of agate and chalcedony. Those studies had revealed that in the iridescent layers of banded agate, the crystallites of quartz are orientated predominantly along the *a*-axis, while in other regions the orientation is less specific. There were also indications of an alternative orientation for the fibre axis in chalcedony, namely the direction perpendicular to the first-order prism face of

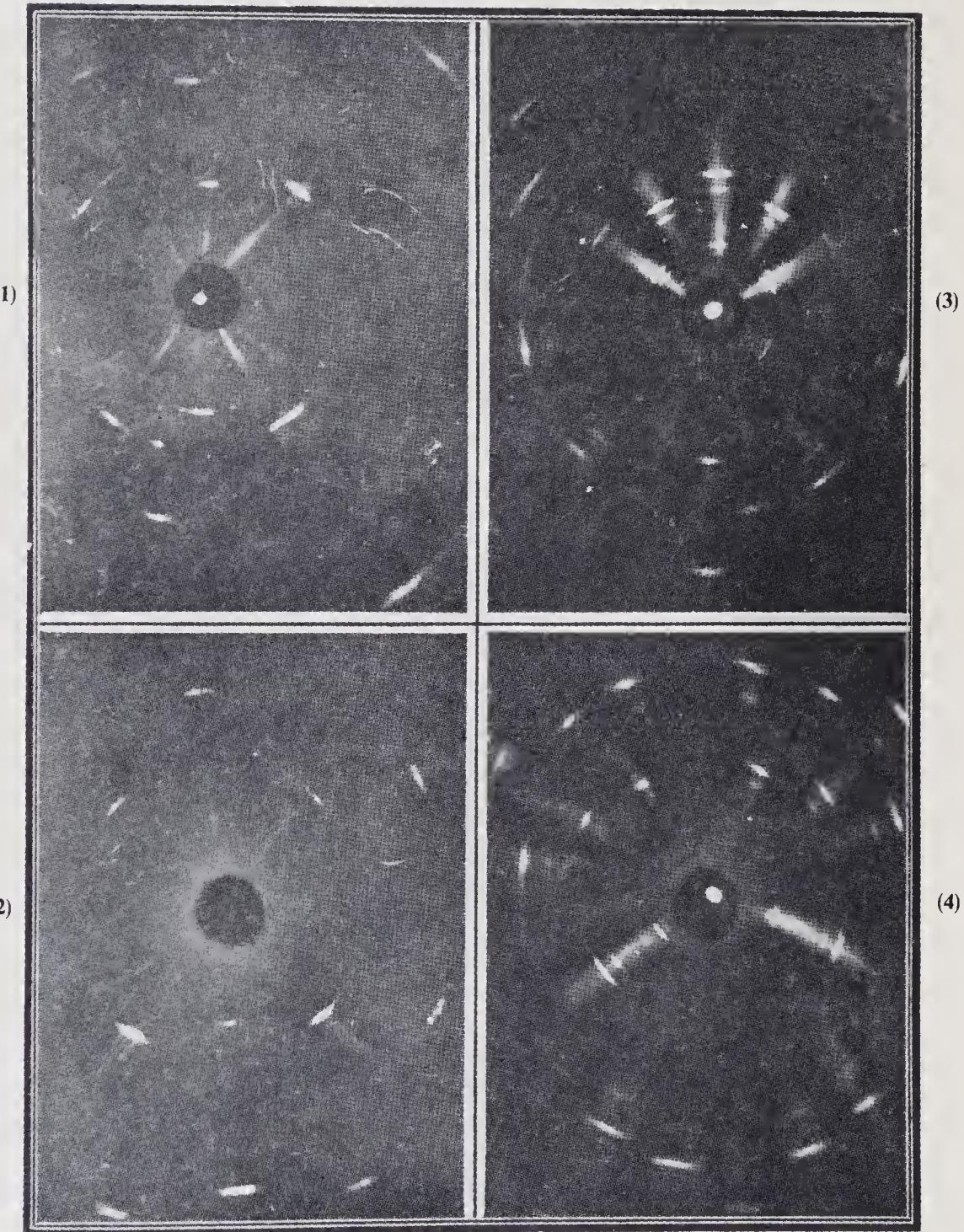
quartz. No case in which the fibering in chalcedony is parallel to the *c*-axis had been encountered by us. Had such a case been forthcoming, optical theory indicates that the material would have been transparent, almost resembling a single crystal of quartz in its behaviour.

### 5. Summary

The results of optical and X-ray examination of specimens of fibrous quartz from the Bababudan Hills in Mysore are described. They indicate that the material may be described as polycrystalline quartz with a strongly preferred orientation for the crystallographic *c*-axis along the length of the fibres.

### References

1. Hintze Carl *Handbuch der Mineralogie*, Erster Band, Zweite Abtheilung, 1915, p. 1348.
2. Pichamuthu C S *Mysore Univ. J.*, 1935, **8**, 1-48.
3. Raman C V and Jayaraman A *Proc. Indian Acad. Sci.*, 1953, **38A**, 199.
4. Jayaraman A *Ibid.*, 1953, **38A**, 441.



Figures 1-4

Plate I

## On the polycrystalline forms of gypsum and their optical behaviour

SIR C V RAMAN and A K RAMDAS

(Memoir No. 48 from the Raman Research Institute, Bangalore)

Received April 5, 1954

### 1. Introduction

Gypsum occurs in nature both as well-developed crystals and as polycrystalline masses. The best known of the massive forms is alabaster; this is a fine-grained white solid. Another naturally occurring variety of gypsum is satin-spar, which is a fibrous material presenting a highly characteristic sheen or lustre from which its name is derived. The present paper is chiefly concerned with a form of gypsum which has come under our notice and which is distinct from either alabaster or satin-spar. It is noteworthy by reason of the very beautiful and interesting optical effects which it exhibits. We have been unable to find any reference to these phenomena in the mineralogical literature, and it would seem that though the material is clearly a distinct species of gypsum, this has not been hitherto recognised and its remarkable optical behaviour has remained unnoticed. We shall proceed to describe the phenomena and explain them in terms of the structure of the material. We have thought it desirable also to include in this paper some observations we have made with alabaster and with satin-spar, and their interpretation in terms of the physical constitution of these varieties of gypsum.

### 2. Nature of the material

The species of gypsum which forms the principal subject of this paper presents some external features which enable it to be readily distinguished from the other recognised varieties of gypsum, viz., selenite, satin-spar and alabaster. Like selenite, it may be readily split into slabs or sheets of any desired thickness, but the surfaces thus exposed do not exhibit the smoothness and optical perfection characteristic of the cleavages of selenite. Indeed, they are more appropriately described as planes of parting rather than as cleavages. Another distinctive feature of the material which at once distinguishes it from selenite is that the edges

of the blocks or slabs are not smooth but exhibit parallel ridges, suggesting that the material is an aggregate of rod-shaped crystals having a common orientation perpendicular to the planes of parting. Optically, the material does not show the perfect transparency in all directions characteristic of selenite; neither does it, on the other hand, exhibit the sheen or lustre characteristic of satin-spar. The fact that it readily splits into parallel sheets indicates a certain measure of similarity of its structure to that of the tabular forms of selenite. We infer that the planes of parting are parallel to the crystallographic symmetry plane of gypsum, while the rod-shaped crystals are orientated along the crystallographic symmetry axis. We shall see later that these inferences are supported by the results of a more detailed investigation and we accordingly propose to designate this species of gypsum (which appears to be by no means uncommon) as "fascicular gypsum".

### 3. The circles of internal reflection

When a plate of this species of gypsum is held in front of the eye and a distant source of light is viewed *normally* through it, the phenomena illustrated in figure 1, plate I are observed. A brilliant circle of light is seen; at the centre of this circle, the source of light appears, but is overlaid by a diffraction pattern consisting of a central disc with concentric surrounding rings. As the plate is tilted away from the normal setting, the outer circle enlarges while the inner diffraction pattern expands and becomes a second circle. This is initially somewhat diffuse by reason of its being a circular diffraction ring with fainter concentric rings on either side (figure 2 in plate I). The circle, however, sharpens when the plate is more obliquely set. With a further tilt of the plate, a third circle emerges at the centre of the whole pattern, firstly as a diffraction disc accompanied by rings and later as a well-defined circle of light (figure 3 in plate I). As the plate is held more and more obliquely, the angular diameters of all the three circles continue to enlarge, but they remain concentric with each other, and also tend to come closer together (figure 4 in plate I). The source itself continues to be visible as a bright point on the second ring in every case. The brightest parts of all the three circles are the regions in the immediate vicinity of this image of the source. However, in a dark room, the complete circles can be seen, and their angular diameters may be increased to any desired extent by giving an appropriate tilt to the plate. At the most oblique settings of the plate, the angular separations of the three circles from each other reach a minimum and then increase once again. Except when they emerge at the centre of the field and display the colours associated with diffraction, the bright circles appear white, thus unmistakably indicating their origin as due to *internal reflection*.

It should be mentioned that the photographs reproduced in figures 1 to 4 in plate I, were obtained using a sheet about 1 mm thick cleaved from a block of the material. Thin glass plates were fixed on either side with a little Canada balsam

to eliminate the effect of the optical imperfections of the exterior faces. Essentially the same phenomena are observed with either thicker or thinner sheets. With thick plates, however, the rings become a little broad and the whole field is overlaid by diffuse light; the light source also ceases to be visible on the second ring when the plate is tilted sufficiently. This is not the case with thinner plates; the source of light continues to be visible even at very oblique incidences. The diffraction effects of the kind referred to above are also more conspicuous with the thinner plates.

#### 4. Polarisation of the internal reflections

We shall now proceed to describe and illustrate the remarkable features of polarisation exhibited by the circles of internal reflection. These features may be observed by placing a polaroid between the eye and the light source either before or after the plate, and rotating either the polaroid or the plate in its own plane. Strangely enough, the effect of the introduction of the polariser is quite different according as it is set before or after the plate of gypsum. The extent to which the plate is tilted away from the normal is not a matter of importance, since a particular circle of reflection exhibits much the same features of polarisation irrespective of its angular diameter. On the other hand, the orientation of the plate in its own plane with respect to the vibration direction of the polaroid is of the utmost importance. One finds by trial that there are two directions in the plane of the plate perpendicular to each other which we may designate as OX and OZ respectively, with one or the other of which the vibration direction of the polaroid should coincide to produce the maximum effects. If the vibration direction of the polaroid bisects the angle between OX and OZ, the polarisation effects are not observed.

Figures 5, 6, 7 and 8 in plate II illustrate the changes in the relative intensities of the three circles of reflection resulting from the insertion of a polaroid. (The plate of gypsum was set obliquely, and the camera recorded only the more intense parts of the circles.) The legends entered below each figure indicate the location of the polaroid and its setting. P indicates that the light was polarised before entering the plate of gypsum, while A indicates that light was unpolarised at entry but passed through a polaroid after reflection. On a comparison of figures 5 and 6 it will be seen that a transfer of the polaroid from the front to the back of the plate results in reversing the behaviour of the first and the third circles of reflection leaving the second or middle circle unaffected. A comparison of figure 7 with figure 8 shows a similar change in the opposite direction, while a comparison of figure 5 with figure 7 or of figure 6 with figure 8 exhibits the effect of setting of the vibration direction of the polaroid along OZ instead of along OX.

The significance of the facts stated above is clear, namely, that in the internal reflections which give rise to the first and third circles, the vibration direction

changes from OX to OZ or *vice versa* in the act of reflection; the former change gives us the first circle of reflection, while the third circle of reflection is associated with a change of the vibration direction from OZ to OX. On the other hand, in the middle or second circle of reflection, there is no change of the vibration direction, OX remaining as OX and OZ as OZ.

If both a polariser and an analyser are used, their effects are combined, as will be seen from figure 9 to figure 12 reproduced in plate II; the legends below each figure give the settings of both the polariser and analyser. It will be noticed that when they are crossed, the second or middle circle is greatly weakened, while the first appears with maximum intensity and the third circle is totally extinguished or *vice versa*. On the other hand when the polariser and the analyser are set parallel, both the first and the third circle appear greatly weakened, while the second or middle circle appears with maximum intensity.

It may be remarked that the photographs reproduced as figures 5 to 12 in plate II, were recorded with a specimen which exhibited the polarisation effects most conspicuously. Other specimens indeed show similar effects but not always in such a striking manner. The degree of perfection of polarisation was also found to vary over the area of the specimens.

## 5. Origin of the reflections

It is evident that the phenomena described above are all interconnected and that an explanation of the same has to be sought for on the basis of the geometric and optical characters of the polycrystalline aggregate. Earlier in the paper, we have suggested that the material consists of rod-shaped crystals having a common orientation for their crystallographic symmetry axis. The latter is an axis of the optic ellipsoid of gypsum. Had the two other optic vibration directions also been the same for all the rods, the material would be optically homogeneous and indistinguishable from selenite. Hence we are compelled to assume that the two other optic vibration directions in the plane perpendicular to the rods are not identical for all of them.

Holding a plate of the material between crossed polaroids and viewing an extended source of light through it, we find on rotating the plate in its own plane, two mutually perpendicular settings in which there is a maximum restoration of light and two others intermediate between them which there is nearly but not quite complete extinction of light. A *small* bright source of light viewed through the combination at the latter settings is, however, extinguished more or less perfectly.

The situation indicated above may be summed up by the statement that the plate considered as a whole has two mutually perpendicular directions as its optic vibration directions, though the individual rods in the aggregate may deviate therefrom to a greater or less extent. That this is the actual situation is indicated

by the appearance of the plate under a microscope when viewed between crossed polaroids. Rotating the plate in its own plane, two settings are found in which there is a minimum of light in the field but by no means complete extinction everywhere. The greater part of the plate appears dark, but there are areas in which there is a notable restoration of light. At these two settings, the directions in the plate designated as OX and OZ in the description of the polarisation effects are also the vibration directions of the polariser and the analyser. It is noticed further that the regions on the plate which give the most marked extinctions are those which give the most perfect polarisation of the circles of reflection, while the areas in which the extinctions are imperfect, also show marked imperfection of the polarisation of the circles of reflection.

## 6. The geometric character of the reflections

It is a familiar result in geometrical optics that when a pencil of light is incident on a cylindrical rod in a direction making an angle  $\theta$  with its generators, the rays reflected by its surface lie along the generators of a right circular cone whose semi-vertical angle is also  $\theta$  and which has its axis parallel to the length of the cylinder. In the present case, however, the reflections occur at intercrystalline boundaries within a birefringent solid, and hence the angles of incidence and of reflection of the light at these boundaries are not necessarily equal. Actually, as a result of the birefringence of the material, an incident pencil of light would divide on entry into the plate into two pencils polarised differently which travel in different directions with different velocities. A further subdivision would occur in the act of reflection at the boundaries, giving us four reflected pencils in all. However, owing to the special circumstance that the external surfaces of the plate are normal to an axis of its optic ellipsoid, two of these pencils would obey the ordinary laws of reflection and would emerge from the plate in identical directions, though their planes of polarisation are mutually perpendicular. For the two other pencils, the angle of reflection would be greater or less than the angle of incidence as a consequence of the planes of polarisation and therefore also the wave-velocities being different for the incident and reflected pencils. Thus, in the final result, we would have, instead of a single cone of reflected rays, three such cones exhibiting the polarisation effects already described; the central or the middle one would have the direction of the light source as one of its generators, and hence the source would appear as a luminous point on that circle.

The correctness of the explanations set forth above is confirmed by few simple calculations and observations. The angles of incidence and of reflection of light inside a birefringent medium are connected by the relation  $\mu_i \cos \theta_i = \mu_r \cos \theta_r$ , where  $\theta_i$  and  $\theta_r$  are the glancing angles which incident and reflected rays make with the reflecting boundary, and  $\mu_i$  and  $\mu_r$  are the corresponding refractive

indices. In our present problem, the two refractive indices under consideration are 1.521 and 1.530. For normal incidence on the surface of the plate,  $\theta_i = 0$ , while the values of  $\theta_r$  comes out respectively as  $6^\circ 18'$ ,  $0^\circ$ , and imaginary for the three circles of reflection. Accordingly, the angles of emergence for the first and second circles come out as  $9^\circ 39'$  and  $0^\circ$  respectively while the third circle is non-existent, in close agreement with the observations. For the case in which the third circle is just visible, the angular radii of the first, second and third circles on emergence come out as  $13^\circ 42'$ ,  $9^\circ 39'$  and  $0^\circ$  respectively, once again in close agreement with the results of observation.

The reflections at the intercrystalline boundaries arise from the fact that the optical polarisabilities of the material on either side of such a boundary differ in magnitude or direction or both. The birefringence of gypsum being very weak, such differences would necessarily be small. The strong reflections actually observed are a consequence of the incidence of the light being very oblique in the cases under study. This is clear from the fact that the circles of reflection display their maximum intensity in the regions not too remote from the image of the light source appearing located on the second circle (see figures 2, 3 and 4, plate I). The variation of intensity exhibited by the first circle of reflection over its circumference (figure 1 in the same plate) has a different origin: it exhibits the fact that the reflecting power is a function of the azimuth of incidence of the light on the boundary, besides being dependent on the angle of incidence which in this case has the maximum value of  $90^\circ$ .

A few brief remarks must suffice in explanation of other features which are observed and which have been referred to earlier. The diffraction phenomena associated with the circles of internal reflection are evidently a consequence of the limitation of the effective aperture due to the oblique incidence of light on the reflecting surfaces. They naturally become most conspicuous when such incidence is nearly grazing. Phenomena closely resembling them may be observed when light from a distant source is reflected obliquely at the surface of a short cylinder of glass.

The reflections of light at the intercrystalline boundaries in the material would necessarily result in a progressive extinction of the incident light beam in traversing the material. The greater the thickness of the plate and the more it is tilted away from the normal, the larger would be the number of reflecting surfaces traversed by the incident light, and hence also the more rapid would be its extinction, as is actually observed.

The diffuse radiation which appears overlying the circles of reflection, especially with thick plates, and the broadening of the circles of reflection which is noticed with such plates when they are held obliquely may be the result of a lack of perfect parallelism in the orientation of the rod-like crystals within the material. Another factor which would also result in a diffusion of light is the *refraction* of the light beams in their passage through the successive intercrystalline boundaries. That such refraction does play an important role is suggested

by the partial polarisation of the second circle of reflection which is noticed when the plate is tilted considerably away from the normal.

## 7. Optical behaviour of transverse sections

In the foregoing, it has been assumed that the rod-like crystals of which the material is composed are parallel to each other and to the crystallographic symmetry axis. If this were strictly the case, a plate of the material so cut that its faces are parallel to the rods should exhibit the following optical behaviour: (1) a light beam polarised with its electric vector parallel to the rods should be freely transmitted by the plate without diffusion or extinction; (2) on the other hand, if the electric vector is perpendicular to the rods, the optical heterogeneity of the material should exhibit itself and result in a strong diffusion and extinction of the light in its passage through the plate, the diffused radiation appearing as a fan of rays in a plane transverse to the rods.

These indications of theory can be tested by observation and are found to be in general accord with the facts but not completely so. A distant source of light viewed through such a plate held normally continues to be visible in focus. Further, it is also completely polarised with its electric vector parallel to the length of rods. However, one also observes a fan of diffracted rays accompanying the transmitted light spread out in a plane transverse to the rods, and this exhibits a partial polarisation in the same sense as the transmitted light. A tilt of the plate away from its normal setting results in extinguishing the transmitted light, if such tilt is in a plane parallel to the rods. On the other hand, a tilt in the perpendicular plane has no such effect.

From the foregoing observations one infers that the structure of the material is approximately but not quite accurately that assumed. This also becomes evident when a plate cut in the same fashion is examined between crossed polaroids under a microscope. A complete extinction is not obtained in any setting of the plate. There is, however, a notable diminution of intensity of the light seen in the field, when the direction of the rods coincides with the vibration direction of either the polariser or the analyser.

## 8. Some observations with alabaster

Alabaster is opaque to light, evidently as a consequence of the birefringence of gypsum, though light can penetrate by diffusion through very considerable thicknesses. Then extent of such penetration is highly variable and such variations appear to be connected with the structure of the material including especially the size of the crystallites of which it is composed.

It appeared to be of interest to investigate whether a transmission of light in the

true optical sense could be observed with alabaster if it be thinned down sufficiently. With coarse-grained varieties the test does not succeed, since we soon arrive at a stage at which the thickness of the test plate is comparable with the size of the individual crystallites which can then be observed to transmit light independently of each other. Fine-grained varieties of alabaster, however, can be thinned down sufficiently to enable a true optical image of a distant and brilliant source of light to be seen through the plate. The image appears overlaid by a diffuse halo, the structure and angular extension of which are determined by the thickness of the plate and the grain size of the substance. The optical transmission is readily distinguished from the overlying halo by its brilliance and its perfect sharpness. It is completely extinguished when the plate is held between crossed polaroids, whereas the halo continues to be visible in the same circumstances though with diminished intensity.

## 9. The structure and optical behaviour of satin-spar

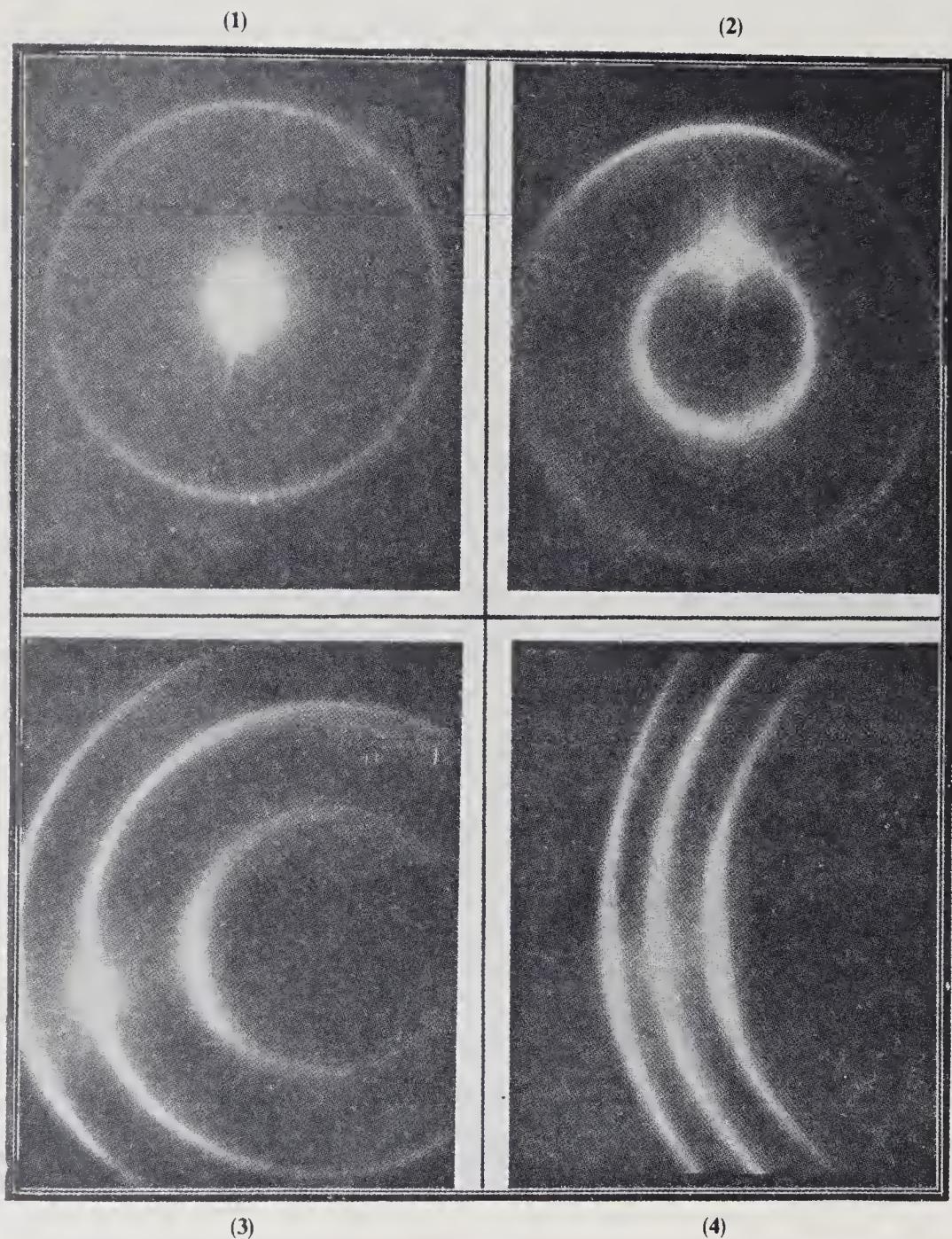
The fibrous nature of satin-spar is conspicuously evident from its very appearance. A beam of light is spread out by reflection at the surface into a fan of light in a plane transverse to the length of the fibres. A plate of the material having its faces parallel to the fibres differs very strikingly in its behaviour from that described in section 7 above. A distant source of light is invisible when viewed through it, all that is observed being a fan of diffracted rays transverse to the fibres and this is found to be completely unpolarised. This behaviour is readily explicable as a consequence of the birefringence of gypsum and the known crystallographic orientation of the fibres.

As is to be expected, light is found to penetrate along the fibres rather more freely than in the transverse direction. A distant bright source of light can indeed be seen if viewed through a rod of the material exactly along its fibres, but appears spread out into a diffuse patch of light. If the rod be tilted a little, this transforms into a diffuse circle of light with a darker area within, the diameter of which increases with the tilt. The brilliancy and sharpness of the phenomena observed with fascicular gypsum are conspicuously absent in the present case, neither are any polarisation effects observed.

## 10. Summary

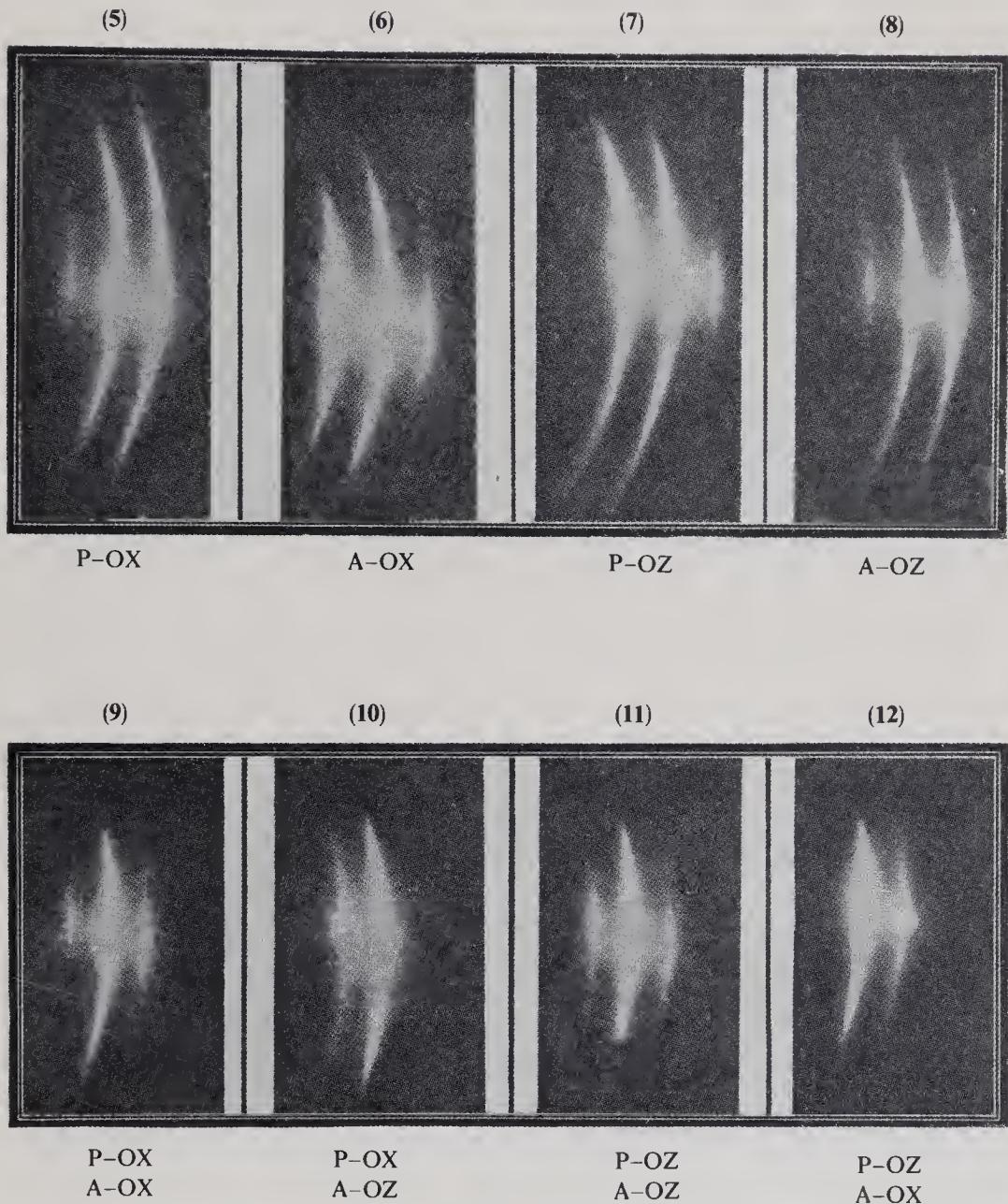
The paper brings to notice the remarkable optical effects exhibited by a polycrystalline form of gypsum which is different from both alabaster and satin-spar in its structure. It is not a fibrous material but consists of fine rods orientated nearly parallel to the *b*-axis of gypsum and exhibits a ready cleavage along planes perpendicular to that axis. A source of light viewed through a plate of the material

exhibits, in general, three concentric circles which are polarised in a characteristic fashion. The source itself appears as a luminous point on the second or middle circle. It is shown that these circles arise by reason of the reflection of light at the boundaries between the rod-like crystals composing the material, for which the name "fascicular gypsum" is accordingly proposed. A theoretical explanation of the phenomena is given and photographs of the same are reproduced. Observations on the optical behaviour of alabaster and of satin-spar are also reported.



Figures 1-4

Plate I



Figures 5-12

Plate II

## X-ray studies on polycrystalline gypsum

SIR C V RAMAN and A JAYARAMAN

(Memoir No. 56 from the Raman Research Institute, Bangalore)

Received August 16, 1954

### 1. Introduction

Gypsum is one of the most important of the commoner minerals and the different forms in which it is found and their structural characters are therefore matters of considerable interest. Brauns' *Das Mineralreich*<sup>1</sup> and Hintze's *Handbuch der Mineralogie*<sup>2</sup> contain illustrated accounts of the subject. We are concerned in this paper with the polycrystalline forms of gypsum. Of these the best known is the white and semi-opaque material known as alabaster. Mineralogists recognise another form which they designate as "fibrous gypsum". As the name indicates, this form is an aggregate of parallel fibres or rods. Hintze mentions that when the fibres in such gypsum are very fine, their direction is parallel to the mineralogical *c*-axis, while if the material consists of coarser fibres, their direction may depart to a greater or less extent therefrom.

In a recent paper in these *Proceedings*,<sup>3</sup> it has been shown that we must recognize *three* polycrystalline forms of gypsum with specific characters which are readily distinguishable from each other. The first is *alabaster* which is an aggregate of small crystals more or less randomly orientated: the second is *satin-spar* which is a truly fibrous variety of gypsum in which the fibres lie along the mineralogical *c*-axis, while the third form has been designated as *fascicular gypsum* and is an aggregate of rods more or less exactly parallel to the *b*-axis which is also the symmetry axis of the crystal-structure. This third form is readily distinguished from the other two by its external appearance. It exhibits optical phenomena of great beauty and interest which have been fully described and explained in the paper referred to above. In the present communication, we report the results of X-ray studies undertaken to confirm and reinforce the conclusions already reached in that paper from the optical evidence. We have thought it desirable to carry out such an investigation for the reason that the third form of gypsum is of common occurrence and it would seem that those who have noticed it have mistaken it for the second or fibrous species. Our X-ray studies show clearly that the direction of the rods in *fascicular gypsum* is along the *b*-axis, while in the truly fibrous forms it is along the *c*-axis. Further, while the X-ray patterns

show that satin-spar gives a typical fibre diagram, fascicular gypsum does not do so, showing thereby that it is not fibrous in the proper sense of the word.

## 2. Alabaster

This polycrystalline form of gypsum varies greatly in its appearance in different specimens, some being chalky-white and opaque even in thin layers, while other specimens appear translucent. These differences are evidently connected with the extent to which light can penetrate through the material and this again appears to depend on the size of the crystallites of which it is composed. Selecting a translucent specimen of alabaster and thinning it down to a plate about a millimetre thick, the X-ray diffraction diagram reproduced as figure 1 in plate I was recorded. A collimated beam of  $\text{MOK}_\alpha$  radiation was employed. The slit width was one millimetre and a flat film camera was used with a specimen to film distance of three centimetres. It will be seen that the diagram exhibits spotty rings. Though the pattern is not altogether symmetric, it is sufficiently nearly so to justify our regarding the material as consisting of crystallites randomly orientated in space.

## 3. Satin-spar

The specimens employed were detached from the surface of a beautiful museum piece which externally manifests a fibrous and brilliant silky lustre. Figure 2 in plate I is an X-ray diagram taken with a flat camera and unfiltered MO radiation: the incident beam travelled along the fibre direction. The specimen employed was about a millimetre in length and of about the same cross-section. It will be seen that the pattern exhibits numerous and nearly complete concentric circular rings.

Figure 4 in plate II was recorded with a cylindrical camera and  $\text{CuK}_\alpha$  radiation. The specimen in this case was a rod about one centimetre long and about half a millimetre in thickness. It was held inside the camera with its length parallel to the axis of the cylinder and the X-ray beam traversed the specimen in a direction perpendicular to its length. The specimen was kept stationary during the exposure. Nevertheless it will be seen that the pattern is a typical rotation diagram. It was verified by measurement of the separation of the layer lines that the length of the fibre was parallel to the mineralogical *c*-axis of gypsum. The conclusion thus indicated that satin-spar is a truly fibrous material orientated along the morphological *c*-axis is, however, only valid for the material used which was detached from the external surface of the museum specimen. When a thin

plate cut from the latter with its faces transverse to the fibre direction was normally irradiated by an X-ray beam in a flat-film camera, the record appeared both spotty and irregular, thus indicating a departure from the regularity of orientation shown by the material detached from its outer surface.

#### 4. Fascicular gypsum

As already stated, this material exhibits highly characteristic external features which enable it to be readily identified. It may be readily split into slabs or sheets of any thickness, but the surfaces thus exposed do not exhibit the smoothness and optical perfection characteristic of the cleavage of selenite and are more appropriately described as planes of parting. The most distinctive feature of the mineral is that the edges of the blocks or slabs are not smooth but exhibit parallel ridges. The inference suggested by the external appearance of the material is that it is an aggregate of rods in parallel setting, their direction coinciding approximately with the *b* or the symmetry axis of gypsum.

Figure 5 in plate II is an X-ray pattern recorded with cylindrical camera and CuK<sub>α</sub> radiation. The specimen examined was a rod detached from the material and set with its length parallel to the axis of the camera. It was kept stationary during the exposure. The pattern exhibits irregularly disposed spots. The configuration of the latter indicated that the length of the rod was not quite parallel to the *b*-axis, but was slightly inclined to the latter. The rod was turned through 3½° from the previous position, but nevertheless the pattern then obtained did not exhibit the characteristic features of a rotation diagram. However, when the specimen was oscillated through 30° each way, a record was obtained which is reproduced in figure 6 in plate II and clearly exhibits layer lines. These are much closer to each other than those appearing in figure 4 in the same plate. Measurements indicated that the oscillation axis coincided with the *b* or symmetry axis of gypsum.

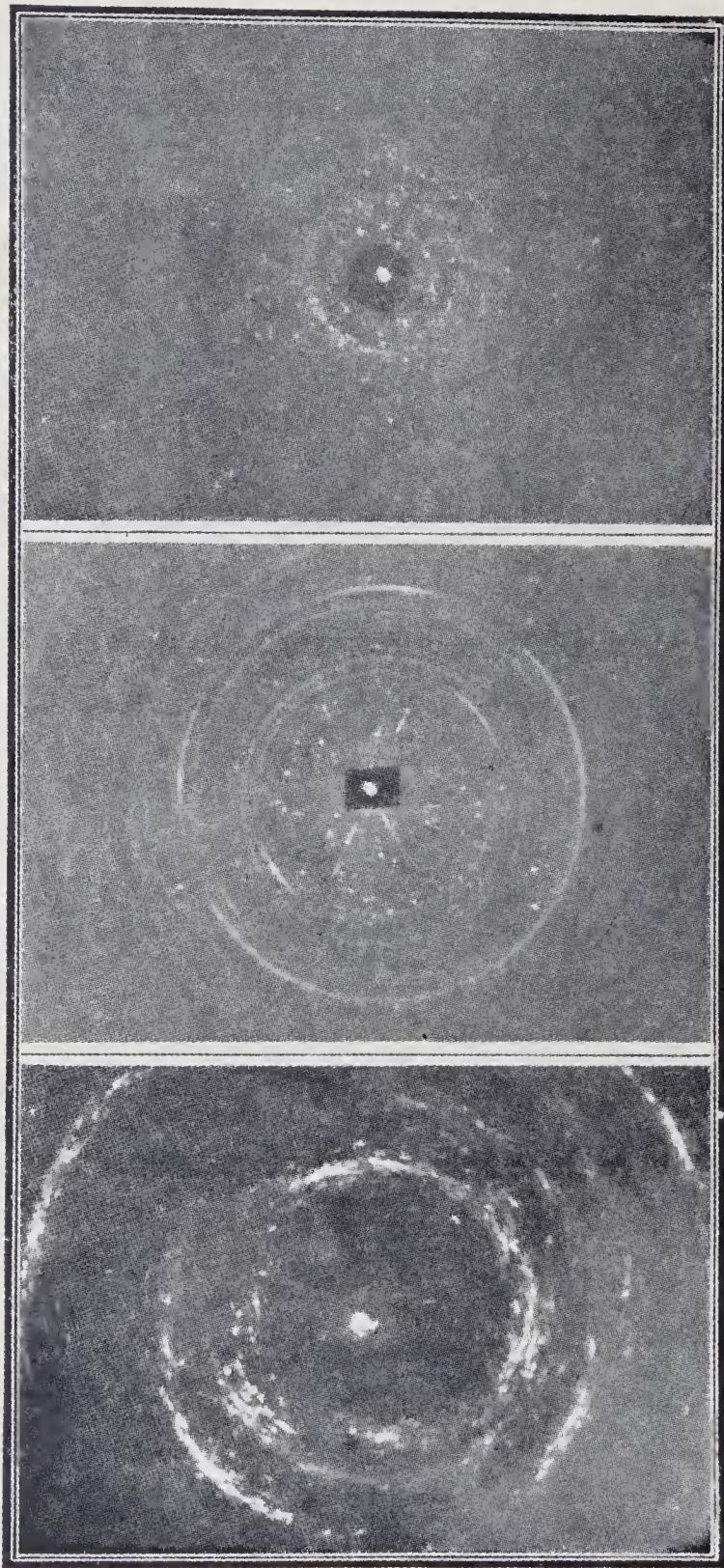
Figure 3 in plate I shows an X-ray diagram obtained with a flat film camera and the MO radiation, the beam being parallel to the length of the rods. It will be seen from the pattern that the X-ray reflections recorded appear as patches located roughly on short arcs of circles. The picture indicates that while the rods consist of individual crystals having their *b*-axes parallel, the variations of orientation of the other two crystallographic axes are insufficient in magnitude to give a complete pattern of circular rings. The inferences regarding the nature of the material indicated both by the longitudinal and transverse X-ray photographs thus support each other. The X-ray results are also in agreement with the conclusions already drawn from the optical investigations and described in the earlier paper.

### 5. Summary

X-ray diffraction patterns have been recorded and are reproduced in the paper showing clearly the existence of *three* polycrystalline forms of gypsum with specific structural characters which are readily distinguishable from each other: (a) alabaster; (b) satin-spar, which is a truly fibrous material with the fibres orientated along the mineralogical *c*-axis; and (c) fascicular gypsum which is an aggregate of rods having their *b*-axes or crystallographic symmetry axes parallel to each other and the two other axes showing only a limited range of variation, and hence not fibrous in the proper sense of the word.

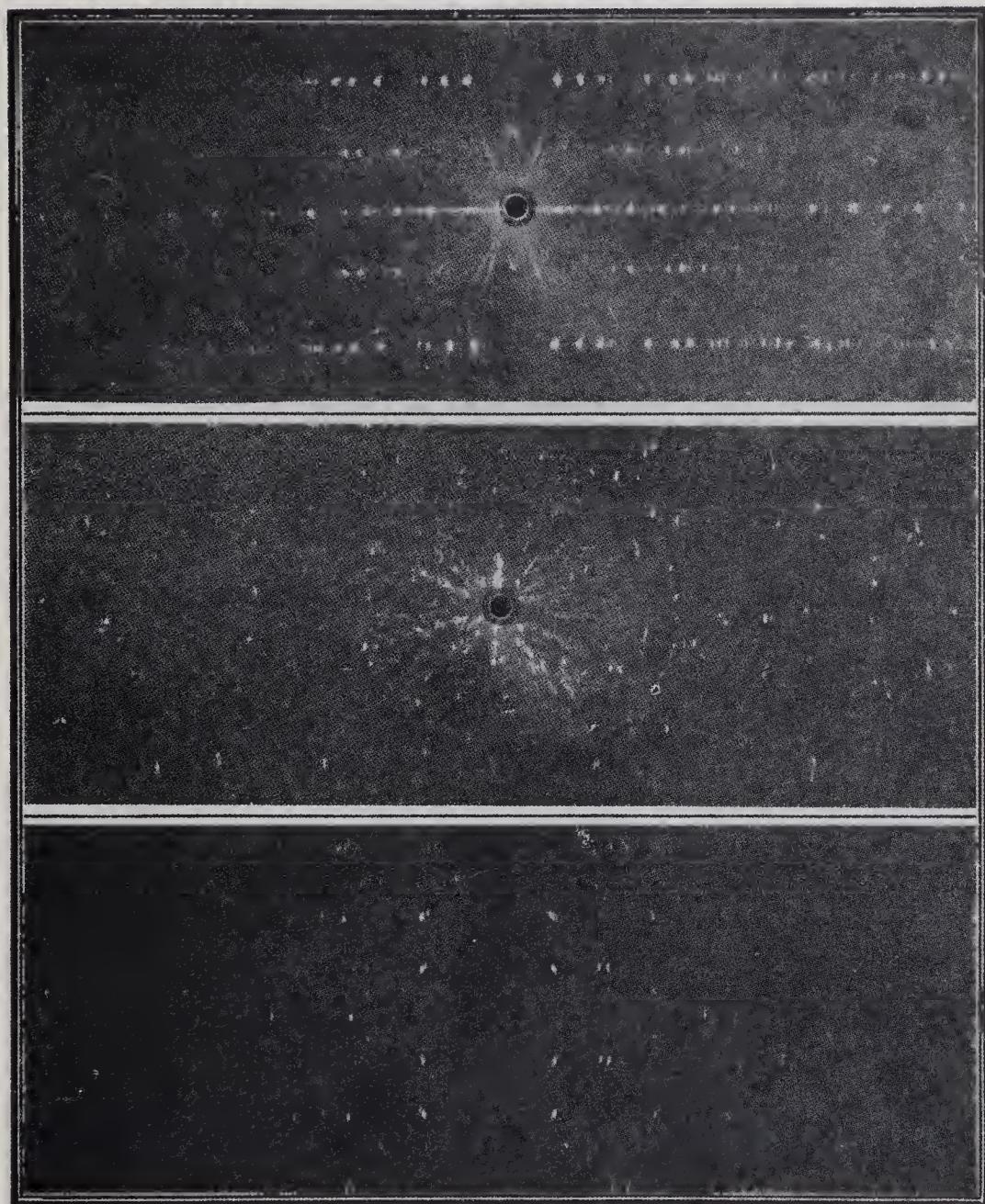
### 6. References

1. Brauns R, *Das Mineralreich*, J F Schreiber, 1912, 408–14.
2. Hintze Carl, *Handbuch der Mineralogie*, Erster Band. Dritte Abteilung, Zweite Halfte, Walter De Gruyter and Co., 1930, 4274–4323.
3. Raman C V and Ramdas A K, *Proc. Indian Acad. Sci.*, 1954, **39A**, 153.



Figures 1-3

Plate I



Figures 4-6

Plate II

## The luminescence of fluorspar

SIR C V RAMAN

Calcium fluoride ( $\text{CaF}_2$ ) appears widely distributed in nature in the form of the mineral known as fluorspar or fluorite. In the year 1529, the usefulness of fluorspar as a flux in metallurgical processes was recognised, and after a lapse of four centuries this application of the material continues to be one of its most important uses, especially in the metallurgy of steel. Fluorspar is the only common mineral containing a large proportion of the element fluorine and it is therefore employed for the production of hydrofluoric acid by treatment with sulphuric acid, and therefrom also the production of the many organic and inorganic compounds of fluorine which find application in the arts and industries. Fluorspar is also used in the ceramic industries as an opacifier in the production of enamels and of glass. There are also other miscellaneous uses. It will be readily understood that in these circumstances, fluorspar is a much sought-after mineral. Indeed, at the present time, the world production of this material is over a million tons per annum.

Many countries possess workable deposits of fluorspar amongst which may be mentioned particularly the United States of America, the USSR, Great Britain, Germany, Spain and so forth. Until the present time, the deposits of fluorspar known in India were few and of small productivity. The recent discovery at Amba Dongar in the Baroda District of substantial deposits of fluorspar is therefore an event of more than ordinary interest and importance. The announcement which appeared in the Press greatly interested the author and led him immediately to contact the Geological Survey of India. Through the kindness of the officers of the Survey, he was enabled to obtain an ample supply of this fresh material. This served as an encouragement to the author to undertake a fact-finding investigation aimed at discovering the nature and origin of the luminescence exhibited by fluorspar, a phenomenon with which he had long been familiar and which had interested him for many years.

Fluorite, it should be mentioned, is a material of importance to the physicist for other reasons. It has a low refractive index and a low dispersive power in the visible region of the spectrum,  $\mu$  being equal to 1.432 and 1.440 respectively at its red and violet ends. It has also a very low aqueous solubility. The melting point of  $\text{CaF}_2$  is  $1360^\circ\text{C}$ , and synthetic optical crystals of as large a size as 150 millimetres in diameter and 125 millimetres in length have been successfully prepared by the well-known method of melting, casting and annealing in cylindrical platinum

containers. The material thus fabricated is transparent throughout the spectral range from 0·125 microns to 9 microns. It finds uses as windows and prisms in ultra-violet, visible and infra-red spectroscopy, in telescope and microscope optical systems, apochromatic lenses and camera objectives.

Fluorite as found in nature displays some remarkable peculiarities of behaviour. It crystallises beautifully, the simple cube being the form most commonly found, though octahedra and other forms are also known. It also exhibits a perfect octahedral cleavage. Surprisingly enough, however, colourless crystals are rather rare; in the majority of cases, the mineral exhibits colours which both in respect of hue and saturation exhibit a great range of variation. By reason of the beautiful crystallisation and of the attractive colours displayed, fluorite specimens are spectacular exhibits in a museum. Some fifty such exhibits from different countries and from India are included in the author's collection. They are representative of the forms and colours exhibited by the mineral. Included in it are several single crystals which are transparent and colourless, as also single crystals in the form of octahedra and cubo-octahedra exhibiting nuances of colour; also clusters of cubes or octahedra attached to the matrix from which they crystallised out, aggregates of various kinds and also massive lumps. All colours ranging from yellow through green and blue to violet and purple are represented in the collection.

Another remarkable optical anomaly exhibited by the natural fluorite was long ago noticed and remarked upon by mineralogists. This is the fact that though it is a cubic crystal and hence should be optically isotropic, it very commonly exhibits a weak birefringence. This usually appears in the form of bands parallel to the cubic planes when a section is viewed between crossed nicols. A lamellar structure parallel to the faces of the cube is thus indicated for the material.

Still another property of fluorite as exhibited by some richly tinted specimens is the appearance of colours as seen by reflection at the surface of the crystal which are different from those seen by transmission through it. It is this phenomenon which led to the name "fluorescence" being given to effects of the same nature exhibited by other materials as well.

The present communication is a first report on the facts which have emerged from a study of the material at the author's disposal. With such an extensive collection of material, even the simplest observations when made on a comparative basis serve to reveal the broad features of the case and to indicate the lines on which a more detailed and comprehensive investigation should proceed. We may, therefore, begin with the simplest of all the methods of study, viz., the visual observation of the luminescence as exhibited by the various specimens. For this purpose, the most convenient way of examining the specimens is to view them in a darkened room under ultra-violet illumination. This is provided by a mercury arc of small size completely enclosed in a bulb of black glass which transmits the near ultra-violet radiation of the arc freely but cuts out all visible light except at the extreme red end of the spectrum. The luminosity of the

specimen under ultra-violet excitation can then be readily observed. The red light escaping through the black-glass envelope of the lamp makes itself evident to the observer by reason of the reflection or diffusion of the light by the specimen. But this is readily recognised by its colour, and its disturbing effect may be greatly reduced by giving the surfaces of the specimen a smooth polish. By using specimens in the form of polished plates, the effect may even be completely eliminated. With a set of three lamps held together and backed by aluminium reflectors, the intensity of the ultra-violet excitation is notably enhanced. It is then possible to detect even the weakest luminescence.

The spectacular character of the effects exhibited by fluorspar under ultra-violet irradiation is illustrated in figure 1 which is a photograph of one of the specimens in the author's collection as thus seen. The largest dimension of the piece is some 20 centimetres. It is a close aggregate of cubic crystals of various sizes adhering to the matrix from which they were formed. The surface of the crystals is mostly covered by a thin deposit of quartz, and the specimen has therefore a very unattractive appearance in ordinary circumstances. But under the ultra-violet lamp, the superficial deposits are invisible and the entire specimen glows with a resplendent blue. This is the characteristic colour of the luminescence of fluorspar which is much the same for all the specimens which exhibit the phenomenon, though the intensity of the glow varies enormously from specimen to specimen, and in a few cases the glow appears of a darker hue.



Figure 1. Luminescence of fluorspar.

A remarkable feature exhibited by the crystal aggregates from Amba Dongar is that the luminescence is manifested in strata running roughly parallel to the external faces of the aggregate, a luminescent layer being located between layers on either side which are non-luminescent. The luminescent layer can be distinguished even in daylight from the non-luminescent layers on either side by its appearance and transparency, the luminescent layer being more transparent and colour-free than the non-luminescent ones.

That fluorspar can crystallise in two distinct forms which are respectively luminescent and non-luminescent is demonstrated in a very striking fashion by the single crystals from Amba Dongar of which many are in the author's possession. The surprising fact emerges that part of the volume of the same crystal may be luminescent and the other part may be non-luminescent, the boundary between the two parts being a sharply defined plane. Irregular lumps which do not exhibit well-defined crystal faces may be ground down into the form of plates and their two faces then polished. It is then found that part of the area of the plate may be luminescent and the other part non-luminescent, the boundaries between them being sharply defined. A great number of section-plates of this kind showing these features have been prepared in the course of the investigation.

The most perfect specimens of fluorite in the author's collection exhibit the usual blue luminescence. This is weak, but readily observable. On the other hand, there are numerous single crystals, both large and small, in the collection in which the effect is unobservable and which therefore must be designated as belonging to the non-luminescent class of fluorite. The question arises whether the artificially prepared fluorite of optical quality would or would not exhibit luminescence. This question can only be answered by actual study of such material. Three specimens were available for examination, which were obtained respectively from Great Britain, USA and Germany. The British and American specimens were found to be blue-luminescent, though only weakly so and to an extent comparable with natural fluorite of the best quality. On the other hand, the product from Germany showed not a trace of the phenomenon.

The most important questions regarding the luminescence of fluorite which need to be answered are firstly, why does it appear in the region of the spectrum where it is observed, and secondly, why it does vary so enormously in its intensity from specimen to specimen? Highly instructive in regard to both of these issues is the result of a spectroscopic study of the luminescence. Visually observed, the spectrum appears as a continuous band extending from the violet into the blue and perhaps a little beyond. This is confirmed by a photographic record of the spectrum. A remarkable change in the character of the emission however appears when the specimen is held continuously at the temperature of liquid air during the exposure. This change is exhibited by the spectrographs reproduced as figure 2. The two spectra (*a*), (*b*) appearing at the top of the picture were recorded with different exposures with the specimen held at room temperature, while the three spectra below (*c*), (*d*) and (*e*) were likewise recorded but with the specimen cooled

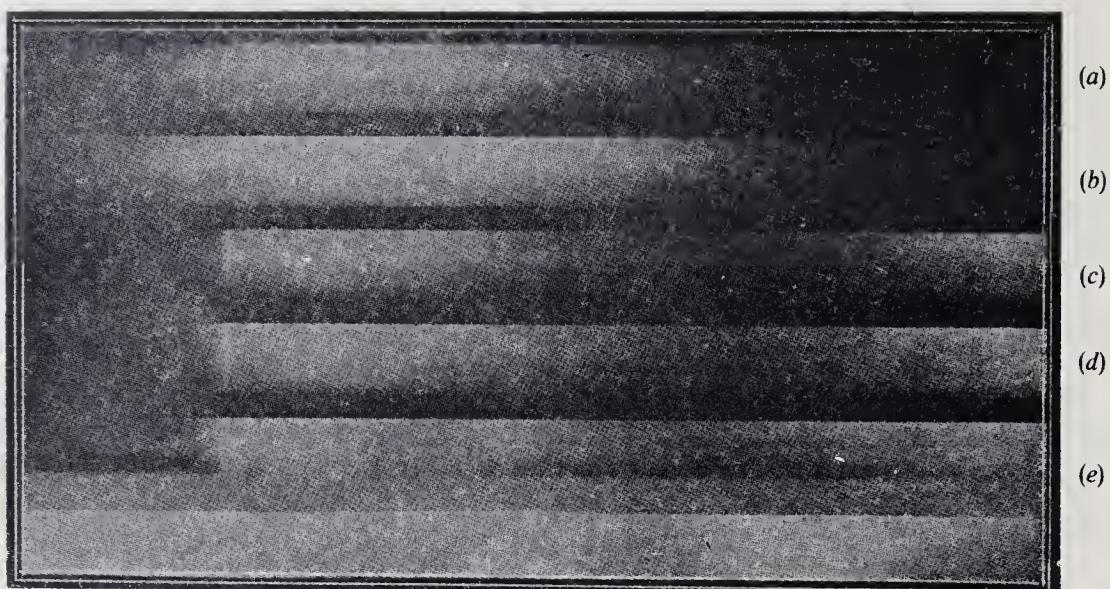


Figure 2. Luminescence spectra of fluorite. (a), (b) Room temperature; (c), (d), (e) liquid air temperature.

down to liquid air temperature. The heavily-exposed spectrum at the foot of the record is that of the mercury arc after removal of the black glass filter held in front of it for exciting and photographing the luminescence spectrum. It will be noticed that the lowering of the temperature of the luminescent fluorite has resulted in the continuum extending to the violet end of the spectrum being replaced by a sharply defined emission located at  $4125\text{ \AA}$ , followed by a set of imperfectly resolved bands extending into the blue; further, an emission appears in the region of longer wavelengths which is not recorded when the specimen is at room temperature.

The emission at  $4125\text{ \AA}$  has been recorded with several different specimens and it is clearly a characteristic feature of the luminescence of fluorspar. That it appears only when the crystal is cooled down to low temperature is a readily understood feature. Such a sharpening of the emission spectra at low temperatures is known in other cases, as for example, the luminescence of the uranyl salts. We are, therefore, justified in inferring that the luminescence of fluorspar is an inherent property of the crystals which show the phenomenon and that it indicates the presence of specific electronic levels between which a transition can occur in their cases.

Comparative study of the luminescence of numerous specimens of fluorite shows very clearly that the intensity of luminescence is correlated with the appearance of visible colour in the specimens. In particular, it is noticed that fluorite exhibiting lighter shades of green emits a luminescence of extraordinary intensity, but that on the other hand, the strength of the luminescence is less when the colour of the fluorite is of a deeper green. These facts indicate that visible

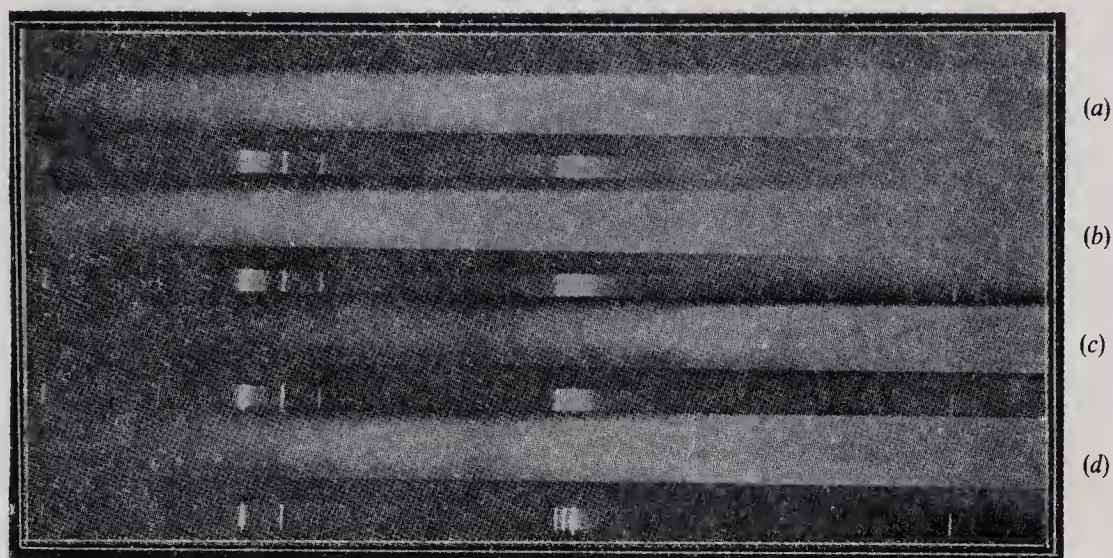


Figure 3. Absorption spectra of green fluorite. (a), (b) Room temperature; (c), (d) liquid air temperature.

colour in fluorite arises from the possibility of inner electronic transitions, which if they occur in one direction result in luminescence and if in the opposite direction result in absorption and the manifestation of visible colour by the specimen.

Accepting the foregoing view of the origin of the colours observed in natural fluorite, we should expect to find that their absorption spectra should, as in the case of the emission spectra, resolve themselves into well-defined bands when the material is cooled down to liquid air temperatures. That this is actually the case is shown by the spectra reproduced in figure 3. They were obtained with a piece of fluorspar exhibiting a bright green colour and which also showed a strong luminescence. The two spectra at the top of the picture record the light of a tungsten filament lamp after transmission through the piece of fluorspar when the latter is held at room temperature. The two lower spectra represent the effect of cooling down the specimen in the temperature of liquid air on the transmission. The appearance of specific absorption bands is very clearly seen in the latter two spectra. The mercury arc spectrum has been recorded in the plate to indicate the positions where the bands appear.

The appearance of weak birefringence patterns in natural fluorite is a feature of great interest calling for an explanation. The present investigation has revealed that this is a field of investigation which is not unrelated to the explanations of the luminescence and of the colours exhibited by natural fluorite. Amongst the facts which indicate such a connection is that a marked difference is noticeable between the appearance of the luminescent and non-luminescent areas in a section-

plate of fluorite when it is viewed between crossed polaroids. In several cases, also, it has been noticed that the luminescence resolves itself into a set of parallel laminae in positions adjacent to or coincident with the lamellae visible in birefringence. The further unravelling of these relationships can, however, well await the results of a more detailed and elaborate investigation of the whole subject.

## The two species of fluorite

SIR C V RAMAN

Amongst the many interesting properties of the mineral fluorspar or fluorite is the luminescence which it exhibits under ultra-violet illumination. In many cases and especially with the larger specimens, the effect observed is indeed spectacular. The nature and origin of the phenomenon are thus problems of great scientific interest. In an earlier article (*Curr. Sci.* 31, 361 (1962)), the present author gave a preliminary account of his investigations in this field. One of the significant discoveries recorded in that article is that when fluorite is cooled down to the temperature of liquid air, the spectrum of its luminescence undergoes a remarkable transformation. The diffuse band stretching from the violet end into the blue region of the spectrum seen at ordinary temperature is replaced by a sharply defined emission line or band centred at 4132 Å of which the spectral width is only a few Angstroms. This is accompanied by various subsidiary features which are noticeable in the part of the spectrum at greater wavelengths. Further studies have shown this behaviour to be entirely characteristic of fluorspar. The emission located at 4132 Å appears at the same position in all cases, irrespective of the place of origin of the mineral or the absolute intensity of its luminescence which indeed in some cases is enormously greater than in others.

The observations reported in the earlier article were made with naturally occurring fluorite specimens. It seemed to be of great importance to carry out similar studies with synthetically prepared fluorite of optical quality which is now commercially available. This material, as is well-known, is prepared from carefully purified  $\text{CaF}_2$  by fusion and slow solidification. It is perfectly colourless and isotropic and its transparency extends into the far ultra-violet. Three specimens of such fluorite were available for the studies. One of them was a rectangular block 37 mm × 37 mm in area by 9 millimetres thick which was supplied by a well-known British firm. A piece 6 millimetres wide was sawn off from the block and employed for the study of the infra-red absorption spectra of plates of fluorite of various thicknesses. The results of this study will be reported in a separate communication. The second specimen was a polished window of synthetic fluorite 25 mm × 25 mm in area and 2 millimetres thick which was gifted to the author by Dr E K Plyler of the National Bureau of Standards at Washington. A third specimen was a smaller plate 1.7 millimetres thick which was sent by Professor R Mecke from his Institute at Freiburg. The infra-red transmission by the two plates was spectrophotometrically studied and did not

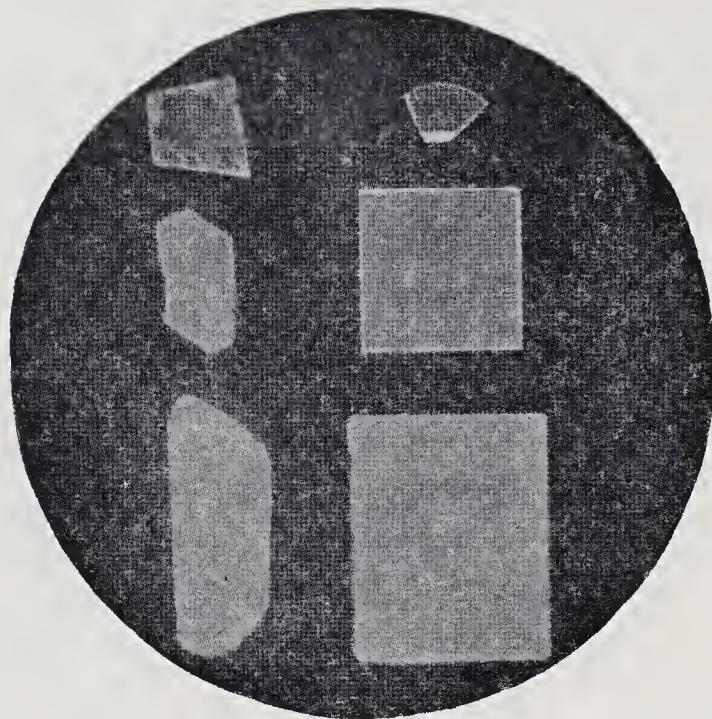


Figure 1. Six specimens of fluorite under ultra-violet illumination.

exhibit any noticeable differences as between themselves. The infra-red behaviour of the British specimen studied with thicknesses of 2 millimetres and one millimetre respectively was also similar to those of American and German manufacture.

Figure 1 is a photograph of six specimens of fluorite as seen under intense ultra-violet illumination. They were placed on a sheet of black paper and an appropriately chosen filter was placed before the lens of the camera to cut off the ultra-violet radiation scattered by the black paper or reflected at the surfaces of the specimens. The three specimens seen on the right-hand side of the picture are the synthetic crystals of German, American and British origin respectively. The three specimens seen on the left of the picture are pieces of natural fluorite whose thicknesses were about the same as that of the synthetic specimens set alongside of them and seen on the right-hand side of the photograph. It will be noticed that the two specimens (one natural and the other synthetic) at the top of the picture are non-luminescent. The two other pairs of specimens, on the other hand, exhibit a readily observable luminescence, of which the intensity is noticeably greater in the case of the natural fluorite.

It should be mentioned here that the spectrum of the luminescence of the synthetic fluorite supplied by the British firm has been studied with the material held at liquid air temperature. A very satisfactory spectrum has been recorded



Figure 2. Luminescent and non-luminescent fluorspar.

with it, exhibiting the well-defined feature at  $4132\text{ \AA}$  accompanied by other details in the region of greater wavelengths. Figure 1 may in the circumstances be regarded as a demonstration of two results of fundamental importance. In the first place, it is clear that luminescence is a characteristic property of fluorite. Secondly, there are two species of fluorite, (either natural or synthetic), of which one exhibits luminescence and the other does not. The difference between the two species is not a difference in degree, but an absolute difference in the sense of luminescence being either present or being totally absent. The total absence of luminescence in one species and its visible presence in the other specimens becomes most clearly evident when the specimens of the two species are set side by side under ultra-violet illumination of the greatest obtainable intensity and against the darkest possible background and are compared visually. Such a comparison made photographically instead of visually is exhibited in figure 2. The specimen of fluorspar on the left is one of the numerous examples of the mineral finding a place in the museum of the Raman Research Institute. It is a block of colourless fluorite which is an aggregate of cubic crystals, and was selected for the comparison by reason of the fact that the luminescence which it exhibits is of extremely low intensity. The specimen on the right is a large transparent single crystal in the shape of a cubo-octahedron with well-defined faces. Under the ultra-violet lamp, it is scarcely visible. Indeed it is only seen in the



Figure 3. Luminescent layer in Amba Dongar fluorite.

photograph by reason of the reflection at its faces of the illumination from the neighbouring luminescent sample.

Why one species of fluorite exhibits luminescence and the other does not is a problem in itself. Much useful light is thrown on this question by the author's studies of the material from the newly discovered deposit of fluorite at Amba Dongar near Chota Udaipur in the Baroda District. Through the kindness of the officers of the Geological Survey of India, a considerable quantity of this material has been made available to the author for his studies. Much of it is in the form of fairly thick blocks which are close aggregates of cubic crystals. The crystal forms are visible on one external face of each block, while the other face shows evidence of the mother rock from which the fluorspar crystallised.

Placing a block under the ultra-violet lamp, it is immediately evident that the material is not all of the luminescent variety. This becomes most clearly evident when the edge of the block is viewed under ultra-violet illumination. The feature then noticed is that a layer of luminescent material which is more or less exactly parallel to the external faces of the block is sandwiched between two layers of non-luminescent fluorspar, while the external face of the block showing the individual crystals usually exhibits an observable luminescence. The former feature is illustrated in figure 3 which shows *the edge of one block*, the upper face of the block seen in profile being only dimly visible in the picture. The luminescent

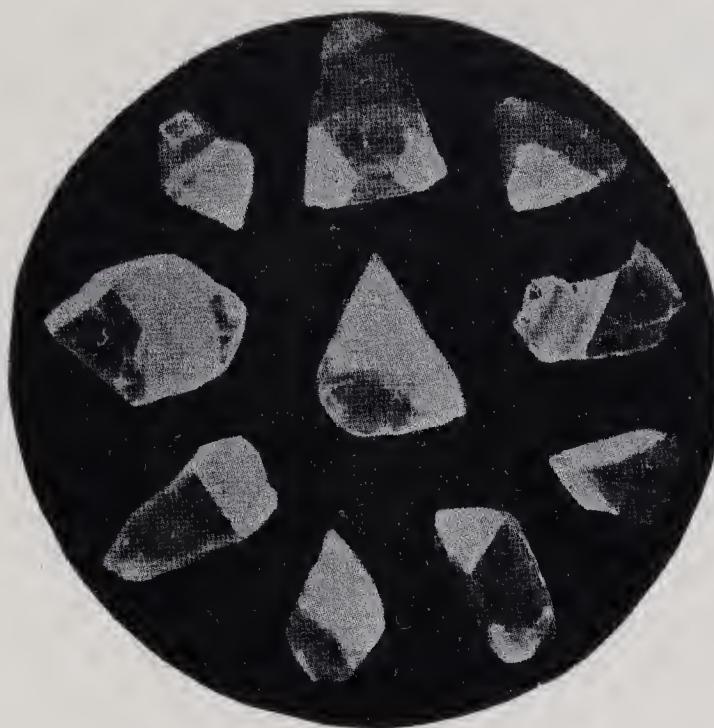


Figure 4. Single crystals of fluorite exhibiting luminescent and non-luminescent sections.

layer is clearly seen in the photograph, while the non-luminescent layers on either side of it are only seen by reason of the light from the luminescent layer which penetrates both above and below and is reflected or scattered within those layers. It should be mentioned that the luminescent layer can easily be distinguished in ordinary daylight from the non-luminescent ones above and below it, by reason of its being clearer and more transparent.

A considerable part of the Amba Dongar fluorite as it came into the hands of the author consisted of small individual fragments and individual crystals which had evidently broken off from the bulk of the mineral during its excavation from the site. Many of the fragments were found to be totally non-luminescent, while others showed luminescence which in most cases did not extend over the whole volume of the fragment. The reason for this becomes clear when such pieces were shaped by grinding and polishing into flat plates with optically good faces. A collection of such plates as photographed under ultra-violet illumination is illustrated in figure 4. The luminescent and non-luminescent areas appear side by side in the same individual crystal, the surfaces of separation being nearly always sharply defined planes.

The facts of observation set forth above indicate that whether fluorspar exhibits luminescence or does not is determined by the ultimate structure or

texture of the crystal which is determined by the temperature and other conditions under which the crystallisation took place. That the difference in the two species arises from the presence or absence of extraneous impurities is a hypothesis which can be scarcely regarded as tenable in the light of the overwhelming factual evidence to the contrary.

## The physics of the diamond

By reason of its remarkable properties, diamond is a substance of extraordinary interest to the physicist interested in the study of solids. It exhibits in a characteristically striking fashion, many phenomena which are scarcely noticeable with other solids in ordinary circumstances. As an instance, we may recall the variation of specific heat with temperature. This was known as an experimental fact in the case of diamond for at least fifty years before it was recognised as a universal property of the solid state; the data for diamond published by Weber in 1875 formed the basis of Einstein's epoch-making paper of 1907 introducing the quantum theory of specific heats. History has a way of repeating itself, and the study of diamond should therefore appeal strongly to the experimenter seeking new avenues of research and to the theorist seeking new and fruitful lines of physical thought concerning the solid state.

For the reasons stated, I have since the year 1930 been deeply interested in physical investigations on the diamond. The difficulty of obtaining the material in a form suitable for exact studies has, however, been a serious obstacle to progress. Indeed, in the early days, I was reduced to the expedient of borrowing diamond rings from wealthy friends who, though willing to oblige, were slightly apprehensive about the fate of their property! More recently, these difficulties have diminished as the result of the discovery that flat plates of diamond of excellent quality are not very expensive and can be purchased in useful sizes from many jewellers in India. The collection of diamonds got together in this way has enabled studies with this crystal to figure prominently in the Bangalore researches on the solid state. Results of fundamental importance have been reached by spectroscopic investigations on light-scattering, on absorption in the visible and ultra-violet, on fluorescence and phosphorescence, and by X-ray studies on numerous diamonds. It is no exaggeration to say that the experimental facts revealed by these researches have opened up a completely new view of the physics of the crystalline state.

My knowledge of diamonds in their natural condition has improved and my personal collection of material for study has been notably enlarged, following a visit by me to the State of Panna in Central India where diamond-mining and diamond-working have been carried on since ancient times. I carried with me to Panna, a microscope, a strain-viewer, an ultra-violet lamp and a small quartz spectrograph. With the aid of this apparatus and with the kind cooperation of Mr Balkrishna who is Director of Industries in the State, Mr Nayar and myself were enabled to examine several hundred diamonds in their natural condition.

We were also graciously permitted by His Highness the Maharaja of Panna to examine his famous garland of 52 large diamonds strung together in their natural state as crystals. The 25 uncut diamonds I purchased and brought back to Bangalore form a representative collection chosen for their scientific interest. There is little doubt that their detailed examination will yield a rich harvest of results.

## 2. The crystal forms of diamond

The reports on the diamond deposits in the Panna State published by E W Vredenburg (1906) and by K P Sinor (1930) include a good deal of information of interest to the physicist and crystallographer. Sinor has a whole chapter in his book, accompanied by drawing and illustrations, concerning the physical characters of the Panna diamonds. Personal observation, however, is necessary to enable one to appreciate the remarkable beauty of these diamonds in their natural condition. With their exquisitely perfect geometric form and their smooth lustrous surfaces, they look absolutely fresh from Nature's crucibles, though actually taken from sedimentary formations which according to the geologists, are a thousand million years old. The strongly-marked curvature of the crystal faces and smoothly rounded edges of the octahedral forms are a surprising feature of these crystals. It is clear, however, from the symmetry of shape, the smoothness of the faces and the fact that forms more complex than the octahedron are represented by sharp edges that the diamonds as we now see them are exactly in the same state as when they were first formed.

I wish to put forward tentatively a suggestion which seems to me to offer a reasonable interpretation of the facts stated above. If carbon liquefied under suitable conditions of temperature and pressure when surrounded by molten silicious material, the form of the drops of the liquid diamond would be determined by the interfacial tension and would be spherical, provided the valence bonds between the atoms of carbon in the liquid were oriented completely at random. If, however, some measure of regularity in the orientation of the valence bonds could be assumed, the conditions within the liquid would roughly approximate to those in the solid crystal; in other words, *diamond in the molten state would be a liquid crystal*. The interfacial tension would then vary with direction and the surfaces of minimum energy would not be spherical, but would tend to show some resemblance to the forms exhibited by a cubic crystal. If the shapes assumed by diamond in the liquid crystalline state persisted on solidification or else suffered only minor changes, we would have an explanation of the forms now observed.

### 3. Accidental birefringence in diamond

Mr Sinor examined many of the Panna diamonds under the polarisation microscope and writes as follows—"Very clear crystals in which all the faces were symmetrically developed showed very little or no double refraction. Crystals full of flaws and inclusions and distorted crystals showed the colour bands very well." This important finding agreed with the observations made by Mr Nayar and myself at Panna with numerous diamonds placed between the nicols of a simple strain-viewer. It has since been fully confirmed by careful observations under the polarising microscope made at Bangalore with the 25 Panna diamonds, the disturbing effects produced by their external surfaces being eliminated by immersion of the specimens in a highly refractive liquid.

The absence of birefringence in clear and symmetrically developed diamonds and its presence in defective and distorted diamonds are precisely what we should expect if a liquid crystalline condition of molten carbon preceded the formation of solid diamond. If the fluid material attained complete uniformity as well as mechanical and thermal equilibrium with its surroundings before solidification, a homogeneous crystal would have formed, while if it did not, the resulting solid would exhibit a lack of homogeneity with consequent development of internal stresses and strains manifesting themselves in an observable birefringence. On this view, the birefringence when observed is essentially a macroscopic effect which does not differ in its physical nature from the birefringence artificially produced by the imposition of external stress on a homogeneous crystal. This interpretation is supported by the fact that the restoration of light is most strongly marked in the vicinity of visible flaws and defects and that by cleaving off the defective parts, the rest of the material may be freed from strain, with the result that the birefringence in it disappears. I have in my collection a plate of diamond which was cleaved into two pieces: as the result of the cleavage, one part was freed from birefringence and is now perfectly dark between crossed nicols, while the other part continues to show a marked restoration of light. It is clear from all these facts that the belief entertained by some writers that a condition of strain is an inherent characteristic of diamond is completely without foundation.

Examination of the specimens in my collection also shows the lack of foundation for the idea which has gained currency in the literature that diamonds whose transparency extends into the ultra-violet beyond 3000 Å are strain-free, while those which transmit radiations only up to 3000 Å are subject to strains. Actually, I have several specimens of the less transparent variety which appear quite dark between crossed nicols, while the four plates of the more transparent kind in my possession all exhibit an intense restoration of light when viewed under the polarising microscope.

#### 4. The scattering of light in diamond

Beliefs in arbitrary or artificial hypotheses, however plausible they may appear, is contrary to the spirit of science which should rely rather on well-ascertained facts of observation as the foundation of its activities. Galileo when he made his famous experiment of dropping weights from the leaning tower of Pisa, showed the way to deal with all such *ad hoc* beliefs, namely, to confront them with the results of a direct experimental test. Diamond which is the prince of crystalline solids gives us the means of making such tests of the assumptions on which Debye's theory of specific heat and the so-called lattice theory of Born are based.

The spectroscopic examination of the light scattered by a crystal when it is traversed by a beam of monochromatic radiation is perhaps the simplest of the experimental methods available for investigating the possible modes of atomic vibration in a crystal. Diamond is readily examined in this way and yields very interesting results. Even with tiny diamonds, the spectroscope records a remarkably intense and perfectly sharp line displaced from its parent radiation by 1332·1 wave numbers at room temperature. Bhagavantam (1930) has shown that this line is many times more intense than the sharp bright line with a displacement of 992 wave numbers observed with benzene which arises from the symmetric vibrations of the carbon ring. Using an exceptionally fine and clear diamond 20 carats in weight, he also recorded several other comparatively faint lines, their wave number shifts being 1158, 1288, 1382, 1431, 1480 and 1585. More recently, Nayar (1941) has studied the scattering of light in diamond over a wide range of temperature and finds that the principal line remains sensibly sharp over the whole range from 83° T to 1130° T; its frequency-shift, however, falls from 1333·8 at the lowest to 1316·4 at the highest temperature of observation.

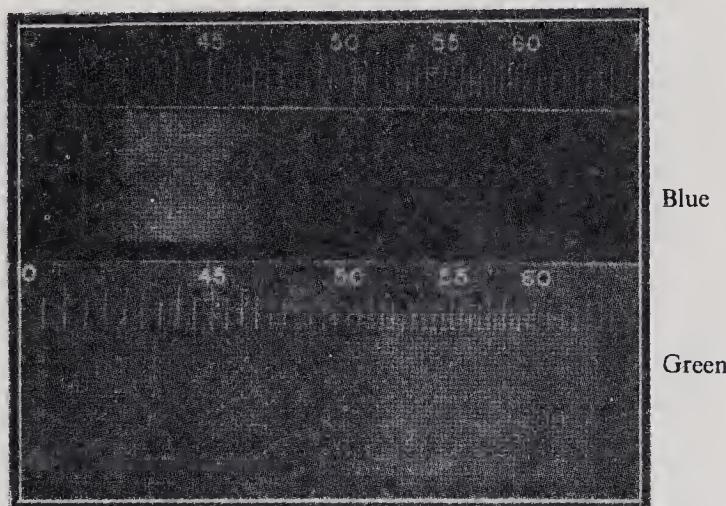
The appearance of no less than seven discrete frequencies as sharp lines in the spectrum of such a simple crystal as diamond is not easy to reconcile with the ideas underlying the Debye and Born theories of the solid state. If we lay aside the preconceived notions underlying these theories, the plain reading of the experimental facts is that the infra-red vibration spectrum of diamond is essentially similar to that of a polyatomic molecule and consists of discrete monochromatic lines. The experiments do not offer any *prima facie* support for the assumption inherent in the theories of Debye and Born that the lattice spectrum is a continuous one.

#### 5. The blue fluorescence of diamond

The experimental situation becomes even clearer in the light of the facts revealed by the recent studies of Nayar (1942) of the blue fluorescence spectrum of diamond and of the corresponding absorption spectrum observed with the crystal held at liquid air temperature. Both in fluorescence and in absorption,

diamond when so cooled down exhibits a close doublet centred at 4152 Å in the spectrum, the same appearing bright in fluorescence and dark in absorption. Spreading out towards lower frequencies in fluorescence and towards higher frequencies in absorption, appears depicted the lattice spectrum of diamond; this is located with perfect mirror-image symmetry of frequency respectively on the two sides of the 4152 doublet. Even at liquid air temperature, the width of the 4152 band is sufficiently small to enable the details of the lattice spectrum to be seen clearly resolved. No fewer than 19 discrete frequencies can be made out, the values derived from the fluorescence and absorption spectra being in complete agreement. These frequencies range from 1387 wave numbers down to 178 wave numbers, and include (within the limits of experimental error) those found by Bhagavantam from his studies on light-scattering in the same region.

Three distinct methods of spectroscopic study, namely, scattering, fluorescence, and absorption, thus agree in indicating that the lattice spectrum of diamond is essentially similar to that of a polyatomic molecule, consisting of a



**Figure 1.** Blue and green fluorescence spectra.

series of discrete monochromatic frequencies. The experimental facts are evidently irreconcilable with the basic ideas of the Debye and the Born theories of the solid state according to which the diamond lattice should have a continuous spectrum of frequencies.

## 6. X-ray reflections of the second kind

The spectroscopic evidence showing that the vibration spectrum of diamond consists of discrete monochromatic frequencies has very important consequences

for the X-ray physics. Since diamond has a rigid structure which is a three-dimensional repeating pattern in space, each of the possible vibrations of this structure must be assumed to occur in the same way in all the volume elements chosen as the units of the space-pattern, since otherwise we would have an infinite number of possible frequencies, instead of a finite number of discrete vibrations as actually observed. In other words, a diamond in which the atoms oscillate with any one of its infra-red frequencies continues to be a three-dimensionally periodic structure in space. Thus, for the same reason which enables the crystal planes of the static crystal to give the well-known Laue and Bragg reflections of unaltered frequency, the crystal planes of the vibrating crystal should also give dynamic reflections with altered frequency.

It has been shown by Dr Nilakantan and myself that the (111) crystal planes in diamond do exhibit dynamic X-ray reflections of the kind indicated above and that their characters as actually observed in experiment, namely, their perfectly specular sharpness, the geometric law which they follow and their practical independence of temperature, can only be understood if they are associated with the high-frequency infra-red vibrations of the crystal structure in the manner suggested. Indeed, exact experimental studies have confirmed this view of their origin in a most remarkable and complete fashion. In particular, it may be remarked that the theory indicates that corresponding to the principal or 1332 vibration of the diamond lattice, the (111) planes should give *three* quantum reflections and not one, the geometric position of these varying with the setting of the crystal, being strictly calculable when it is known. The beautiful confirmation of this prediction furnished by the experiments is illustrated in the accompanying Laue diagram obtained by R V Subramanian, where the three quantum-reflections appear as sharply defined lines in displaced positions on one side of the usual Laue reflection.

An important feature of the new X-ray reflections observed with diamond is that the crystal-spacing associated with such reflections, if calculated on the basis of the ordinary Bragg formula, is not constant but varies rapidly with the setting of the crystal. It is also a function of the wavelength of the X-rays employed. Further, the orientation and azimuth of the plane in which the reflections are observed are also dependent on the setting of the crystal and the wavelength of the X-rays. These facts and especially the existence of three simultaneous

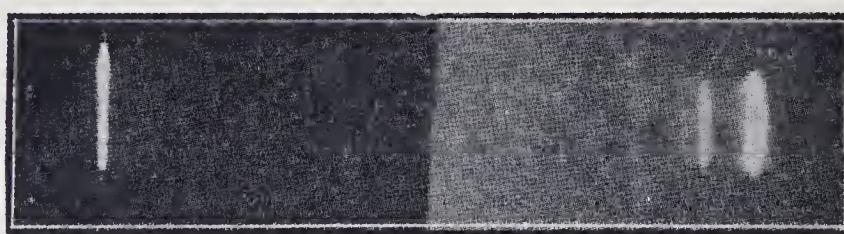


Figure 2. The triple quantum X-ray reflections.

reflections in geometric relation to each other are in complete accord with the dynamic view of their origin. It is evident, on the other hand, that attempts to explain away these phenomena by *ad hoc* assumptions, e.g., an arbitrarily postulated inherent static "strain" in diamond are wholly inadmissible and indeed quite meaningless. It should be emphasised also that the perfect sharpness at all settings of the crystal exhibited by these reflections excludes any attempt to explain them as due to the disturbance of the crystal lattice by vibrations of the kind assumed in the Debye and Born theories of the solid state.

## 7. The lattice spectrum of diamond

The spectroscopic and X-ray results obtained with diamond and briefly summarised above thus compel us to reject the Debye and Born theories as incompatible with the facts. We may summarise the experimental situation by stating that the possible vibrations of the crystal lattice of the diamond are spectroscopically similar to those of a polyatomic molecule, while geometrically they must be considered as repeating themselves in space with three-dimensional periodicity. A simple way of reconciling these results is to regard the entire crystal as an aggregate of interpenetrating space-lattices of a very simple kind, and to assume that these lattices oscillate as rigid wholes relatively to each other, while their common centre of gravity remains at rest. Such an oscillation would cause the structure of the crystal to vary with time periodically, while retaining its perfect three-dimensional periodicity in space. This picture is, however, only an idealisation, since the X-ray results show that a slow variation of phase of the lattice oscillation at different parts of the crystal is permissible.

The crystal structure of diamond is well known, and the various possible normal modes of vibration of the lattice which can arise in this way can therefore be theoretically ascertained. Their frequencies can also be calculated in terms of the force resisting the movements of the carbon atoms, namely, those involved in an alteration of the length of the valence bonds and those resisting a change of the angles between them. The lattice spectrum of diamond can thus be theoretically worked out and compared with the experimental data. In particular, it becomes clear that the vibration having a frequency of 1332 wave numbers is that in which the adjacent planes of carbon atoms parallel to the (111) faces of diamond alternately approach and recede from each other. It is readily understood why such an oscillation results in an intense reflection of the X-rays with altered frequency by those planes. Other lattice frequencies observed in the fluorescence spectrum may be similarly identified as various types of oscillations relative to each other of the atomic planes parallel or perpendicular to important faces of the diamond, e.g., the cube, the octahedron and the dodecahedron. A complete account of the X-ray phenomena exhibited by diamond would include a detailed

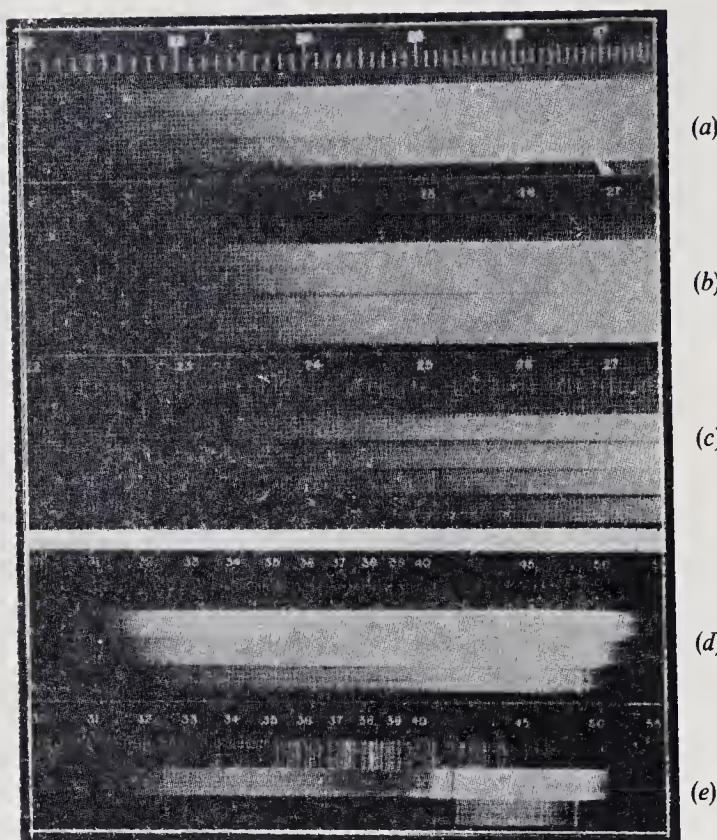


Figure 3. The absorption spectra of different diamonds.

consideration of the effects of each of these possible modes of oscillation on the lattice planes capable of giving sufficiently strong X-ray reflections.

### 8. The absorption spectrum of diamond

It has already been mentioned that the blue fluorescence of diamond is associated with a corresponding absorption in the violet and near ultra-violet regions of the spectrum. The intensity of this fluorescence and of the corresponding absorption varies enormously from diamond to diamond, though their spectral characters remain otherwise sensibly the same. For instance, in a small octahedral diamond in my possession, the 4152 band is only recorded after extremely prolonged exposures. The fluorescence, when present, is accompanied by phosphorescence in the green, yellow and red regions of the spectrum. Several of the Panna diamonds in my collection, on the other hand, show an intense fluorescence in the green, yellow and red regions, the blue fluorescence though present being weak in comparison. There are other diamonds again which show both the blue and green fluorescence in roughly comparable intensities.

These remarkable variations in the luminescence properties of diamond appear to bear a relation, not yet fully elucidated, to the equally obvious variations in the transparency of diamonds in the visible and ultra-violet regions of the spectrum. So far as transparency in the ultra-violet is concerned, Mr. Nayar's studies show that at least *three* distinct kinds of variation should be recognised, as they are accompanied by clearly recognisable features in the absorption spectra. *The first and most transparent kind of diamond* has a sharp cut-off at about 2250 A.U. in the ultra-violet. The *second type* has a clearly marked absorption band at about 2370 A.U. followed by a very feeble transmission at shorter wavelengths. The *third type* has a cut-off at about 3000 A.U., accompanied by subsidiary absorption bands at longer wavelengths. The majority of diamonds appear to belong to the third type, a characteristic of which is the emission of the blue fluorescence with greater or less intensity. It is noteworthy also that some diamonds exhibit simultaneously more than one or even all the three types of spectroscopic behaviour. A continuous transition between the three types of behaviour is thus shown to be possible. The ultra-violet absorption of the third or ordinary type has been pretty fully investigated by Nayar. No fewer than some 25 sharply defined electronic absorption frequencies have been recorded by him between 3000 A.U. and 3600 A.U. at liquid air temperatures.

## 9. Concluding remarks

It will be obvious from what has been stated above that the investigation of the physics of the diamond is full of promise for the future. I have made no reference in this article to further results of great interest which have been obtained but which could not appropriately find a place in a general account of the subject. I may, however, briefly mention the progress which has been made in the study of the relations between the spectroscopic behaviour of different specimens of diamond and the X-ray phenomena exhibited by the same specimens. It is sufficient here to remark that the results obtained in this connection do not in any way contradict the broad results stated above, but on the other hand afford them the fullest support.

C V RAMAN

## The structure and properties of diamond\*

SIR C V RAMAN

As is well known, a study of the forms and properties of crystals enables them to be grouped in 32 symmetry classes, five of which appear in the cubic system. These symmetry classes are identified in theoretical crystallography with the 32 point-groups, these having as their sub-classes the various space-groups which specify the patterns of atomic arrangement within the crystal. In actual experience, crystals exhibiting a high degree of symmetry often contain far fewer atoms in each lattice cell than the full number of asymmetric particles required by theory to give such symmetry. This becomes possible when the atoms are located at special positions in the space-lattice, namely, at the intersection points of the axes and planes of symmetry of the crystal. If the atoms were mere geometrical points, their positions alone would determine the symmetry of the crystal. Actually, however, the atoms with their enveloping electronic clouds have a finite extension. It follows that the atoms themselves must possess certain symmetry characters to permit of their occupying such privileged positions in the space-lattice. The orientations of the atoms must accordingly be taken into consideration, and should be such as to satisfy the symmetry requirements of the crystal. Indeed, it may well happen that in an actual case, the orientations of the atoms are such that the crystal has a lower degree of symmetry than would be the case if the atomic positions alone determined its form and physical properties.

### 2. The allotropic modifications of diamond

That a situation of the kind stated above may arise in the case of a diamond is *a priori* evident. As is well known, the structure of this crystal embodies two interpenetrating face-centred cubic lattices of carbon atoms so located that each atom in either lattice is symmetrically surrounded by four atoms in the other. The number of atoms per unit cubic cell in the structure is eight, four belonging to each lattice. To permit of such a simple structure for a cubic crystal, each carbon atom must itself possess a high degree of symmetry. The minimum symmetry

---

\*Presidential address to the eighth annual meeting of the Indian Academy of Sciences, at Bangalore, on the 26th December 1942.

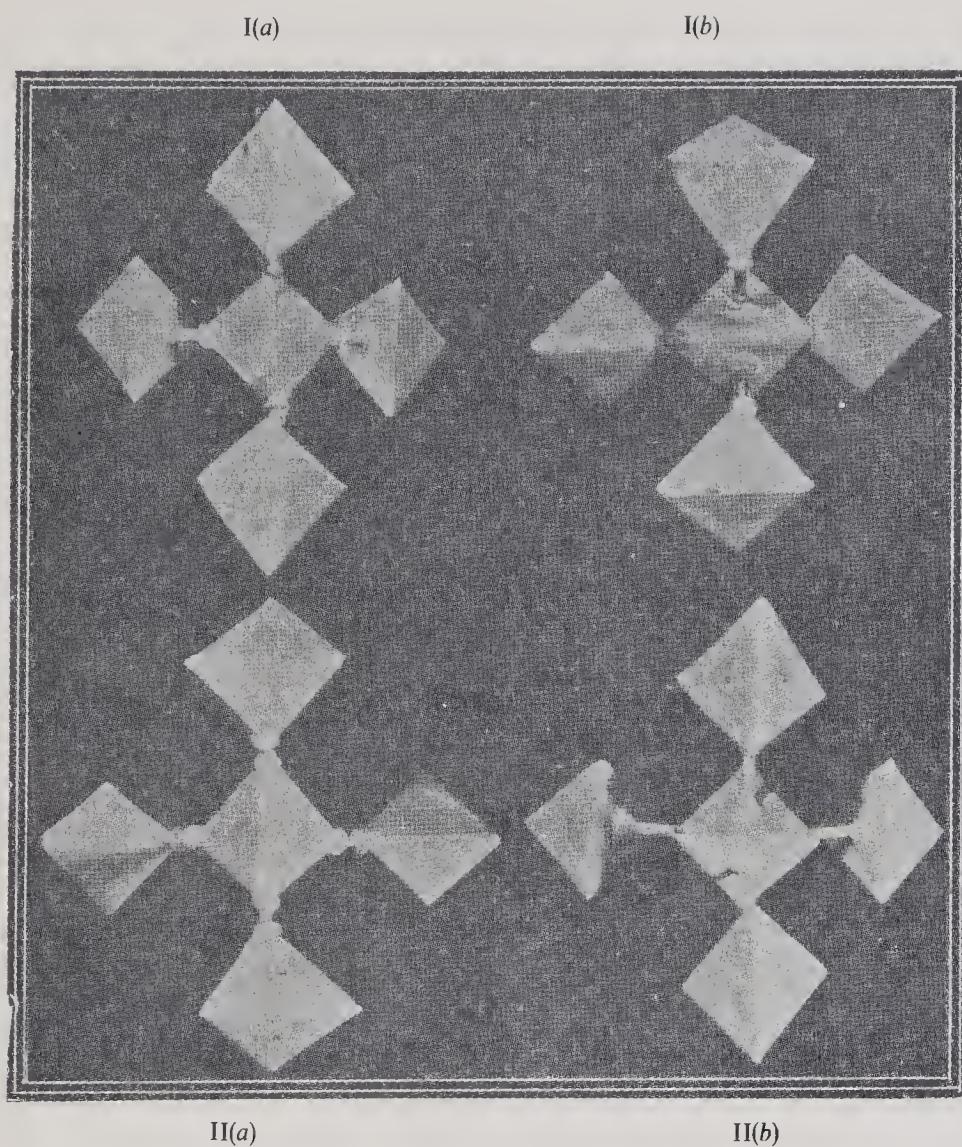


Figure 1. Possible orientations of the carbon atoms in diamond. (Models and photographs by Dr C S Venkateswaran)

which must be assumed is that of a tetrahedron. Assuming the atoms to possess only tetrahedral symmetry, the question arises as to how they are orientated in the unit cell. Several distinct possibilities may be envisaged. We may, for instance, assume each atom to be orientated in the same way as its four nearest neighbours along the body-diagonals of the cube, in the positive or negative sense. The structure would then not possess any centre of symmetry and would belong to the space-group  $T_d^2$  in the hexakis-tetrahedral class of symmetry (E V Chellam 1942).

Alternatively, each atom may be oppositely orientated to its four nearest neighbours. Here again, there are two distinct possibilities, since either the vertices or the bases of the opposing tetrahedra may face each other. In either of these two cases, it is apparent that the crystal would exhibit the full symmetry of the cubic system, its space-group being  $O_h^7$  in the hexakis-octahedral class. It is thus seen that there are four distinct possibilities, in two of which the diamond has only tetrahedral symmetry, and in the other two, the full symmetry of the octahedron.

It is possible that we may also be concerned with combinations (in a quantum-mechanical sense) of the different arrangements represented in figure 1. If, for instance, types I(a) and I(b), or if similarly types II(a) and II(b) are superposed, the individual atoms as well as the crystal as a whole would possess octahedral symmetry. On the other hand, combinations of I and II (one each) would make the atoms in the two lattices possess different symmetries, while the crystal as a whole would possess only tetrahedral symmetry. Mr G N Ramachandran (1942) has shown that all the different arrangements here contemplated would give zero intensity for the X-ray reflections by the (200) planes of the crystal, in agreement with observation. On the other hand, the so-called "forbidden" X-ray reflections, e.g., those by the (222) and (622) planes, would appear with some models and not with others, the actual intensity varying with the combination chosen.

### 3. The crystallographic facts

Mineralogists are familiar with various special types of twinning as the result of which the true symmetry of a crystal is often disguised and forms of higher symmetry are closely imitated. In the hexakis-tetrahedral class, for example, an interpenetration twinning of "positive" and "negative" tetrahedra would enable the forms of highest symmetry of the cubic system to be exhibited. Since the positive and negative forms are physically similar and differ only in external orientation, such interpenetration would not easily be detectable by ordinary methods. The true symmetry of the crystal in such cases may, however, be inferred from its physical properties and also from the evidence of such facts as the unequal but symmetric development of four out of the eight octahedral faces, the appearance of octahedra with grooved edges, as also occasionally of single tetrahedra, of duplex tetrahedra, and of complete crystals exhibiting the 24 faces of the hexakis-tetrahedron. That the majority of diamonds have in reality only tetrahedral and not octahedral symmetry and that the higher kind of symmetry exhibited by the observed crystal forms arises from an interpenetration of positive and negative tetrahedra, is indeed evident from a study of the observed crystal forms of diamond. Examples illustrating each of the special crystal forms mentioned above will be found pictured by Sutton in his book (1928) based on 35

years' study at the South African mines. There is no doubt, however, that diamonds do occasionally appear which possesses the true symmetry of the hexakis-octahedral class.

The exact nature of the interpenetration twinning which appears in diamond cannot, of course, be predicted from purely theoretical considerations. It may, of course, be the case that the boundaries of separation within the crystal of the interpenetrating species are wholly arbitrary, viz., of irregular form and variable size. This may well happen when the two types are physically similar, e.g., the positive and negative tetrahedra of the hexakis-tetrahedral class. On the other hand, it may reasonably be expected that interpenetration twinning of physically different modifications may also, as in the case of quartz, occur parallel to certain crystallographic planes. An inspection of the models illustrated in figure 1 suggests that when twinning layers appear in diamond, they should be parallel to the octahedral planes. It is noteworthy in this connection that a lamellar structure parallel to one or more of the cleavage planes of the crystal is a characteristic feature exhibited by certain diamonds. The observed facts thus find a natural explanation in the ideas set forth above.

#### 4. The infra-red absorption of diamond

Since the difference between the tetrahedral and octahedral types of diamond arises only from the relative orientations of the atoms, neither variety of diamond would give any indication of electric polarity. A striking difference should, however, appear between the two kinds of diamond in respect of their infra-red absorption spectra. For the tetrahedral variety of diamond lacks a centre of symmetry, while in octahedral diamond this is present. Accordingly, a periodic motion of the two interpenetrating lattices with respect to each other should give rise to an oscillating electric moment in tetrahedral diamond and should therefore be infra-red active, while in octahedral diamond such oscillation would give zero moment and would be infra-red inactive. In both cases, however, such oscillation should give rise to a periodically varying optical polarisability and should therefore be active in light-scattering. As was first shown by Nagendra Nath (1934), the intense line with a spectral frequency shift of 1332 wave-numbers which appears in the light-scattering by diamond is due to such an oscillation of the interpenetrating lattices. This frequency corresponds to a wavelength of about  $8\ \mu$  in the infra-red spectrum. The well-known fact that an intense infra-red absorption in the neighbourhood of this wavelength is exhibited by the majority of diamonds, while such absorption is absent in a less common variety of diamond thus receives a simple and natural explanation. Indeed, this variation in the infra-red behaviour furnishes the clearest proof that we are dealing with distinct allotropic modifications of diamond.

## 5. The luminescence of diamonds

One of the most remarkable properties of diamond is the visible luminescence which it exhibits under ultra-violet irradiation. Unlike that of pearls or rubies, the luminescence of diamond varies very greatly from specimen to specimen, both in intensity and colour. This is illustrated in figure 2 of which the left and the right

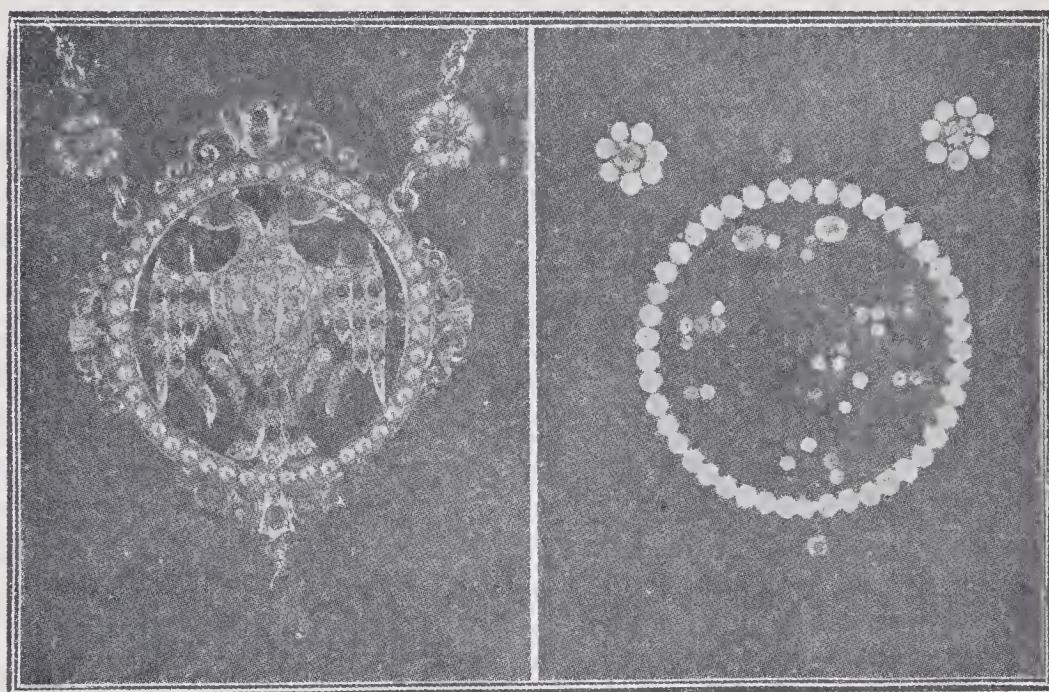
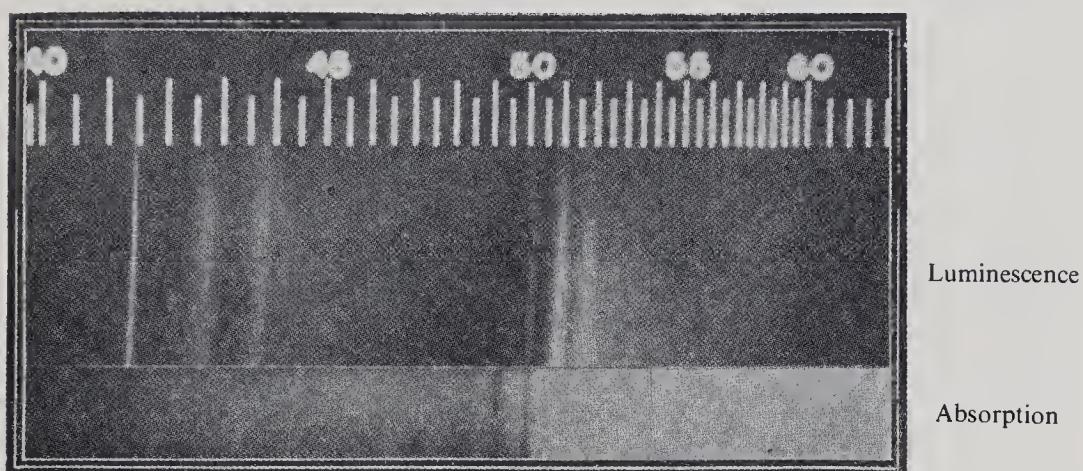


Figure 2. Luminescence of diamonds, pearls and rubies. (Photographs by Mr T M K Nedungadi.)

halves are photographs of the same jewel taken respectively by ordinary reflected light and by the luminescence in ultra-violet light. The 88 diamonds with which the jewel is set (unlike the pearls, rubies and emeralds also seen in it) luminesce with enormously different intensities. Indeed, only the more strongly luminescent diamonds have come out in the picture owing to the moderate exposures used, while the rest remain invisible. In the majority of diamonds, the colour of the emitted light is blue. Greenish-blue, green or greenish-yellow luminescence is, however, also observed in some diamonds. Strongly blue-fluorescent diamonds show a greenish-yellow phosphorescence which continues when the ultra-violet irradiation is cut off. Even when the luminescence is of the same colour – blue for example – its intensity may vary by a large factor – up to say 10,000 in different diamonds.

The spectroscopic studies of P G N Nayar (1941) and of Miss Anna Mani (1942) at Bangalore have greatly advanced our knowledge of the luminescence of

diamonds. These investigators have found that in spite of the enormous differences mentioned above, the luminescence spectra of all diamonds (irrespective of their origin) are essentially similar and that this is also the case for the associated absorptions in the visible region of the spectrum. The principal features in all the spectra are the two narrow electronic bands at 4152 A.U. and 5032 A.U.



**Figure 3.** Luminescence and absorption spectra of green-fluorescent diamond at liquid air temperature. (Photographs by Mr P G N Nayar.)

respectively, appearing as bright lines in emission and as dark lines in absorption. Other radiations appear at longer wavelengths in emission and at shorter wavelengths in absorption than these electronic bands; these frequencies of emission and of absorption in every case exhibit perfect mirror-image symmetry about the electronic frequencies, thus showing that the frequency differences represent the vibration-frequencies of the crystal lattice. The differences in intensity and colour of the luminescence are brought about the variation of the absolute and relative intensities of the electronic emissions at 4152 A.U. and 5032 A.U. as well as of the associated radiations of longer wavelengths. Corresponding differences in the absorption intensities are also exhibited.

The spectroscopic evidence clearly suggests that the luminescence is a characteristic property of diamond itself and not of any extraneous impurities which may happen to be present. This indication is further strengthened by the definite correlation which is found between luminescence and the other properties which differentiate the allotrophic modifications of diamond. It is noticed, for instance, that diamonds which exhibit a blue luminescence, even if only feebly, possess the other properties, e.g., the absorption in the near ultra-violet, which characterise the lower type of symmetry. On the other hand, if diamond is completely non-fluorescent, it is usually found to be of the higher type of symmetry. Another interesting fact is that the fractured edges of cleavage plates

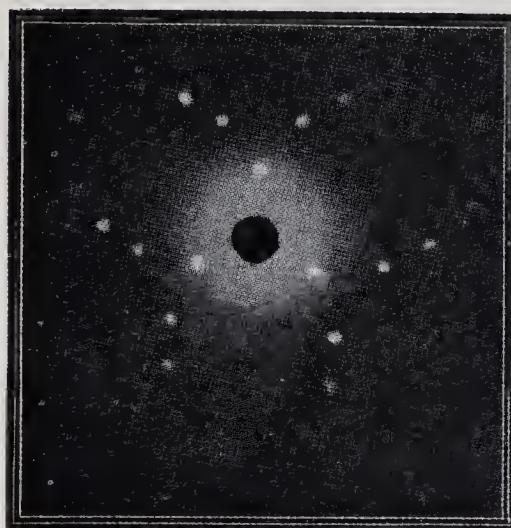
of diamond luminesce far more strongly than either the polished faces or the interior of the crystal. This is an indication that the luminescence is excited by a purely physical cause, namely, a disturbance of the regularity of the crystal structure. The variations in the intensity of the luminescence are then readily explicable as arising from the variation in the number and extent of such irregularities within the diamond. It is evident that an intimate interpenetration of positive and negative tetrahedra in the diamond of lower symmetry, if it occurs, would constitute a disturbance in the regularity of crystal structure. Such interpenetration should therefore operate as an exciter of luminescence in diamond of this type, its intensity being determined by the area and distribution of the surfaces of separation. It is then unnecessary to postulate the presence of extraneous impurities in the diamond, and indeed if such impurities were the cause of luminescence, it would be difficult to understand why diamonds having the higher type of symmetry do not exhibit luminescence to anything like the same extent. On our present view, the latter fact finds a natural explanation in the circumstance that such interpenetration does not exist in the octahedral variety of diamond. The chemical or impurity theory is also discredited by the observation that strongly blue-luminescent diamonds are often of the highest quality in respect of transparency and freedom from colour.

## 6. X-ray phenomena

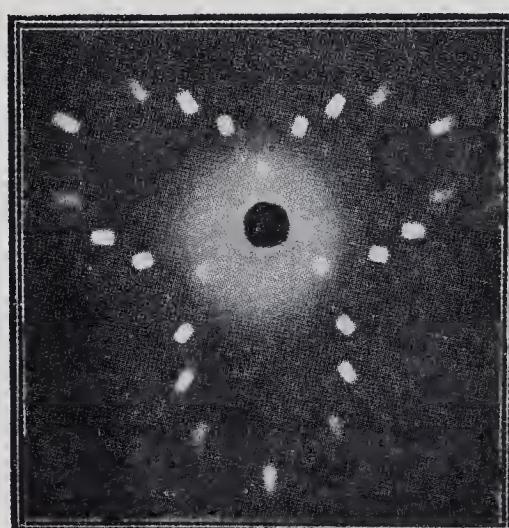
The explanation of the luminescence of diamond put forward above has found striking support in an investigation by P S Hariharan (1942) of the X-ray reflections by diamond, both by the Laue and the Bragg methods, in the latter case with oscillating crystals. He found that the X-ray reflections increased conspicuously in intensity *pari passu* with the strength of the blue luminescence of the diamond under ultra-violet irradiation. His results leave little doubt that the exciting cause of luminescence is to be found in the irregularities of crystal structure. He also found that the diamonds which belong to the lower symmetry class and exhibit the blue luminescence with the least observable intensity are also the diamonds which give the least observable intensities of X-ray reflection and are therefore the nearest approach to the ideal diamond. *Per contra*, the diamonds which are non-fluorescent and belong to the higher symmetry class give extremely large intensities of X-ray reflection. The (111) Laue spots in the X-ray patterns of these latter crystals show a fine ripple-like structure of straight lines parallel to the atomic reflecting layers; from this, it may be inferred that the atomic layers in these diamonds are not strictly plane but have a periodic waviness or rugosity. The enormously increased strength of the Bragg reflections given by an oscillating crystal of this class thereby becomes intelligible. It is scarcely to be doubted that these rugosities made evident by the X-ray reflections are closely associated with the lamellar structure of these diamonds and with the

streaky restorations exhibited by them in the polariscope which run parallel to one or more of the octahedral cleavage planes of the crystal.

The difference between the tetrahedral and octahedral types of diamond also manifests itself in respect of the phenomenon of quantum or modified X-ray reflection. All diamonds of the tetrahedral class, whether weakly or strongly luminescent, exhibit the triple quantum reflections by the (111) planes in a conspicuous manner. These reflections have been explained by the present writer as due to the excitation of the lattice vibrations of wave-number 1332 by the impact of the X-ray photons. Certain writers, notably Born and Lonsdale, have, on the other hand, supported the suggestion that they may arise from a "peculiar state of strain having cubic symmetry present in such diamonds". It is obvious that a state of strain having cubic symmetry cannot possibly maintain itself in a finite crystal free from external stress, and that even if such strain existed, it would not give any observable effect other than a minute alteration of the crystal spacings. It is also important to remark that it is precisely the kind of diamond



I. Weakly fluorescent tetrahedral diamond

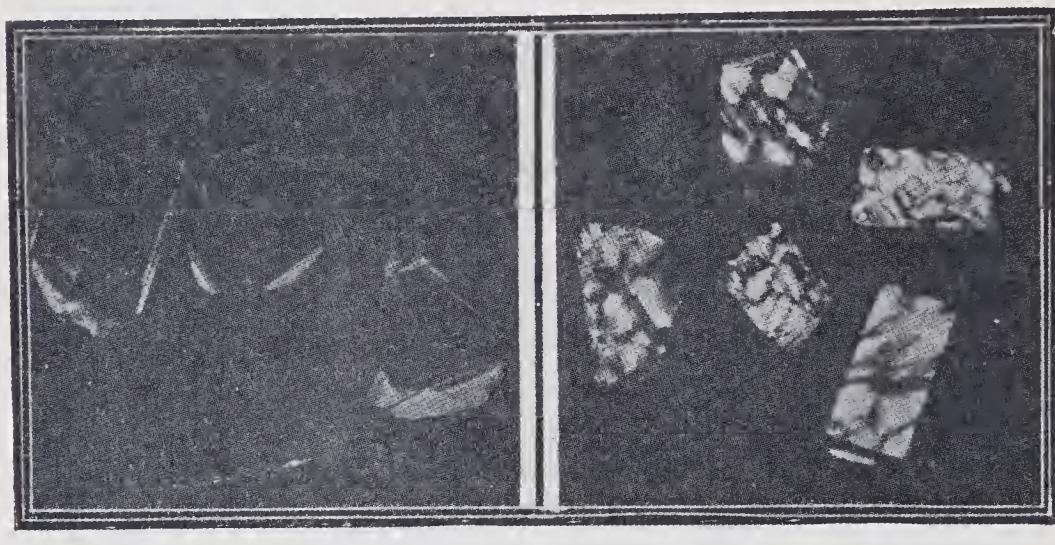


II. Strongly fluorescent tetrahedral diamond

**Figure 4.** Laue patterns of weakly and strongly blue-fluorescent diamonds. (Photographs by Dr R S Krishnan.)

which exhibits the quantum X-ray reflections that can be obtained as cleavage plates completely from any strain detectable between crossed nicols. It is also found that such strain-free plates exhibit the quantum reflections to exactly the same extent as other plates of the same variety of diamond which show a strong and irregular restoration of light between crossed nicols as the result of visible faults or inclusions. These facts are sufficient to show that the *ad hoc* suppositions made by Born and Lonsdale are wholly without any physical foundation.

As already mentioned, the classical X-ray reflections of the octahedral variety of diamond are extremely intense. Remarkably enough, however, the diamonds of this class fail to exhibit the triple quantum reflections. This is regarded by Born and Lonsdale as a refutation of the ideas put forward by the present writer for explaining the phenomena observed with the other type of diamond. A closer consideration of the facts shows, however, that this difference in X-ray behaviour actually forms strong evidence for the correctness of the views put forward by the present writer. It will be recalled that the two types of diamond differ in their infra-red behaviour in respect of the lattice vibration of wave number 1332, this being inactive in octahedral diamond and active in the tetrahedral variety. This difference is a direct consequence of the difference in crystal symmetry. Similar



(A) 5 Strain-free plates of tetrahedral diamond

(B) Strain-patterns in 5 plates of octahedral diamond

**Figure 5.** Plates of diamond between crossed nicols. (Photographs by Mrs K Sunanda Bai.)

considerations of crystal symmetry may be expected also to apply to the quantum-mechanical excitation of the same lattice vibration by the X-ray photons. The appearance of the quantum X-ray reflections with one kind of diamond and their non-appearance in the other kind then follows as an immediate consequence. In other words, this difference in X-ray behaviour of the two kinds of diamond is actually a proof that the movement of the crystal lattice which gives rise to the modified X-ray reflection is the same high-frequency vibration in respect of which the two types of diamond show such a remarkable difference of behaviour in infra-red absorption.

## 7. Photo-conductivity

Diamond, as is well known, exhibits the very interesting property of becoming electrically conducting when illuminated by visible or ultra-violet light. Gudden and Pohl who studied this effect found that the diamonds which freely transmit ultra-violet radiations of shorter wavelength than 3000 A.U. exhibit the effect in a more striking manner than the diamonds which are practically opaque beyond that wavelength. They attributed this difference to the impurities which they assumed were present in the less transparent variety of diamond. This assumption, of course, has no foundation, and we have to seek for a different explanation of the very remarkable experimental facts. Robertson and Fox (1934) showed that the greater transparency in the ultra-violet goes hand in hand with the absence of infra-red absorption at the wavelength  $8\ \mu$ . It follows that the difference in ultra-violet transparency also arises from the difference in crystal structure, the tetrahedral diamonds being the less transparent and the octahedral diamonds the more. This difference in transparency cannot however, by itself, account fully for the striking differences in photo-conductivity, and it is evident that we have to seek for a further explanation on the same basis as for the difference in the luminescence properties. This question has been examined by Mr D D Pant (1942) who has made observations with numerous specimens from the collection of diamonds in the possession of the present writer. From Mr Pant's studies, it appears quite definitely that there is an inverse correlation between the primary effect in photo-conductivity and the luminescence of the diamond. Taking, for instance, the diamonds of the tetrahedral class, it is found that the more strongly luminescent they are, the smaller the photo-conductivity they exhibit. Indeed, the most feebly luminescent diamonds of this class exhibit the effect to an extent which is not vastly smaller than the non-fluorescent diamonds of the octahedral variety.

## 8. Some concluding remarks

Many of the physical properties of the allotropic modifications of diamond differ very little. Other properties, however, as we have seen, exhibit striking differences which enable us to distinguish between them. The luminescence exhibited under ultra-violet irradiation is by far the most easily observed and striking of these, and as already remarked, it exhibits most remarkable variations in colour and intensity. Numerous specimens in the possession of the writer even show variations of colour and intensity in different areas of one and the same specimen. These variations often take the form of bands and patterns of colour parallel to the octahedral cleavages of the crystal. The observations suggest that the tetrahedral and octahedral species of diamond may intermingle in the same

specimen and that such intermingling is responsible both for the development of strain patterns and of luminescence patterns in the specimen. This is confirmed by the existence of corresponding local variations of the ultra-violet transparency of the diamond. The fuller consideration of these matters must be reserved for some future occasion.

## The four forms of diamond\*

SIR C V RAMAN

From the earliest times, the diamond has rightly been recognized as Nature's choicest product in the mineral world. Its claims to the attention of the scientific investigator are also of the strongest kind. The crystal form and the structure of diamond afford the clearest possible proof of the tetrahedral symmetry of the carbon atoms and the most striking illustration of their quadrivalence and of their capacity to combine with each other in limitless number. To the physicist, diamond is the prince of solids, and the study of its properties opens up many new pathways of knowledge into the domain of the crystalline state of matter.

Purely crystallographic considerations indicate that the structure of diamond should have four possible forms. This follows at once from the fact that the structure may be described as a repetition pattern in which the unit consists of two carbon atoms, each of which possesses only tetrahedral symmetry. The four axes characteristic of such symmetry have both direction and sense, and while the directions are necessarily the same for the two representative atoms, the senses may be different, and we have, therefore,  $2 \times 2$  or four possible settings in space of these axes relative to each other. In two of them, the crystal as a whole would have only tetrahedral symmetry, and they may be described in the language of geometric crystallography as the positive and negative tetrahedral forms, which are physically identical, and are only geometrically different from each other. In the other two settings which are both physically and geometrically different from each other, the crystal would have full octahedral symmetry.

These theoretical considerations are confirmed in a remarkable way and independently by the crystallographic evidence, and by the spectroscopic behaviour of diamond. The appearance of crystal forms characteristic of ditesseral polar symmetry had led the earlier crystallographers to assign to diamond only the lower or tetrahedral symmetry and to explain the frequent appearance of octahedral forms as due to interpenetration twinning of the positive and negative tetrahedral forms. The correctness of their verdict, at least as regards the majority of diamonds, is triumphantly vindicated by the spectroscopic evidence, which shows that the characteristic lattice frequency of

\*Symposium on the Structure and Properties of Diamond, Proc. Indian Acad. Sci. A19 189–342 (1944) and plates III to XXX.

$1332\text{ cm}^{-1}$  is *active* in infra-red absorption in most diamonds. It is known, however, that, in some diamonds, this characteristic frequency is infra-red *inactive*, thereby indicating that such diamonds possess the full octahedral symmetry of the cubic system. Theory indicates, however, that *the characteristic frequency should be active in light-scattering in both cases*, and this again is in agreement with experiment. The evidence thus makes it clear that the considerations set forth above stand on an irrefutable basis.

The energy of binding of the carbon atoms with each other, though of a covalent nature, is essentially of electrostatic origin. Hence, if the distribution of static charge were noticeably different in the different possible structures, they would easily be distinguishable from each other by such simple tests as density or refractivity. Since this is not the case, we are led to recognize that the differences are of a more subtle kind, and are probably connected with the configuration of the orbits and the intrinsic spins of the electrons within the crystal. Diamond is diamagnetic, and the orbits and spins must be so arranged that the magnetic moments associated with them cancel out in the aggregate. In the structures having only tetrahedral symmetry, the individual moments associated with the carbon-carbon bonds should persist, while the aggregate moment vanishes by reason of their tetrahedral setting in space. On the other hand, an octahedral symmetry of structure is only possible when the magnetic moments associated with each carbon-carbon bond cancel out individually.

The close similarity in structure of the four possible forms of diamond suggests that the simultaneous appearance of two or even all four in an individual diamond should be a common occurrence. The least disturbance to the regularity of crystal structure would occur when the positive and negative tetrahedral forms interpenetrate, since these are physically identical. The interpenetration would occur without setting up strains in the crystal, and such a diamond should, therefore, appear isotropic when examined under the polariscope. On the other hand, the two forms having octahedral symmetry being physically different, their mutual interpenetration may be expected to take the form of an alternating or lamellar twinning, and even the smallest difference in the lattice-spacings of the two forms would result in such twinning making itself evident under the polariscope by reason of the birefringence set up. Interpenetration of the tetrahedral and octahedral structures also should give rise to observable birefringence on account of the physical differences between them. These inferences from the theory are found to be in complete accord with the facts.

Apart from the birefringence resulting from the interpenetration of structures differing from each other as explained, there are other physical properties which arise from, or are influenced greatly by, such interpenetration. Amongst these should be mentioned specially the power of the diamond to luminesce or emit visible light under ultra-violet irradiation or the impact of X-rays, the extent of transparency of the diamond in the visible and the ultra-violet regions of the spectrum, its photoconductivity under visible or ultra-violet irradiation, and the

reflecting power of the crystal planes for X-rays. The symposium contains reports of investigations on all these topics. Not only are these properties capable of enormous variations from specimen to specimen, but such variations may also occur within an individual crystal or cleavage plate of diamond. Thus the possibility arises of individual diamonds exhibiting *patterns of luminescence*, *patterns of ultra-violet transparency*, and *patterns of X-ray reflection or X-ray topographs*. The discovery of the existence of such patterns and of the similarities and differences between them as observed in the same diamonds forms a notable contribution to the physics of the diamond made in the symposium. Numerous photographs of them are reproduced together with the catalogue numbers of the diamonds to enable the reader to compare the different kinds of patterns of the individual diamonds.

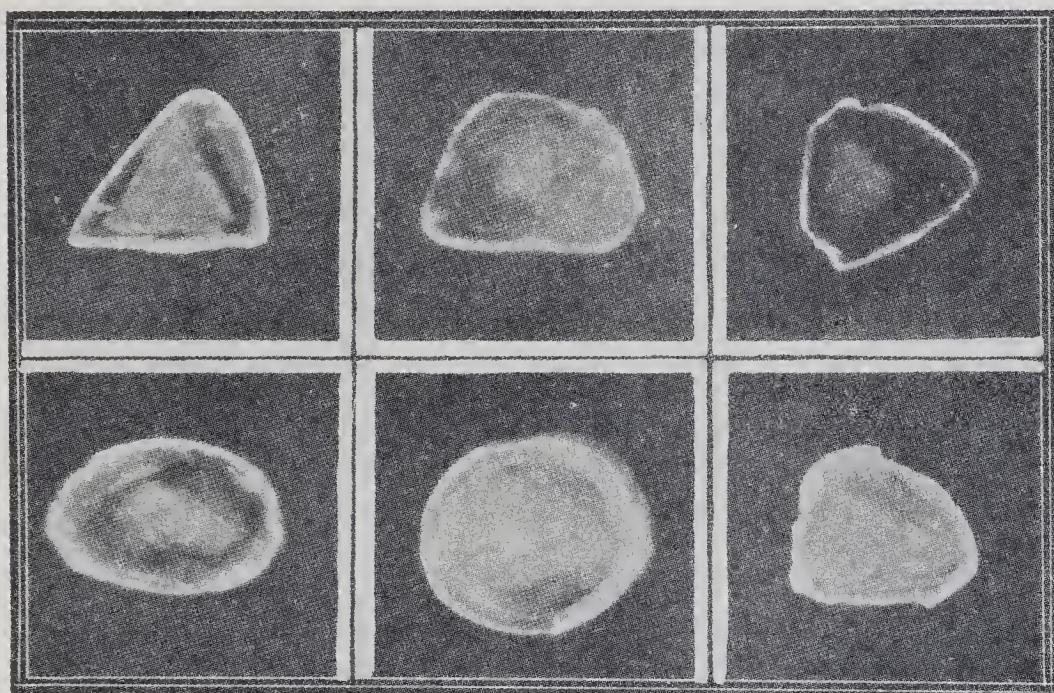


Figure 1. Luminescence patterns in diamond.

The luminescence of diamond in its various aspects forms the subject of a series of papers in the symposium. The intensity as well as the colour of the luminescence is highly variable, while some diamonds are definitely non-luminescent. A very thorough investigation by Miss Anna Mani shows that the spectral character of the emitted light may be described in terms of two distinct systems, which may be referred to as the blue and the yellow luminescence spectra. The former is associated with a sharp bright line at  $4152\text{ \AA}$ , while the latter is similarly associated with a sharp bright line at  $5032\text{ \AA}$ , these being in each

case accompanied by subsidiary lines and bands. The absolute and the relative intensities of the 4152 and the 5032 systems vary enormously from diamond to diamond, thus fully accounting for the observed variations of the colour and intensity of luminescence. While the 4152 system alone appears in some diamonds giving a blue luminescence, the 5032 and the 4152 systems invariably appear together when the luminescence exhibits other colours such as green or yellow. No trace of either system is recorded with non-fluorescent diamonds.

An explanation for these facts comes directly out of the theory indicated above. Blue luminescence arises whenever the tetrahedral structures interpenetrate into one another. On the other hand, the lamellar twinning of the octahedral structures produces no luminescence; but if the octahedral structure intermingles with the tetrahedral, then yellow luminescence results. In an actual specimen, the nature and extent of the interpenetration of the different structures may vary, and this is the origin of the high variability of the intensity and colour of fluorescence. Precisely the same explanation is sufficient to account for the patterns of luminescence exhibited by many diamonds. The local variations of colour and intensity in such cases clearly arise from corresponding variations in the structure of the diamond.

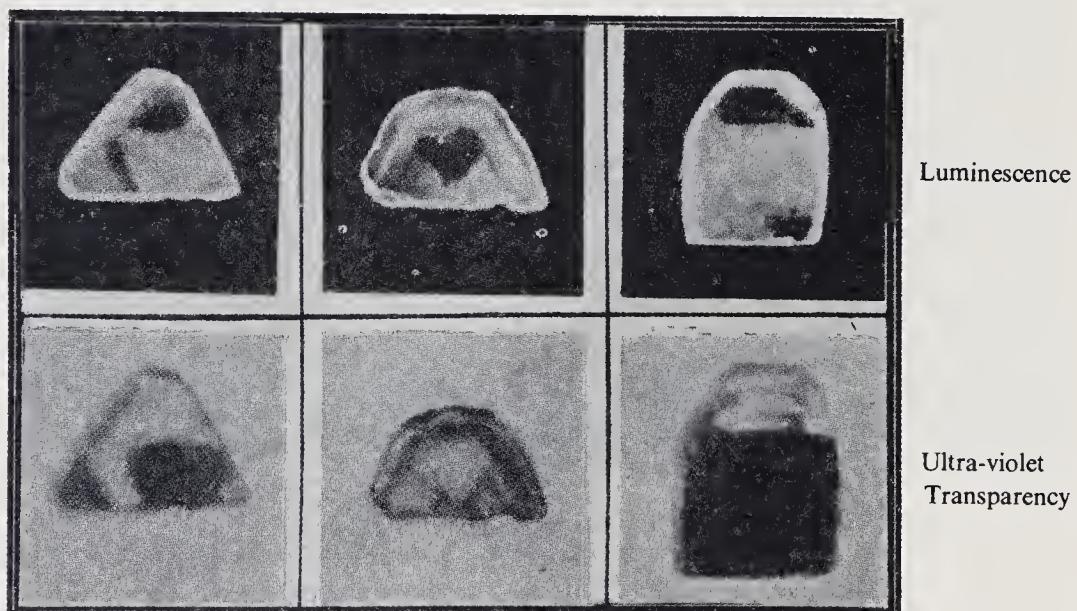
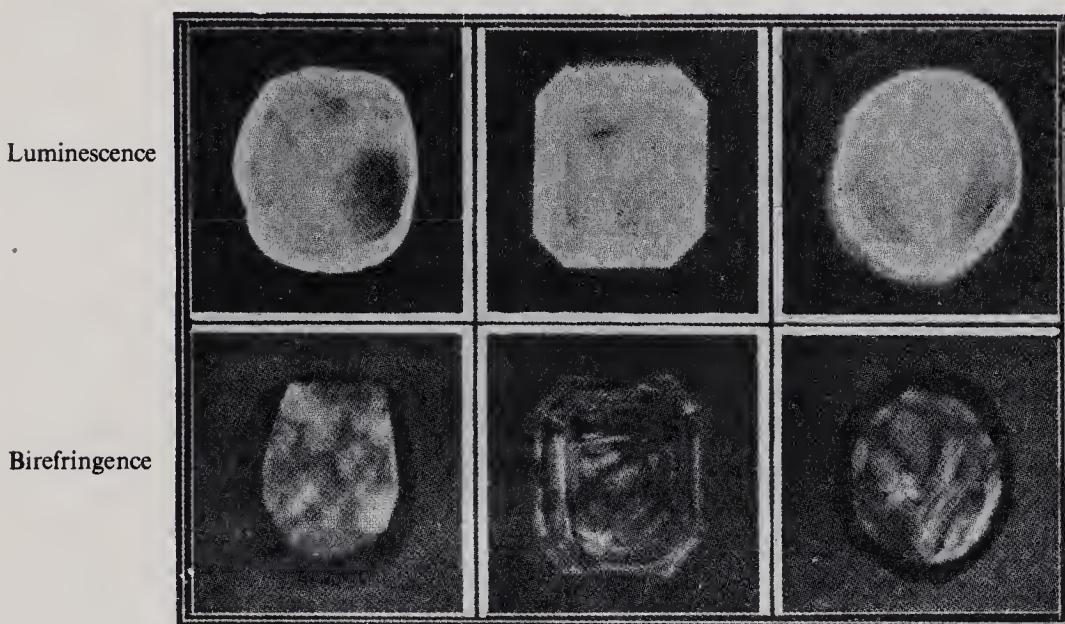


Figure 2. Comparison of luminescence and ultra-violet transparency patterns.

The foregoing interpretation of the origin of luminescence in diamond and of the appearance of luminescence patterns therein finds a striking confirmation in the results of a spectroscopic study of the ultra-violet transparency of diamonds by Sunanda Bai, and of direct observations of the transmission through diamond of the 2537 Å radiations of the mercury are made by Mr Rendall. It is found that

blue-luminescent diamonds are invariably of the ultra-violet opaque type; but the opacity diminishes with increasing intensity of luminescence. The spectrum shows a cut-off at 3050 Å in weakly blue luminescent diamonds, but progressively extends into the ultra-violet in intensely luminescing diamonds even up to 2450 Å. The non-fluorescent diamonds are ultra-violet transparent, transmitting freely up to 2250 Å, or even beyond. On the other hand, in diamonds of the yellow luminescing kind, the transparency in this region is very imperfect. A strong absorption doublet, accompanied by subsidiary bands on either side appears at about 2360 Å in diamonds that show both the 4152 and the 5032 systems.



**Figure 3.** Comparison of luminescence and birefringence patterns.

X-ray studies furnish a further striking confirmation of the ideas stated above. As already described, the two tetrahedral structures can interpenetrate freely without setting up stresses in the crystal. Nevertheless, the mixed structure is not ideally homogeneous, so that its lattice planes should give stronger X-ray reflections than those given by either structure individually, the intensity being larger, the greater the extent of interpenetration. Hence, one should expect a close correlation between the intensity of blue-luminescence, and of X-ray reflection. This inference has in fact been confirmed by Dr R S Krishnan both by the Laue and the Bragg methods. The interpenetration of the octahedral structures, on the other hand, sets up strains in the crystal, so that such a mixed structure should show much more intense X-ray reflections than the blue-luminescing diamonds. For the same reason, the yellow-luminescent diamonds should exhibit an X-ray reflection intermediate between the above two types. These conclusions have also

been borne out by the investigations of Mr P S Hariharan. A natural consequence of the above considerations is that one should also expect variations in the X-ray reflecting power over the area of a cleavage plate of diamond. Such variations have in fact been made manifest by a new method of obtaining Laue reflections using X-rays diverging from a pinhole, adopted by Mr G N Ramachandran. By suitably tilting the crystal, and the photographic plate, an almost perfect reproduction (X-ray topograph) of the variations in the crystal structure can be obtained. A comparison of these topographs with the other patterns is very interesting, and shows that the enhanced intensity may be of two types. It may be caused either by an increased interpenetration of the tetrahedral structures or by the intrusion of the octahedral type. Mr Ramachandran has found that this increase is different for the different crystal planes, the factor of increase being greatest for those having the largest structure-amplitude, and decreasing to unity for feebly reflecting planes.

Observations of the characteristic streaky birefringence of the ultra-violet transparent type of diamond suggests that it has a piezo-optic effect due to the crystal spacings of the two modifications of octahedral diamond being different from each other. We should expect on this basis that the optic axes of the birefringence should be parallel and perpendicular to the intruding layers, and this is actually the case. It is gratifying also to be able to report that direct experimental proof has been obtained for the difference in the lattice spacing of the two octahedral modifications. Using the oscillating crystal method, and a diamond in which the two structures coexist in adjacent layers of the crystal, Dr Krishnan has found that the Bragg reflections exhibit a waviness, showing clearly that there is a difference in the crystal spacing of the alternate layers. These observed differences suggest that there should also be a difference in the spectral frequency of the lattice vibrations. Dr Krishnan has also obtained evidence of this by a careful study of the width of the 1332 line observed.

Reference must also be made to other results of importance announced in the symposium. Dr Krishnan has studied the scattering of light in diamond in great detail, using the Rasetti technique, and has obtained ten other lines, besides the well-known line with a frequency shift of  $1332\text{ cm}^{-1}$ . These new lines have been identified as the octaves and the allowed combinations of the eight frequencies of oscillation of the diamond structure, calculated according to the principles of crystal dynamics developed by the present writer. These lines are not permitted to appear as fundamentals in light-scattering by reason of the selection-rules, but appear in fluorescence in combination with electronic frequencies. The frequencies calculated from Dr Krishnan's results are found to agree well with the frequencies deduced from fluorescence spectra by Dr Nayar and Miss Mani. Using the experimental values for the fundamental frequencies, Mr Bisheshwar Dayal has evaluated the specific heat of diamond, the calculated values agreeing perfectly well with the experimental data throughout the entire range of temperatures.

There is only space here for a brief reference to a paper by Mr A Sigamony on the magnetic susceptibility of diamond, and to two papers by Mr Pant on the photoconductivity of diamond. The latter has studied the photoconductivity of a large number of diamonds, and has interpreted his results on the basis of the variations in the structure of the crystal as described above. Mr Ramaseshan reports some interesting studies of the crystal forms of the Panna diamonds, and particularly of the nature of the curvature exhibited by their surfaces.

## The crystal symmetry and structure of diamond

SIR C V RAMAN

Department of Physics, Indian Institute of Science, Bangalore

Received April 17, 1944

### Contents

1. The crystal symmetry of diamond
2. The four possible structures of diamond
3. Confirmation of the theory by infra-red spectroscopy
4. Interpenetration of positive and negative tetrahedral structures
5. Lamellar twinning of octahedral structures
6. Inter-twinning of tetrahedral and octahedral structures
7. Summary

### 1. The crystal symmetry of diamond

Diamond was assigned by the earlier crystallographers (*vide* Groth 1895; Liebisch 1896; Hintze 1904) to the ditesseral polar or tetrahedrite class of the cubic system. The assignment was based on the fact that though diamond commonly exhibits octahedral symmetry of form, specimens showing only the lower tetrahedral symmetry were forthcoming, and it was therefore natural to suppose that the higher symmetry when observed was the result of a supplementary twinning of the positive and negative tetrahedral forms. In particular, the appearance of octahedral forms with grooved or re-entrant edges could be explained in this way. We may here quote from the first edition of Miers' *Mineralogy* (1902) where the forms of diamond are discussed at considerable length: "Much controversy has taken place upon the question whether the diamond is really octahedral as it appears or tetrahedral as is suggested by the grooves; the problem may now be regarded as decided in favour of the tetrahedrite class by the following two facts: (1) several crystals have been found which are undoubtedly simple crystals of tetrahedral habit..... (2) the supplementary twinning of such crystals sufficiently explains all the other peculiarities of form." Sutton (1928) who has written a treatise on the South African diamonds gives illustrations of crystals having the forms of hexakis-tetrahedra, truncated

tetrahedra, duplex-tetrahedra and others which are entirely typical of ditesseral polar symmetry.

Van der Veen (1908) noticed that diamond does not exhibit any pyro-electric properties and expressed the view that this is irreconcilable with the assignment of tetrahedral symmetry. The results of the X-ray analysis of the crystal structure of diamond by W H Bragg and W L Bragg (1913) have also usually been regarded as demonstrating that diamond possesses holohedral symmetry (Tutton 1922; W L Bragg 1937). These contentions are, however, open to question. It may, in the first place, be pointed out that the evidence of the crystal forms on which the earlier assignment was based cannot be lightly brushed aside. Secondly, it is very significant that the X-ray data show the structure of diamond to be analogous to that of zinc blende which is a typical crystal of the tetrahedrite class, and this is a hint that the crystal symmetry of diamond might also be of the same class. It is thus evident that the matter deserves more careful consideration than it appears to have received so far. It is the purpose of the present paper critically to examine the question whether the crystal symmetry of diamond is octahedral or only tetrahedral. The investigation reveals that there are several alternative possibilities and thereby furnishes the key to an understanding of many remarkable and hitherto imperfectly understood facts regarding the diamond and its physical properties.

## 2. The four possible structures of diamond

We shall accept the X-ray finding that the structure of diamond consists of two interpenetrating face-centred cubic lattices of carbon atoms which are displaced with respect to one another along a trigonal axis by one-fourth the length of the cube-diagonal. Each carbon atom in the structure has its nucleus located at a point at which four trigonal axes intersect. Hence, we are obliged to assume that the electronic configuration of the atoms possesses tetrahedral symmetry. It must also be such that the alternate layers of carbon atoms parallel to the cubic faces have the same electron density. This is shown by the X-ray finding that the crystal spacings parallel to the cubic planes are halved. Hence, the possibility that the two sets of carbon atoms carry different total charges is excluded. In other words, diamond is not an electrically polar crystal in the ordinary sense of the term. It is readily shown, however, that the charge distributions may satisfy both of these restrictions and yet not exhibit a centre of symmetry at the points midway between neighbouring carbon atoms. To show this, we remark that when two similar structures having tetrahedral symmetry interpenetrate, centres of symmetry would not be present at the midpoints between the representative atoms unless the tetrahedral axes of the two structures point in opposite directions. We may, in fact, have *four* possible kinds of arrangement as indicated in figure 1. Of these the arrangements shown in Td I and Td II have tetrahedral symmetry,

while Oh I and Oh II would be distinct forms, both having octahedral symmetry.

The tetrahedral symmetry of the atoms required by virtue of the special positions which they occupy in the crystal lattice must be satisfied both by the electrostatic distributions of charge and by the orientations of the orbital and spin moments of the electrons. When the structure as a whole is considered, the magnetic moments should be fully compensated, since the crystal is diamagnetic. But such compensation may be secured in several distinct ways which would endow the structure with different symmetry properties. On the one hand, four equal magnetic moments directed either all inwards or all outwards along the four tetrahedral axes of a cubic crystal would automatically cancel each other. On the other hand, if the pair of electrons which bind neighbouring atoms have opposite magnetic moments (directed inwards or outwards as the case may be), these would directly cancel each other. Considering these two pairs of possibilities, we have four different ways in which the extinction of the resultant

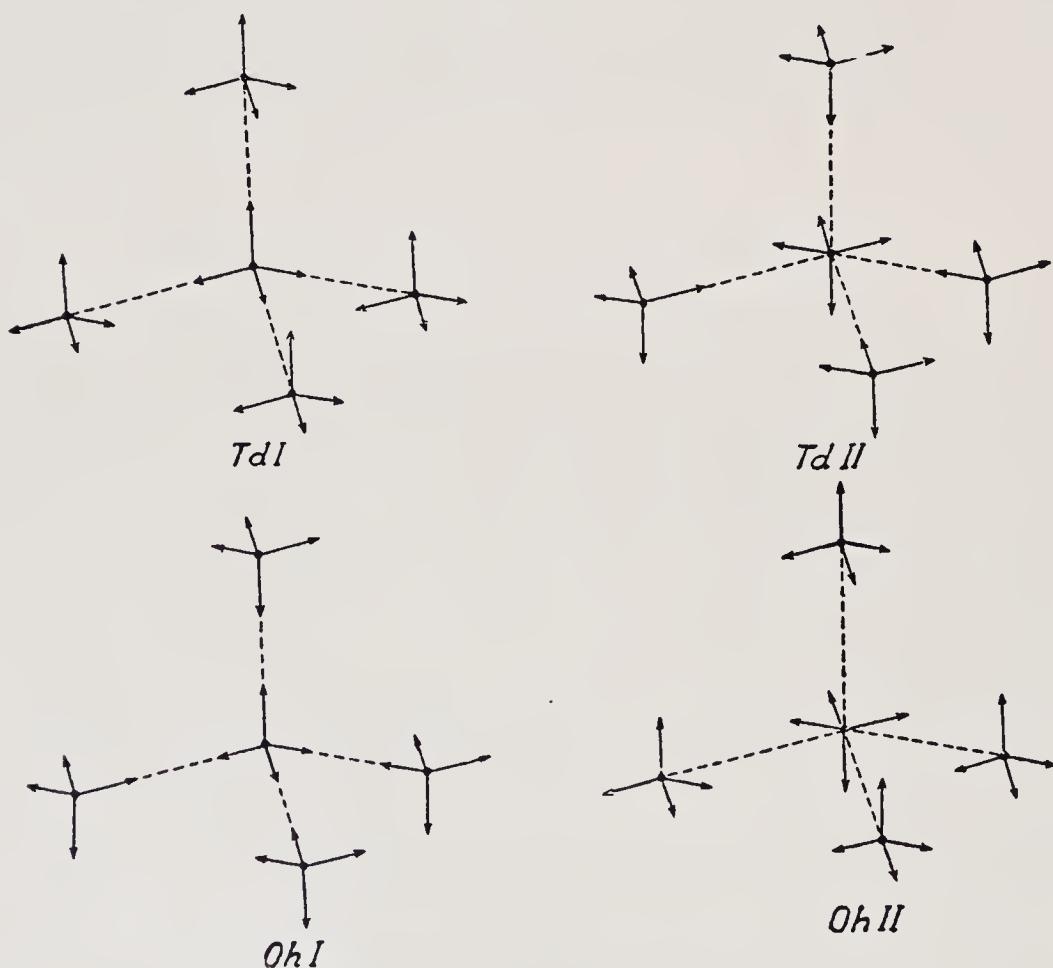


Figure 1. The four possible structures of diamond.

magnetic moment may be secured. It is seen that these correspond to the four possible structures of diamond indicated in figure 1.

It is readily shown that if the charge distributions which differ in their angular setting as shown in figure 1 are otherwise identical, the electron density in the alternate layers of atoms parallel to the cubic planes would be the same. This follows immediately from the fact that these planes are equally inclined to the tetrahedral axes. Hence, all the arrangements shown in figure 1 would be consistent with the observed halving of the spacing of these planes. Hence, the X-ray findings leave the question whether diamond possesses tetrahedral or octahedral symmetry entirely open.

The expectation that diamond would have pyro- or piezo-electric properties would only be justified if the neighbouring carbon atoms carry different electric charges. Since this is not the case, the absence of such properties cannot be regarded as a contradiction of the views of the earlier crystallographers regarding the symmetry class to which diamond belongs.

### 3. Confirmation of the theory by infra-red spectroscopy

Placzek (1934) has discussed the relation between the symmetry class of crystallographic groups and their activity in infra-red absorption, as also in the scattering of light with change of frequency. He has shown that for the groups which contain a symmetry centre, the selection rules for infra-red absorption and for light-scattering are complementary, viz., the modes of vibration which can appear in light-scattering are forbidden in infra-red absorption, and vice versa. For those groups which do *not* have a centre of symmetry, there is a possibility that the same vibrations may appear both in the scattering of light and in infra-red absorption. The simplest illustration of these principles is furnished by the case of a diatomic molecule, its vibrations being active in light-scattering and inactive for infra-red absorption provided the atoms are similar, and active in both if they are dissimilar. Placzek's rules successfully explain the experimentally observed behaviour of many crystals in light-scattering and in infra-red absorption. Taking, for instance, the case of rock-salt which has holohedral symmetry, its fundamental frequency is that of the triply degenerate oscillation of the sodium and chlorine lattices with respect to each other. This is observed to be active in infra-red absorption and inactive in light-scattering, in accordance with the behaviour indicated by the selection rules.

The infra-red absorption of diamond was studied by Angstrom (1892), Julius (1893) and by Reinkober (1911), and has been investigated with especial thoroughness by Robertson, Fox and Martin (1934). From these studies, and especially from the work of the last mentioned investigators, the remarkable fact emerges that diamonds are not all identical in respect of their behaviour in infra-red absorption. In the majority of diamonds the infra-red absorption coefficient

rises very steeply from a comparatively moderate value to a maximum of about 90% in the wave-number range  $1350-1300\text{ cm}^{-1}$ . This steep rise in absorption as well as the entire band of which it is the head are, however, wholly absent in other diamonds which evidently form a second and rarer variety.

The significance of these facts becomes clearer when it is remarked that the fundamental frequency of the diamond structure is that of the triply-degenerate oscillation of the two lattices of carbon atoms with respect to each other, and that this falls precisely within the range of wave-numbers where the sudden rise of infra-red absorption occurs in the common variety of diamond. This is proved by the appearance of an intense line with a frequency-shift of  $1332\text{ cm}^{-1}$  in the spectrum of the scattering of monochromatic light by diamond; the wave-number of the fundamental vibration of the diamond structure calculated from its specific heat data is also  $1332\text{ cm}^{-1}$  (Ramaswamy 1930). The investigations of Robertson and Fox (1930) have shown that both the commoner variety of diamond which exhibits the infrared absorption in this region of frequency and the rarer variety in which it is missing, alike exhibit the strong line with a frequency shift of  $1332\text{ cm}^{-1}$  in the spectra of the scattering of light.

Placzek's selection rules (*loc. cit.*) for the point-groups of the cubic system show that a triply-degenerate vibration in a crystal having octahedral symmetry can manifest itself *only* in infra-red absorption *or* in light-scattering *but not in both*. On the other hand, in a crystal with tetrahedral symmetry, such a vibration must appear *both* in absorption and light-scattering or else can appear in *neither*. Taking these selection rules in conjunction with the experimental facts, it follows at once that the commoner variety of diamond has only tetrahedral symmetry, while the rarer variety of diamond has octahedral symmetry. *The views of the earlier crystallographers assigning only the lower symmetry are thus completely vindicated by the infra-red absorption data and the selection rules so far as the commoner variety of diamond is concerned. The rarer variety of diamond must however be credited with the full or holohedral symmetry of the cubic system.*

Infra-red spectroscopy thus compels us to recognize the existence of two forms of diamond, a commoner form having only tetrahedral symmetry of structure, and a rarer form having octahedral symmetry. We have now to consider the further implications of the theory which indicates that each of these forms has two variants, namely those whose symmetry characters are indicated in figure 1 as Td I and Td II respectively for the tetrahedral type of diamond, and as Oh I and Oh II respectively for the octahedral type. The question arises whether there is any physical evidence for the existence of these four types of diamond and in what manner, if any, it is possible to differentiate between them. In this connection, it is worthy of note that both the tetrahedral and octahedral types of diamond, as we may now designate them, exhibit the same frequency shift ( $1332\text{ cm}^{-1}$ ) in the scattering of light within the limits of observational error. This indicates that the forces which hold the carbon atoms together in the two kinds of diamond do not differ sensibly, despite the difference in the symmetry of their structures.

Accepting this as an experimental fact, it follows that in respect of the energy of formation and the lattice spacings in the crystal, and therefore also all the commoner physical properties, such as density, elasticity, specific heat, refractivity, dielectric constant, diamagnetic susceptibility etc., any differences which may exist between the four types of diamond must be small. It is very remarkable that though the symmetry of the electronic configuration is not the same in the two types of diamond, the strength of binding between the carbon atoms is not sensibly different. *Prima facie*, this result indicates that the electrostatic distributions of charge are the same. We are therefore led to assume that the differences which exist lie essentially in the orientations of the orbital and spin moments of the electrons, as already indicated.

#### 4. Interpenetration of positive and negative tetrahedral structures

As the commoner type of diamond has only tetrahedral symmetry, crystallographic considerations compel us to admit the existence of two variants of the tetrahedral type, namely the positive and negative structures indicated by Td I and Td II respectively in figure 1. It is evident that these two sub-classes would be completely identical in respect of energy of formation and lattice spacing, and consequently also in respect of density, refractive index and such other physical properties. The question then arises how we can distinguish between them.

It is possible, of course, for diamond having the positive or negative tetrahedral structure to have an external form with octahedral symmetry. For, both positive and negative tetrahedral faces may appear in the same diamond—as they actually do in zinc-blende—and it is quite possible that they are equally well developed with nothing whatever to distinguish one from the other. The comparative infrequency of crystals having a simple tetrahedral habit would, however, be easier to understand on the basis of the supplementary twinning of the positive and negative tetrahedral forms. That such twinning is possible and indeed common finds support in the various peculiarities of form (e.g., the grooving of the octahedral edges) observed in actual specimens. Further, the identity of the physical properties of the positive and negative tetrahedral structures makes the assumed interpenetration highly probable on theoretical grounds. We are therefore justified in assuming that such interpenetration twinning is a phenomenon of very general occurrence.

It is well known that when interpenetrative twinning occurs, there is no “plane of composition”, in other words, the interpenetrating forms are separated from each other in an irregular way. In the present case, the interpenetration is often complete and it is a reasonable assumption that it may occur on a microscopic or even ultra-microscopic scale. Whether this is so or not, the identity of density and refractive index would make the direct observation of such internal twinning

impossible, and we would have to depend on the study of structure-sensitive properties to demonstrate its existence. Diamond is rightly regarded as one of the most perfect crystals, if not the most perfect of them all, as shown by the extreme sharpness of the setting for the reflection of monochromatic X-rays exhibited by well-chosen specimens. It is evident however, that unless a specimen consists exclusively of sub-type Td I or of sub-type Td II, we cannot consider it as ideally perfect and homogeneous. Hence, the existence of the interpenetrative twinning should be capable of detection by X-ray methods. The *smaller* the volume-elements inside the crystal which are exclusively of one or the other sub-type, the more numerous would be the elementary blocks of which the crystal is built up, and the easier, therefore, would it be to observe the resulting non-homogeneity of the crystal by its X-ray behaviour or by other delicate methods of study.

## 5. Lamellar twinning of octahedral structures

Figure 1 indicates that the sub-types Oh I and Oh II cannot, unlike the sub-types Td I and Td II, be regarded as necessarily identical with each other in observable physical properties. They would nevertheless resemble each other sufficiently closely to make it highly probable that the Oh I and Oh II types would frequently appear together in the same specimens of diamond of the octahedral variety.

It is significant in this connection that a laminated structure in which layers parallel to one, two, three or even all the four faces of the octahedron appear simultaneously has been recognised as a characteristic phenomenon exhibited by some diamonds. Sutton (1928) describes and illustrates this kind of structure in diamond. He recognises that it is quite different from the macling or twinning which has been often observed in diamond, since in the latter case, the components differ in orientation as shown by the difference in their planes of cleavage, and also, of course, by their X-ray patterns. Sutton therefore considers the lamellar structure to be an "illusory" type of twinning. Since, however, it is a real phenomenon it is no explanation of its existence to call it by such a name. Indeed, the appearance of a finely laminated structure is a well known experience in crystallographic studies. It is observed for instance, in iridescent crystals of potassium chlorate and in various other substances. Hence, it is a reasonable assumption that when it is observed in diamond, it is also a specific form of twinning. We have already seen that an interpenetrative twinning of the Td I and Td II types would not exhibit any specific planes of composition. Hence, the presence of a lamellar structure in diamond parallel to the octahedral planes is a definite indication of the presence of the Oh types in the specimen and if, further, the specimen consists exclusively of these types, we may explain it on the basis that the Oh I and Oh II sub-types appear in alternate layers within the crystal. The simultaneous appearance of laminations parallel to more than one of the octahedral planes presents no difficulty of explanation on this view, since it would

indicate merely that the two sub-types appear in the diamond as small blocks bounded by surfaces parallel to the laminations instead of as thin layers.

## 6. Inter-twinning of the tetrahedral and octahedral structures

Though diamonds having the lower and higher symmetry are physically different, yet they are so closely alike in their structure that the appearance of the two types simultaneously in the same individual crystal must be a not uncommon event. Indeed, since diamond has usually the lower symmetry, it may be expected that the higher symmetry would appear as an intrusion in diamond of the lower symmetry more frequently than as a type by itself. Since there are altogether four types of diamond, the number of possible modes of combination amongst them is fairly large, and we may have a wide range of possible space distributions of the different kinds of structure within the crystal.

Inter-twinning of the tetrahedral and octahedral forms of diamond may ordinarily be expected to exhibit a composition plane or planes parallel to each other within the crystal, thus dividing up the latter into layers which are physically different. The alternate layers may consist exclusively of the Td I or Td II types and of the Oh I or Oh II respectively. On the other hand, it is also possible that the Td I and Td II types may appear together in the layers having tetrahedral symmetry, while similarly, the Oh I and Oh II types may appear as alternate finely-spaced laminae within the layers having octahedral symmetry. Besides such cases, others may conceivably arise in which diamond of the lower symmetry is dispersed in microscopically small volume elements or even ultra-microscopically in diamond of the higher symmetry, or *vice versa*. The possibility of such cases is distinctly suggested by the situation which exists in relation to the individual types of diamond.

## 7. Summary

By virtue of the special positions which they occupy in the crystal lattice, the carbon atoms in diamond must have a tetrahedrally symmetric configuration of the electron orbital movements and spins. A tetrahedral axis has both direction and sense, and the carbon atoms in the two Bravais lattices may therefore be orientated in space and with respect to each other in four distinct ways, each of which corresponds to a possible structure for diamond. In two of these structures, diamond has only tetrahedral symmetry and in the two others the full or octahedral symmetry of the cubic system. The selection rules require that the fundamental vibration of the diamond lattice having a frequency  $1332\text{ cm}^{-1}$  should appear both in light-scattering and infra-red absorption if the crystal has tetrahedral symmetry, while it would appear only in light-scattering and not in

the infra-red absorption spectrum if the symmetry is octahedral. These predictions are in accord with the observed spectroscopic behaviours respectively of the commoner and rarer types of diamond recognised as such by Robertson, Fox and Martin. Hence, the assignment of tetrahedral symmetry to diamond by the earlier crystallographers is confirmed for the commoner type of diamond, while on the other hand, the rarer type is shown to have the full symmetry of the cubic system. The crystallographic facts also support the theoretical result that there should be two sub-types of diamond for each kind of symmetry. The positive and negative structures having tetrahedral symmetry have identical physical properties and can therefore interpenetrate freely. The two sub-types having octahedral symmetry cannot be considered as physically identical and their inter-twinning would therefore have composition planes. The lamellar structure parallel to the octahedral planes observed in some diamonds thereby becomes explicable. The possibility that diamond having the higher and lower types of symmetry may appear inter-twinned in the same crystal has also to be recognised.

### References

- Angstrom K 1892 (quoted by Reinkober).  
 Bragg W H and Bragg W L *Proc. R. Soc. A* **89** 277 (1913).  
 Bragg W L *Atomic structure of mineral* Oxford University Press (1937) p. 52.  
 Groth P *Physikalische Kristallographie*, Engelmann (1895) p. 515.  
 Hintze C *Handbuch der Mineralogie* (Veit 1904) **Band 1**. Abt. 1, p. 3.  
 Julius 1893 (quoted by Reinkober).  
 Liebisch T *Physikalische Kristallographie* (Veit 1896) p. 88.  
 Miers H E *Mineralogy*, MacMillan (1902) p. 291.  
 Placzek G Rayleigh-Streuung und Raman-Effekt, *Handbuch der Radiologie* (1934) **Band 6**, 2nd Auf., Teil. II, p. 231, table 9 on p. 297 and p. 305.  
 Ramaswamy C *Nature (London)* **125** 704 (1930); and *Indian J. Phys.* **5** 97 (1930).  
 Reinkober *Ann. Phys.* **34** 343 (1911).  
 Robertson R, Fox J J and Martin A E *Philos. Trans. R. Soc. A* **232** 482 (1934).  
 Robertson R and Fox J J *Nature (London)* **126** 279 (1930).  
 Sutton J R *Diamond*, Murby (1928) Plates II, IV, XVII, XVIII, XX and XXI. Also pp. 9 and 32–33.  
 Tutton A E H *Crystallography and practical crystal measurement*, MacMillan **1** 502 (1922).  
 Van der Veen *Proc. Acad. Sci., Amsterdam* **10** 182 (1908).

# The nature and origin of the luminescence of diamond

SIR C V RAMAN

Department of Physics, Indian Institute of Science, Bangalore

Received April 17, 1944

## Contents

1. Introduction
2. The material for study
3. Intensity and colour of luminescence
4. Luminescence patterns in diamond
5. Luminescence and ultra-violet transparency
6. Luminescence and structural birefringence
7. Interpretation of the experimental facts
8. The spectral characters of luminescence
9. Luminescence and X-ray reflection intensities
10. Excitation of luminescence by X-rays
11. Phosphorescence
12. Summary

### 1. Introduction

Not the least interesting of the many remarkable properties of diamond is that it emits visible light on excitation by appropriate methods. Many investigators have studied the luminescence of diamond since Robert Boyle in 1663 published his observations of the phenomenon. To the methods of exciting luminescence described by him, viz., light, heat and friction, the advance of knowledge has added others, viz., cathode-ray bombardment and X-rays. It has also provided instruments, viz., the phosphoroscope and the spectroscope for the critical study of the phenomenon and extended the range of temperatures over which it may be observed downwards to the lowest values. A full summary of the earlier investigations is given in the fourth volume of Kayser's *Handbuch* (1908). In view of the fact that diamond is an elementary solid and is the typical valence crystal, it might have been supposed that its behaviour would figure prominently in any

account of the subject of luminescence. Far from this being the case, the luminescence of diamond does not even find a mention in the two bulky treatises written by Lenard for the *Handbuch der Experimental Physik*, or in Pringsheim's article of 1928 in the *Handbuch der Physik*. The reason for this lack of interest is clear from the brief reference made in Pringsheim's book (1928) and in his earlier *Handbuch* article (1926), namely the belief that the centres of luminescence in diamond are not the atoms of carbon of which it is composed, but some foreign atoms of undetermined identity present in it as impurity. The basis for this belief has been the variability of the intensity and colour of the emitted light, and the fact that not all diamonds show the phenomenon. The impurities suggested in the literature as the origin of the luminescence make a lengthy list, viz., samarium, yttrium, sodium, aluminium, chromium, iron and titanium, and include even some hydrocarbons!

The considerations regarding the crystal symmetry and structure of diamond developed in the introductory paper of this Symposium (Raman 1944) enable us to make a fresh approach to the problem of its luminescence. It is proposed to give a general outline of the experimental facts regarding the luminescence properties of diamond and to show that they fit naturally into the framework of the ideas developed in that paper, while, on the other hand, the facts remain wholly unintelligible on the impurity hypothesis. On the basis of the new ideas, it follows that the behaviour of diamond in respect of luminescence should stand in the closest relationship with its other properties, namely the absorption spectra in visible, ultra-violet and infra-red regions of the spectrum, the isotropy or birefringence observed in the polariscope, the X-ray reflection intensities, and so on. The evidence that such relationships actually exist, thereby placing the new ideas on a firm basis of experimental fact, is briefly set out in the present paper, and in fuller detail in others following it in the symposium.

## 2. The material for study

Opportunities for observing the luminescence of diamond in an impressive fashion first presented themselves to the writer in the year 1930 in connection with spectroscopic studies on the scattering of light in crystals. Several diamonds of exceptional size and quality (one of them as large as 143 carats) had been loaned by kind friends for use in those investigations. It was then found that the luminescence spectrum of diamond recorded itself on the spectrograms simultaneously with the scattering of light in the crystal, its leading feature being a band at 4155 A.U., and its intensity varying enormously from specimen to specimen (Bhagavantam 1930). These observations on photo-luminescence suggested a comparison with the case of cathode-ray luminescence. A spectroscopic investigation of the latter phenomenon was then undertaken and showed very clearly the similarity between the results in the two cases (John 1931). The very striking

character of the photo-luminescence as observed visually with some of the diamonds indicated that its further study should prove a fascinating line of research. The difficulty of obtaining suitable material, however, discouraged the pursuit of the subject.

About five years ago, the writer became aware that cleavage plates of diamond of good size and of excellent quality could be obtained at very modest prices. It was also recognized that diamond in this form is often more suitable for physical investigations than the high-priced brilliants of the jeweller's trade. The difficulty of obtaining material having thus disappeared, a sufficient number of specimens was acquired to make a start with the research, and a very fruitful series of investigations on the scattering and absorption of light in diamond and its photo-luminescence at various temperatures was carried out (Dr P G M Nayar 1941a, b, c, d; 1942a, b).

In June 1942, the writer was enabled through the kindness of the Maharaja of Panna to visit his State in Central India where diamond-mining has been carried on since very early times. The necessary instruments were transported to Panna and set up in a room in the State Treasury, and with the assistance of Dr Nayar, a physical examination was made of some hundreds of diamonds in their natural state. In particular, the valuable opportunity was afforded to us of observing the crystal form and luminescence properties of a unique set of 52 large diamonds of the finest quality belonging to the Maharaja. The writer was also enabled during this visit and also a subsequent one in December 1942 to purchase a representative collection of the diamonds mined in the State and of enlarging his collection of polished cleavage plates. Preliminary reports of the observations made on the Panna diamonds have already appeared (Raman 1942, 1943).

The observations made at Panna and the more detailed systematic studies made at Bangalore with the diamonds in the writer's collection have furnished ample material on which to base trustworthy conclusions. The material available for the laboratory investigations includes 310 specimens which may be classified as under:

- (a) 29 Panna crystals in their natural condition, selected so as to be representative of the forms and qualities of diamond as found in the State.
- (b) 65 Polished cleavage plates, for the greater part of Indian origin.
- (c) 88 Brilliants, made from South African diamonds, and set together as a jewel.
- (d) 10 Diamonds of various origins specially chosen for their interesting behaviour in regarding to luminescence or colour.
- (e) 118 Other-diamonds mostly of Indian origin.

### 3. Intensity and colour of luminescence

*The 88 South African Diamonds*—These diamonds are in the form of brilliants of varying size. Set in gold surrounded by a circle of pearls and interspersed by lines

of rubies and emeralds, the pattern formed by them represents the double-headed eagle which is the heraldic emblem of the Mysore State (figure 1 in plate I). The brilliants are not quite large enough to exhibit the inherent colour, if any, of the diamonds. So far as can be seen, however, they appear to be clear and colourless.

The ensemble of diamonds, pearls, rubies and emeralds formed by the ornament makes a striking exhibit when irradiated by ultra-violet light in the wavelength range 3500–3900 A.U. obtained by filtering the rays of the sun or of an electric arc through a plate of Wood's glass. The circle of pearls shines brightly with a uniform bluish-white lustre, while the lines of rubies appear a brilliant red and the emeralds a very faint yellow. The diamonds on the other hand, vary enormously in their appearance. A few of them irregularly scattered over the set emit a bright blue light of great intensity, while others not so luminous are also to be seen here and there. A cursory inspection suggests that only some ten or twelve of the diamonds emit any visible light. On a closer examination, however, it becomes evident that this is not really the case and that *all the 88 diamonds excepting three or four are luminescent*, though with enormously different intensities. This fact becomes particularly clear when the ultra-violet rays are focussed on each individual diamond so that the intensity of the light emitted by it is as great as possible. It is then noticed that the great majority of the diamonds exhibit luminescence of various shades of blue, the fainter ones appearing an indigo-blue and the brighter ones purer blue. Half a dozen of the diamonds, however, exhibit other colours, viz., greenish blue, greenish yellow, or pure yellow.

The range of variation of intensity between the different diamonds may be roughly estimated from the photographic exposures necessary to record them on a plate. The appearance of the ornament as seen by daylight is shown in figure 1 and photographed by (Miss) Mani with different exposures under ultra-violet light in figures 2 to 6 in plate I. A cell containing a concentrated solution of sodium nitrite was placed in front of the camera lens as a complementary filter when obtaining the luminescence photographs. Its effectiveness is shown by the fact that the gold setting and all the gems with the exception of the diamonds and one of the emeralds remain completely invisible. An exposure of two seconds was found to be sufficient to record the three mostly strongly luminescent diamonds. Exposures of 5 seconds, 15 seconds and 30 seconds respectively resulted in substantial increases in the number of diamonds visible in the photograph (figures 2, 3 and 4 respectively). An exposure of two minutes (figure 5) was necessary before the pattern bore any recognizable resemblance to its appearance as seen by daylight, while an exposure of 30 minutes was necessary in order to record the most feebly luminescent diamonds (figure 6). The brightest diamonds are, of course, then heavily overexposed. A ratio of the order of 1000:1 or even more, between the strongest and the feeblest emission intensities, is thus indicated.

*The 52 large Panna diamonds*—Crystals having smooth and lustrous faces and exquisitely beautiful geometric forms (rounded hexakis-octahedra or tetrakis-hexahedra) are to be found amongst those mined in the Panna State. Mr Sinor's book (1930) on the diamond mines of Panna contains an illustration of a remarkable and probably unique set of 52 diamonds of this kind, all having the form of hexakis-octahedra, every one of them of the finest water, and their sizes forming a regular gradation from 24 carats for the largest to  $1\frac{1}{2}$  carats for the smallest. The diamonds are strung together as a garland in their natural state by thin girdles of gold which leave the crystal faces exposed. The luminescence properties of the entire set of diamonds could therefore be very conveniently examined one after another in succession. For this purpose, the light of a carbon-arc was filtered through a plate of Wood's glass and focussed by a lens on one of the faces of the crystal, and the track of the beam inside the diamond as made visible by the luminescence could be observed through another face. In this way, besides noting the colour of the luminescence, some idea of its relative intensity in the different diamonds could also be obtained.

Of the 52 diamonds in the set, the luminescence of 3 diamonds was visually classified as "intense", of 12 as "strong", of 21 as "weak", of 14 as "very weak" and of the remaining 2 diamonds as "unobservable". The luminescence as observed in all the 50 fluorescent diamonds was of a blue colour, though, as stated, its intensity varied enormously.

*The writer's collection of 29 Panna diamonds*—The specimens in this collection fall into two groups. Group A comprises 10 diamonds of the best quality, colourless and transparent, having well-developed crystal forms and smooth lustrous faces. Group B comprises 19 so-called "industrial" diamonds, mostly of irregular shape and having a noticeable colour, grey, brown or yellow. From a scientific point of view, however, some of these diamonds are of great interest, thereby justifying their inclusion in the collection.

The diamonds were in the first instance tested in the usual manner under ultra-violet irradiation and all of them were found to be luminescent. At a later stage in the investigations, it was found useful to immerse the diamonds, while irradiated, in a cell containing a highly refractive liquid and thereby diminish the disturbing effect of reflections and refractions at their external surfaces. The behaviour of the diamonds in the two groups showed many notable differences. Those in Group A were all blue-luminescent. So far as could be made out, the intensity was uniform within the substance of each crystal, though it differed enormously as between the different diamonds. The diamonds in Group B showed a very varied behaviour. Some exhibited a blue luminescence very similar to that given by the diamonds in Group A, but its intensity varied greatly, not only as between the different specimens but also within the volume of each individual crystal. Others, again, of the diamonds in Group B showed a greenish-yellow luminescence of which the intensity varied from specimen to specimen. Careful examination showed that

luminescence of this colour was, in general, not uniformly distributed within the specimen, but appeared in parallel bands or stripes running through the volume of the crystal. The remaining crystals in Group B showed a mixed type of luminescence in which yellow bands or stripes of varying width appeared crossing a background of blue colour. In some of them, the yellow luminescence was most pronounced near projecting tips or bosses on the surface of the crystal, while the blue luminescence appeared in the interior.

The observations made with the Panna diamonds are of particular value, as the specimens were studied individually in their natural state and were in some cases also of considerable size. The observations with the brilliants of South African origin were not made under such favourable conditions, and hence they are not scientifically so significant. Broadly speaking, however, the results obtained with the two sets of diamonds are in excellent accord. The experimental situation may be summarised as follows:

- (a) Luminescence under ultra-violet excitation is exhibited by the vast majority of diamonds, including especially those of the finest quality.
- (b) A blue luminescence is characteristic of nearly all diamonds which are colourless and crystallographically perfect, its intensity, however, varying enormously from specimen to specimen.
- (c) Imperfect diamonds show sometimes a blue luminescence, sometimes a greenish-yellow luminescence and sometimes a mixed type of luminescence, the intensity of which varies not only from specimen to specimen but also within the volume of each specimen.
- (d) A few diamonds are definitely non-luminescent.

#### 4. Luminescence patterns in diamond

The difficulties which arise in working with the immersion method are altogether avoided by the use of polished cleavage-plates of diamond. 65 such plates are included in the writer's collection. Their thickness is generally small (from half a millimetre to one millimetre or more), but this is far from being a disadvantage in these investigations. The luminescence of the plates may be conveniently studied by placing them on a polished sheet of copper and irradiating them normally with ultra-violet light, a complementary filter of sodium nitrite solution being used when photographs are desired.

The enormous variations in the intensity of luminescence are best appreciated by viewing a group of diamonds at the same time (see figure 7, in plate II which includes 46 diamonds). Six plates in the collection exhibit no observable luminescence except very feebly at their edges, as shown by the bottom row in the figure. The luminescence of 34 plates is a blue, of 6 plates a yellowish-green, and of the remaining 19 plates a mixture of the two. The blue-luminescing plates may be

divided into two groups of approximately equal number; in the first group, the luminosity is more or less uniform over the plate except at the unpolished edges which shine out brightly; in the second group, the luminosity is highly non-uniform over the area of the plate and exhibits a pattern of bright and dark regions, usually with geometric features related to the crystal structure, the lines of equal brightness running parallel to the inter-sections of one, two or three sets of octahedral planes with the surface of the plate. Most of the yellow-luminescent diamonds show a pattern of fine streaks running parallel to one another within the plate. In the plates showing the mixed type of luminescence, sets of yellow bands running parallel to one another in one or two or even three different directions within the crystal are a conspicuous feature. The appearance of these yellow bands is found to depend on the angle at which the plate is viewed; they appear as fine sharp lines at some angles of observation and as broad bands at others, thereby indicating that they represent thin luminescent layers within the substance of the crystal.

Many of the 46 cleavage plates appearing in figure 7 in plate II exhibit luminescence patterns, as may be seen in that figure. The scale of this photograph is however rather too small and the exposures in most cases either too great or too small to record the patterns satisfactorily. Six typical patterns photographed on a larger scale are reproduced as figure 8 and figure 9 respectively in plate III, appearing in the upper half of these pictures. The geometric character of the patterns shown by D38 in figure 8 and by D179 in figure 9 is particularly noteworthy. These, as well as D224 appearing in figure 8 are blue-luminescent diamonds. The non-uniform intensity and the appearance of dark streaks in the luminescence of D179 and D224 are also worthy of remark. D200 seen in figure 8 has a greenish-yellow luminescence in which the most prominent feature is a set of four parallel bands. D188 and D190 appearing in figure 9 are typical diamonds exhibiting the mixed variety of luminescence. The former shows an extremely interesting pattern consisting of an intense blue spot surrounded by a faint blue ground which is crossed by sets of parallel yellow bands running in different directions across the plate. D190 exhibits a pattern of parallel bands running in different directions, blue in one part of the diamond and yellow in other parts.

Many other examples of luminescence patterns and a detailed description of the same will be found in a paper by Mrs K Sunanda Bai (1944) appearing in this symposium.

## 5. Luminescence and ultra-violet transparency

It has long been known that while the majority of diamonds are opaque to ultra-violet radiation of wavelengths smaller than about 3000 A.U., there are some diamonds which transmits the ultra-violet rays freely up to about 2250 A.U. The investigations of Robertson, Fox and Martin (1934) have shown that this

difference in ultra-violet transparency goes hand in hand with other notable differences in behaviour, especially in respect of infra-red absorption and in respect of photo-conductivity. It is therefore of obvious importance to ascertain whether the luminescence properties are in any way correlated with the empirical classification of diamond into two types which has been suggested by these investigators.

The ultra-violet transparency of diamond may be studied with a suitable source of radiation and a quartz spectrograph, and if quantitative results are desired, also an ultra-violet spectro-photometer of some kind. When a cleavage plate is employed, it is also possible by traversing its area in successive steps to investigate whether its ultra-violet transparency varies over the surface. A much simpler and more satisfactory procedure adopted by the author and Mr Rendall for this purpose is to place the plate in contact with a sheet of uranium glass and illuminate the latter *through* the diamond with the 2537 A.U. radiations of a water-cooled quartz mercury arc, its other radiations being deflected aside with a quartz prism and a couple of quartz lenses. The plates which are opaque to the 2537 rays are then seen as dark areas in the surface of the uranium glass lit up by these radiations, while those which transmit them are seen as bright areas. On placing a group of cleavage plates together on the sheet of uranium glass, it may be seen at a glance that a few of them transmit while others are opaque to the 2537 A.U. radiations. Further, it is noticed that the plates which are not opaque to the 2537 radiations may differ greatly in their degree of transparency. The method of observation also reveals that the extent of transparency may vary greatly over the surface of a given plate. Indeed, a plate may be perfectly opaque to the 2537 radiation in certain areas, perfectly transparent to it in other areas, and exhibit an intermediate behaviour elsewhere. *The procedure thus enables as visually to observe and photograph the ultra-violet transparency patterns of the cleavage plates of diamond.* Using this method of study, the following relations between luminescence and ultra-violet transparency have been established:

- (a) A blue-luminescent diamond is invariably of the ultra-violet opaque type, but the opacity diminishes with increasing intensity of luminescence.
- (b) Non-luminescent diamonds are invariably of the ultra-violet transparent type.
- (c) The diamonds which exhibit an yellowish-green luminescence are of the intermediate type, in other words, are neither perfectly transparent nor perfectly opaque to the 2537 radiations.
- (d) These statements are also valid in respect of the individual areas in a cleavage plate which exhibits a luminescence pattern.

It follows that the luminescence pattern should show a close resemblance to the ultra-violet transparency pattern to those cases where part of the diamond is blue-luminescent and another part is non-luminescent, or when the plate exhibits a greenish-yellow banded luminescence. On the other hand, if a cleavage plate

consists exclusively of blue-luminescent diamond, it is ultra-violet opaque and can therefore show no transparency pattern, even though it may exhibit local variations in the intensity of the luminescence.

To illustrate these remarks, the luminescence and ultra-violet transparency patterns of the diamonds numbered D48, D198 and D235 in the collection are reproduced side by side in figure 10. D48 exhibits three different types of behaviour simultaneously in different areas, viz., non-luminescence, blue-luminescence and the greenish-yellow banded luminescence, as can be seen from the pattern reproduced in the upper part of figure 10, while the corresponding variations in ultra-violet transparency are noticeable in the lower part of the same figure. D198 is non-luminescent at the centre and around it shows a geometric pattern of bands of greenish-yellow luminescence, changing to blue at the outer margin. It will be noticed that the resemblance between the luminescence and ultra-violet transparency patterns is extremely striking. D235 shows patches which are non-luminescent and ultra-violet transparent, while in the main it is blue-luminescent and ultra-violet opaque. Where the opaque and transparent diamonds mix, we have an imperfect transparency, and streaks of greenish-yellow luminescence are observed. It may be remarked that none of these three diamonds shows the least trace of nonuniformity when critically examined in ordinary daylight.

Illustrations of many more ultra-violet transparency patterns and a detailed discussion of the same will be found in a paper by Mr G R Rendall (1944) appearing in this symposium.

## 6. Luminescence and structural birefringence

Diamond is a cubic crystal. Hence, if the structure is the same throughout the volume of a specimen, it should be optically uniform and isotropic. If, however, structures which differ from each other ever so little in their lattice spacings are incorporated in the same specimen, it is inevitable that stresses would be set up, with the result that a strain pattern indicating the inhomogeneity of the specimen would be visible between crossed nicols in the polariscope. Cleavage plates with polished faces are particularly well-suited for such studies, as disturbing effects due to oblique reflection or refraction at the surfaces do not arise. Further, the cleavage which enables the plate to be detached from the crystal automatically releases the stresses arising from flaws, cracks or inclusions located outside the plate, and hence eliminates the purely accidental birefringence due to such causes, thereby enabling the true structural birefringence, if it exists, to be perceived.

The examination of the 65 cleavage plates in the writer's collection has furnished much valuable information regarding the nature and origin of the birefringence sometimes observed in diamond. These results will be fully dealt with in another paper appearing in the symposium. It will be sufficient here to

state the following relations which the observations show to exist between luminescence and the presence or absence of birefringence in diamond.

- (a) Diamond may be perfectly isotropic and strain-free; it is then invariably of the blue-luminescent type.
- (b) Non-luminescent diamond exhibits a characteristic and readily recognisable type of birefringence, consisting of closely-spaced parallel streaks running in several directions through the crystal.
- (c) Diamond exhibiting the greenish-yellow luminescence invariably shows a characteristic type of structural birefringence consisting of parallel dark and bright bands, usually rather wider apart than those shown by non-luminescent diamonds.
- (d) Diamond in which the blue-luminescent and non-luminescent types, or the blue-luminescent and the greenish-yellow luminescent types are simultaneously present invariably shows structural birefringence.

To illustrate the structural birefringence which appears associated with luminescence in the particular circumstances explained above, the patterns seen between crossed polaroids of the diamonds D38, D224, D200, D188, D179 and D190 are reproduced in figures 8 and 9 (plate III, side by side with the corresponding luminescence patterns. In all these cases, the general resemblance between the two kinds of pattern can be made out easily. It is most obvious in the case of the three diamonds which exhibit a greenish-yellow luminescence, viz., D200, in figure 8, and D188 and D190 in figure 9. Diamonds D38 and D224 in figure 9 and D179 in figure 10 are blue-luminescent, the two former strongly, and the latter weakly. The dark streaks appearing in their luminescence-patterns correspond to bright streaks in the birefringence patterns and arise from the intrusion of non-luminescent diamond into the blue-luminescent kind.

## 7. Interpretation of the experimental facts

We are now in a position to consider the question of the origin of the luminescence. As we have seen, Indian and South African diamonds exhibit essentially similar phenomena. The fact that the effects observed do not depend on the locality of origin makes it highly improbable that impurity atoms are responsible for the luminescence. Then again, it is the clearest and most colourless, in other words, the chemically purest diamonds which exhibit the blue luminescence in the most striking fashion. The necessity for rejecting the impurity hypothesis becomes even clearer when we consider the luminescence patterns exhibited by individual diamonds. In numerous cases, as we have seen, particular regions with sharply defined boundaries show a vivid luminescence, while adjoining regions are non-luminescent. The patterns observed in many cases have geometric configurations clearly related to the symmetry of the crystal,

indicating that the luminescence is fundamentally connected with the crystal structure.

Positive proof that the luminescence is an inherent property of the diamond itself is furnished by the relationships between the phenomenon and the other physical properties of diamond which are also dependent on crystal structure. Particularly significant is the fact that non-luminescent diamonds are completely transparent to the 2537 radiations of the mercury arc. According to the investigations of Robertson, Fox and Martin (*loc. cit.*), such ultra-violet transparency goes hand in hand with the absence of a prominent infra-red absorption band which is markedly present in diamonds opaque to the 2537 radiations. This infra-red absorption band has its head at the characteristic frequency of the diamond lattice ( $1332\text{ cm.}^{-1}$ ), and its absence and presence respectively indicate, as shown in the preceding paper, that the diamond has full octahedral symmetry or only tetrahedral symmetry as the case may be.

In the light of the foregoing remarks, the experimental facts set out in the preceding sections may be re-stated in the following words:

- (a) Diamonds with tetrahedral symmetry of structure are, in general, blue-luminescent.
- (b) Diamonds with octahedral symmetry of structure are non-luminescent.
- (c) Diamonds in which the tetrahedral and octahedral types of structure are intimately mixed exhibit the greenish-yellow type of luminescence.

It remains to explain the enormous variations found in the intensity of the luminescence. In the case of the blue-luminescent diamonds, the most natural interpretation of the facts is that the luminescent property arises from the interpenetration of the positive and negative tetrahedral structures and consequent heterogeneity of the crystal. The intensity of the luminescence would then be determined by the nature and extent of such interpenetration. Similarly, in the case of the greenish-yellow luminescence, its intensity would be determined by the extent and distribution of the tetrahedral structure which is present as an admixture with the octahedral type. The features exhibited by the luminescence patterns and the analogies and differences noticed between them and the patterns of ultra-violet transparency and of structural birefringence give strong support to these ideas.

## 8. The spectral characters of luminescence

The blue and greenish-yellow types of luminescence should evidently show different spectra. Since as we have seen, the greenish-yellow luminescence is exhibited by diamonds in which the non-luminescent and blue-luminescent varieties are mixed, it follows that the spectrum of the greenish-yellow type should always be accompanied, feebly or strongly, with that of the blue type.

Non-luminescent diamond, on the other hand, should show neither type of spectrum, even under the most prolonged exposures.

A striking experimental confirmation of these conclusions is furnished by the investigations of the luminescence and absorption spectra in the visible region carried out by (Miss) Anna Mani with 32 representative diamonds and reported in this symposium (Mani 1944). She has shown that the spectra are of two types which may be designated as the 4152 and 5032 systems, these being respectively characteristic of the blue and greenish-yellow luminescence. These always appear together, though with varying intensities whenever a diamond is luminescent, while neither appears when it be non-luminescent. Each system consists of a principal electronic line appearing at the wavelength stated in emission as well as absorption, and this is accompanied by weaker electronic lines at other wavelengths and by a subsidiary lattice spectrum in which the principal electronic frequency combines with the various possible frequencies of vibration of the crystal lattice. The lattice spectrum appears with mirror-image symmetry about the principal electronic frequency, towards longer wavelengths in emission and towards shorter wavelengths in absorption.

The significant facts which emerge from the spectroscopic studies of Nayar (*loc. cit.*) and of Miss Mani (*loc. cit.*) are the following:

- (a) Given sufficient exposures, the type of diamond which is opaque to the 2537 A.U. radiations invariably records the 4152 system with an intensity which varies enormously as between different specimens.
- (b) No trace of either the 4152 or the 5032 systems is recorded, either in emission or in absorption, with diamonds which are perfectly transparent to the 2537 A.U. radiations. But diamonds which are imperfectly transparent to these radiations show both the 4152 and 5032 systems, with varying relative strengths.
- (c) Whenever the 5032 system is recorded with any specimen, the 4152 system is an invariable accompaniment, though its strength may be greater or smaller than that of the former system.

These facts fit naturally into the ideas regarding the structure of diamond and the origin of its luminescence developed in these pages. But it is not easy to reconcile them with the 'impurity' hypothesis.

## 9. Luminescence and X-ray reflection intensities

A further striking confirmation of the idea that the luminescence of diamond is associated with the interpenetration of different crystal structures and the inhomogeneity resulting therefrom is furnished by X-ray studies. Actually, we have four possible structures, two with tetrahedral symmetry designated as Td I and Td II, and two with octahedral symmetry designated as Oh I and Oh II. The

two tetrahedral structures are physically identical but geometrically different. Hence, they can interpenetrate freely without any composition planes and without setting up stresses in the crystal. The mixed structure is nevertheless not ideally homogeneous, and its lattice planes should therefore give X-ray reflections stronger than those given by either structure individually. The smaller the blocks in which the structure is homogeneous, the more intense would be the X-ray reflections, as also the luminescence. Hence, a close correlation must exist between luminescence and X-ray reflection intensity. The lowest reflection-intensities should be given by the most feebly blue-luminescent diamonds which accordingly are the nearest approach to the ideal crystal. *Per contra*, the strongest X-ray reflection intensities and the largest departures from crystal perfection would be provided by the intensely blue-luminescing diamonds.

The theoretical inferences stated above have been confirmed experimentally by Dr R S Krishnan. The effect is conspicuously seen in the two Laue diagrams obtained by him and reproduced in an article by the present writer (Raman 1943). One of the diamonds (D31) is weakly blue-luminescent, while the other (D224) shows an extremely strong luminescence of the same colour and gives a much more intense Laue pattern than the other. A similar effect has also been observed by Dr R S Krishnan on comparing the intensities of the Bragg reflections by the oscillating crystal method.

If the Oh I or Oh II type of diamond structure exists by itself, it should give the weak X-ray reflections characteristic of an ideal crystal. Actually, when the two structures appear in the same diamond, they exhibit planes of composition and a characteristic streaky birefringence, indicating that they are physically different and that their juxtaposition sets up stresses in the solid. Hence the Oh I–Oh II mixed type should show much more intense X-ray reflections than the most intensely blue-luminescing diamond having the Td I–Td II structure. For the same reason also, diamonds having the Td–Oh mixed structures and exhibiting the yellow luminescence should stand half-way between these in respect of X-ray reflection intensities, just as they do in respect of ultra-violet transparency. That this is actually the case has been shown by Mr P S Hariharan by photometric comparison of the intensity of the Bragg reflections by a series of cleavage plates of diamond having different luminescent properties. A report of his work appears elsewhere in the symposium (Hariharan 1944).

Luminescence patterns, ultra-violet transparency patterns and structural birefringence patterns are the various different ways in which the non-uniformity of structure of a plate of diamond may be made manifest to the eye at a glance. Still another and quite different way of doing this is by the aid of X-rays, and the technique necessary for this purpose has been successfully worked out by Mr G N Ramachandran. His results are reported in another paper in the symposium (Ramachandran 1944). White X-radiation from a tungsten-target tube diverges from a pin-hole and falls upon the plate of diamond held at a sufficient distance from it. Each of the spots in the Laue pattern recorded on a photographic film is

then seen as a topographic map of the diamond in which the variations of crystal structure are indicated by corresponding variations of X-ray reflection intensity. Very striking and interesting pictures are obtained in this way, the plate and the photographic film being so tilted that the Laue spot is recorded as an undistorted representation of the diamond.

## 10. Excitation of luminescence by X-rays

The preceding discussion concerned itself with the effects observed under ultra-violet irradiation in the wavelength range 4000 A.U. to 3500 A.U. Luminescence is also excited by longer wavelengths (5000 A.U. to 4000 A.U.) and by shorter waves (3500 to 2000 A.U.). This is readily demonstrated using the appropriate light-sources and a monochromator to isolate the desired exciting radiations. The intensity with which the 4152 and 5032 systems are excited would necessarily depend on the wavelength of the exciting radiation, being greatest when it coincides with the wavelength of the principal electronic radiation of the system concerned and becoming negligible when it is larger, while it would persist with appreciable but greatly diminished intensities for shorter wavelengths. This has been shown to be the case for the 4152 system by Nayar (1941). In the ultra-violet beyond 3000 A.U., the imperfect transparency of the diamond also comes into play and causes the luminescence to be superficial and to be markedly enfeebled, these effects being the less conspicuous the more transparent the diamond under study is for the exciting radiations.

Diamonds also luminesce under the action of X-rays, unlike pearls and rubies which remain completely dark under such excitation. The intensity and also the colour of the luminescence varies as between different specimens, but the range of such variation is far less conspicuous than in the excitation by ultra-violet light. This is evident on a comparison of the series of figures 11 to 14 in plate IV with the sequence of figures 2 to 6 in plate I. Mr G N Ramachandran who has made some observations on the subject has noticed a remarkable brightening up of the luminescence by increasing the voltage under which the X-ray tube is run, while the milliamperage seemed to have little or no obvious effect on the intensity. These effects obviously merit further investigation.

## 11. Phosphorescence

Diamonds which are strongly blue-luminescent emit a yellow phosphorescence when the exciting radiation is cut off. It follows that the spectrum of the emitted light should change rapidly with time when the incident radiation is cut off. Nayar (1941, *b, c*) has recorded some fluorescence and phosphorescence spectra showing this effect, as also the change in the spectrum of the emitted light when the

wavelength of the incident light is altered by steps over the range 4000 A.U. to 6000 A.U. It is obviously desirable that the studies of the phosphorescence spectra should be extended to diamonds which show the 4152 and 5032 systems in fluorescence with comparable intensities. In this connection, it is noteworthy that strongly yellow-luminescent diamonds have a scarcely noticeable phosphorescence, thus markedly differing in their behaviour from blue-luminescing ones.

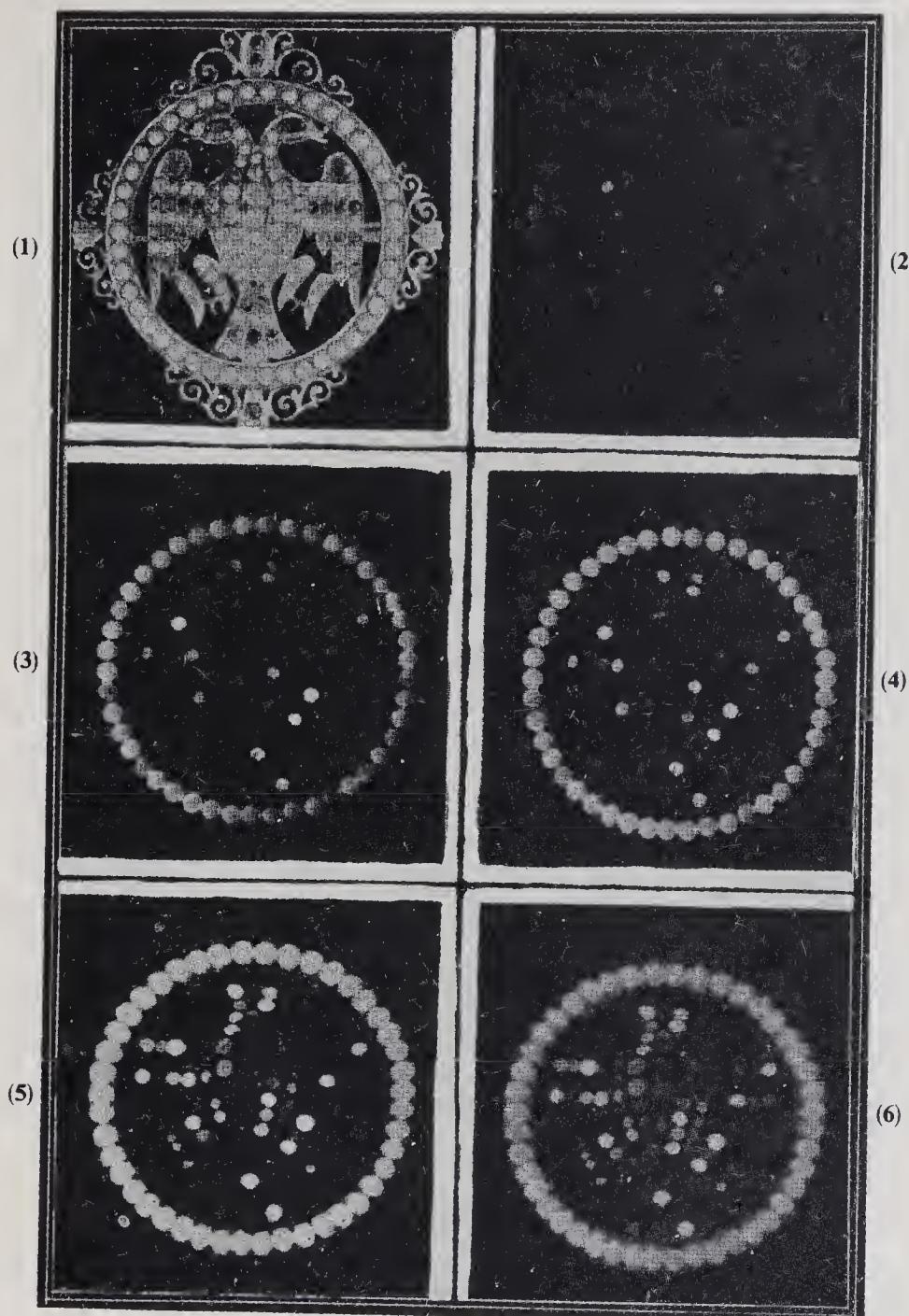
## 12. Summary

Luminescence is exhibited by nearly all diamonds, though with enormously varying intensities. Numerous specimens, both Indian and South African, in the form of natural crystals as also of cleavage plates, have been studied and the results are described and discussed. Observations with the cleavage plates are particularly significant, as many of them exhibit *luminescence patterns* having geometric characters obviously related to the structure of the crystal. The comparison of these luminescence patterns with the *patterns of transparency in the ultra-violet* beyond 3000 A.U. and with the *patterns of structural birefringence* observed between crossed polaroids is very instructive and shows that all these patterns have an essentially similar origin, viz., the interpenetrative or lamellar twinning of the different possible crystal structures in diamond. The interpenetration of the positive and negative tetrahedral structures gives rise to blue luminescence without any structural birefringence, the diamond remaining ultra-violet opaque. The interpenetration of the tetrahedral and octahedral structures gives rise to the yellow luminescence accompanied by a banded structural birefringence and an imperfect ultra-violet transparency. The lamellar twinning of the two possible octahedral structures gives diamond which is both non-luminescent and ultra-violet transparent but with a characteristic finely streaky birefringence. Spectroscopic study of the emission and absorption spectra of diamonds in the visible region, and a study of the variation of the reflecting power of the lattice planes for X-rays confirm these conclusions and show that the luminescence is essentially physical in origin and not due to foreign atoms present as impurities.

## References

- Bhagavantam S *Indian J. Phys.* **5** 169 (1930).
- Hariharan P S *Proc. Indian Acad. Sci.* **19** (1944).
- John M V *Indian J. Phys.* **6** 305 (1931).
- Kayser *Handbuch der Spectroscopie* **4** 830 (1908).
- Mani A *Proc. Indian Acad. Sci.* **19** (1944).
- Nayar P G N *Ibid.* **13** 284 (1941a).

- Nayar P G N *Ibid.* **13** 483 (1941b).  
Nayar P G N *Ibid.* **13** 534 (1941c).  
Nayar P G N *Ibid.* **14** 1 (1941d).  
Nayar P G N *Ibid.* **15** 293 (1942a).  
Nayar P G N *Ibid.* **15** 310 (1942b).  
Pringsheim P *Handbuch der Physik Band 23* Ziff. 60 (1926).  
Pringsheim P *Fluorescenz und Phosphorescenz* 318 (1928).  
Ramachandran G N *Proc. Indian Acad. Sci.* **19** (1944).  
Raman C V *Curr. Sci.* **11** 261 (1942).  
Raman C V *Ibid.* **12** 33 (1943).  
Raman C V *Proc. Indian Acad. Sci.* **19** 189 (1944).  
Rendall G R *Ibid.* **19** (1944).  
Robertson, Fox and Martin *Philos Trans. R. Soc. A* **232** 463 (1934).  
Sunanda Bai K *Proc. Indian Acad. Sci.* **19** (1944).



Luminescence of South African diamonds

Figure 1. Photograph in daylight.

Figures 2 to 6. Luminescence in ultra-violet with increasing exposures.

Plate I

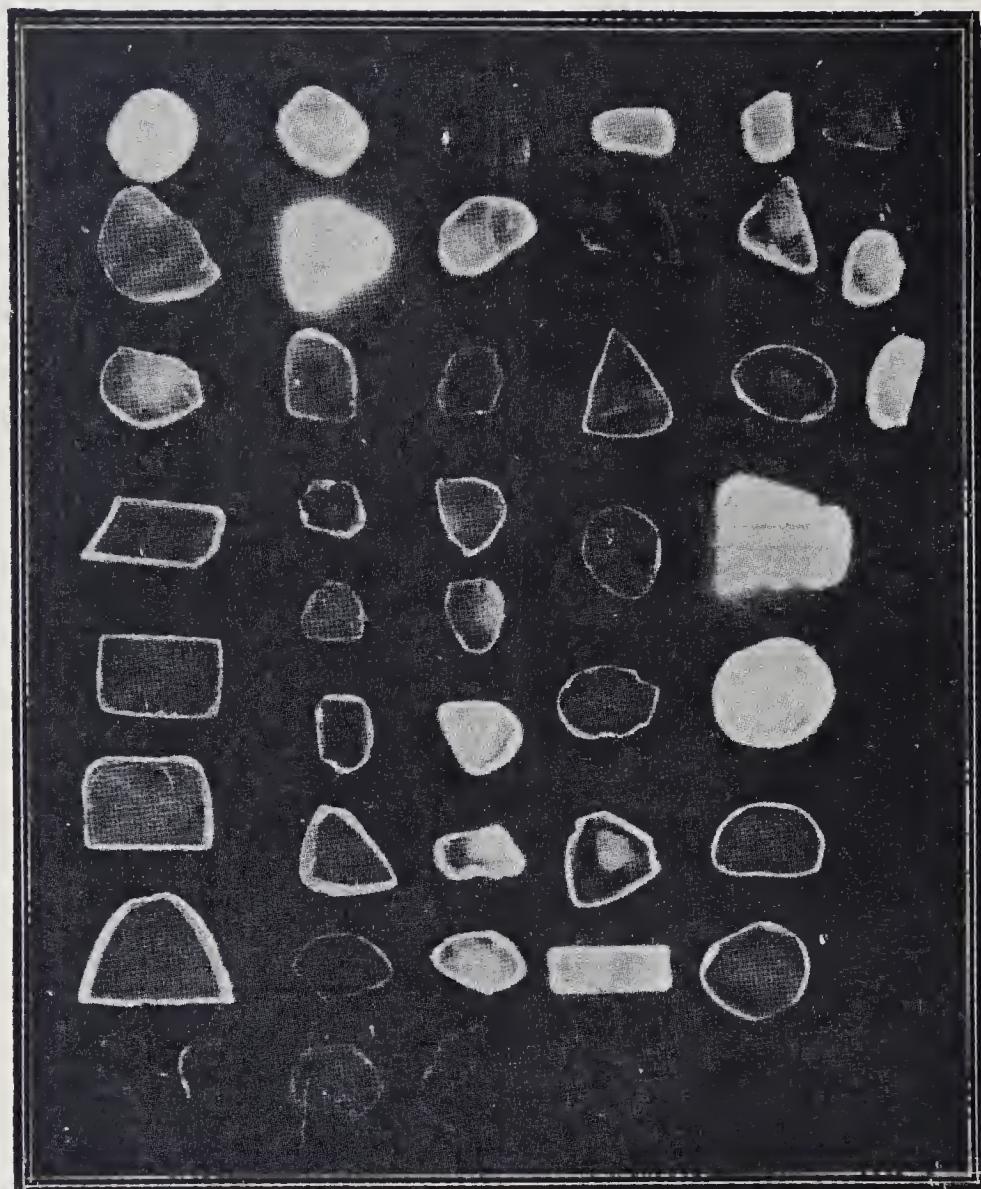
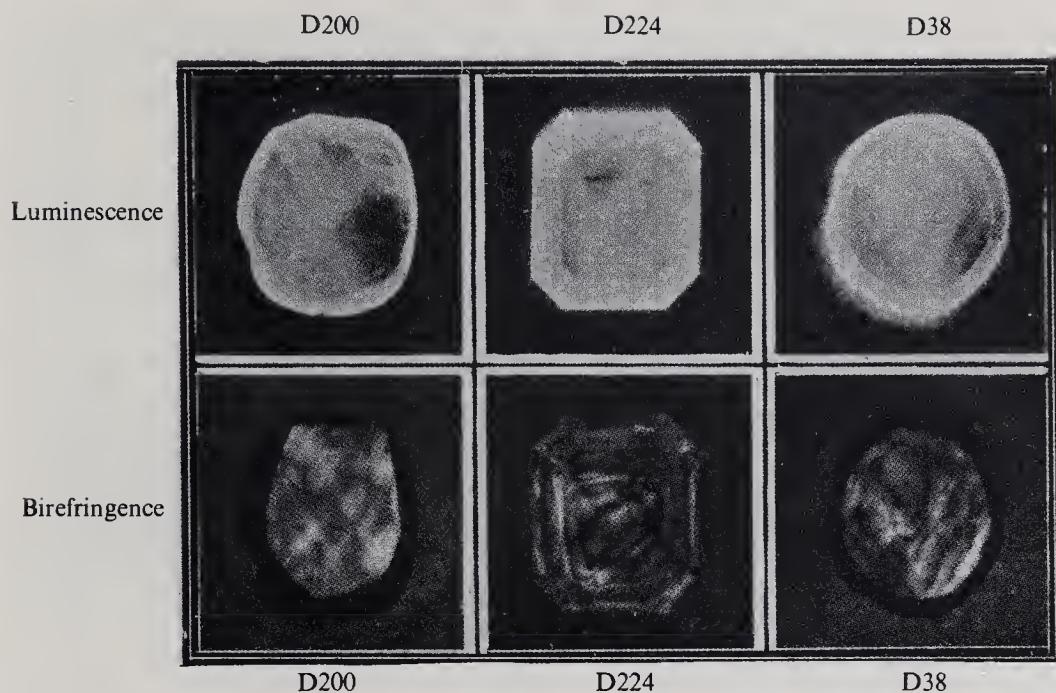
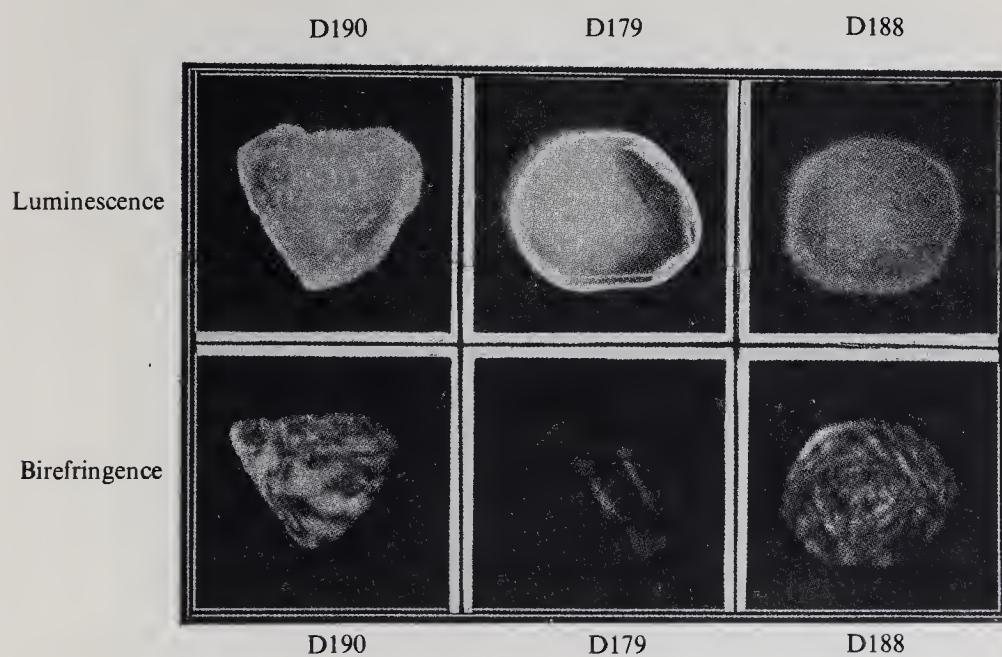


Figure 7. Luminescence of cleavage plates of diamond.

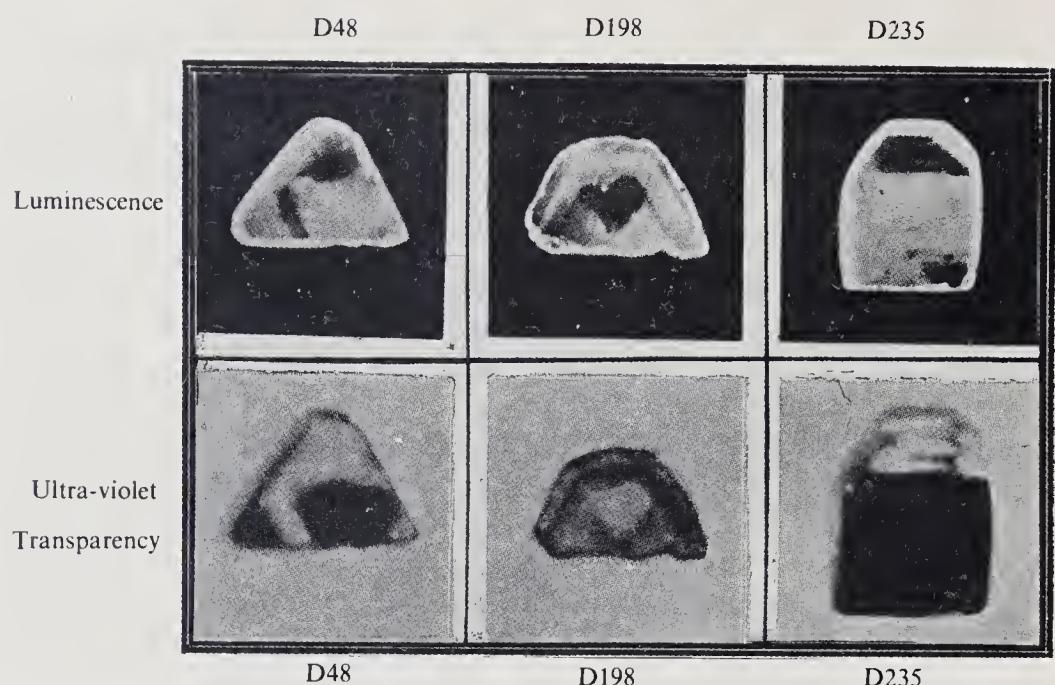
Catalogue numbers					
D 188	200	199	196	193	191
175	190	192	198	48	194
185	210	211	195	177	202
31	231	182	178	34	
	176	183			
221	52	187	173	38	
36	174	189	180	181	
222	172	186	42	179	
52,208	209	206	39	207	Non-luminescent



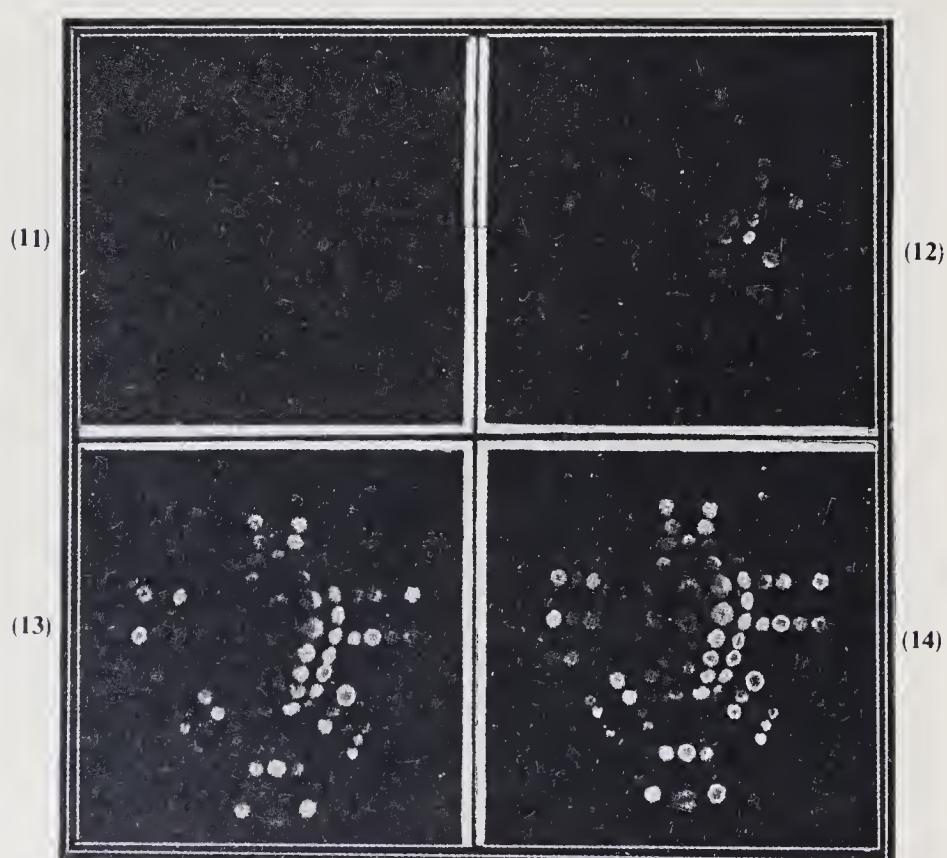
**Figure 8.** Comparison of luminescence and birefringence patterns.



**Figure 9.** Comparison of luminescence and birefringence patterns.



**Figure 10.** Comparison of luminescence and ultra-violet transparency patterns.



**Figures 11 to 14.** 11. 50 K.V. 10 minutes 12. 56 K.V. 30 minutes, 13. 70 K.V. 30 minutes; 14. 70 K.V. 60 minutes.

## Birefringence patterns in diamond

SIR C V RAMAN and G R RENDALL

Department of Physics, Indian Institute of Science, Bangalore

Received May 11, 1944

### 1. Introduction

Mineralogists have long been familiar with the fact that diamonds exhibit a very varied behaviour when examined under the polarising microscope. Sinor (1930) made extensive observations on the diamonds mined in the Panna State and found that very clear crystals in which all the faces were symmetrically developed showed very little or no double refraction. On the other hand, crystals containing flaws and inclusions, distorted crystals, and brownish tinted crystals showed bands and stripes of colour between crossed nicols. Since perfection of external form and of optical quality are both indicative of a homogeneity of structure, the specimens exhibiting them should naturally also show the optical isotropy characteristic of a cubic crystal. *Per contra*, it is not surprising that diamonds having an irregular form or visible internal flaws or inclusions should exhibit birefringence. Even a small difference in crystal orientation in the different parts of a diamond which has solidified under unsatisfactory conditions would result in enormous stresses and strains being set up which would reveal themselves in the polariscope. Such birefringence would necessarily be irregular. The variations of crystal orientation within the diamond giving rise to it should be evident on an X-ray examination, e.g., in a Laue photograph, the spots in the pattern being distorted or drawn out into streaks or even appearing multiplied in number.

Birefringence of a wholly different kind which may be described as *structural* and not as accidental, is also exhibited by many specimens of diamond. Such birefringence is distinguished by the geometric character of the figures observed in the polariscope, as also by the relationship of the figures to the crystal architecture and symmetry. Birefringence of this kind in diamond and its interpretation forms the subject of the present paper. Somewhat analogous patterns are exhibited by crystal plates of isomorphous mixtures of substances crystallising in the cubic system, e.g., the nitrates of barium, strontium and solids, and especially by crystal plates of the mixed alums when examined between crossed nicols (Liebisch 1896). As is shown in the introductory paper of this symposium, crystallographic considerations as well as spectroscopic evidence

compel us to admit the possibility of four different structures for diamond, two with tetrahedral and two others with octahedral symmetry, which may coexist in one and the same specimen. This fact opens the way to an understanding of the geometric birefringence patterns observed in diamond, as also of other properties which vary with its structure, e.g., its luminescence, its transparency in the visible, ultra-violet and infra-red regions of the spectrum, its reflecting power for X-rays and its photoconductivity, all of which stand in close relation to each other.

## 2. Crystals in their natural form

Observations with diamonds in their natural state placed between crossed nicols are of interest in view of the fact that the absence of birefringence is a very delicate test of crystal perfection. Consider for instance, an octahedral diamond of 20 carats which would be about a centimeter thick and the optical path through which would be some 50,000 wavelengths of visible light. A difference of one part in a million in the refractive indices for vibrations in different directions would produce an easily observable restoration of light between crossed nicols, while a difference of one part in a hundred thousand would give polarisation colours. It will be evident that the test is an extraordinarily sensitive one for crystal perfection, especially where large diamonds are concerned.

Owing to the high refractivity of diamond, such observations are necessarily be confined in any one setting of the crystal to small portions of it bounded by parallel faces. These regions would be further restricted if, as is often the case, the surfaces of the crystal are curved. The difficulties mentioned are least serious in the case of large regular crystals with nearly plane faces and most serious for small crystals having highly curved surfaces and with irregular diamonds. They may, however, be minimised by immersing the crystal in a cell containing a transparent liquid of sufficiently high refractive index.

The optical behaviour of numerous diamonds, including some of large size and in particular, the Maharajah's necklace of 52 octahedral crystals was studied by Sir C V Raman and Dr P G N Nayar during their visit to Panna State in July 1942. More recently at Bangalore, 42 Panna crystals of various sizes and qualities have been critically examined for birefringence when immersed in liquid monobromnaphthalene. The conclusions indicated by these studies are as follows:

- (a) Diamonds which are of the blue luminescent and ultra-violet opaque type are optically isotropic, their birefringence, if any, being less than 1 part in 100,000. This is subject to the proviso that the crystal is of perfect form, free from flaws and inclusions, and colourless.
- (b) Small diamonds of the kind stated above may be optically isotropic even if the crystal form is not absolutely regular.

- (c) Other diamonds usually exhibit marked birefringence of which there are two kinds, appearing each by itself or together, viz., birefringence which is wholly irregular, and birefringence which is related to the crystal architecture and exhibits a geometric character.
- (d) While birefringence of the latter kind may appear in blue-luminescent diamonds, it is an invariable feature in the yellow-luminescing ones.

### 3. Observations with polished cleavage plates

There are notable advantages in the study of the birefringence patterns in diamond gained by the use of polished cleavage plates, such as are readily obtainable. As these plates are parallel to the octahedral planes (more rarely to the dodecahedral planes) in the crystal, the relationship of the pattern seen in the polariscope to the crystal architecture is immediately apparent. Moreover, the pattern over the whole area of the plate is visible and can be photographed at the same time, while the disturbing effects due to oblique reflection and refraction which are so troublesome in working with crystals in their natural form do not arise at all. There is also another notable gain in the use of cleavage plates. The act of cleavage releases the material in the plate from stresses having their origin in faults or irregularities elsewhere in the original crystal from which it is split off. The accidental or irregular birefringence due to those stresses is thereby eliminated and the real optical character of the material in the plate made accessible to observation.

A beautiful illustration of the foregoing remarks is furnished by the case of the cleavage plates D36 and D45, the birefringence patterns of which are reproduced in juxtaposition in figure 4 of plate IV. These two diamonds originally formed a single plate, the whole area of which exhibited a strong restoration of light between crossed nicols. This had its origin in certain irregularities located in the lower part included in D36 and which are clearly seen in the pattern of the latter. When D45 broke off, the stresses in it were released with the result that the birefringence in it has disappeared, while that in D36 remains undiminished (possibly even a little enhanced).

The birefringence patterns as seen between crossed polaroids of several cleavage plates are reproduced as figures 1, 2, 3 and 4 in plates I to IV accompanying this paper. These were chosen from amongst a large number so as to be generally representative of the whole and at the same time to illustrate points of special interest. The significance of these patterns becomes evident when they are carefully compared with the luminescence patterns, the ultra-violet transparency patterns and X-ray topographs of the same diamonds appearing with the papers immediately following the present one in the symposium.

#### 4. Description of the patterns

The diamonds D221 (figure 1) and D45 (figure 4) are opaque to the 2536 Å radiations of the quartz mercury arc lamp and are both feebly blue-luminescent. It will be noticed from the figures that they give no sensible restoration of light between the crossed polaroids, thereby confirming the essentially isotropic character of diamonds of this class already made evident from the study of the best Panna crystals. The statement made by Robertson, Fox and Martin (1934) that type I or ultra-violet opaque diamonds are optically anisotropic is thus clearly not justified.

D174, D178 and D179 (figure 1) are three diamonds which exhibit rather striking patterns of geometric type. These diamonds are, over the greater part of their area, of the blue-fluorescent and ultra-violet opaque type. That they are optically isotropic in the same regions is evident from the fact that nearly the whole area of D178, the central region of D174 and the major part of the area of D179 remain quite dark as seen at all settings between crossed polaroids. The symmetric patterns shown rather feebly in D178 and more strongly in D174 and D179 consist of bands running parallel to the octahedral planes in the crystal. The region of the diamond which appears as a particularly bright line in the birefringence pattern of D179 appears as a dark line in its luminescence pattern and as a line of diminished opacity in its ultra-violet transparency pattern, thereby clearly showing that it is an intrusive layer of diamond having different properties from the rest of the material in the plate. The same result is indicated by the X-ray topographs of D174 and D179 obtained by Mr G N Ramachandran (1944), where the intruding layers reveal themselves by the increased intensity of X-ray reflection at precisely the same regions in the plates. D181 and D38 illustrated in figure 1 are also blue-luminescent diamonds. The strong birefringence which they exhibit has essentially the same explanation, viz., the intrusion into the blue-luminescent diamond of thick layers of non-luminescent diamond. This is clearly shown by the X-ray topographs which exhibit a perfect correspondence with the birefringence patterns.

The appearance between crossed polaroids of D206, D207, D208, D209 and of D39 and D57 is illustrated in figures 2, 3 and 4. All these six diamonds are of the ultra-violet transparent and non-fluorescent class, and it will be seen that the birefringence which they exhibit is of a highly characteristic type, viz., sets of parallel dark and bright streaks running through the crystal in various directions. The spacing of these streaks is extremely variable, and indeed, both coarsely and finely-spaced streaks may often be seen at the same time in any particular specimen. A special remark is necessary regarding D39, which at first sight seems different in its behaviour from the others. In this diamond, an irregular birefringence is present, due to some obvious imperfections in the crystal which are also revealed by X-ray examination. This obscures the characteristic streaky birefringence of diamonds of this class over a greater part of its area. Careful

examination under higher magnification, however, reveals the presence of the latter, and especially clearly when the irregular birefringence is eliminated in a particular area by an appropriate setting of the plate between the crossed polaroids. The patterns of D57 appearing in figure 4 have been reproduced under rather high magnification in order to exhibit the characteristic criss-cross streakiness of the field more clearly.

The case of D39 (and also of some other diamonds in the collection) shows clearly that diamonds of the ultra-violet transparent class *may* exhibit irregular birefringence. The statement made by Robertson, Fox and Martin in their paper that diamonds of this class are optically isotropic is therefore not justified. While all diamonds may exhibit irregular birefringence if they have imperfections, perfect crystals of the blue-fluorescent ultra-violet opaque type are, as we have seen, essentially isotropic and free from birefringence, while diamonds of the non-fluorescent ultra-violet transparent type have a characteristic structural birefringence of the kind illustrated in figures 2, 3 and 4 in the plates. The situation is thus actually the reverse of that stated to exist by Robertson, Fox and Martin.

The remaining patterns illustrated in the plates accompanying the paper fall into two groups. Some of them are essentially of the same nature as the patterns of the six ultra-violet transparent diamonds considered above. The diamonds D199 and D202 are of this kind. They exhibit a yellow fluorescence. They are not fully ultra-violet transparent, but as has been shown in the paper by Sunanda Bai (1944), if adequate exposures are given, the recorded absorption spectra of these diamonds extend to the same limit as that of the fully ultra-violet transparent diamonds. It is therefore scarcely surprising that the birefringence patterns are also of the same nature for the two sets of diamonds. The other two plates whose patterns have been reproduced, viz., D48 and D235, are typical *mixed* diamonds, showing in different parts of their area all the three kinds of behaviour in respect of luminescence, viz., blue-luminescence, non-luminescence and yellow-luminescence, and the corresponding three different behaviours in their ultra-violet absorption, viz., opacity, perfect transparency and partial transparency. The respective regions in the areas of the plate can be distinguished in the luminescence and ultra-violet transparency patterns, while the X-ray topographs show clearly the intrusion into each other of the different types of diamond. The corresponding variations in the nature of the birefringence in different areas of the plate can also be readily made out in figures 2 and 4.

## 5. The origin of structural birefringence

The origin of *irregular* birefringence has already been considered and pointed out earlier in the paper, viz., accidental imperfections of the crystal structure. The appearance of such imperfections is scarcely surprising when the structure of

diamond and the nature of the atomic forces in it are considered. The binding forces acting directly between neighbouring atoms of carbon are the strongest of these and are sufficient to secure the coherence of all the atoms in a specimen even when the circumstances of formation of the crystal are such that complete uniformity of the inter-atomic distances and especially of the valence angles throughout its volume is not possible. Atomic equilibrium can then only be secured by the existence of a system of macroscopic stresses and strains in the solid.

The origin of the kind of birefringence with which we are principally concerned in this paper is, however, of an altogether different nature. As we have seen, it arises from the co-existence in the same specimen and interpenetration into each other of kinds of diamond having different physical properties. Considering, first, the diamonds of the blue-luminescent ultra-violet opaque class, these have tetrahedral symmetry, the two variants Td I and Td II having this symmetry being co-existent and interpenetrating to varying extents. The absence of birefringence in such diamonds indicates that the crystal spacings of these two structures are perfectly identical and that they can therefore fit into each other without any stresses or strains arising. Indeed, the relationship between neighbouring carbon atoms in Td I and Td II is physically the same, but geometrically different. Hence, the identity of crystal spacing and the absence of any birefringence in diamonds of this class is fully to be expected. *Per contra*, the appearance of a characteristic streaky or lamellar birefringence in the non-luminescent ultra-violet transparent diamonds indicates that the Oh I and Oh II structures of which these diamonds consist, and the co-existence and interpenetration of which gives rise to their lamellar structure, are not physically identical. It is evident that even a small difference in the crystal spacing of the two interpenetrating forms would give rise to a streaky or lamellar birefringence, and that it would also give rise to marked inhomogeneities giving a greatly increased intensity of X-ray reflection.

The explanation of structural birefringence in diamond indicated above is confirmed in a striking manner by the existence of observable variations of crystal spacing in diamonds of the ultra-violet transparent class. This is shown in another paper by Dr R S Krishnan (1944) appearing in this symposium. His experiments were made with the diamond D209 whose birefringence pattern is reproduced in figure 2 of the plates accompanying this paper. The variations in crystal spacing in alternate layers of the diamond were revealed by X-ray methods and found to be accompanied by periodic variations in the intensity of the X-ray reflections from these layers, indicating the existence of a close physical relationship between the two effects. The periodic variations in crystal spacing found were of the order of 5 parts per 10,000. Small though these are, they are clearly sufficient to explain the observed birefringence which is itself small and is so readily noticed only because of the delicacy of the method of observation.

X-ray observations with specimens, such as D48 and D235, in which the

tetrahedral and octahedral varieties of diamond appear juxtaposed in adjacent areas should similarly be capable of ascertaining the differences in crystal spacing of the Td structures from those of the Oh I and Oh II types. A knowledge of these differences would assist in a fuller elucidation of the birefringence patterns observed in such cases. In some of these patterns, e.g., those of D174 and D178 appearing in figure 1, only the intruding layers of octahedral diamond show an appreciable restoration of light, while in others e.g., the patterns of D181 and D38, the entire diamond shows a restoration though of varying intensity, though the intrusions extend over only part of its area. It would seem that in cases of the latter kind, the stresses set up by the presence of the intruding layers extend over the entire diamond and are of sufficient magnitude to cause an appreciable birefringence to be exhibited by it.

## 6. Nature and magnitude of the stresses

Since the birefringence patterns are photoelastic effects due to the variations of the crystal spacing in diamond, it follows that the axes of birefringence should be related to the orientation of the layers in the crystal in a determinate way. In particular, when there is only one set of laminations in the crystal, the axes of birefringence should be parallel and perpendicular respectively to the laminations. This is readily tested by placing the diamond between crossed polaroids and observing the changes in the pattern as the diamond is rotated in its own plane. As is to be expected, it is found that the bands in the pattern appear most intense when they run at an angle of  $45^\circ$  with the axes of the polaroids and vanish when they are set parallel or perpendicular to them.

In more complicated cases when there are two or more sets of parallel laminations running in different directions and intersecting each other, both the nature of the pattern and the axes of birefringence would be determined by their joint effect, and not by any one of them separately. A striking illustration of this is furnished by D209, the birefringence patterns of which taken at two different settings of the diamonds are reproduced in figure 2. It will be noticed that in one setting, the pattern is very bright and shows a rectangular patchwork of dark and bright lines, while in the other setting, it is of much smaller intensity and of irregular character. It is found that the pattern is most intense when the bands in the birefringence pattern are inclined at  $45^\circ$  to the axes of the crossed polaroids, and least intense when they are parallel and perpendicular respectively to these axes. It may be remarked that the X-ray topograph of D209 shows the presence of two sets of strongly reflecting layers of diamond which are inclined to each other at an angle of  $60^\circ$ , while the birefringence pattern, on the other hand, shows a rectangular pattern of bright and dark bands. This difference is, however, entirely to be expected in view of the remarks made above. Indeed, the resemblances as well as the differences noticed between the birefringence pattern of this diamond and

its X-ray topograph form a striking confirmation of the explanations put forward of the origin of the former pattern.

Quantitative measures of the birefringence are obviously desirable to enable a more complete account of the subject to be given. A knowledge of the elastic-optic constants of diamond, the orientation and thickness of the intruding layers, and of their crystal spacings, should enable the expected birefringence to be computed and compared with the observed values. Such an investigation should be well worth undertaking. It should be remarked also that the birefringence patterns reveal only the *differences* in the refractive index for vibrations along the principal axes of stress. Observations of interference patterns may conceivably reveal the *absolute* variations of the refractive index, though these would naturally be very small. A knowledge of them would be necessary for a complete evaluation of the stress system of pressures and shears present in the diamond.

## 7. Summary

Birefringence in diamond may be either *irregular* or of *geometric* character. In the former case, it is due to structural imperfections, but its magnitude is negligible in well-formed perfect crystals. *Geometric* or *structural* birefringence manifests itself in regular patterns related to the symmetry of the crystal. It arises from the co-existence in the crystal of structures with different properties and crystal spacings. Extensive studies prove that diamond of the blue-luminescent ultra-violet opaque type is isotropic, while diamond of the non-luminescent ultra-violet transparent type invariably shows a structural birefringence. These facts find a natural explanation when the relationships existing between the four possible structure-types in diamond namely Td I, Td II, Oh I and Oh II are considered. A difference in the crystal spacings of the Oh I and Oh II structures present in the ultra-violet transparent diamonds is proved by X-ray studies and is the origin of the streaky or laminar birefringence exhibited by such diamonds. Birefringence patterns may also arise from the intrusion of the Oh structure into Td diamonds. This is fully confirmed by the variations of luminescence, ultra-violet transparency, and of X-ray reflection intensities over the area of the specimen exhibited by such diamonds.

## References

- Krishnan R S, *Proc. Indian Acad. Sci.* **A19** (1944)
- Liebsch T, *Physikalische Krystallographie Veit*, Leipzig **325** (1896)
- Ramachandran G N, *Proc. Indian Acad. Sci.* **A19** (1944)
- Robertson, Fox and Martin, *Philos. Trans. R. Soc.* **A232** 463 (1934)
- Sinor *The diamond mines of Panna* (1930).
- Sunanda Bai K, *Proc. Indian Acad. Sci.* **A19** 253 (1944)

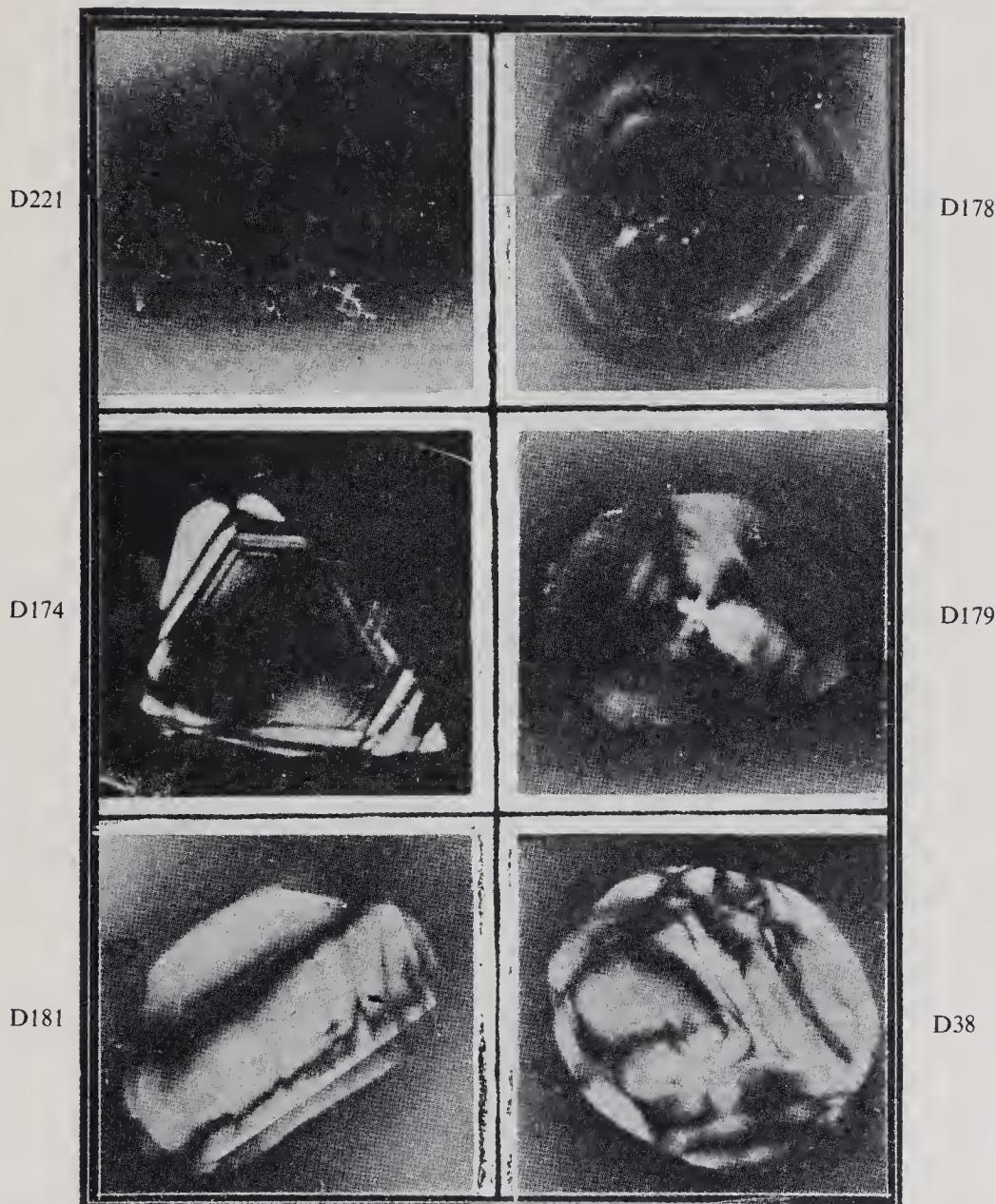


Figure 1. Birefringence patterns in blue-luminescent diamonds.

Plate I

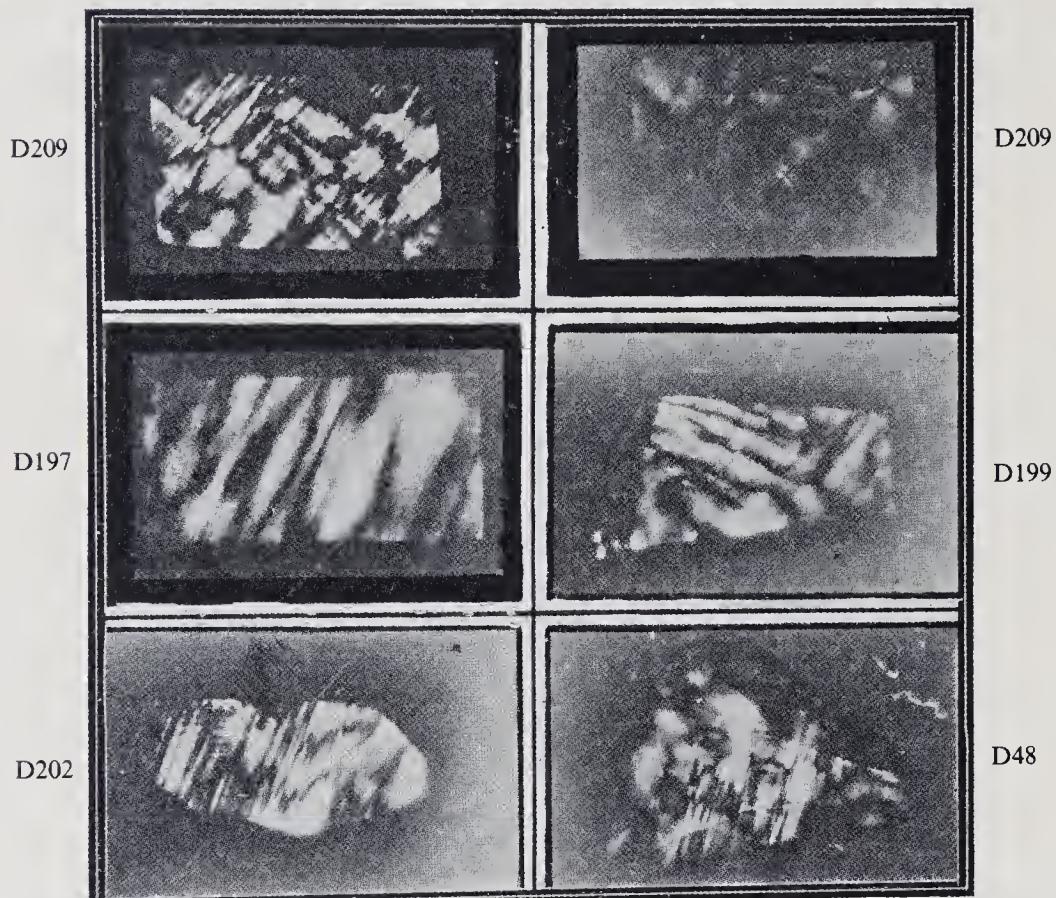
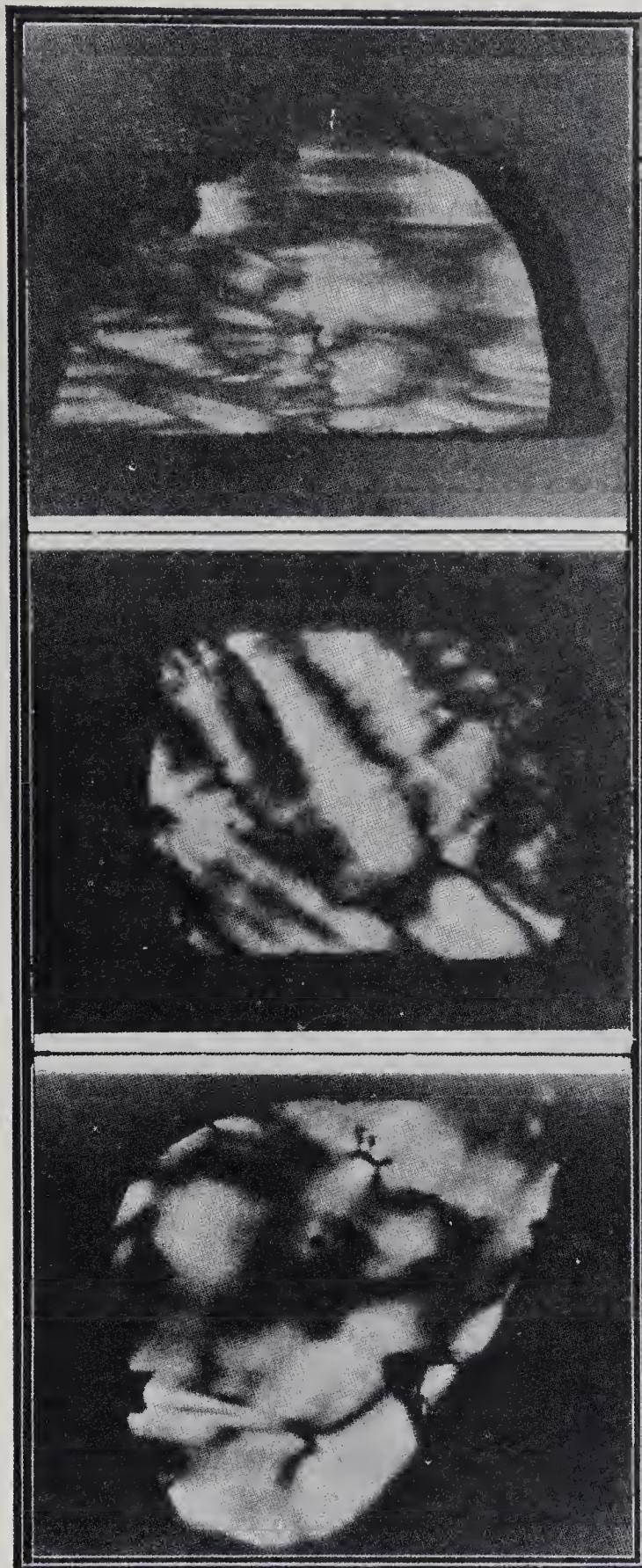


Figure 2. Streaky birefringence in diamonds.

Plate II



D206

D208

D39

**Figure 3.** Birefringence in non-luminescent diamonds.

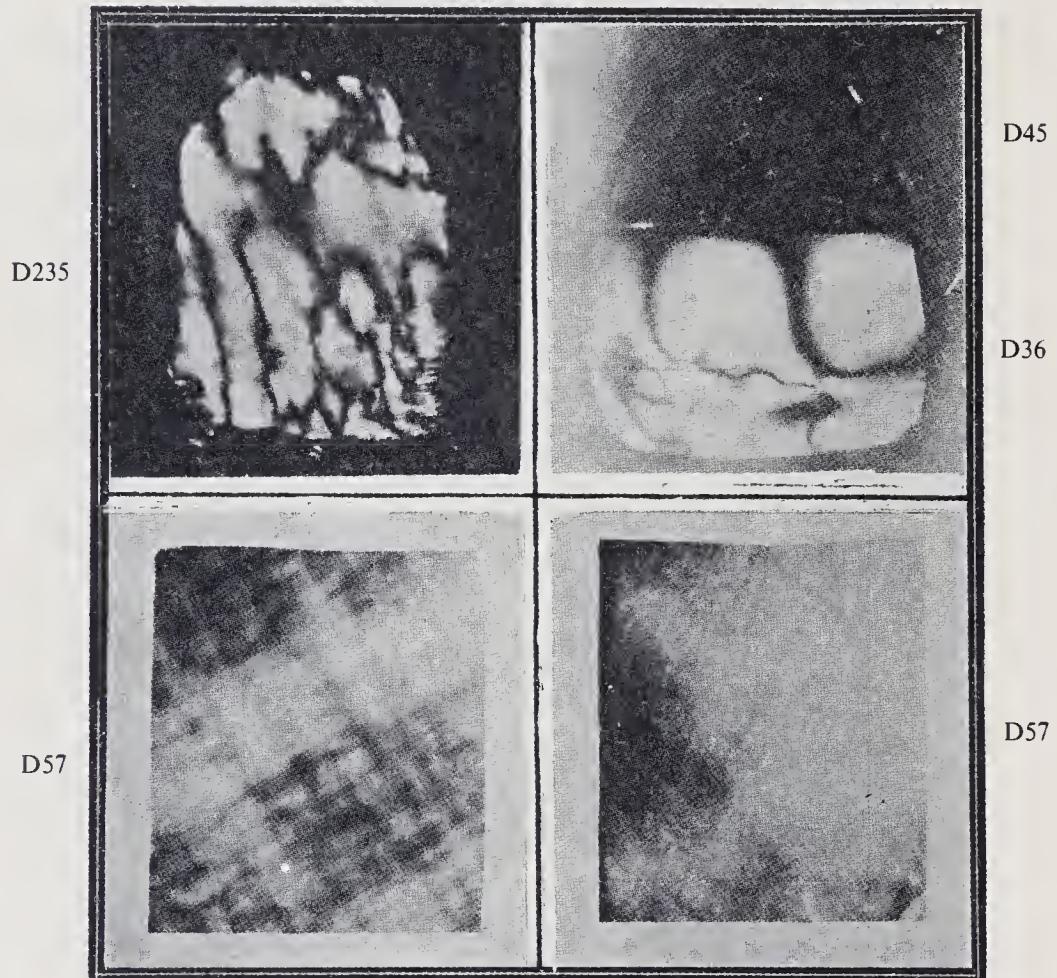


Figure 4. Birefringence in diamonds.

Plate IV

# The crystal forms of diamond and their significance

SIR C V RAMAN and S RAMASESHAN

Department of Physics, Indian Institute of Science, Bangalore

Received for publication, June 4, 1946

## Contents

1. Introductory statement
2. General descriptive characters
3. Some theoretical considerations
4. Geometric preliminaries
5. The configuration of the edges
6. The crystal symmetry of diamond
7. Classification of the crystal forms
8. The Haidinger diamond
9. The triangular twins
10. Some descriptive notes
11. The allotropic modifications of diamond
12. Summary. References. Plates

### 1. Introductory statement

The crystallography of diamond presents problems of peculiar interest and difficulty. The material as found is usually in the form of complete crystals bounded on all sides by their natural faces, but strangely enough, these faces generally exhibit a marked curvature. The diamonds found in the State of Panna in Central India, for example, are invariably of this kind. Other diamonds – as for example a group of specimens recently acquired for our studies from Hyderabad (Deccan) – show both plane and curved faces in combination. Even those diamonds which at first sight seem to resemble the standard forms of geometric crystallography, such as the rhombic dodecahedron or the octahedron, are found on scrutiny to exhibit features which preclude such an identification. This is the case, for example, with the South African diamonds presented to us for the purpose of these studies by the De Beers Mining Corporation of Kimberley. From these facts it is evident that the crystallography of diamond stands in a class by itself apart from that of other substances and needs to be approached from a

distinctive standpoint. It is essential, at the very outset, to emphasise the point—seemingly obvious but often overlooked—that a crystal which exhibits curved faces cannot properly be described in the usual terminology which is based on the existence of plane faces obeying the crystallographic law of rational indices.

One of the most firmly established results of physics is the dependence of the physical properties of a crystalline solid on the symmetry of its structure of which the external form is an indication. There can be little doubt, therefore, that a study of the crystal forms of diamond, pursued from an appropriate standpoint, would prove most helpful in understanding and interpreting the many remarkable properties of this substance. These considerations and the availability of the material referred to above—some 72 specimens in all—encouraged us to undertake a critical examination of the subject. The investigation had for its object the discovery of the factors determining the general shape and other distinctive features of the crystal forms, and of the connection between them and the internal architecture of the crystal. The studies have enabled us to establish some definite propositions concerning these matters which are stated below. The evidence on which our conclusions are based will be set out fully in the course of the paper.

- I. Both the internal architecture of diamond and its external form are determined by the quadrivalence of the carbon atom and its intrinsic tetrahedral symmetry in the crystal.
- II. The sharply defined edges appearing on the curved surface of the crystal are its intersections with the six symmetry planes of the fundamental tetrahedron, each containing two of the valence directions.
- III. The general shape of a diamond crystal stands in the closest relation with the configuration of the edges on its surface.
- IV. An edge is most pronounced when it coincides exactly with a valence direction and becomes less conspicuous as it deviates from the same.
- V. The vertices of the crystal are the points where four or six edges meet.
- VI. The crystal symmetry of diamond as revealed by the edges on its surface is in the majority of cases that of the tetrahedral class only.
- VII. While many diamonds exhibit the features characteristic of tetrahedral symmetry, there is a manifest tendency towards the assumption of forms which are common to the tetrahedral and octahedral symmetry classes.
- VIII. The crystal forms of diamond exhibit a recognizable sequence on which it is possible to base a theory of their formation.

## 2. General descriptive characters

*The Panna diamonds:* Fortythree of our specimens are from the State of Panna in Central India. They are of widely differing shape, size and quality and may be

considered as fairly representative of the diamonds mined in that area. As stated in the Introduction, the Panna diamonds invariably exhibit curved faces. During the senior author's two visits to the Panna State Treasury, he had the opportunity of examining several hundreds of these diamonds, including several very large and exceptionally fine specimens and never once came across a crystal showing plane faces either alone or in combination with the usual curved forms. It is very remarkable also that though the Panna diamonds are found in conglomerate beds of obviously sedimentary origin, it is exceptional to find a specimen exhibiting signs of having undergone any wear and tear during the transit from the original site of formation to its final resting place in those beds. Indeed, amongst our 43 specimens, there are only two which give any indication of having suffered in this manner. Most of our specimens, in fact, exhibit a remarkable transparency and smooth lustrous faces on which the details are seen beautifully clear and sharp. There cannot therefore be any doubt that the Panna diamonds exhibit precisely the same form as that in which they originally crystallised.

In an earlier symposium, a paper appeared by one of us (Ramaseshan 1944) describing and depicting the forms of the Panna diamonds. At that time, our Panna collection was not so extensive as it is now, having since been enriched by the addition of fourteen specimens of great interest from the scientific point of view. Further, at that time, we did not recognise as fully as we do now, the futility of describing curved crystal forms in the usual language of geometric crystallography. At that time also we had not discovered the physical significance of the details seen on the surface of these diamonds. The shortcomings arising from these circumstances, however, do not effect the scientific value of the diagrams, photographs and descriptive detail set out in the earlier paper. It was, in fact, the attempt to explain the facts described in that paper which led us to the present investigation.

We may here briefly recapitulate the main facts which emerged from the earlier studies. The curved surface of a Panna diamond is not a single continuous sheet, but consists of distinct sections meeting sharply along well-defined edges. These edges appear elevated above the general level of the surface to an extent depending on the angle between the sections on either side of them. This angle and the prominence of the edge vary enormously. An edge may at one part of the surface be so pronounced as to form a visible ridge, while elsewhere it may be so little conspicuous as to be seen only on careful examination under suitable illumination. The points on the surface where four or six prominent edges meet appear as protuberances or vertices of the crystal form. On the other hand, regions where the edges are inconspicuous are areas of relatively small curvature of the surface, even at points where they intersect. In a general way and subject to certain variations determined by the general shape of the diamond, the pattern of edges may be described by the statement that it divides the superficies of the crystal into 24 triangular sectors. These sectors are approximately similar to each other if the diamond is of fairly symmetric shape, while on the other hand, the

sectors may differ greatly in size and shape if the diamond is of unsymmetrical form.

*The Hyderabad diamonds:* Eleven of the diamonds having their natural form as crystals included in our collection are a recent addition. They were picked out and purchased from the stock of unset stones in the possession of a firm of jewellers at Hyderabad (Deccan). No information was available regarding the origin of these stones beyond the statement that they had been detached for sale from some ancient jewellery. Since the city of Hyderabad is the nearest market to various places in the Deccan where diamonds are found, it is not improbable that the stones are of South Indian origin. All the eleven specimens are small, but they are of particular interest, being, with one exception, quite different from the Panna diamonds in their general features. They represent a combination of plane and curved forms, but the proportion of plane to curved surface varies in the different specimens. Taken together, the ten stones illustrate the successive stages of the transition from the curved faces and edges of the Panna diamonds to the form having eight plane faces separated by grooves which is the nearest approach made by diamond to the standard forms of geometric crystallography.

*The South African diamonds:* The sixteen specimens presented to us by De Beers of Kimberley for the purpose of this investigation have proved very useful in enabling us to compare the South African forms with the Indian ones and determine the relationships between them. Two items of particular interest in the collection may be mentioned here. One is a remarkably perfect example of the form of diamond first described by Haidinger, illustrations of which are to be found in the standard texts on mineralogy. The other is a triangular twin of flat tabular form with beautifully sculptured edges, presenting an interesting comparison with the rounded contours of the triangular twins found at Panna. We shall have occasion to refer to both of these specimens later in the course of the paper.

### 3. Some theoretical considerations

Geometric crystallography is based on the fact that crystals exhibit plane faces bounded by straight edges, and the descriptions given of them specify the directions of the face-normals with reference to the crystallographic axes. The obvious advantages of this system are that the directions of the face-normals are readily determined by goniometry, and that no changes are necessitated in the description by reason of any unequal development in different direction—a very common feature in actual crystals. When, however, we seek to depict a crystal by means of a figure, what we actually do is to delineate its edges. It follows that a crystal can be described by specifying the directions of its edges instead of its face-normals, and that such a description should enable us to determine the symmetry

class to which the crystal belongs quite as definitely as the orientation of its faces. In this connection, however, a minor complication which may arise has to be borne in mind, namely, that the unequal development of a crystal in different directions would not only alter the lengths of its edges, but may also bring into existence new edges along which faces which do not meet in a perfectly developed crystal intersect each other.

When the faces of a crystal are curved, as in diamond, it becomes impossible to specify the directions of the face-normals by a finite set of numbers. But it remains possible to depict the form of the crystal exactly by delineating its edges. The edges would then naturally be curved, but it may very properly be assumed that if a crystal does exhibit a set of well-defined edges on its surface, the configuration of these edges must be related in some specifiable manner to its internal structure, and hence that a study of the same would enable us to determine the symmetry class of the crystal in an unequivocal manner.

X-ray studies have made it clear that the structure of diamond is essentially based on the quadrivalence of the carbon atom. The four axes of trigonal symmetry of the crystal are, in fact, also the directions of the valence bonds which link each atom of carbon in the structure with its four nearest neighbours. It stands to reason therefore that the visible signs of crystallinity exhibited by diamond in its natural forms should also be related in some simple manner to these valence directions. A specific indication as to the nature of such relationship is obtained by considering the form of the regular rhombic dodecahedron. It is readily proved that if a diamond had this form, every one of its 24 edges would coincide with one of the valence directions. Many actual diamonds do roughly resemble a rhombic dodecahedron, but they also exhibit features which cannot be reconciled with such a description. Nevertheless, a simple examination shows that the observable edges on such diamonds do approximately coincide with the valence directions. A more exact statement would be that the edges lie in the planes which contain the valence directions taken two at a time. This statement immediately makes intelligible the features observed on such diamonds which are irreconcilable with a description of them as rhombic dodecahedra.

We summarise the considerations set out above in the form of two propositions.

- A. The configuration of the edges on the surface of a diamond is determined by the structure of the crystal and hence should exhibit its symmetry properties.
- B. The configuration of the edges is also related in a simple way to the valence directions.

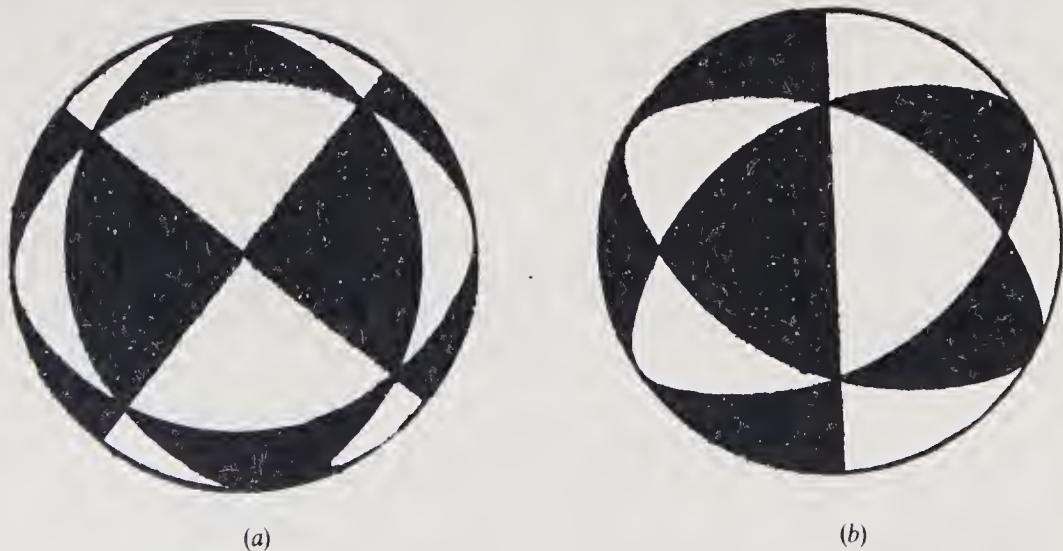
#### 4. Geometric preliminaries

Before we proceed to discuss the observed forms of diamond in the light of the two foregoing propositions, it is useful to recall the symmetry properties of the crystal classes belonging to the cubic system. All five classes in that system have as a

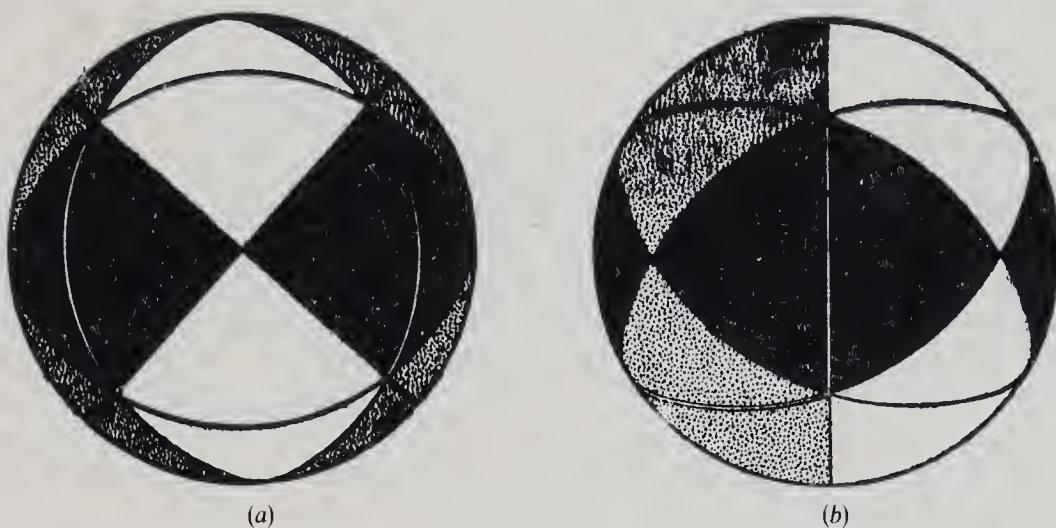
common feature the four axes of trigonal symmetry which are the cube body-diagonals. Taking these axes in pairs and drawing planes through them, we obtain the six diagonal planes of the cube. If these are symmetry planes, the crystal would belong to the tetrahedral class. All the elements of symmetry appearing in that class are represented by drawing through the centre of a sphere the six diagonal planes. The sphere then appears divided up into 24 equal spherical triangles.

Figures 1(a) and (b) represent two views of a spherical surface divided up in this way. It will be seen that there are six points on the surface where four sectors meet and eight points where six sectors meet. There are respectively the intersections with the spherical surface of the three axes of diagonal symmetry and the four axes of trigonal symmetry. Any crystal of the tetrahedral class having a regular form, viz., a positive or a negative tetrahedron, a cube, a rhombic dodecahedron, a tetrakis-hexahedron or a hexakis-tetrahedron may be represented by its projection on the surface of a sphere. The edges of the crystal would appear as the sharp dividing lines between the areas on the surface of the sphere, the number of distinct areas being the same as the number of faces in the crystal, viz., 4, 6, 12 or 24 as the case may be. To illustrate this, the case of the rhombic dodecahedron is represented in figures 2(a) and (b). The shorter diagonals of the rhombic faces have been retained in the figures so as to enable the similarity between figures 1 and 2 to be perceived.

If, besides the six diagonal planes, the three axial planes of the cube are also planes of symmetry, the crystal would belong to the octahedral class. The elements of symmetry appearing in that class may be represented by drawing all the nine planes through the centre of a sphere. The surface of the latter would then appear divided up into 48 equal spherical triangles.

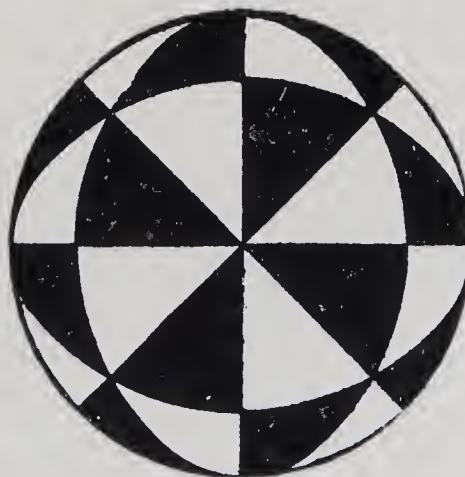


**Figures 1(a) and (b).** Division of a spherical surface by the tetrahedral symmetry planes.



**Figures 2(a) and (b).** Rhombic dodecahedron projected on a sphere.

Figure 3 illustrates the division of a spherical surface in this way by the symmetry planes of the octahedron. A regular crystal having the most general form of this class with 48 similar faces could be represented by its spherical projection, the edges of the crystal appearing as the dividing lines between the sectors of the sphere. Particular cases of the class with a smaller number of similar faces could also be represented in the same way by the simple device of leaving out some of the dividing lines on the surface and thereby reducing the number of distinct areas into which it appears divided. For instance, a regular octahedron would be represented by figure 3 with the six diagonal planes of symmetry omitted and only the three axial planes of symmetry retained, the surface of the sphere would then appear divided into 8 equal areas separated by sharp dividing lines. It would, of course, be impossible to exhibit the form of an octahedral



**Figure 3.** Division of spherical surface by the octahedral symmetry planes.

crystal with the aid of figure 1, since the three axial planes of symmetry are not present in that figure.

### 5. The configuration of the edges

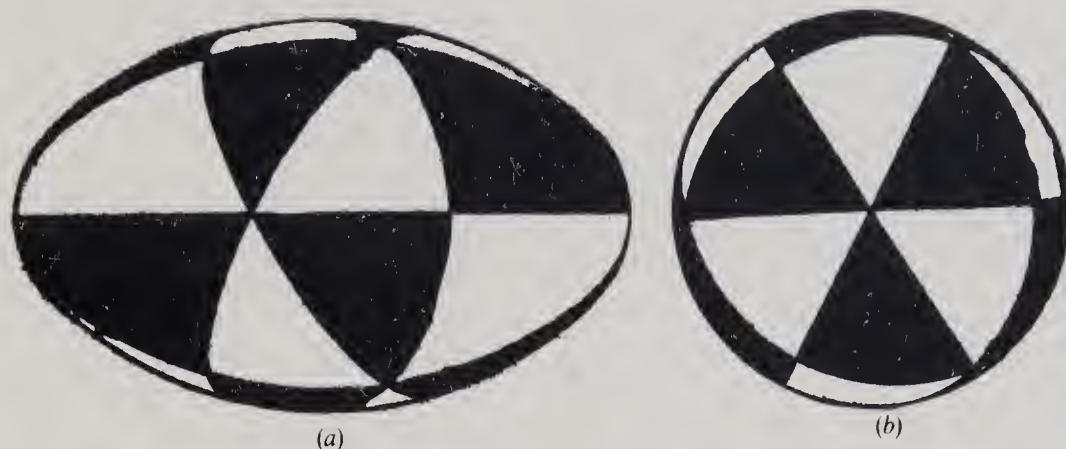
Even from the results of the earlier studies of the forms of the Panna diamonds referred to above (Ramaseshan, *loc. cit.*), it is evident that the edges seen on the surface of these diamonds represent the division of the superficies of the crystal into 24 sections by the symmetry planes of the fundamental tetrahedron. Many of the diamonds do indeed show marked deviations from the simplicity and regularity of the pattern depicted in figure 1. These deviations are however readily explained and do not represent any essential departure from the principles which determine the configuration of the pattern.

In the first place, the actual shape of the diamond has to be taken into consideration. The influence of this may be illustrated by considering the intersection of the symmetry planes of a tetrahedron with various surfaces other than a sphere, e.g., a prolate spheroid, an oblate spheroid or an ovaloid of revolution, which roughly represent the shape of the smaller Panna diamonds. In dealing with such cases, it is natural to suppose that the orientation of the tetrahedral axes with respect to the surface would not be arbitrary, but would be related to it in some specific fashion, viz., one of the trigonal axes of symmetry would coincide with the rotation axis of the surface. It is noteworthy that this view is borne out by the actual facts, viz., that the configuration of the edges on the surface of a diamond is very clearly related to the general shape of the crystal.

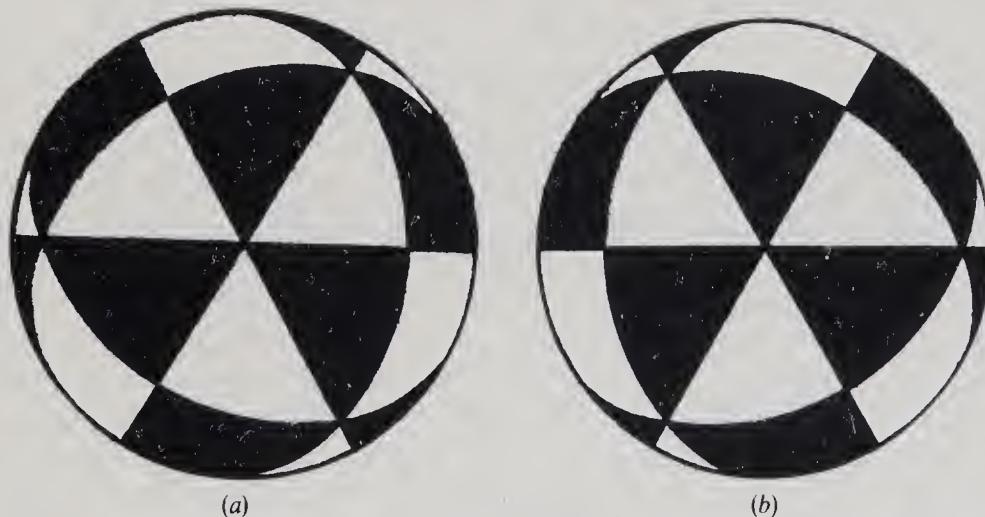
The division of the surface of a prolate spheroid into 24 sectors by the six diagonal planes of symmetry is shown in figure 4. Figure 4(a) is a side view and figure 4(b) is an end view. The sectors of the surface are still of roughly triangular form, but they are now of unequal area, those near the ends being considerably enlarged in relation to the others. A prolate spheroid has an axis of rotation and a plane of symmetry bisecting that axis. But the pattern on its surface evidently does not exhibit these features.

The division of the surface of an oblate spheroid into 24 segments by the six diagonal planes of symmetry is illustrated in figures 5(a) and (b), the two figures being the front and back views of the surface. It will be noticed that the front and back views are different and that one of them would require to be rotated through  $180^\circ$  to enable them to be brought into coincidence, thereby showing clearly that while the oblate spheroid has a plane of symmetry bisecting its axis of rotation, the pattern on its surface does not share that feature. Later in the paper, we shall have occasion to consider the features appearing in figures 5(a) and (b) in relation to the theory of formation of the flat triangular twins of diamond.

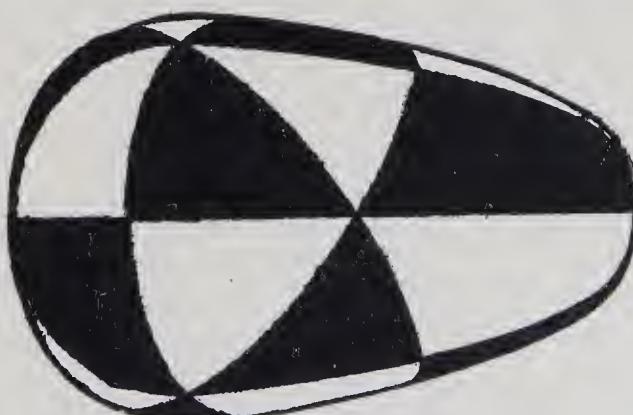
Figure 6 illustrates the division of the surface of an ovaloid of revolution into 24 segments by the symmetry planes of a tetrahedron. The figure of the ovaloid



**Figures 4(a) and (b).** Division of a prolate spheroid by the tetrahedral symmetry planes.



**Figures 5(a) and (b).** Division of an oblate spheroid by the symmetry planes of a tetrahedron.



**Figure 6.** Division of an ovaloid of revolution by the symmetry planes of a tetrahedron.

does not possess a centre of symmetry and hence a pattern drawn on its surface exhibits the tetrahedral symmetry in a more obvious fashion than similar patterns on the surface of a sphere or spheroid of revolution.

In the models illustrated in figures 4, 5 and 6, the six diagonal planes of symmetry were drawn so as to pass through a single point within the surface, viz., the centre of the spheroid or the centre of mass of the ovaloid. As a consequence, the patterns are similar to that drawn on the surface of a sphere in their general features, viz., the division of the surface into 24 segments of triangular shape, four of which meet at six common points on the dyad axes and six at eight common points on the triad axes. The patterns are thus fundamentally related to the pattern of edges presented by a hexakis-tetrahedron or a tetrakis-hexahedron with 24 exactly similar faces. We know, however, that when the general shape of a crystal departs from regularity, the pattern of edges exhibited by it is substantially altered. While the *directions* of the edges which persist remain the same, their positions are altered, and new edges appear along the lines of intersection of the planes which did not previously meet. A similar situation would arise in our present problem of the configuration of the edges on a curved surface, and similar results would naturally follow. Hence, the configuration of the edges in the vicinity of the dyad and triad axes would be altered to an extent varying with the general shape of the diamond and to different extents at the various points. The nature of such variations may be readily deduced by shifting the edges laterally while retaining their general directions and drawing intermediate edges connecting the broken ends together.

This has been done in figure 7 for the case of four edges which fail to meet exactly on a dyad axis, with the result that a fresh edge connecting up the broken ends appears on the surface. It may be remarked that this type of irregularity is seldom noticed in diamond. The reason for this is that in the vicinity of the dyad axes, the valence directions lie in two perpendicular planes and the edges meeting on these axes are usually very pronounced.

On the other hand, the six edges which run towards a triad axis often fail to meet exactly on that axis when they traverse a part of the surface which is very nearly flat. The various types of deviation which may be expected to occur are

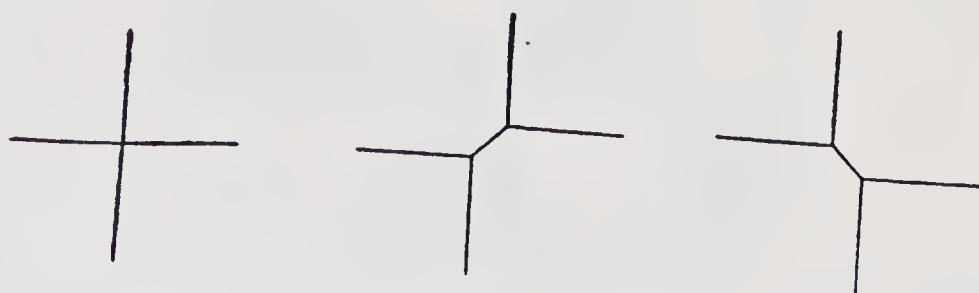
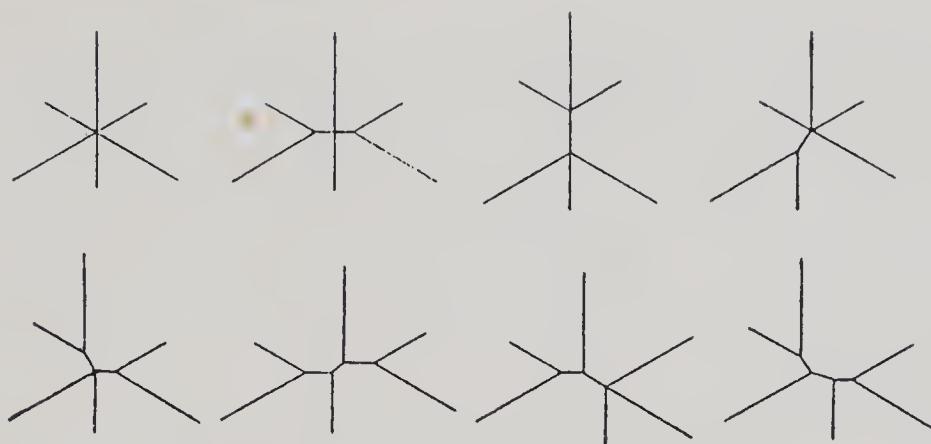


Figure 7. Pattern of edges in the vicinity of a dyad axis.



**Figure 8.** Pattern of edges in the vicinity of a triad axis.

indicated by the diagrams in figure 8. It may be remarked that they correspond closely to the features actually observed in our specimens.

All the Panna diamonds without exception exhibit on their surface a pattern of edges which may be described as its intersections with the tetrahedral planes of symmetry of the structure—subject to the modifications described and illustrated above. This fact is all the more remarkable when it is recalled that some of the specimens in our collection bear no resemblance whatever to the conventional descriptions of a crystal. The actual configuration of the edges varies with the shape of the diamond and when this is irregular, the edges meander in their course. We shall refer to the points on the surface where four and six edges meet respectively as the dyad and triad vertices of the crystal. The actual shape of any particular specimen is closely connected with the configuration of the edges in the vicinity of the dyad and triad axes and the relative prominence of the two types of vertices. There are, of course, various possibilities, and many of them are illustrated by the specimens in our collection. We shall return to these matters later in the paper, but meanwhile we may turn to the fundamental question—What is the crystal symmetry of diamond?

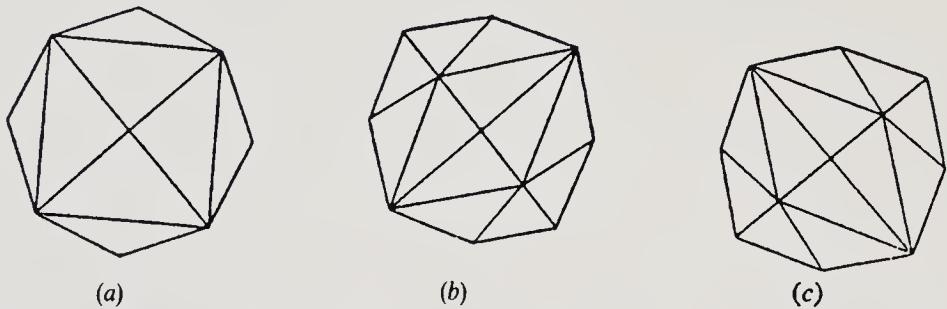
## 6. The crystal symmetry of diamond

As illustrated in figure 3, the planes of symmetry in the octahedral class divide the sphere into 48 equal sectors. If diamond had octahedral symmetry of structure, we may expect it to exhibit such a subdivision, or at least the edges lying in the axial planes of symmetry. There is not the slightest hint or indication of any such edges in the Panna diamonds. Geometric crystallography tells us that the tetrahedral and octahedral symmetry classes have some forms in common, viz., the cube, the rhombic dodecahedron, and the tetrakis-hexahedron. If a substance

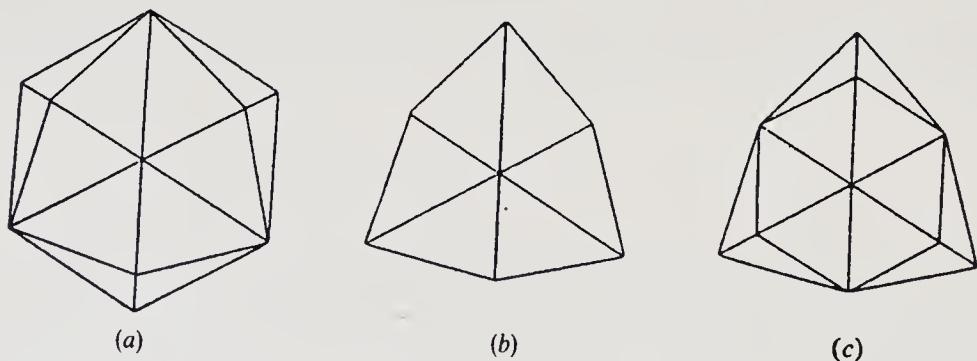
crystallised exclusively in these forms, it would not be possible to decide between the two alternative possibilities. A decision can only be based on the appearance or non-appearance of forms definitely indicative of the higher or the lower symmetry as the case may be. We are accordingly justified in applying similar tests in the case of diamond. The non-appearance in the Panna diamonds of the edges lying in the axial symmetry planes is an indication that we are dealing with only the lower and not the higher symmetry. But evidence of a more positive character is desirable. We must however know what it is we have to look for. Here, again, we may usefully draw upon the ideas and results of geometric crystallography.

Figure 9(a) represents a tetrakis-hexahedron viewed along a dyad axis in either direction, while (b) and (c) represent a hexakis-tetrahedron also viewed along a dyad axis in the two opposite directions respectively.

Figure 10(a) represents a tetrakis-hexahedron viewed along a triad axis in either direction, while figures 10(b) and (c) represent a hexakis-tetrahedron



**Figures 9(a), (b) and (c).** (a) Tetrakis-hexahedron; (b) and (c) hexakis-tetrahedron viewed along a dyad axis.



**Figures 10(a), (b) and (c).** (a) Tetrakis-hexahedron; (b) and (c) hexakis-tetrahedron viewed along a triad axis.

viewed along a triad axis in the two opposite directions respectively. The forms illustrated in figures 9 and 10 both belong to the tetrahedral symmetry class, but the tetrakis-hexahedron can also be regarded as exhibiting octahedral symmetry, the dyad axis then becoming a tetrad axis passing through a centre of symmetry. As can be seen from a comparison of the figures, the characteristic feature of tetrahedral symmetry is that the dyad vertices appear as ridges instead of as peaks, while the triad vertices appear as peaks and as domes respectively at the opposite ends of each axis instead of as peaks at both ends.

Examination of our Panna collection discloses in numerous cases the specific features of tetrahedral symmetry indicated above. It is a very common occurrence to find the dyad vertices appearing as elongated ridges formed by the meeting of two edges nearly parallel to each other, while the two other edges which are transverse to them go up and down the slopes of the ridge. Then, again, one frequently finds the eight triad vertices falling clearly into two groups, one set of four forming fairly well-defined peaks, while the other set of four opposite to them appear as flattened domes. It is very significant also that such configurations of the dyad and triad vertices appear in association with each other. In other words, it is the same diamonds that either show or do not show the stated features in respect of the dyad and triad vertices. Further, these features are clearly related to the general shape of the diamond. The crystals that do not exhibit these features are of highly symmetrical form. On the other hand, the specimens that do exhibit these features possess a symmetry of general shape which is obviously of a lower order. Some of the finest diamonds in our Panna collection—beautiful water-white crystals with smooth lustrous faces—present an external form which does not possess a centre of symmetry. It is impossible in the face of these facts to doubt the truth of the proposition that *the internal symmetry of the diamond structure is that of the tetrahedral class only and not that of the octahedral*, at least in all the cases now under consideration.

It remains to be explained, however, why diamond seems to prefer the forms whose symmetry may be indifferently assigned either to the lower or the higher class, and why even in the forms in which the lower symmetry is observable, it does not appear as conspicuously as might have been expected. One possible explanation is that the more symmetric forms have a smaller surface per unit volume than the less symmetric ones. If, as the curvature of the surfaces suggests, diamond was formed by solidification from carbon liquefied under pressure, the form having the smaller surface would have less surface energy and is therefore more likely to be assumed at the instant of solidification. The second possible answer, which is supported by much relevant evidence, is that the positive and negative tetrahedral forms appear intermingled in the crystal. If this be the case, the crystal form would tend to imitate octahedral symmetry even if it does not exhibit the specific characters of that symmetry.

## 7. Classification of the crystal forms

A survey of all the specimens in our collection indicates that in spite of the great variety of forms exhibited by diamond, it is possible to arrange them in a regular sequence which is evidently connected with the physical circumstances of their formation. The ordering of the forms in such a sequence is obviously an advantage. It avoids the necessity for a minute description of all the individual specimens, and it also enables us, at least tentatively, to put forward a physical explanation of the features appearing in them. Indeed, we may advantageously reverse the order and derive from physical considerations an idea of what the forms of diamond should be and then proceed to fit the observed forms into a sequence based on such considerations.

It appears highly probable that diamond results from the solidification of carbon which has assumed the liquid state under conditions of high pressure and temperature. The state of the atoms in the liquid state is an important point needing consideration. The thermal agitation would certainly prevent a perfect ordering of the valence bonds within the liquid. Hence, it follows that the molten carbon would assume a rounded shape and this would be the more likely, the smaller the volume under consideration. Solidification is accompanied by a fixation of the valence bonds but not necessarily by any radical change of shape. On this basis, it is easy to understand why the crystals formed have curved faces. It may be remarked that the smaller diamonds in our Panna collection exhibit a highly marked curvature of the surface on which a pattern of edges appears as described earlier in the paper. The formation of these patterns is readily explained. At the surface of the molten carbon there would be some free valences which may attach themselves to the surrounding material. The valences not thus disposed of would link each carbon atom to its three nearest neighbours on the surface and hence would tend to align them with respect to its position in the valence directions. Accordingly, the first indication of the regular internal structure manifesting itself on the surface of the solidified material would be the formation of edges along the directions of the valence bonds, or in the planes containing them which are also the tetrahedral planes of symmetry of the structure.

If the edges of the crystal could align themselves completely along the valence directions, the surfaces between them would be plane, and the form of the crystal would be that of the rhombic dodecahedron. However, the curvature of the surfaces would prevent such a complete ordering of the edges. In consequence, the form would only approximate to a rhombic dodecahedron; the edges would not stop at the triad vertices but would be continued along the shorter diagonals, thereby dividing the superficies into 24 parts and not 12. Since these "continuation edges" deviate considerably from the valence directions, they would be relatively inconspicuous and would also meander on the surface to fit its varying curvature. These features are exhibited by several of our South African

specimens. One of them (N.C. 26) is a beautiful crystal which might easily be mistaken for the regular rhombic dodecahedron of geometric crystallography, but is seen on a more careful examination to exhibit the features indicated above. The other dodecahedroid diamonds are less symmetrical in shape and exhibit corresponding variations in the configuration of their edges. These variations, however, are fully explicable on the same basis as in the case of the Panna diamonds already discussed in the foregoing pages.

If the valence bonds within the liquefied carbon have at least a semblance of the regular ordering which exists in the crystal, it would follow that the form assumed by the mass would deviate notably from a spherical shape. In a separate paper by Ramaseshan appearing in the present symposium, it is shown that the surface energy per unit area varies with the orientation of the surface in respect of the valence directions, being a minimum in the directions normal to the triad axes and a maximum in directions normal to the dyad axes. Accordingly, the liquid mass would tend to assume the shape of an octahedron with rounded edges, the largest proportion of the area appearing in the vicinity of the triad axes and the smallest near the dyad axes. On solidification, this general shape would be maintained but modified by the formation of the usual pattern of edges in the planes containing the valence bonds. Many of the larger Panna diamonds, including three examples in our collection (N.C. 2, N.C. 4, N.C. 8), have the shape indicated here. They may be referred to as "octahedroid" diamonds, but are not true octahedra, since they do not exhibit any edges in the axial planes. It may be remarked that the edges in the vicinity of the triad axes are much less conspicuous in the octahedroid diamonds than in the dodecahedroids, since they necessarily deviate more from the valence directions.

A further stage in the sequence of the crystal forms of diamond is reached when the influence of the thermal agitation is diminished sufficiently to enable the surface of the molten carbon to adjust itself exactly to the condition of minimum surface energy. This would exhibit itself by the surface in the immediate vicinity of the triad axes appearing as perfect planes in the solid crystal. The subsequent stages in the sequence would correspond to increasing areas of such plane areas in the crystal and a corresponding contraction of the curved surfaces, until finally a crystal form is attained in which nearly the whole surface consists of optical planes normal to the triad axes of symmetry.

The appearance of optically plane or "splendent" faces in combination with curved surfaces is represented in all its stages in our collection. The first indication of it to appear is a peculiar waviness or rippling of the surface in the vicinity of the triad vertices, often of a regular character and forming a hexagonal network of lines surrounding these vertices. The next stage in the sequence is the appearance of plane areas at and around these vertices. If these are continuous and of sufficient extent, they appear as a truncation or slicing off of the curved surface of the crystal and indeed have the form which would result from such a process, viz., a hexagon with three acute and three obtuse angles, the vertices appearing exactly

at the points where the edges running across the curved surfaces meet the plane. Not infrequently also, the planes appear at the top of a succession of terraces. These terraces run parallel to the perimeter of the plane area, and the edges which have traversed the curved surfaces can be traced through the whole series of terraces up to the plane surface before they finally disappear. As the plane areas enlarge further in extent and the curved surfaces diminish correspondingly, the terraces or slopes—sometimes both terraces and slopes—fringing the plane areas persist, with the result that the crystal presents finally the appearance of an octahedron with deep grooves along its edges. The successive stages by which this result is reached can be followed in the Hyderabad specimens in our collection, thereby making it evident that it is not an accidental circumstance but a specific feature of the crystal forms of diamond.

## 8. The Haidinger diamond

As mentioned earlier, our South African collection includes a magnificent example (N.C. 25) of the particular form of diamond originally observed and figured by Haidinger and of which illustrations are to be found in the standard treatises on mineralogy. The general form is that of an octahedron, but the octahedral edges are absent. In their place, we have the special feature of the form, namely, conspicuous V-shaped grooves with smooth surfaces which widen from the middle outwards. Four of these grooves meet at each vertex of the octahedron and terminate in four sharp straight edges converging to a point on the symmetry axis. *These edges lie in the planes containing the valence bonds, and our measurements indicate that they are parallel to the valence directions.* They form part of the system of edges lying in the valence planes characteristic of all diamonds. Continuations of them, though much less conspicuous, may be traced running up the terraces on the faces of the octahedron and disappearing at the vertices with acute angles on each face. Another set of edges can be seen cutting across each groove and dividing it at its narrowest part into two parts sharply inclined to each other. These same edges can also be traced climbing the terraces and meeting the plane octahedral faces at the vertices with obtuse angles.

Apart from the fact that the particular specimen is a remarkably perfect one, the features which it exhibits can also be seen in several of our Hyderabad diamonds. It is therefore clear that the Haidinger diamond is not a rare or accidental occurrence but is a typical form of deep significance in the crystallography of this substance. The appearance of grooves or re-entrant edges is a characteristic feature of twinning, and in view of the independent evidence showing that the crystal symmetry of diamond is ordinarily that of the tetrahedral class, the only reasonable description of the Haidinger form is that it is an interpenetration twin of positive and negative hexakis-tetrahedra truncated by planes normal to the trigonal axes. Further, since the form mimics octahedral

symmetry, it furnishes an excellent example of the result of such interpenetration in suppressing the external manifestation of the inherent tetrahedral symmetry of diamond.

### 9. The triangular twins

The ideas developed in the preceding pages enable us to offer a simple explanation of the formation and peculiar shape of the well known "macles" or twin diamonds of triangular form and of small thickness, examples of which are often forthcoming. Referring again to figures 5(a) and (b) on an earlier page in which the front and back views of an oblate spheroidal model were represented, the remark may be recalled that for these two views to become identical, it would be necessary to rotate one through  $180^\circ$  with respect to the other. In the figures, the pattern of edges is represented as lying on the surface of the model. Actually, however, the dyad vertices would appear elevated above the surface, while the triad vertices would tend to be suppressed and become relatively inconspicuous, as is indeed the case in the majority of diamonds for reasons already explained. Hence, an oblate spheroidal diamond would tend to assume a triangular shape having its vertices on the dyad axes of the pattern, but the triangles on the two faces would be set oppositely, viz., vertex to base and base to vertex. Indeed, some of the specimens in our Panna collection (N.C. 6, N.C. 12) show such a form. The thinner the diamond, however, the greater would be the probability that this incompatibility between the front and the back of the same crystal would be redressed during its formation by one half of the form swinging round through  $180^\circ$  with respect to the other, thereby resulting in the formation of a triangular twin in which the two halves fit each other perfectly, vertex to vertex and base to base.

The pattern of edges formed by the intersections of the tetrahedral symmetry planes with the two surfaces of a model twin of triangular form is represented in figure 11. Only one side of the model is shown, since the other would be identical in the twin. Examination of the triangular twins in our Panna collection (N.C. 9 and N.C. 23) reveals a pattern of edges on their faces and their edges which corresponds closely with that represented in figure 11.

One of the South African specimens in our collection (N.C. 30) is also a triangular twin, but of a different type. It is much thicker, and also much more "like a crystal", that is to say the faces are much flatter and the edges much steeper than in the Panna examples. Examination of this specimen reveals the remarkable fact that its two faces and also the edges up to a third of the way down from each face exhibit a close similarity to the Haidinger form of diamond. We have the same triangular faces with terraces, the same steep grooves below them and the same set of four sharp edges in the valence planes meeting near the vertices of the form. These features are incompatible with the usual description of



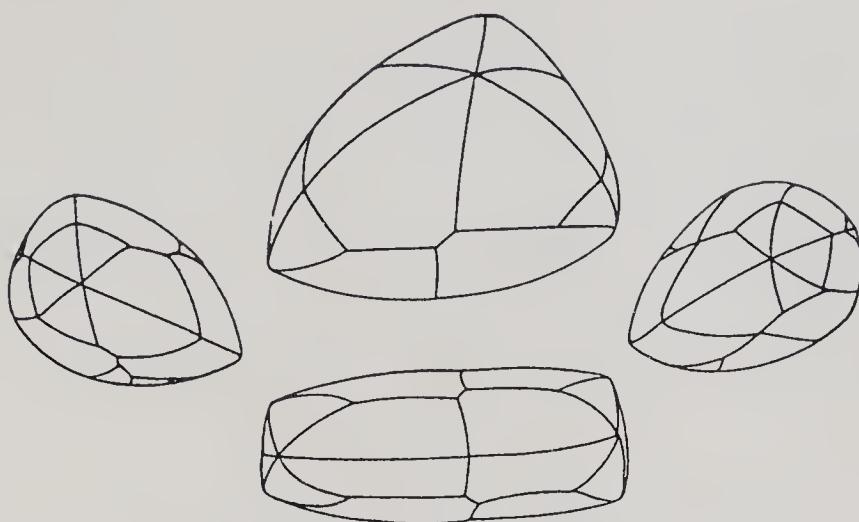
**Figure 11.** Intersection of the tetrahedral symmetry planes with the surfaces of a triangular twin.

the triangular diamonds as "spinel twins" obtained by cutting an octahedron in two and rotating one half through  $180^\circ$ . On the other hand, the specimen does exhibit in the vicinity of its median plane, the characteristic features of the form obtained in that way. It may accordingly be described as a remarkable but only partially successful attempt by a crystal of the tetrahedral class to mimic one of the characteristic form of octahedral symmetry.

## 10. Some descriptive notes

In the paper by Ramaseshan in the 1944 symposium, descriptions, drawings and photographs have already been given of several of our Panna diamonds. There is little need for reproducing the same of similar material here, especially as the numerous figures in the text of the present paper represent the theoretical counterparts of the features described in the earlier one. Since, however, several additions have been made to our collection, some of which are of special interest, it appears desirable to include descriptive notes and illustrations of a few of the new acquisitions.

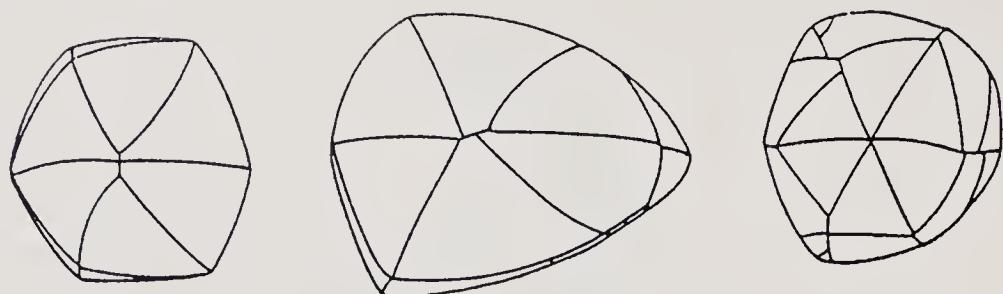
**N.C. 14**—This diamond from Maharajpur (Panna) weighs 143 milligrams, and is water-white in colour, but exhibits a faint greenish surface tinge of the kind which is fairly common in the Panna diamonds. This is the specimen in our collection which makes the nearest approach in its shape to the regular hexakis-tetrahedron of geometric crystallography and hence most clearly demonstrates that diamond is a crystal of the tetrahedral symmetry class. The form is obviously lacking in a centre of symmetry. The eight triad vertices of the form fall into two groups of four each; in one group of four vertices, the edges meet accurately, and on the ridges connecting these vertices appear the six dyad vertices of the form. The other triad



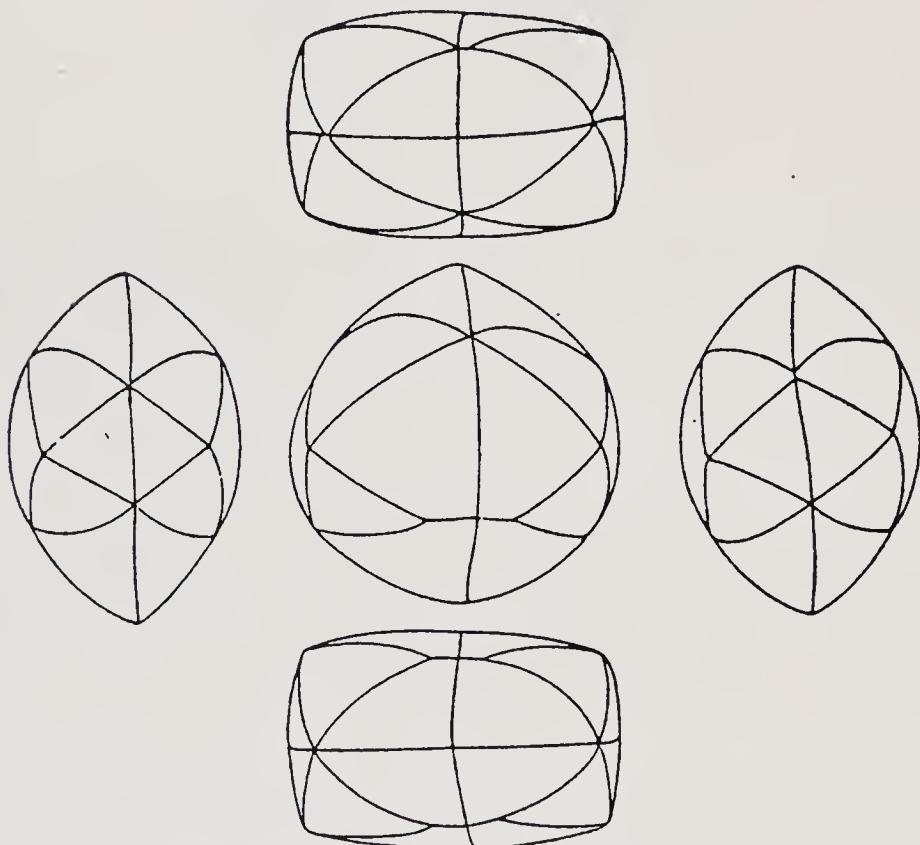
**Figure 12.** Front and side views of N.C. 14.

vertices appear on the four nearly flat faces of the form. In these vertices, the edges fail to meet and give rise to a pattern of broken lines as illustrated in figure 8 on an earlier page. Two of the triad vertices of the former group appear as pointed triangular tips at which three prominent ridges and three fainter ones midway between them meet. These tips are connected by an elongated ridge. The two other triad vertices of the same group are less prominent and are connected by a much shorter ridge, and the dyad vertex appearing midway between them is a prominent feature of the form. As a consequence of these features, both the general shape of the diamond and the details observed on it show only two of the planes of symmetry of the six which a perfect tetrahedron has. The two planes of symmetry are mutually perpendicular and contain between them all the eight triad vertices—four on each. Their intersection is a dyad axis of symmetry for the crystal.

**N.C. 18**—This diamond from Udasna (Panna) weighs 57 milligrams and is perfectly water-white in colour. Being a relatively small diamond, the curvature of the faces is very marked. Nevertheless, the specimen shows clearly enough the characters of tetrahedral symmetry. The form lacks a centre of symmetry, and exhibits a trigonal axis at the two ends of which very different features are noticed. One end of the axis is a sharp triangular tip where six edges meet. The other end is a nearly flat dome with a hexagonal perimeter bounded by three dyad and three triad vertices, all of which are fairly prominent. The four other triad vertices—appearing respectively on the triangular faces of the tip and on the dome at its end—are of a different description, being zig-zag patterns of broken lines. Three of the dyad vertices appear on the ridges which converge towards the triangular tip of the form, and the three others around the base of the dome.



**Figure 13.** Front and end views of N.C. 18.



**Figure 14.** Front and side views of N.C. 10.

**N.C. 10**—This beautiful diamond from Maharajpur (Panna) weighing 182 milligrams, water-white in colour, with smooth lustrous faces, is well worthy of a detailed description as it illustrates a stage in the transition from the “tetrahedroid” to the “octahedroid” forms of diamond. The crystal exhibits a perfect symmetry of shape and of detail about two planes which are perpendicular to each other. These planes are two of the tetrahedral symmetry planes and the line

along which they intersect is a dyad axis also for the actual shape of the crystal. The two ends of this axis are prominent dyad vertices of the form and exhibit the tetrahedroid character, appearing as ridges rather than as peaks. Since one of them is much more pronounced than the other, the crystal form has no centre of symmetry. The four other dyad vertices come next in order of prominence and are all exactly alike each other. They are peaks rather than ridges and thus exhibit an octahedroid character. The triad vertices form pairs, two of which appear in each of the two symmetry planes of the crystal. The four pairs of vertices are of progressively diminishing prominence. They illustrate the successive stages of the transformation of a triad vertex from a perfect meeting of six ridges to an elongated zig-zag of broken lines.

*N.C. 25*—This diamond from Bultfontein, South Africa, water-white in colour and weighing 211 milligrams, is the Haidinger form already described in some detail in section 8 above. A photograph with an accompanying sketch appear in figures 1 and 2 in plate I of this paper. Figure 10 in plate III is a photograph of one of the faces of the form showing its characteristic hexagonal shape, the terraces surrounding it and the triangular depressions or “trigons” appearing on the same. Another photograph of the same diamond reproduced as a negative appears as figure 11 in plate III.

*N.C. 164*—This is one of the Hyderabad diamonds whose forms were described and explained in sections 2 and 7 above. It is a small diamond weighing 62 milligrams and is nearly water-white in colour. It exhibits a combination of optically plane or “splendent” faces with curved surfaces separating them, the latter being smooth and lustrous and exhibiting edges analogous to those observed on the Panna diamonds. In this particular diamond, six of the plane faces are much larger than the other two. The photograph reproduced as figure 3 in plate I shows the smallest of all the plane faces as a dark area. Figure 9 in plate III is an enlarged picture of the same face, showing clearly the curved surfaces surrounding it as well as the edges crossing them and meeting the vertices of the plane face. The sketch reproduced in figure 4 in plate I shows in addition two of the larger plane faces of the diamond and the curved surface lying between them and separated into sections by a system of curvilinear edges. See also figure 12 in plate III where the photograph is reproduced as a negative.

*N.C. 26*—This diamond from South-West Africa, weighing 191 milligrams and water-white in colour, is the “rhombic dodecahedron” the features observed on which have been described and explained in section 7 above. Photographs and sketches of it from two different points of view are reproduced as figures 5, 6, 7 and 8 in plate II and in figures 13 and 14 in plate III.

## 11. The allotropic modifications of diamond

It is useful here to review our findings in so far as they have a bearing on the question of the symmetry of the internal structure of diamond. What the evidence indicates is that in the majority of the cases studied and possibly in all, the crystal symmetry is that of the tetrahedral class only and that none of the crystals appearing in our collection presents conclusive evidence of its possessing a true octahedral symmetry. There is, however, a pronounced tendency towards the assumption of crystal forms which may be indifferently regarded as either tetrahedral or octahedral. This tendency would result from an interpenetration of positive and negative tetrahedral forms, and there is crystallographic evidence that such interpenetration does occur. But it should not be forgotten that the same situation would arise from the existence of diamond having a truly octahedral symmetry of structure but formed under conditions unfavourable for the intrinsic symmetry expressing itself to the fullest extent in the external form. The possibility has also to be borne in mind that the modifications of diamond having tetrahedral and octahedral symmetry of structure appear intertwined with each other in the same crystal. In all such cases, we could scarcely expect the crystal forms to exhibit either tetrahedral or octahedral symmetry exclusively. It would then be necessary to rely on physical evidence, as for instance the infra-red absorption spectrum, to discriminate between the various possibilities and to establish the nature of any particular specimen.

Summing up the situation, we may say that while the study of the crystal forms in our collection shows clearly enough that the majority of diamonds have only a tetrahedral symmetry of structure, the results do not exclude the possibility that diamond has in some cases a truly octahedral symmetry of structure which for one reason or another fails to manifest itself fully in the external form of the crystal.

## 12. Summary

The paper describes the conclusions reached from a critical examination of some 72 diamonds in their natural form obtained from various sources. The curvature of the faces and other special features exhibited by diamond invalidate a description of its forms in the standard terminology of geometric crystallography. The proper basis for description and classification is furnished by the configuration of the sharply-defined edges which appear dividing the superficies of the crystal into 24 distinct sections. Subject to minor modifications, these edges lie along the intersections of the surface with the symmetry planes of a fundamental tetrahedron. These planes also contain the directions of the valence bonds between the carbon atoms in the crystal and the sharpness of the edges is determined by the angle which they make with the valence directions. The

configuration of the edges and the specific features exhibited by them in numerous specimens prove that in the majority of diamonds the crystal symmetry is that of the tetrahedral class only. The crystallographic evidence also shows that the positive and negative tetrahedral forms freely interpenetrate each other, and this explains the frequent appearance of forms common to the tetrahedral and octahedral symmetry classes. That diamond may in some cases possess a true octahedral symmetry is however entirely consistent with the observed facts. A physical theory of the formation of diamond is outlined which explains the observed features of the crystal forms and enables them to be classified in a regular sequence.

## References

### Treatise

- Dana E S *A system of mineralogy* Wiley & Sons (1911) p. 3. *A text-book of mineralogy* Wiley & Sons (1932) p. 395.  
 Groth P *Chemische krystallographie* (1906) Erster Teil p. 12.  
 Hintze C *Handbuch der Mineralogie* (1904) Erster Band, Erste Abteilung p. 14, 26.  
 Miers H A *Mineralogy* Macmillan (1902) p. 291.  
 Sinor K P *The diamond mines of Panna state Times of India* (1930).  
 Sutton J R *Diamond* Van Nostrand Co. (1928).  
 Tutton E H *Crystallography and practical crystal measurement* Macmillan (1922) p. 502.

### Papers

- Goldschmidt V Z *Krystallogr.* **50** 460 (1912).  
 Hirschwald J *Ibid.* **1** 212 (1877).  
 Martin, Weiss etc *Ibid.* **6** 103 (1882).  
 Ramaseshan S *Proc. Indian Acad. Sci. A***19** 334 (1944).  
 Sadebeck A Z. *Krystallogr.* **2** 13 (1878).



Figure 1

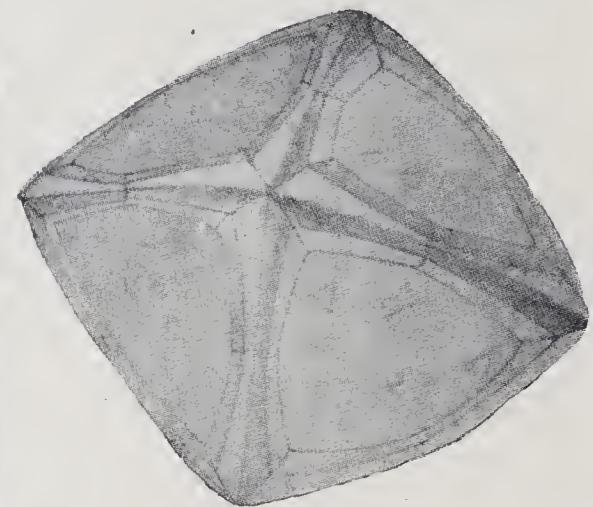


Figure 2

Haidinger diamond (N.C. 25)

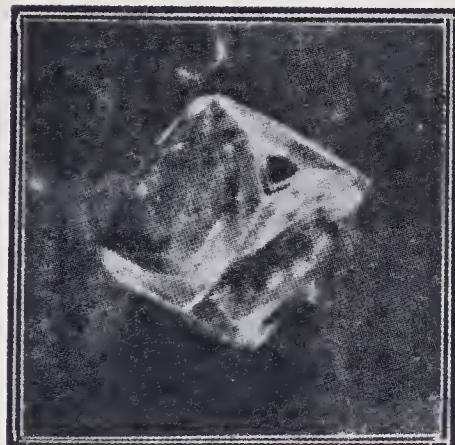


Figure 3

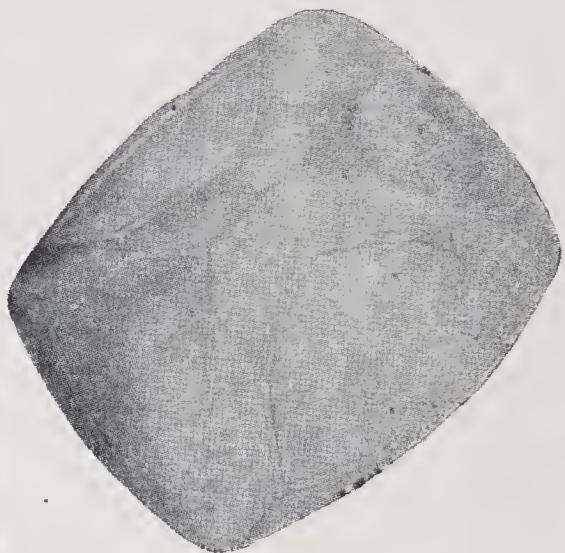


Figure 4

Hyderabad diamond (N.C. 164)

Plate I

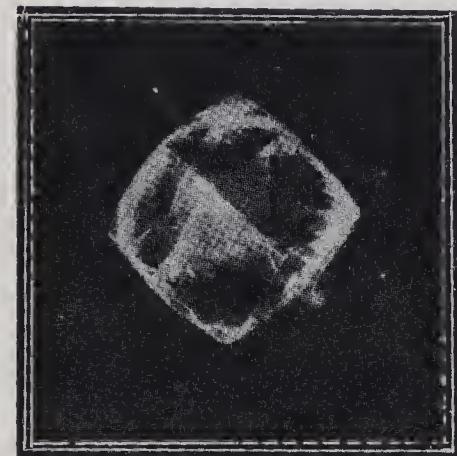


Figure 5

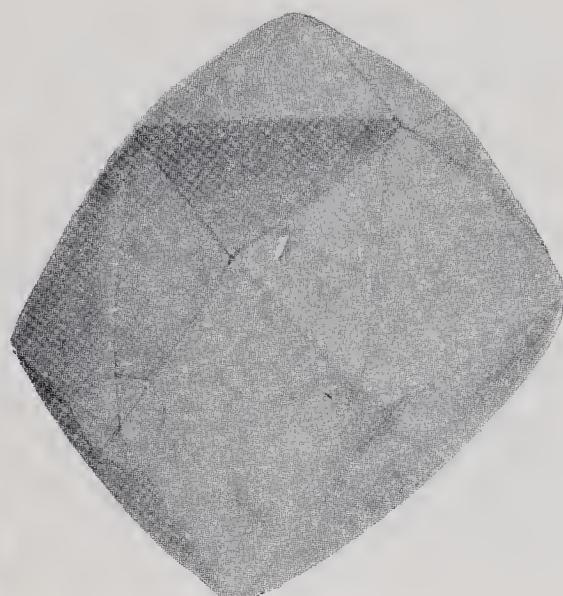


Figure 6

N.C. 26



Figure 7

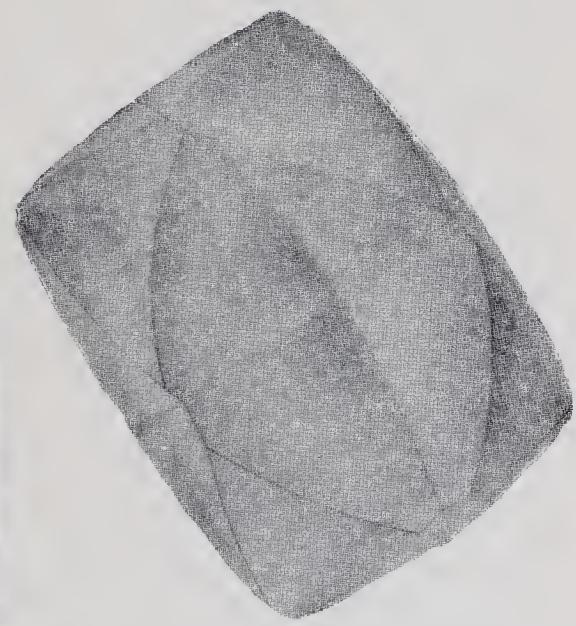


Figure 8

N.C. 26

Plate II

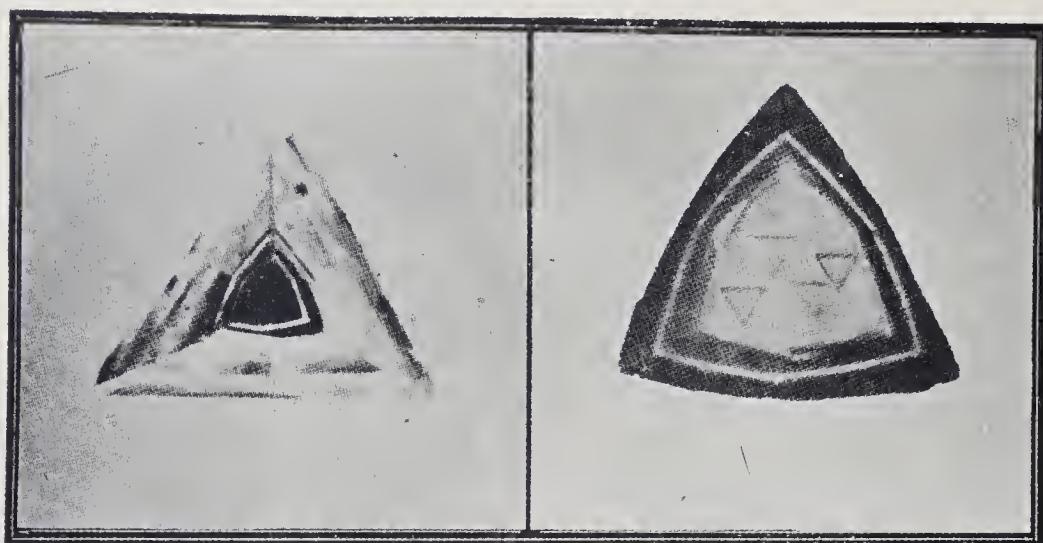


Figure 9

N.C. 164

Figure 10

N.C. 25

Figure 11

Figure 12

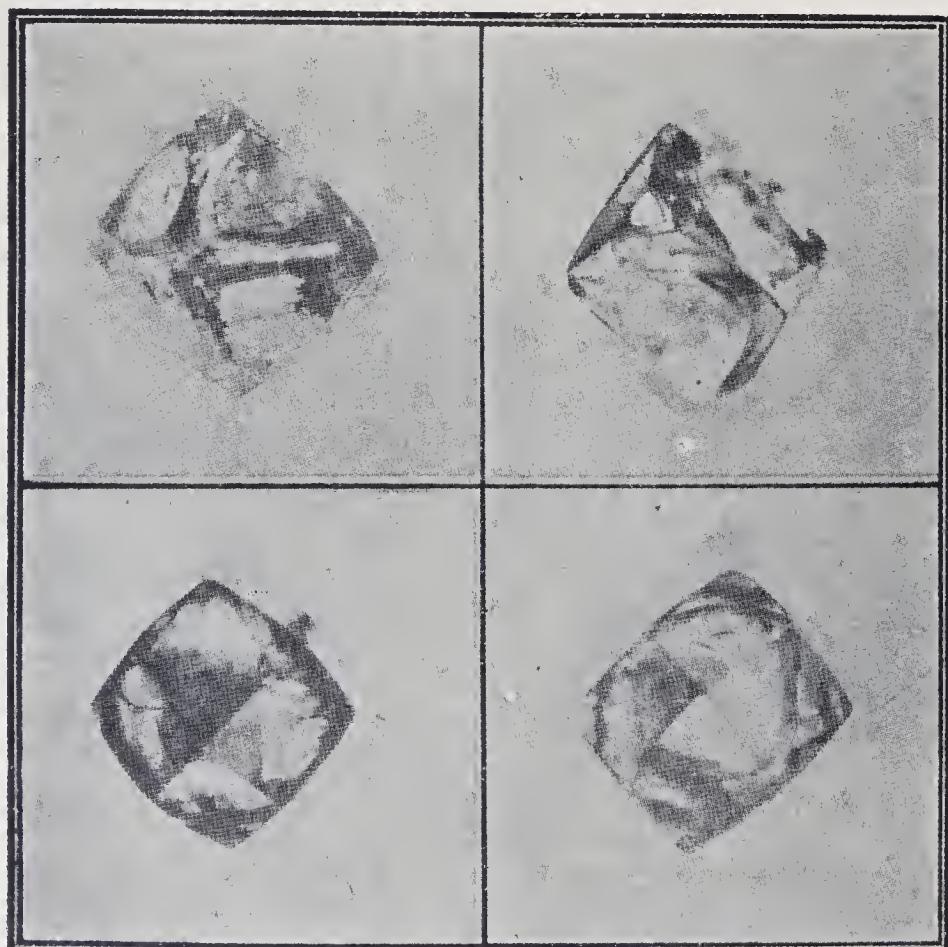


Figure 13

Plate III

Figure 14

## The diamond and its teachings

The Indian Academy of Sciences has once again made scientific history by the publication as its *Proceedings* for July 1946 of a symposium of original papers devoted exclusively to the physics of the diamond. Twenty-one memoirs by eight authors make up a volume of 197 pages illustrated by 23 full-page plates and numerous figures in the text. A similar symposium was issued in May 1944 which contained seventeen papers by eleven authors and ran to a total of 153 pages and 30 full-page plates. This was reviewed in *Current Science* for June 1944. Eight separate papers on diamond by various authors also appeared in the *Proceedings* during the latter half of 1944 and the first half of 1945. The enthusiasm manifested in this output of research possibly needs a few words of explanation. There is good reason to believe that the investigation of the structure and properties of diamond would lead to a deeper understanding of the basic principles of organic chemistry and of crystal chemistry. The crystal forms and the genesis of the diamond also offer problems of great interest to the mineralogist. And to the physicist interested in the theory of the solid state, diamond presents an almost illimitable field for fruitful research. For it is at once the most representative and the most exceptional of solids—representative because of its elementary nature and the simplicity of its structure, and exceptional because in spite of these qualities, it exhibits many remarkable properties and a fascinating variety of behaviour.

The principal difficulty in such studies is that of obtaining suitable material. Diamond shows wide variations in some of its most characteristic properties. Hence, the experimenter should have at his disposal a fairly large collection of specimens. This fact and the expensiveness of the best material is a discouragement to the investigator. The work pursued during the past few years at Bangalore has been made possible by the material gradually got together by the present writer. The additions made recently to the collection have been particularly useful and have enabled definite conclusions to be reached on many important questions.

## The crystal forms of diamond

Diamond presents some peculiar puzzles to the crystallographer. One of these is the strongly marked curvature of the faces of the crystals which is a very general feature, while in some specimens both plane and curved faces appear in

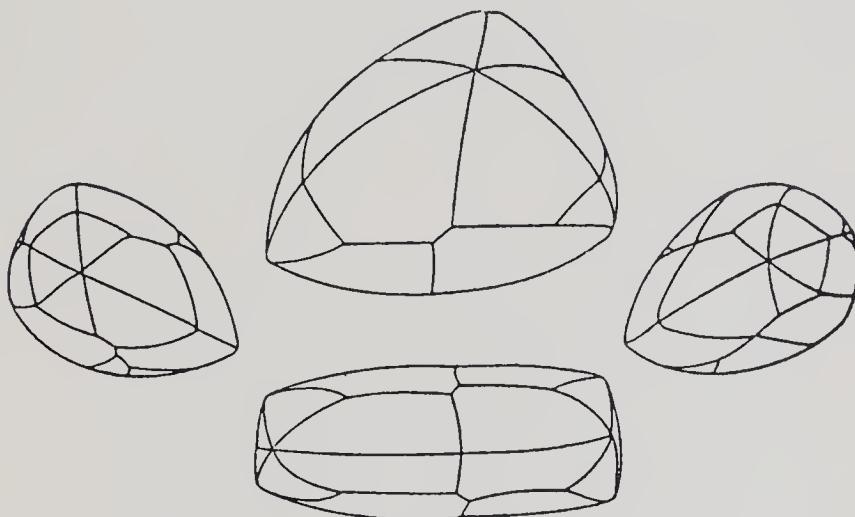
combination. It is obvious that a crystal exhibiting curvature in some or all of its faces cannot appropriately be described in the usual terminology of geometric crystallography and that a new approach is therefore needed. In the introductory paper of the symposium, it is shown that the proper basis for description and classification of the forms is the pattern of sharply-defined edges seen dividing the curved surface of the diamond into distinct sections. These edges lie in the planes which contain the valence directions within the crystal taken two at a time. There are six such planes and if they are drawn passing through a given point in space, their intersections with a closed surface surrounding it would divide up the surface into 24 triangular areas. In the ideal pattern thus derived, there are six points on the surface at each of which four edges meet and eight points where six edges meet. In a general way, these are the features actually seen on the surface of the diamonds, though there are certain modifications in detail. The configuration of the edges is found to be related in a remarkable way to the form of the diamond and the valence directions. The vertices or prominences of a crystal form are invariably points where four or six edges meet sharply. *Per contra*, on relatively flat areas of the surface, the edges are always inconspicuous and show a tendency to meander in their courses and to intersect in a somewhat haphazard fashion forming broken zig-zags. The form of the crystal approximates to a regular rhombic dodecahedron when all the prominent edges are nearly straight and parallel to the valence directions. Even in such cases, however, the rhombic faces are traversed by inconspicuous edges dividing them in two, thereby securing the usual sub-division of the surface into twenty-four distinct sections. This is an example of the general principle that the edges are most conspicuous when they nearly coincide with a valence direction and least conspicuous when they deviate largely from it.

### The crystal symmetry of diamond

The six planes containing the valence bonds are also the symmetry planes of the tetrahedral carbon atom. Octahedral symmetry for the crystal would demand three additional planes of symmetry, viz., the axial planes of the cubic structure. If all these nine planes are drawn through a point in space, they would divide up an enclosing surface into forty-eight sections and not twenty-four. There is no hint or suggestion in the Panna diamonds of any edges lying in the axial planes of symmetry, and it may, therefore, reasonably be inferred that the crystal symmetry of those diamonds is that of the tetrahedral and not that of the octahedral class. The correctness of this inference is confirmed by the fact that the characteristic features of hemihedry are very clearly exhibited by numerous specimens. In particular, the configuration of the edges at the two ends of each triad axis of symmetry are found to be notably different, one end appearing as a sharp vertex or prominence of the crystal, while at the other end the surface is a flattened dome.

Four different views of such a "tetrahedroid" diamond are shown in figure 1.

It may seem surprising that diamond which consists of atoms all of the same kind has the same crystal symmetry as zinc blende which, as is well known, is a polar crystal exhibiting piezo-electric properties. This point is discussed in a paper by Mr G N Ramachandran and it has shown that diamond may possess tetrahedral symmetry without being a polar crystal; a suitable distribution of the electron atmospheres would secure this result without involving any differences



**Figure 1.** Four views of a tetrahedroid diamond.

in the total charge attached to the individual atoms. It must not, however, be supposed that diamond is *invariably* a crystal of the tetrahedral class. The evidence of the crystal forms shows only that the majority of diamonds possess the lower symmetry and that diamonds which unambiguously exhibit the higher or octahedral symmetry are much less common. There is also distinct evidence from the crystal forms that the interpenetration of the positive and negative tetrahedral structures is a very frequent occurrence.

### Atomic vibration spectrum

Being the typical valence crystal, diamond is particularly well-suited to be a test-case for theories of solid behaviour. In particular, its optical properties in the ultra-violet, visible and infra-red regions of the spectrum are of extra-ordinary interest in relation to such theories. It is not surprising, therefore, that these properties have come in for a good deal of attention. Indeed, the majority of the

papers in the symposium are concerned with such questions. In particular, experimental evidence is presented in papers by Dr R S Krishnan and Mr K G Ramanathan which very definitely clears up the fundamental problem of the nature of the atomic vibration spectrum in a crystal lattice.

In principle, the problem of the vibration spectrum of a crystal lattice is a simple one. For, the structure of a crystal is three-dimensionally periodic in space and comes into coincidence with itself when given unit translations in turn along each of the three axes of the space-lattice. The characteristic modes of vibration of the atoms should accordingly also exhibit the same property. Since the phases of vibration of the atoms in a normal mode are either the same or opposite, the result of a unit translation would be that the phases of the atoms brought into coincidence either all remain the same or else are all reversed. We have thus  $2 \times 2 \times 2$  or 8 distinct sets of cases to be considered. The set in which the phase of the vibration is the same in all the units of structure includes  $(3p - 3)$  modes of vibration (excluding simple translations), while the remaining sets give us  $21p$  modes,  $p$  being the number of non-equivalent atoms per unit cell. Thus the result emerges that the crystal structure has  $(24p - 3)$  modes of normal vibration, each having a definite monochromatic frequency. These modes must of course be regarded as very highly degenerate, thereby taking account of the immense number of atoms whose vibrations they describe. The three modes left out in this enumeration represent the degrees of freedom carried over into the elastic or low-frequency spectrum of the vibrations of the solid regarded as a continuum.

The nature of the vibration-spectrum, as revealed by all the spectroscopic investigations on the scattering of light in crystals so far made, is seen to be in perfect agreement with the foregoing indications of the theory, provided the disturbing effect of the thermal agitation on the postulated regular ordering of the atoms is taken into account. The finite amplitudes of vibration and the resulting anharmonicity have also to be considered, as they give rise to the possibility of overtones and combinations of the  $(24p - 3)$  modes. What is needed for a complete demonstration of the theory is observational evidence that besides the  $(3p - 3)$  modes, the remaining  $21p$  modes with sharply defined frequencies and their overtones and combinations also exist. Clear evidence on this point is furnished by the series of investigations recently carried out by Dr R S Krishnan and published in the *Proceedings* of the Academy under the serial title of "Raman spectra of the second order in crystals". The results obtained by him with diamond are particularly significant and conclusive and will now be referred to.

Diamond contains two non-equivalent atoms in its unit cell, and hence the  $(3p - 3)$  modes give us three frequencies which reduce to one by reason of the cubic symmetry of the crystal. This is clearly the mode with the frequency of  $1332\text{ cm}^{-1}$  revealed by the earlier studies. [One of the papers in the symposium gives accurate measurements of the frequency of this mode over a wide range of temperature and reveals both a diminution of this frequency as also a steadily increasing width of the line with rising temperature. These data have also been

discussed in relation to the thermal expansion of diamond for which a set of accurate data is presented.] The remaining eight modes are found to be inactive in light-scattering in agreement with theory, which, however, indicates that they may appear as overtones and combinations in the second order spectrum and this again is found to be the case (figure 2). The figure is a microphotograph and shows a series of well-defined peaks in the positions expected, a relatively feeble continuum overlying them, which evidently owes its origin to the numerous unresolved combinations of the discrete frequencies both amongst themselves and with the lower or continuous part of the vibration-spectrum of the lattice. Particularly noteworthy and significant is the fact that the peaks observed by Dr R S Krishnan in the second-order spectrum of light-scattering agree closely in position with the series of sharply defined peaks observed earlier by Robertson, Fox and Martin in the infra-red absorption spectrum of diamond when examined under adequate resolving powers.

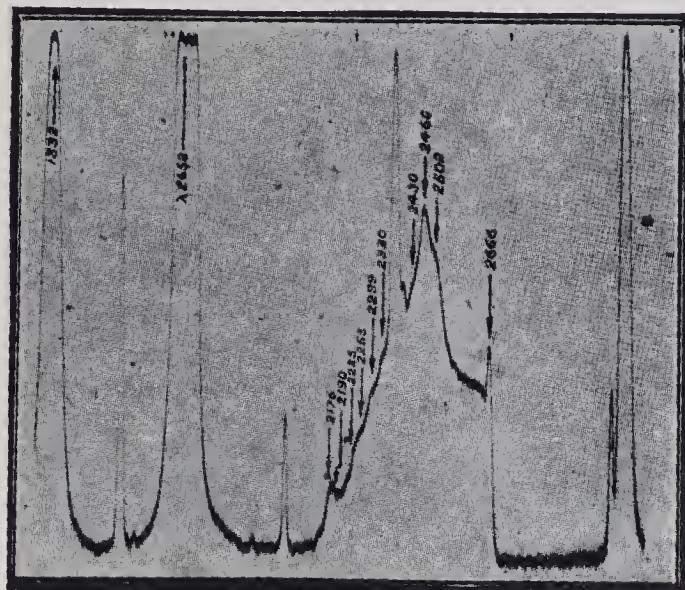


Figure 2. Second order Raman spectrum of diamond.

### Infra-red absorption spectrum

One of the most firmly established results of physics is the relationship between the various physical properties of a crystalline solid and the symmetry of its structure of which the external form of the crystal is an indication. The tetrahedral symmetry of diamond involves as a necessary consequence that the fundamental vibration-frequency of the lattice ( $1332\text{ cm}^{-1}$ ) should be active in

infra-red absorption, while *per contra*, if diamond had an octahedral symmetry of structure, the same vibration would be inactive in such absorption. It had long been known that some diamonds exhibited an absorption-band in the  $8\ \mu$  region, while others apparently did not, but evidently owing to the use of unsatisfactory material, the differences in behaviour hitherto recorded were not as clear as was to be expected, and the data also left much to be desired in other respects. In two papers appearing in the symposium, Mr K G Ramanathan has cleared up the position fairly completely, both by obtaining and presenting new experimental data with numerous specimens of well-ascertained structure, and also by a detailed discussion of his results. As *Current Science* for July 1946 contained a report of his work, it is unnecessary to describe it in detail here. It will suffice to remark that his work settles a very important issue, viz., the existence of allotropic modifications of diamond having tetrahedral and octahedral symmetry respectively and the activity of the frequency  $1332\text{ cm}^{-1}$  in the former and its inactivity in the latter. Of particular importance also is the explanation put forward by him of the observed structure of the infra-red absorption bands in the  $8\ \mu$  and  $5\ \mu$  regions in the light of the theory of the vibrations of a crystal lattice discussed earlier. The demonstration of local variations in infra-red transparency over the area of cleavage plates of diamond is another noteworthy contribution made by this author.

### The electronic spectrum of diamond

That variations exist in the transparency of diamond in the ultra-violet region of the spectrum has long been known. A new complexion is given to the subject by the result established by Mr K G Ramanathan that even the diamonds which in moderate thickness are opaque to radiations below  $\lambda 3000$ , are transparent upto  $\lambda 2250$  provided their thickness is sufficiently reduced (figure 3).

Equally remarkable is the result established by the same author that diamonds of the same type if employed in sufficient thickness completely cut off all wavelengths below about  $\lambda 4140$  and also exhibit a whole series of discrete absorption lines and bands between this wavelength and  $\lambda 4800$ . New detail has also been recorded by him in the absorption-spectra of such diamonds right up to the limit of transmission, viz.,  $\lambda 2240$ , as observed at liquid air temperature.

From these studies, taken in conjunction with the results of the earlier investigations by Dr P G N Nayar, by Mrs K Sunanda Bai and Miss Anna Mani, published in the *Proceedings of the Academy*, a very remarkable fact emerges, viz., that diamond exhibits a whole series of sharply defined electronic frequencies in absorption between  $\lambda 2240$  and  $\lambda 5359$ . Numerous sharply defined emission frequencies have also been recorded by Miss Mani in the luminescence spectra of diamond in the range between  $\lambda 4060$  and  $\lambda 6358$ , and in the majority of cases, corresponding absorption frequencies have been observed. The intensity with

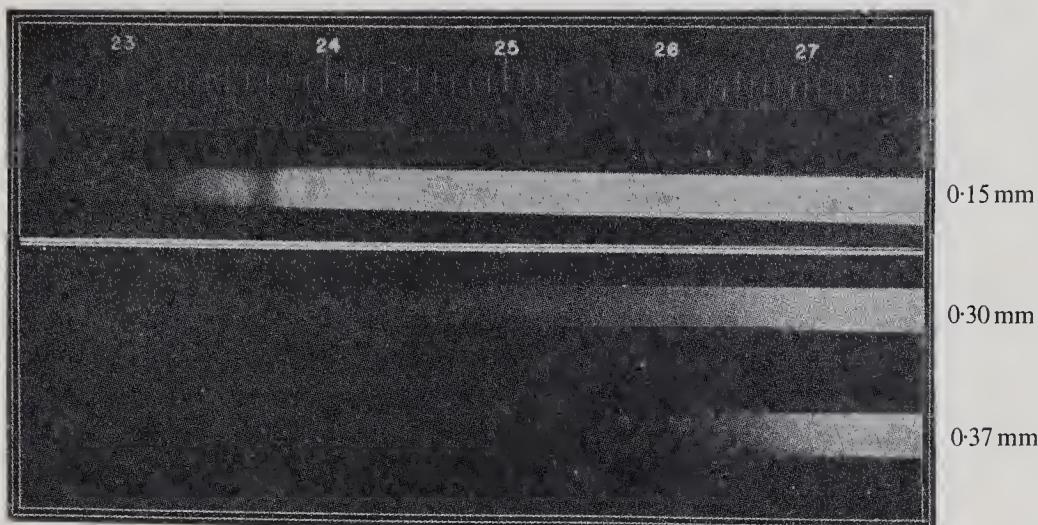


Figure 3. Ultra-violet transparency of thin diamonds.

which these absorption and emission frequencies are recorded with different diamonds differ enormously. But there can be no doubt that they are all characteristic of diamond itself and that the variations arise from the same causes which give rise to the variations in infra-red absorption strength.

### Allotropic modifications of diamond

It is a remarkable fact that though diamond is a cubic crystal it often exhibits birefringence, and that this not infrequently takes the form of geometric patterns very clearly related to the crystal structure. Figure 4 is an illustration of four large flat cleavage plates of diamond as viewed between crossed polaroids exhibiting this geometric character in a very striking fashion. These plates are all of the type of diamond which in moderate thicknesses is opaque to wavelength less than  $\lambda 3000$ . Diamond which is completely transparent up to  $\lambda 2250$  invariably exhibits a characteristic and wholly different type of birefringence that is finely streaky in character. It must not be thought, however, that diamond is always birefringent. Indeed, this is not the case, and in the writer's collection there are several fine specimens of non-birefringent diamond, and these have been very successfully used by Mr S Ramaseshan for the studies of the Faraday effect in diamond described by him in the symposium. They belong to the tetrahedral or infra-red opaque type of diamond.

In the earlier symposium, the present writer suggested that birefringence in diamond—except when due to obvious cracks or other defects—arises from the juxtaposition in the same specimen of different allotropic modifications of diamond. This suggestion has been confirmed and placed on a quantitative basis

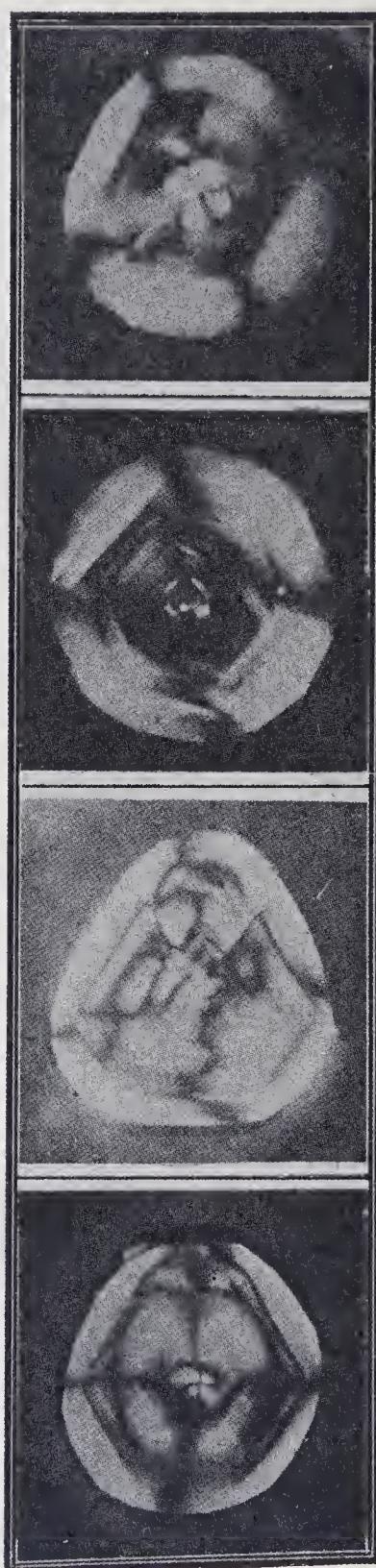
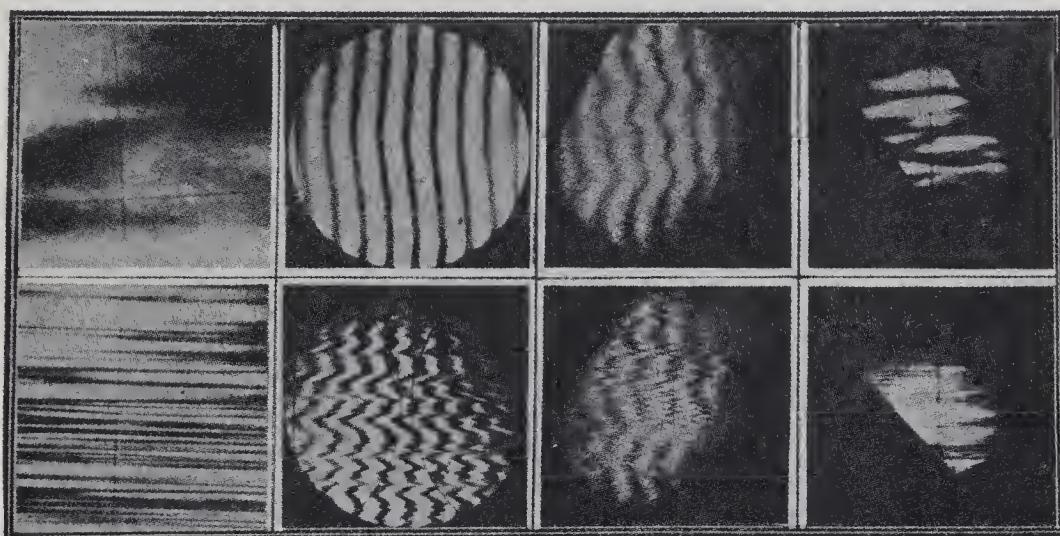


Figure 4. Birefringence patterns in diamond.

by Mr G N Ramachandran using a very ingenious method. The cleavage plate of diamond under examination is placed on the Federov stage of a petrographic microscope, using where necessary the auxiliary glass spheres. Very remarkable changes in the nature of the birefringence pattern are observed when the plate is tilted on the stage and also when the stage is rotated. A Babinet compensator inserted in the microscope so that the image of the diamond is focussed in its plane enables the sign and magnitude of the birefringence to be evaluated under these conditions. In this way it has been shown that birefringence *invariably* arises from the presence of layers lying in the octahedral or dodecahedral planes and different from the material on either side. The upper and lower pictures in figure 5 represent the effects observed in this way of tilting the Federov stage with or without the Babinet compensator in the field. The diamond in this case was of the octahedral variety.



**Figure 5.** Birefringence in diamond observed with Federov stage and Babinet compensator (octahedral diamond).

Figure 6 shows similar pictures of a plate of tetrahedral diamond containing intruding octahedral layers. (The nature of the intrusion was verified in this case by the observation of the ultraviolet transparency of the layers.) The picture shows that some of the layers have a greater and some a lesser refractive index than the rest of the diamond. These pictures clearly prove the existence of two forms of octahedral diamond, as had been suggested earlier by the present writer.

### The luminescence of diamond

The fluorescence of diamond excited in various ways and the subsequent after-glow or phosphorescence form the subject of no less than six papers in the

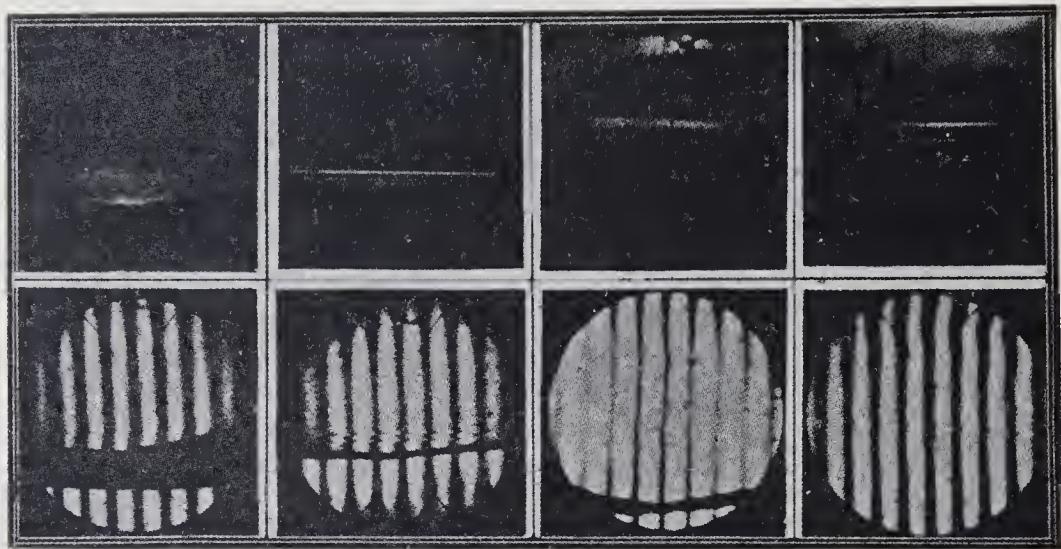


Figure 6. Birefringence observed with Federov stage and Babinet compensator, showing intruding octahedral layer in tetrahedral diamond.

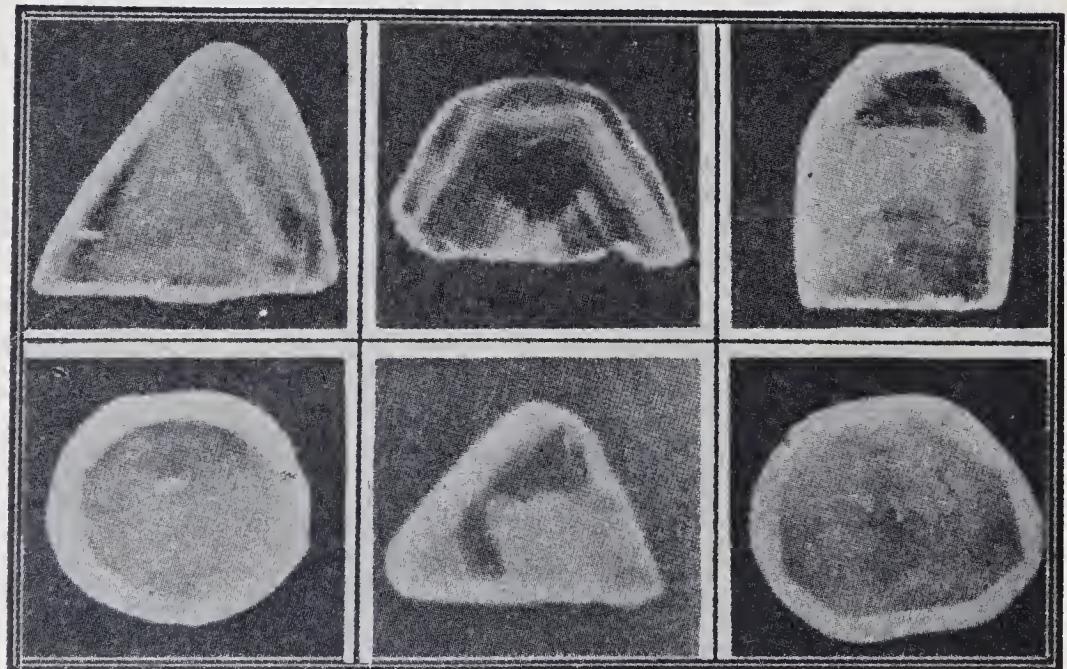
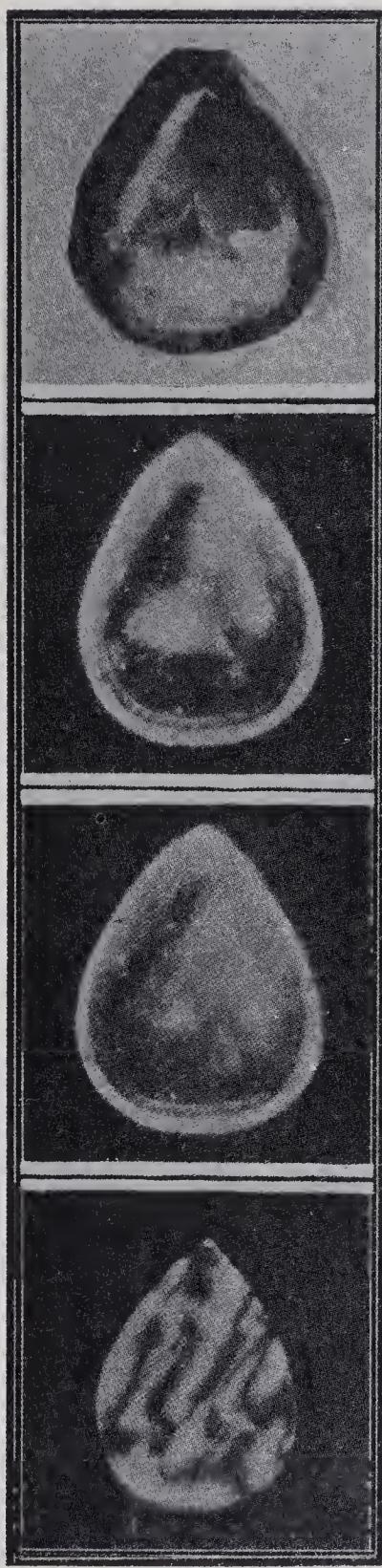


Figure 7. X-ray luminescence patterns.



**Figure 8.** Ultra-violet transparency, blue luminescence, yellow luminescence and birefringence patterns of a cleavage plate of diamond.

symposium which deal with these subjects from different points of view. Mr G N Ramachandran has made a detailed study of the luminescence as excited by X-radiation, the mechanism of its production with special reference to the strength and quality of the X-radiation, and also the remarkable differences between such luminescence and that excited by ultra-violet light in respect of the spectral character of the emission and other features. With Mr G R Rendall's paper are reproduced the luminescence patterns of no fewer than 19 cleavage plates, photographed separately to exhibit the "blue" and the "yellow" luminescence patterns. These are set alongside the ultra-violet transparency patterns and the birefringence patterns of the same diamonds, so as to exhibit the notable resemblances and differences between these patterns. Figure 8 is an example of such patterns, but the difference between the "blue" and "yellow" patterns and the analogy between the latter and the birefringence patterns are usually much more striking.

Mr V Chandrasekharan in one of his papers records a series of phosphorescence patterns obtained by the method of contact photography and shows that only the "blue" patterns as seen in fluorescence are recorded in phosphorescence, though the colour of the latter is "yellow" and not "blue". Mr Chandrasekharan also describes a series of interesting studies on the activation of diamonds by short-wave ultra-violet rays and the release of such activation energy in the form of "blue" luminescence by the impact of red light or other long-wave radiation or by the action of heat. These studies as well as the other papers noticed above demonstrate beyond all possibility of doubt that luminescence is a characteristic of diamond itself and not due to any extraneous impurities. Messrs Ramachandran and Chandrasekharan have a joint paper, the results of which seem to indicate that the luminescence of diamond owes its origin to "forbidden" electronic transitions between various sharply defined energy levels characteristic of its crystal structure. That the intensity of luminescence varies enormously from specimen to specimen is not inconsistent with this view. This is indicated by the fact that increased intensity of blue luminescence goes hand in hand with an increased mosaicity of crystal structure, as is shown in Mr Ramachandran's paper on X-ray topographs. Local variations in mosaicity appear also to be responsible in some cases for the local variations in photoconductivity discovered by Mr Achyutan in the cleavage plates of diamond.

### The genesis of the diamond

Reference should also be made to other papers by Mr S Ramaseshan appearing in the symposium. Besides being the joint author of the introductory paper of the symposium, he has developed the ideas contained in it further and put forward a definite theory of the crystal forms of diamond, connecting them with the circumstances of the genesis of the diamond and with the surface energy of the

molten carbon from which the crystals formed. The calculations made of the surface energy of different crystallographic planes in this connection suggested that diamond should exhibit various other cleavages besides the well-known octahedral one. This prediction has been verified in experiment.

*C V RAMAN*

## New concepts of crystal structure

As is well known, the theory of crystal structure was worked out by Sohncke, Schoenflies and Federov in the 19th century on a purely geometric basis long before the discovery of the diffraction of X-rays by crystals opened up the possibility of the physical exploration of their atomic structure. The results of the geometric theory are embodied in the statement that any crystal must belong to one of the 230 possible space-groups, which in their turn are derivable from the 32 possible point-groups or symmetry classes to which a crystal can be assigned; these symmetry classes can be grouped together so as to yield the well known classification of crystals into six (or seven) divisions. The theory of space-groups rests on the premise that the structure of a crystal exhibits the translational symmetry of a space-lattice or three-dimensional network of equally spaced points; a number of such lattices similar and similarly situated but not coincident interpenetrate each other, and the structure of the crystal is obtained by locating a set of atoms of the same kind at all the points of each such lattice. The enumeration of the possible space-groups is based on a consideration of the various types of symmetry which could be exhibited by such a structure. In passing from the point-groups to the space-groups, some additional types of symmetry become possible, viz., glide-plane reflexions and screw-axes, the effect of which is to multiply the number of lattices which are occupied by atoms of the same kind and to locate these atoms within the unit cell of the structure at equal intervals which are integral submultiples of the lattice spacings. The theory of space-groups is complete in itself and its conclusions are fully borne out by the results of the X-ray investigations made with crystals. The determination of the space-group to which a crystal belongs is possible by X-ray study, the so-called absent reflexions giving the clue to the existence of glide-plane reflexions and screw-axes as elements in the symmetry of the structure. Indeed, assignment in this manner of the crystal to the space-group to which it belongs is a necessary step in the task of completely elucidating its structure.

While the complete generality and utility of the theory of space-groups are unquestionable, the nature of the approach which it makes to the subject of crystal structure is purely formal and geometric, and hence the theory cannot take us far towards a physical understanding of the facts of crystal structure. It only tells us what combinations of the various elements of symmetry are possible and the results of such combination, but is not concerned with the reasons for their appearance. A characteristic feature of the theory of space-groups is the introduction, in all except some special cases, of undetermined parameters in the

description which it affords of crystal structure. The appearance of unknown quantities in the description of a structure characterised by perfect order and symmetry must be considered a disturbing and unsatisfactory feature and is an indication that the foundations of the theory have not been laid deeply enough in the groundwork of physical reality.

### An alternative approach

It is proposed in the following to put forward tentatively a concept of crystal structure which, while it is radically different from that forming the basis of the theory of space-groups, does not come into conflict with the results of that theory, but on the other hand, affords a physical interpretation of them, and also explains many facts known regarding the structure of crystals which have hitherto remained without adequate explanation. The concept proposed may be stated in the form of four propositions or postulates.

- I. All the atoms in a crystal whether of the same or of different kind are located at the points of a common space-lattice: but not all the points of the lattice are necessarily occupied.
- II. The locations of the atoms at the points of the common space-lattice with respect to each other are determined by fixed rules derived from their mutual affinities.
- III. The unit of the structure which results from the grouping of the atoms around each other at the points of the common space-lattice is of the same species as the cells of that lattice, but its dimensions are integral multiples of the cell dimensions.
- IV. The valence directions in the crystal structure obey the law of rational indices.

We shall now proceed to comment upon each of these postulates in turn, offering some sort of justification for each of them and pointing out their interrelations. The first postulate contains the kernel of the proposed new concept of crystal structure. Various considerations may be urged in favour of its acceptance. In the first place, it removes all uncertainty or arbitrariness in the specification of crystal structure, and has thus a purely philosophical or a priori justification. Secondly, it may be remarked that for a variety of atoms of different kinds to settle down to form the regular arrangement in space which we call a crystal, it is clearly necessary that they should all take up places in a common plan and the simplest assumption which we could make regarding the nature of this plan is that it is a three-dimensional network or space-lattice, the points of which provide locations for all the atoms. It is also evident that the existence of such a plan does not necessitate that all the points in the lattice should be filled. *Per contra*, the existence of unfilled places would, in general, be necessary if atoms of

different kinds and, therefore, of different sizes are all to be accommodated in the same lattice.

Our second postulate scarcely needs detailed justification. The atomic interactions would obviously determine the manner in which the atoms would take up positions in the postulated common space-lattice, and unless these interactions are of such a nature that they result in specific types of grouping of atoms of the same kind or different kinds about each other, anything like the regular order characteristic of a crystal would clearly be impossible.

Our third postulate may be regarded as consequential on the first two. If we postulate definite types of grouping of the atoms about each other in a common space-lattice, the final result of such grouping should exhibit the various types of symmetry shown to be possible by the theory of space-groups. In the first place, the structure would repeat itself in three dimensions at regular intervals, which are integral multiples of the spacing of the primitive lattice. In other words, the resulting structure would be such that the atomic co-ordinates in the unit of the structure would all be integral multiples of the spacing of the primitive common lattice, and, therefore, either rational sub-multiples or rational fractions of the dimensions of the structural unit. Thus, our postulates would lead naturally to the appearance in all cases of a translational symmetry in the structure of the crystal and also in appropriate special cases, to the types of symmetry recognised in the space-group theory as arising from glide-plane reflexions or screwaxes. But the existence of rational relationships between the atomic co-ordinates and the dimensions of the structural units is a general consequence of our postulates and is not restricted to such special cases.

Our fourth postulate is not an independent one but is merely consequential on our first and second postulates. But it appeared worthwhile to put it forward as a distinct postulate because of its obvious importance in relation to the views of crystal structure here considered, and also because it appears possible to find an independent justification for it. The idea of a directed valence is a fundamental notion of chemistry and is stressed in organic chemistry with reference to the so-called "tetrahedral" valence directions of the carbon and silicon atoms. But one has only to recall cases like cyclo-propane or cyclo-butane to stress the fact that even in saturated carbon compounds. The valences of carbon are not necessarily tetrahedral and that their directions are influenced by the structure. Thus, if the notion of valency has any meaning at all in relation to the crystalline state of matter, we may expect to find the directions in which it is exerted, in other words, the directions of the lines joining neighbouring atoms to bear some simple and specific relations to the structure of the crystal. If such relationships exist, their nature should be of the law of rational indices which one naturally regards as the most fundamental fact of crystal architecture. Thus, if our fourth postulate is regarded as having an independent theoretical justification, our first postulate would be a consequence of it, and vice versa.

Lest it be thought that our present approach to the theory of crystal structure is

hypothetical and speculative, it may be pointed out that a great many inorganic crystals, both of an elementary and of a compound nature, whose structures have been determined with some assurance of finality may be described in terms of our present concepts. Indeed, all crystals in which the atomic co-ordinates have been found to be simply related to the lattice spacings, either as a rational sub-multiple or as a rational fraction thereof fall naturally into the present scheme of thought. Many such structures may be found on an examination of the tabulated results of X-ray analysis. Particularly significant are those cases in which atomic locations of this kind are not demanded by the results of space-group theory.

### Some outstanding questions

Before concluding, it may be worthwhile to reply briefly to some criticisms which may be urged against the present point of view. The most likely criticism that might be urged is that there are apparently well-attested cases of crystals in which the atomic co-ordinates are *not* expressible as rational sub-multiples or rational fractions of the structural cell-dimensions. The answer to this criticism is that such cases deserve careful re-examination with regard to the facts or their interpretation. The atomic co-ordinates here considered are the positions of the atomic nuclei, while the co-ordinates determined from the study of X-ray reflexion-intensity represent the optical centres of the electronic clouds surrounding the nuclei. If the electronic clouds are not spherically symmetrical, the locations determined from the X-ray intensities would not necessarily be those of the atomic nuclei. Another possible source of error in the X-ray studies is the thermal agitation of the atoms which may be considerable and not necessarily symmetrical about the nuclear positions. Not until these and other possible sources of error in the X-ray studies are carefully considered and eliminated in various simple cases which appear to conflict with the present point of view could their evidence be considered to outweigh the significance of the large number of cases in which it does fit with the facts and offers an intelligible explanation of them.

C V RAMAN

## The luminescence of diamond and its relation to crystal structure

SIR C V RAMAN and A JAYARAMAN  
Raman Research Institute, Bangalore

Received August 14, 1950

### 1. Introduction

Studies on the luminescence exhibited by diamond under ultra-violet irradiation were commenced at Bangalore some ten years ago. Their scope enlarged as the collection of high-grade material available for the investigations grew and became more fully representative in character. The results of the researches of the first few years were reviewed in two papers<sup>1, 2</sup> published together in these *Proceedings* in the year 1944. The conclusions reached in those papers may be stated briefly as follows:

I. *Nearly all diamonds and especially those of the first quality exhibit luminescence: this effect is an inherent property of the material: the variations observed in its intensity and in its spectral character have a structural origin.*

II. *The symmetry of the electronic structure of diamond may be either tetrahedral or octahedral: in individual specimens there is a commingling of the different possible structures having these types of symmetry and the property of luminescence results therefrom.*

Experimental evidence was presented both at that time<sup>3</sup> and also later<sup>4, 5</sup> that variations of behaviour having a structural origin present themselves not only in respect of luminescence, but also in respect of numerous other physical properties of diamond, viz., the intensity and angular divergence of the X-ray reflections by the crystal, its infra-red absorption spectrum of the first-order, the absorption spectra in the remote and near ultra-violet and in the visible region, structural birefringence and photo-conductivity. The variations observed in all these properties are manifestly correlated with each other, thereby demonstrating their common physical origin.

The structural origin of the luminescence of diamond can be very elegantly exhibited with the aid of polished cleavage plates of the crystal and by various methods of observation. One of these is an examination of the behaviour of such plates in respect of luminescence under ultra-violet irradiation and in respect of

birefringence in ordinary light. A remarkable parallelism between these two phenomena was discovered by one of us.<sup>6</sup> Photographs were published in these *Proceedings*<sup>7</sup> which were intended to exhibit them side by side for purposes of comparison. Unfortunately, however, the techniques employed were defective, and the pictures reproduced convey only a feeble idea of the very remarkable and precise character of the relationship between luminescence and birefringence in diamond. The present paper is intended to remedy this defect in the earlier work. The photographs now published in the plates accompanying the paper are a record of the luminescence and birefringence of some of our typical specimens. The photographs are on precisely the same scale and have the same orientation, thus enabling them to be readily compared with each other. There are over a hundred cleavage plates of diamond of the first quality in our collection, and the summary of the facts noticed in the case of the diamonds whose photographs are reproduced is equally a description of the behaviour of the rest of them.

## 2. Technique of study

The spectral character of the luminescence of diamond has been thoroughly investigated by P G N Nayar<sup>8</sup> and by Anna Mani<sup>9</sup> at Bangalore. On cooling the diamond down to low temperatures, it becomes evident that the luminescence has its origin in various electronic transitions in the crystal, either alone or in combination with its vibrational transitions. Comparison of the spectra of numerous specimens shows that the emission is of two distinct kinds, a *blue luminescence* and a *greenish-yellow luminescence* respectively. Their absolute and the relative intensities vary largely. The blue luminescence arises principally from an electronic transition giving a line at 4152 A.U. near the violet end of the spectrum, accompanied by a vibrational spectrum appearing in the blue and green regions. The greenish-yellow luminescence arises *principally* from an electronic transition giving a greenish-blue line at 5032 A.U. accompanied by a vibrational spectrum appearing in the green and yellow regions. The two types of luminescence may be viewed separately by observing the diamond through appropriately chosen colour filters. A piece of cobalt glass transmits only the blue luminescence and cuts off the other. For isolating the greenish-yellow luminescence, we have found that an orange-yellow filter which has a complete cut-off at 5400 A.U. is preferable to an yellow filter with a cut-off at about 5000 A.U., since the blue luminescence has a sensible intensity in the region between 5000 and 5400 A.U.

Sunlight concentrated by a large lens and passed through a nickel-oxide glass filter furnishes ultra-violet illumination of the requisite intensity to excite the luminescence. It is focussed on the diamond which is placed on a plate of black glass, both being carefully cleaned to minimise scattered light. It is arranged that the ultra-violet irradiation is almost tangential to the surface of the specimen and as nearly uniform over it as possible, while the visible luminescence is viewed

nearly normally to the surface. In this way, the trouble due to reflection and scattering of the red light simultaneously transmitted by the ultra-violet filter is minimised. In some cases, entry of light through the faceted edges of the diamond results in a streaky illumination of its interior. This trouble is avoided or minimised by a proper choice of the setting of the diamond in its own plane. The camera with which the specimen is photographed is a vertical one of rigid construction and of fixed focal length. It is fitted with a high-quality short-focus lens of the type used for making enlarged photographic prints from small negatives. The appropriate colour filter is interposed between the camera and the diamond. When the cobalt-blue glass is used as a filter, a cell containing sodium nitrite solution has to be interposed to prevent scattered and reflected ultra-violet radiation from entering the camera.

The birefringence is recorded with the same camera and under the same conditions as the luminescence, except that the illumination is by ordinary light transmitted normally through the diamond held between crossed polaroids, no filters being used. The photographs of luminescence and birefringence are thus on exactly the same scale and therefore strictly comparable. The record of the birefringence is to some extent influenced by the setting of the specimen in its own plane between the crossed polaroids. This is varied until the features which it is desired to exhibit are most clearly visible.

### 3. The facts of observation

Each of the figures 1 to 14 appearing in plates I to VII contains three photographs marked (a), (b), (c); these represent respectively the blue luminescence, the greenish-yellow luminescence and the birefringence of the diamond. They are placed together for ease of comparison. We shall not comment on the figures individually, but proceed to state the facts emerging on a careful study made with the specimens in our collection. The interested reader can readily verify these statements by an examination of the figures reproduced.

A. A few diamonds are non-birefringent. Such diamonds exhibit only blue luminescence, the greenish-yellow type being absent.\*

---

\*During a visit by one of us to Great Britain in May 1948, the opportunity arose of examining the luminescence of a great number of diamonds of the highest grade in their natural form as crystals. These had been sorted and arranged in cages in the order of their excellence, as judged by their water, freedom from colour and the absence of strong birefringence when examined between crossed polaroids. Each cage contained some fifty or sixty crystals. All the diamonds without exception from the first six cages showed luminescence of blue colour. Examples of green or yellow luminescence were very few even in the cages containing the lower grades. A blue or bluish-green luminescence was by far the commonest. The batch of diamonds studied was from the Congo, and the similarity between these results and those observed with Indian diamonds of high grade during a visit to Panna in June 1942 was very striking.

B. A few diamonds show neither the blue nor the greenish-yellow luminescence. Such diamonds exhibit a characteristic type of birefringence consisting of a set of fine streaks parallel to each other, or sets of such parallel streaks intersecting each other.

C. The majority of diamonds exhibit both types of luminescence. They also exhibit a birefringence pattern, the geometric character of which bears a recognisable relationship to the features observed in one or the other or both of the luminescence patterns.

D. The two kinds of luminescence often exhibit certain geometric features in common. In other cases, they appear to be complementary, dark regions in one being bright regions in the other, and vice versa. Frequently, also, the greenish-yellow luminescence exhibits features totally absent in the blue luminescence.

E. The blue luminescence is usually conspicuous in areas where the birefringence is weak or absent. It often exhibits a remarkably uniform intensity over such areas. On the other hand, in areas where there is strong birefringence, the blue luminescence is generally of non-uniform intensity and may exhibit a banding which is often straight, but may sometimes also be wavy.

F. The greenish-yellow luminescence frequently takes the form of sets of bands running parallel to each other. Sometimes, two or even three such sets of bands may be seen. Corresponding sets of bands are visible in birefringence.

G. The greenish-yellow luminescence is often conspicuous in the regions separating areas in which birefringence is weak or absent from those which exhibit a strong birefringence.

H. One can distinguish the character of the birefringence in the areas which display both blue and greenish-yellow luminescence or the latter alone, from the birefringence in the areas which display neither. The areas of the latter kind exhibit birefringence of the same character as the nonluminescent diamonds.

Figures 15 and 16 in plate VIII illustrate an effect observed with all diamonds which exhibit the greenish-yellow luminescence as a set of parallel bands. Inclining the plate about an axis parallel to the bands, it is found that the bands sharpen to fine lines when the plate is tilted to one side, while they become more diffuse when the tilt is on the opposite side. In the same circumstances, the bands in birefringence sharpen to fine lines or become more diffuse respectively, thus displaying a complete parallelism of behaviour with the bands in luminescence. Figures 15(b) and (c) exhibit these effects with a tilt to one side, and figures 16(b) and (c) with the tilt on the other.

In this connection, a reference should be made to the facts elicited concerning the birefringence of polished cleavage plates of diamond in the very thorough study by G N Ramachandran<sup>10</sup>. This author made use of a Zeiss petrographic microscope with a Federov universal stage on which the diamond could be placed and suitably orientated. He examined many plates apparently different in their behaviour, and the investigation showed that in all cases, the birefringence patterns were resolved by the microscope with a suitable tilt of the plate to a set of

laminations having a definite orientation parallel to either the octahedral or the dodecahedral planes in the crystal. This was found to be the case even when no laminations were visible when the plate was viewed *normally* between crossed nicols. Only in the diamonds which exhibited no visible birefringence were such laminations found to be absent. In other words, birefringence when observed in diamond is associated with a laminated structure in the crystal: the laminae run parallel to the octahedral or to the dodecahedral planes in the space-lattice.

#### 4. The origin of the luminescence

The view formerly held regarding the luminescence of diamond was that it did not represent a characteristic property of that substance and that the emission was due to some undetermined impurity present in it; the impurities suggested from time to time made a long list, viz., samarium, yttrium, sodium, aluminium, chromium, iron, and titanium, and included even some hydrocarbons! However, it became clear from even the earliest Bangalore investigations that this view was irreconcilable with the observed spectral characters of the luminescence and of the associated absorption. Nayar in his papers of 1941 recognized that the spectroscopic evidence showed the luminescence to be a characteristic property of diamond itself. He ventured further to suggest that the variations of its intensity were in some way connected with the question of the structural perfection of the crystal. A more extensive collection of material became available soon afterwards, and other methods of investigation were also applied to the problem. These enabled more definite conclusions to be reached and published, as already mentioned in the introduction.

It is clearly not possible to reconcile the view which regards the luminescence of diamond as an emission by some undetermined impurity with the experimental facts which we know today about the subject. It is not possible, either, to entertain the alternative but scarcely less naive hypothesis put forward by some authors, namely that the luminescence is that of diamond activated by a trace of some unknown impurity. Indeed, it is obvious that no activator, however distributed within the crystal, could account for the curious and remarkable relationships between luminescence and birefringence observed to exist, as set out in the foregoing pages. Nor would it be capable of accounting for the quantitative relationships which exist between luminescence intensity and X-ray reflection phenomena in diamond as demonstrated by G N Ramachandran<sup>11, 12, 13</sup> by three different methods. These relationships form a direct and convincing demonstration that luminescence in diamond has a structural origin. In these circumstances, it seems almost superfluous to refer to many other facts which have been fully established for which it would scarcely be possible to offer any reasonable explanation on the "activator" hypothesis. We shall content ourself

here with mentioning the very striking results obtained by K G Ramanathan,<sup>14</sup> who has shown that the luminescence intensity and the infra-red absorption by diamond stand in the closest relation with each other.

### 5. Luminescence and crystal structure

The clue to an understanding of the luminescence properties of diamond is to be found in a consideration of the symmetry properties of the structure of that crystal.\* The leading crystallographers of the nineteenth century, including especially Groth, came to the conclusion that the crystal symmetry of diamond was of the tetrahedral class, and that the octahedral symmetry frequently exhibited by it was a pseudo-symmetry arising from an interpenetration of the positive and negative tetrahedral forms. Fersmann and Goldschmidt made a thorough study of the subject<sup>15</sup> and arrived at the same conclusions. The crystal forms of diamond have been re-examined from completely new point of view,<sup>16</sup> and the results support the earlier findings with one modification, namely that the possibility of the structure of diamond being octahedral in some cases is not excluded. The position thus reached is that there are alternative possibilities, in other words that the symmetry of the structure may be either tetrahedral or octahedral.

The existence of structures belonging to the two different symmetry classes would at once explain why the strength of the infra-red absorption of the first order in diamond is highly variable. Spectroscopic theory permits us to identify the structures which are infra-red active with those possessing tetrahedral symmetry and those which are inactive as possessing octahedral symmetry. We can also understand without difficulty why some diamonds which are infra-red active are optically isotropic. The positive and negative tetrahedral forms are physically identical and only geometrically different. Hence their interpenetration would not lead to birefringence. On the other hand, the lamellar structure of the infra-red inactive diamonds indicates that there are also two sub-types of octahedral structure: but these are physically different and therefore do not interpenetrate but appear in distinct layers, the octahedral or dodecahedral planes of the lattice being the planes of junction, analogous to be the composition

---

\*In the article on diamond in volume 3 (pp. 69–89) of the *Encyclopedia of Chemical Technology* (Edited by Professors Kirk and Othmar of the Brooklyn Polytechnic Institute, and issued by the Interscience Publishers, 1949), it is shown how this also enables the remarkable variations in physical properties exhibited by diamond to be correlated and interpreted in a coherent and intelligible manner.

planes in polysynthetic twinning. Such a juxtaposition naturally results in birefringence.

Viewed against the theoretical background sketched above, the facts stated in the preceding sections naturally fall into place. Tetrahedral and octahedral symmetries do not give us different kinds of diamond but only different kinds of structure. If the positive and negative tetrahedral structures co-exist, interpenetrating each other, we have non-birefringent blue luminescent diamond. If the two sub-types of octahedral symmetry co-exist, we have birefringent non-luminescent diamond. In the great majority of cases, however, the tetrahedral and octahedral structures co-exist with the result that the diamond is birefringent and exhibits both blue and greenish-yellow luminescence. The latter arises at the junction planes between the tetrahedral and octahedral structures, and it is readily understood, therefore, why it exhibits a banded structure.

Similar considerations enable us to understand the variations in the behaviour of diamond in respect of infra-red activity, as also in respect of their ultra-violet absorption. In sufficiently thin layers,<sup>17</sup> all diamonds exhibit ultra-violet transmission up to 2250 A.U., there being an intense absorption at still shorter wavelengths. A weaker absorption at longer wavelengths is characteristic of the electronic structures having tetrahedral symmetry. Hence, the strength of such absorption varies from diamond to diamond in a manner closely correlated with their behaviour in respect of luminescence. If the diamond is completely non-luminescent, the cut-off appears at 2250 A.U. even with thick plates. On the other hand, if the diamond is of the luminescent kind, the thicker plates exhibit absorption at wavelengths greater than 2250 A.U., and in the case of the feebly blue-luminescent non-birefringent diamonds this extends up to about 3000 A.U.

## 6. Some remarks on nomenclature

References continue to appear in the literature which assume that any actual diamond must belong to either the one or the other of two species designated as type I and type II respectively. This assumption does not correspond with reality. The original proposers of that nomenclature noted that the great majority of diamonds showed optical birefringence and also infra-red activity in the  $8\mu$  region of the spectrum. They assumed that such optical anisotropy and infra-red activity were characteristic of a particular type of diamond including the great majority of specimens which they designated as type I. On the other hand, they found that a small minority of diamonds were inactive in infra-red absorption in the  $8\mu$  region and exhibited a lamellar structure. These diamonds, they designated as belonging to type II. Actually as we have seen, diamonds are forthcoming which show the infra-red activity strongly but do not show any visible birefringence. Moreover, examination on the Federov stage with a polarising microscope shows that all diamonds which show birefringence also

exhibit a lamellar structure. Further, the infra-red activity of diamond in the  $8\mu$  region is variable and may be anything from zero upwards. Hence it is not possible to divide diamond into two classes on the basis of the presence or absence of such activity. Neither is it possible to base such a classification on the degree of transparency of diamond in the ultra-violet region of the spectrum between 2250 A.U. and 3000 A.U., since this varies in a continuous manner from diamond to diamond.

It is thus clear that the classification of diamond as belonging to type I or type II was based on erroneous beliefs concerning the actual facts of the case. A proper scientific classification must be based on a definite physical idea of what the structural differences actually observed represent and should be capable of correctly describing and interpreting the observed facts. Since this is not the case for the division of diamond into two types and since such division does not correspond with reality, it is meaningless and quite misleading and should therefore be discarded. The truth of the matter is that the great majority of diamonds have a structure which does not permit of their being labelled as belonging to any single type.

### Acknowledgement

We take this opportunity of acknowledging the generous assistance which was forthcoming when one of us visited London in May 1948, facilities for study and specimens for further investigations having been freely placed at his disposal by several persons and authorities. We wish to mention and specially offer our thanks to Dr Paul Grodzinski and to Mr B W Anderson. The diamond of which the photographs are reproduced as figure 1 was one of the specimens received as a gift during the visit. To the Instruments and Chemicals Ltd. of Ambala, we are also much indebted for the prompt construction of the stand-camera used in obtaining the photographs and for their generosity in making a gift of it to this Institute.

### Summary

The relationships which exist between the luminescence of diamond and its behaviour in respect of birefringence are described and illustrated in the paper by a new series of photographs obtained with improved technique and with diamonds of the first quality. It is shown that the results fully support the conclusions reached earlier, viz., that the luminescence of diamond has a structural origin. It is also pointed out that the classification of diamond into two species as type I and type II does not correspond with reality and must therefore be discarded.

## References

1. C V Raman, *Proc. Indian Acad. Sci.*, **A19** 189 (1944).
2. C V Raman, *Ibid.* **19**, 199 (1944).
3. First symposium on diamond, *Ibid.*, June issue **19** (1944).
4. Second symposium on diamond, *Ibid.*, July issue **24** (1946).
5. Symposium on the vibration spectra of crystals, *Ibid.*, December issue **26** (1947).
6. C V Raman, *Curr. Sci.*, **12** 33 (1943).
7. G R Rendall, *Proc. Indian Acad. Sci.*, **24** 168 (1946).
8. P G N Nayar, *Ibid.*, **13** 483 (1941).  
P G N Nayar, *Ibid.*, **13** 534 (1941).  
P G N Nayar, *Ibid.*, **14** 1 (1941).  
P G N Nayar, *Ibid.*, **15** 293 (1942).
9. (Miss) Anna Mani, *Ibid.*, **19** 231 (1944).
10. G N Ramachandran, *Ibid.*, **24** 65 (1946).
11. G N Ramachandran, *Ibid.*, **19** 280 (1944).
12. G N Ramachandran, *Ibid.*, **19** 304 (1944).
13. G N Ramachandran, *Ibid.*, **24** 95 (1946).
14. G N Ramachandran, *Ibid.*, **26** 469 (1947).
15. Fersmann and Goldschmidt, *Der Diamant, C Winter, Heidelberg* (1911).
16. C V Raman and S Ramaseshan, "Second symposium of diamond," *Proc. Indian Acad. Sci.*, **A24** 1 (1946).
17. K G Ramanathan, *Ibid.*, **24**, 137 (1946).

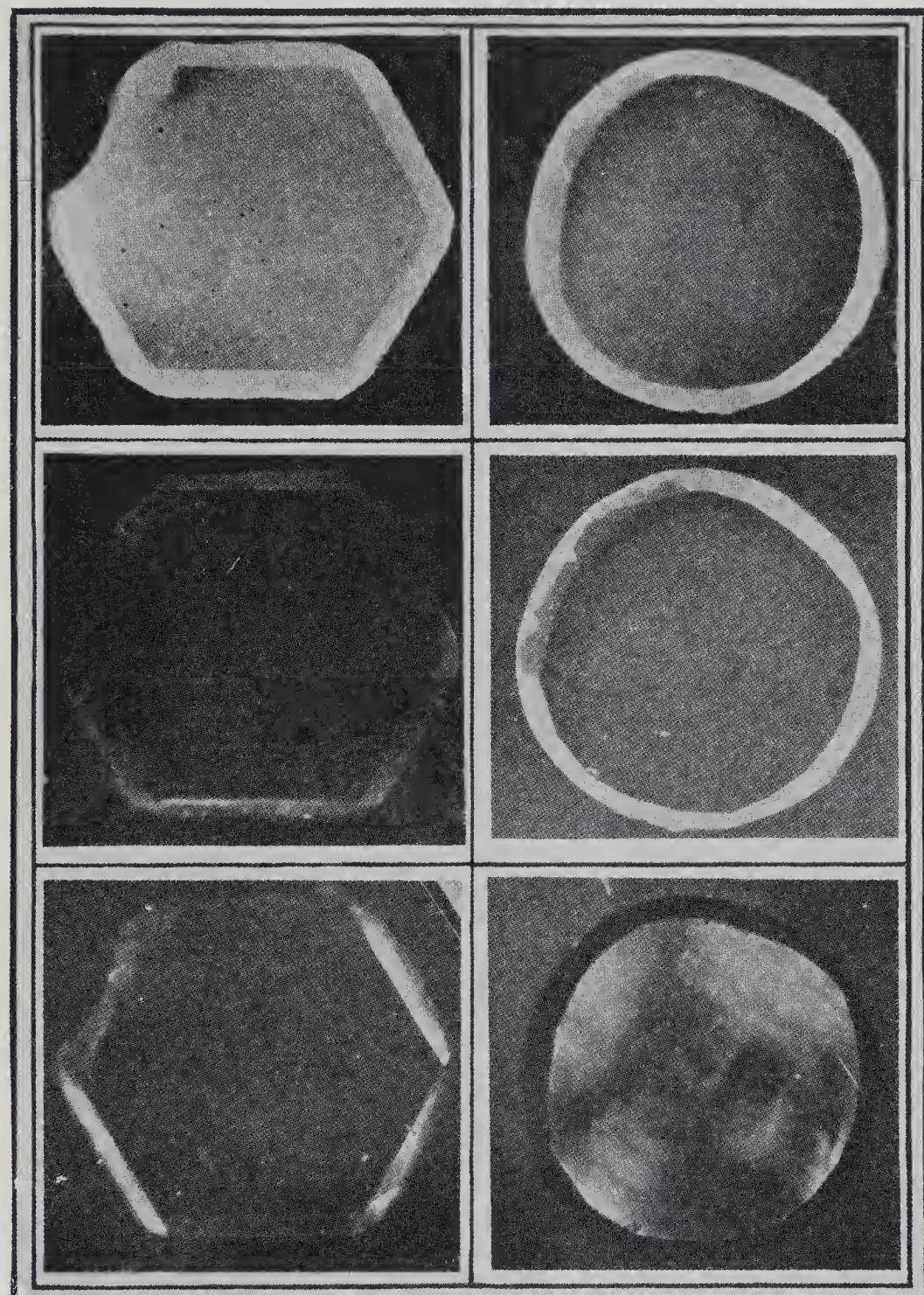
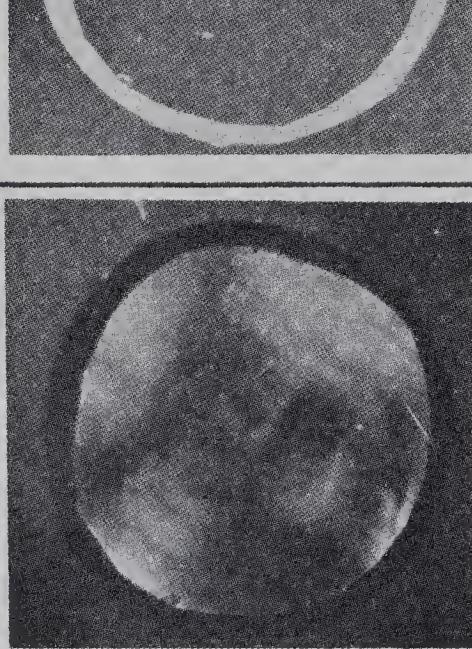


Figure 1

Plate I

Figure 2



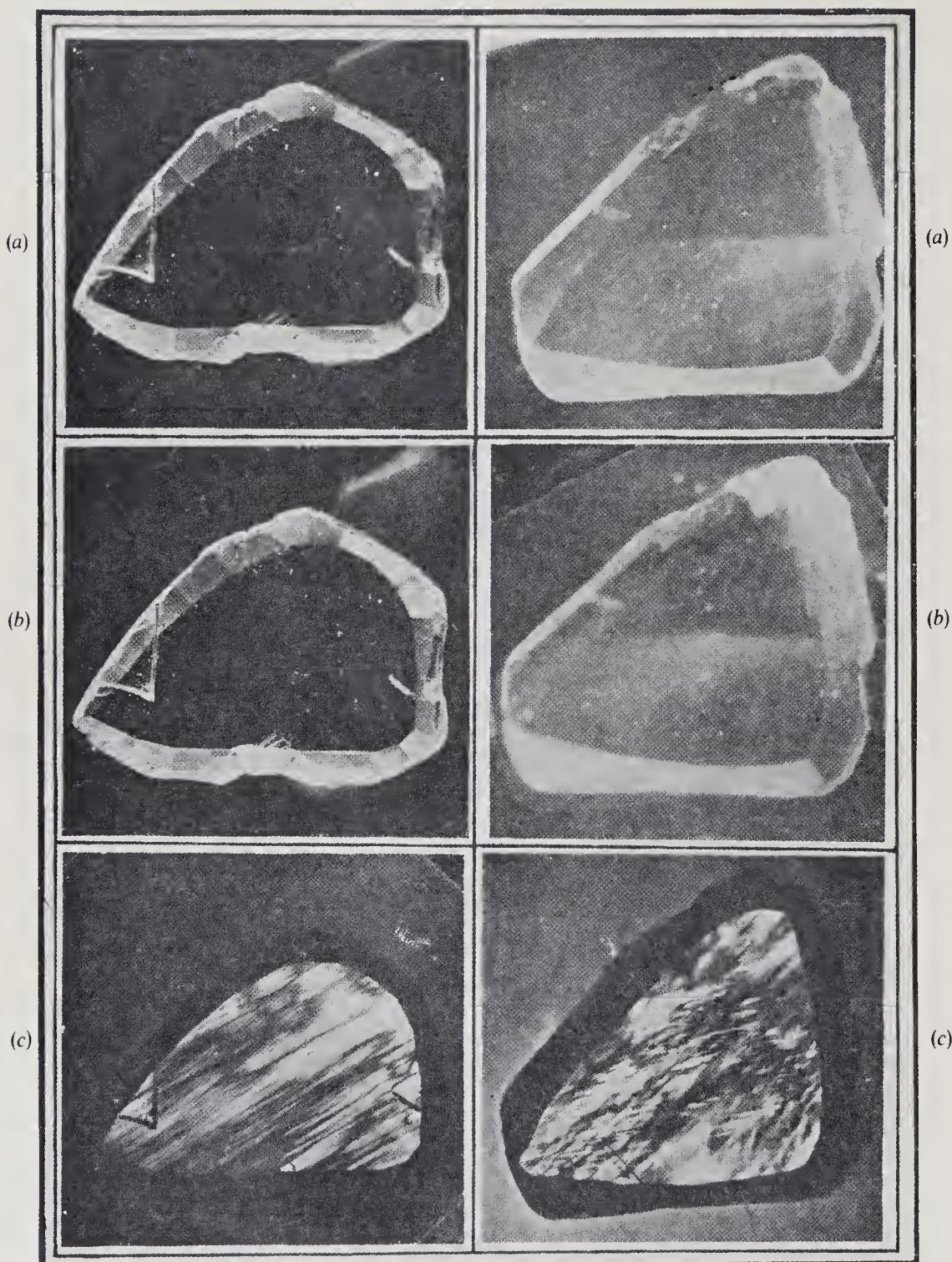


Figure 3

Plate II

Figure 4

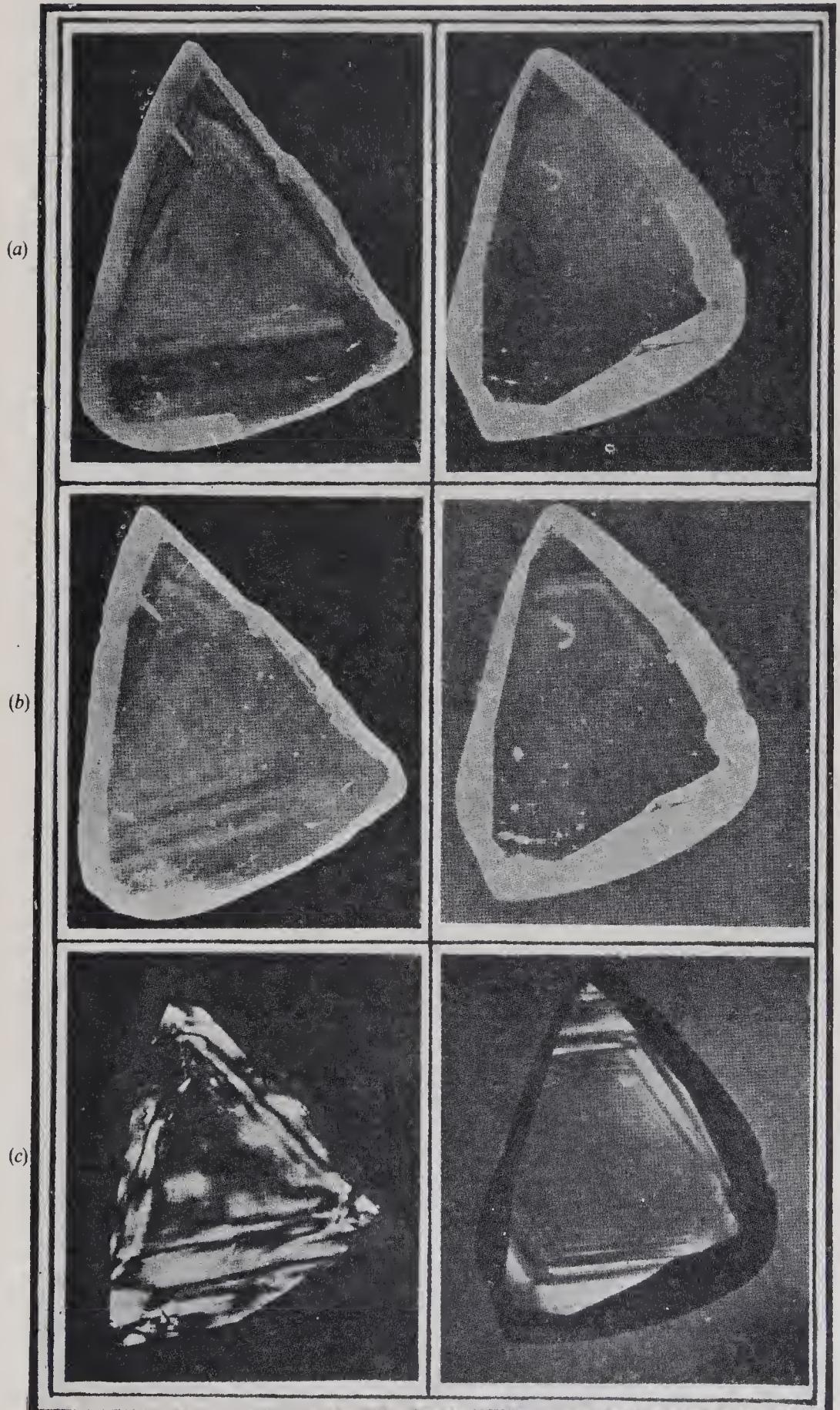


Figure 5  
Plate III

Figure 6

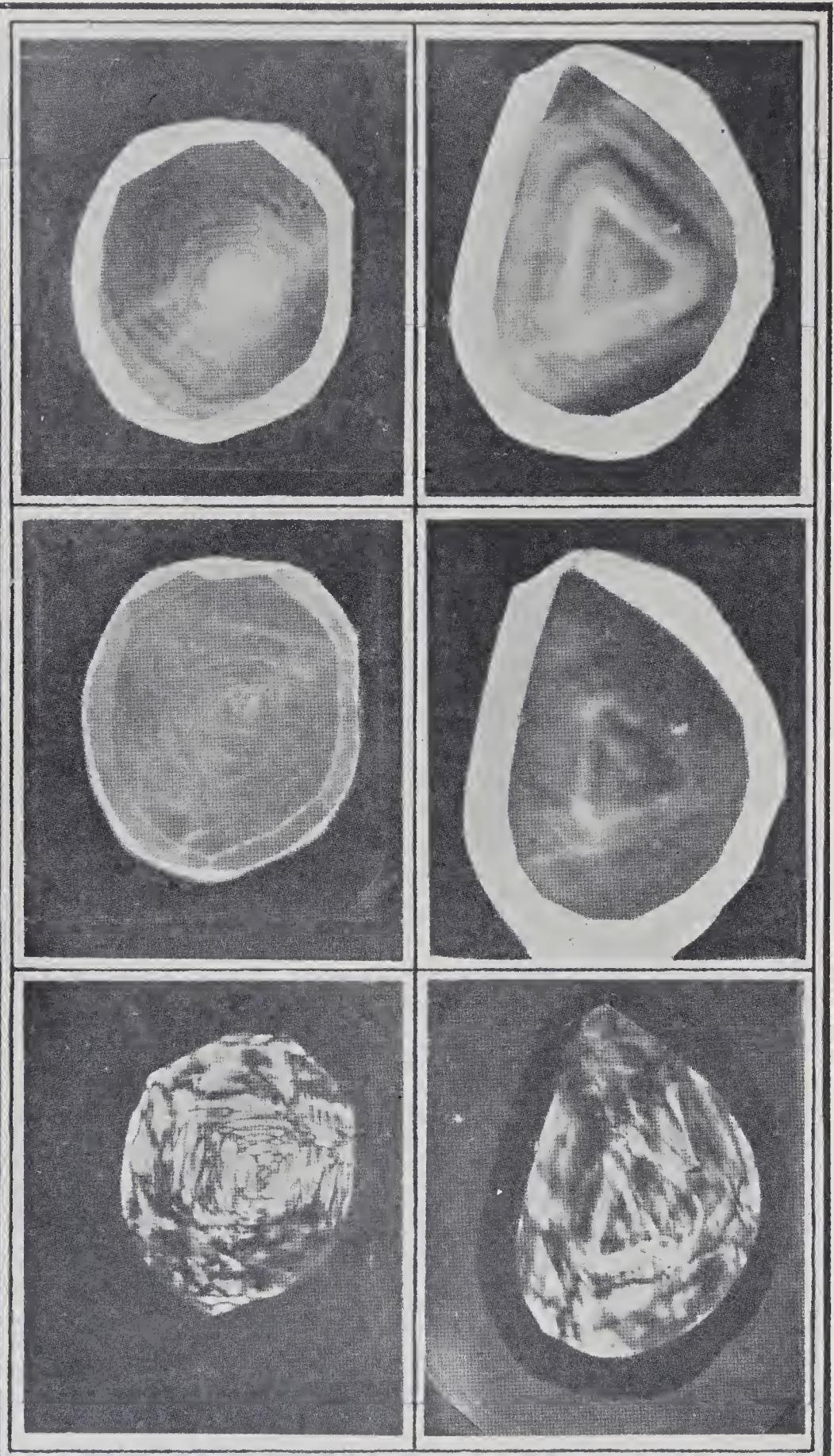


Figure 7

Plate IV

Figure 8

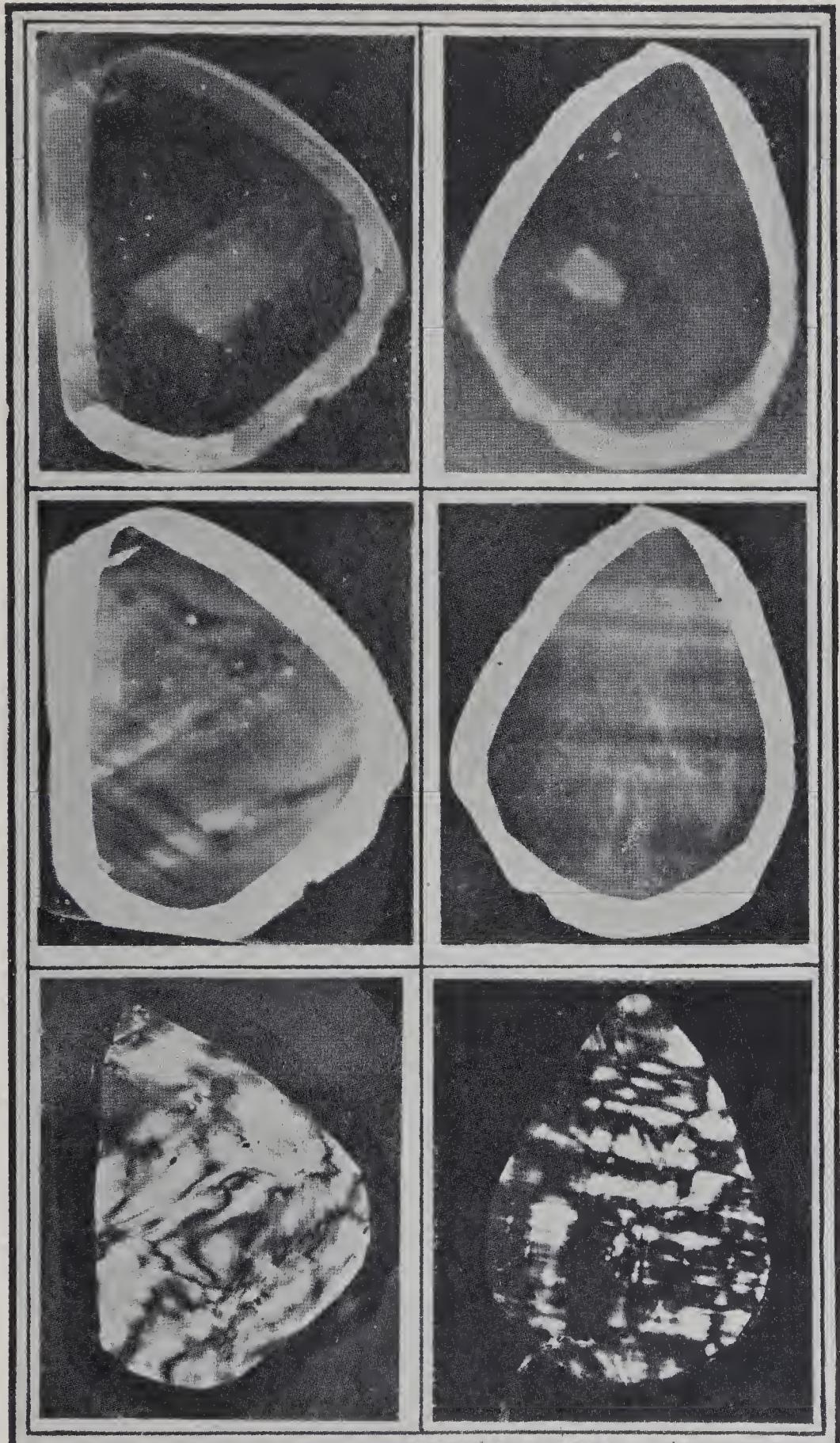


Figure 9  
Plate V

Figure 10

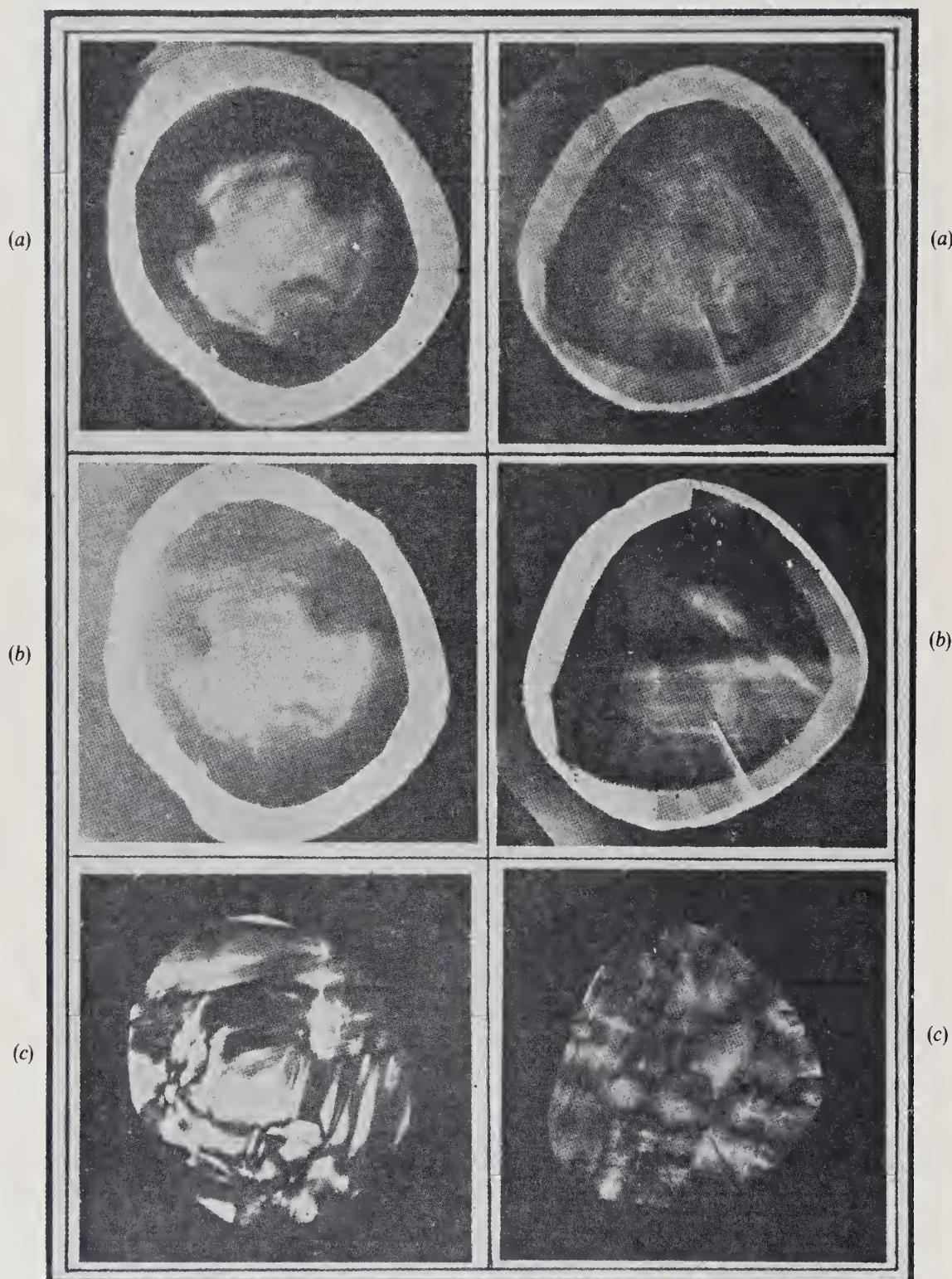


Figure 11

Plate VI

Figure 12

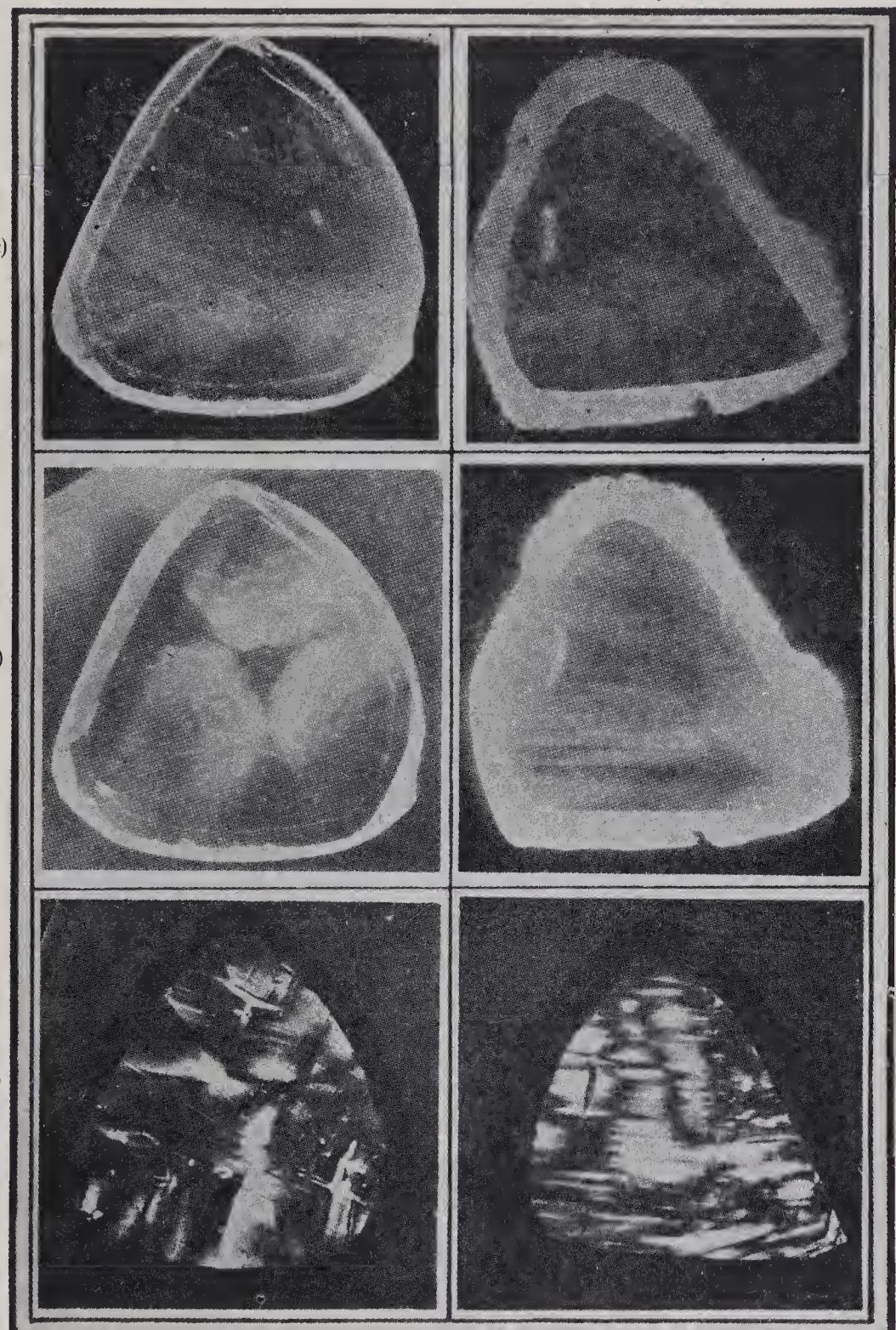


Figure 13  
Plate VII

Figure 14

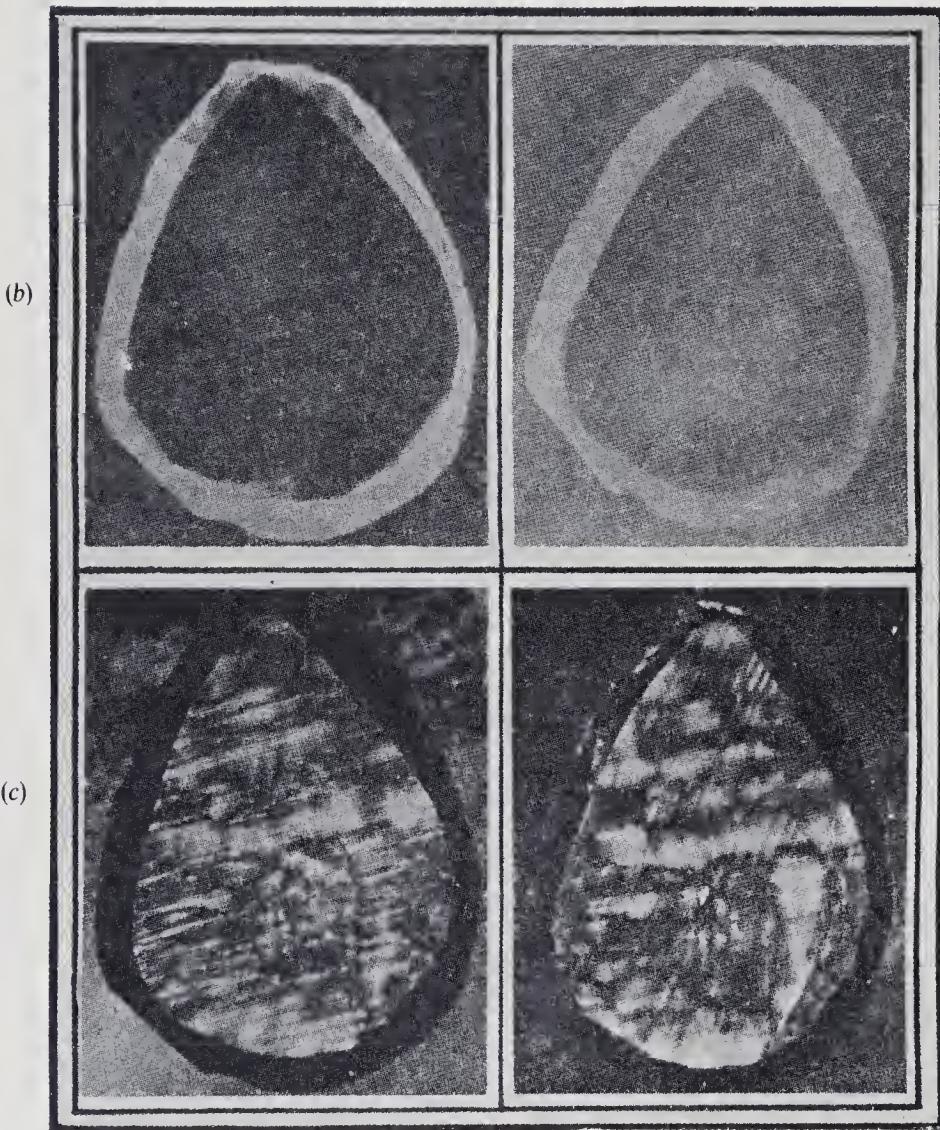


Figure 15

Plate VIII

Figure 16

# The luminescence of diamond—I

SIR C V RAMAN

## 1. Introduction

No less than seventy-five distinct papers which concerned themselves with the structure and properties of diamond were communicated by the present writer and his collaborators and published in the *Proceedings* of the Indian Academy of Sciences between the years 1934 and 1948. Review articles surveying the work of the latter part of this period appeared from time to time in the pages of *Current Science*. Investigations on the diamond have once again been taken up and fresh results have been reported in the *Proceedings* of the Academy for August 1950.\* It appears appropriate in these circumstances to give an account of this recent work in the light of the earlier investigations. In doing so, we shall not trouble to quote literature references, since the interested reader will find a complete bibliography classified under various headings on pages 269 to 287 of the *Proceedings* of the Academy for December 1948.

When the phenomenon of the luminescence of diamond first came under the notice of the present writer in the year 1930, it was not regarded as a subject offering scope for research. Actually, it presented itself as an impediment to the researches then in progress which had for their object the spectroscopic study of the scattering of light in diamond with a view to discover the nature of the *complete vibration spectrum* of that substance. The realisation of this aim had indeed to wait for many years until some non-luminescent diamonds came into the possession of the writer. That the luminescence was itself a phenomenon worthy of study did not suggest itself till the year 1940 when Mr P G N Nayar took up the problem at the instigation of the writer. It soon became apparent that a most fertile field of research awaited exploration.

The photographs reproduced in figure 1 exhibit one of the remarkable features of the luminescence of diamond, namely, the enormous variations in its intensity.

The first of the six pictures in the figure shows a group of 88 South African diamonds set within a circlet of pearls as seen by daylight. The remaining five pictures show the same diamonds made visible by their emission when irradiated

\**Memoirs of the Raman Research Institute*, No. 9. "The luminescence of diamond and its relation to crystal structure," by Sir C V Raman and A Jayaraman.

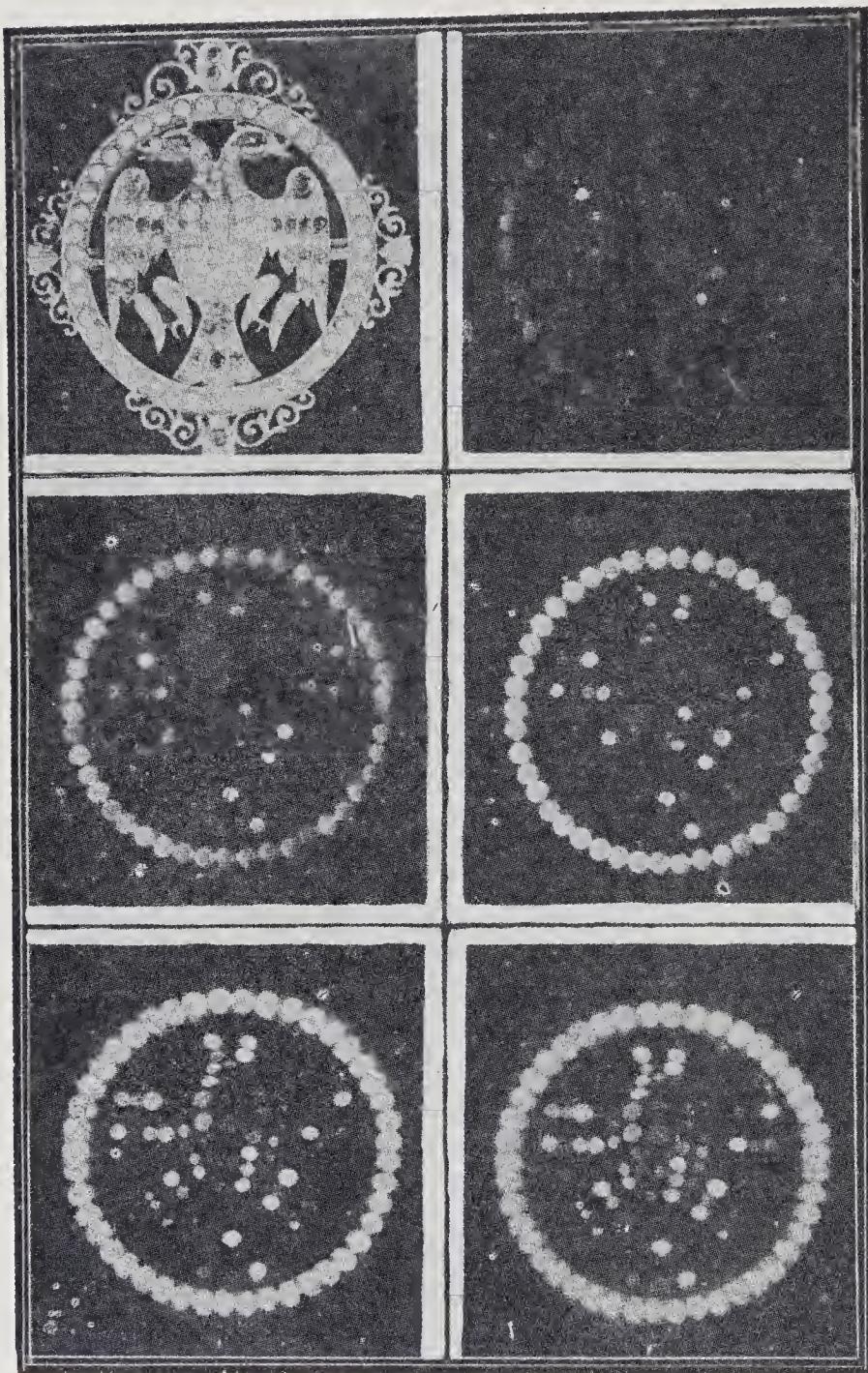


Figure 1. Luminescence of South African diamonds.

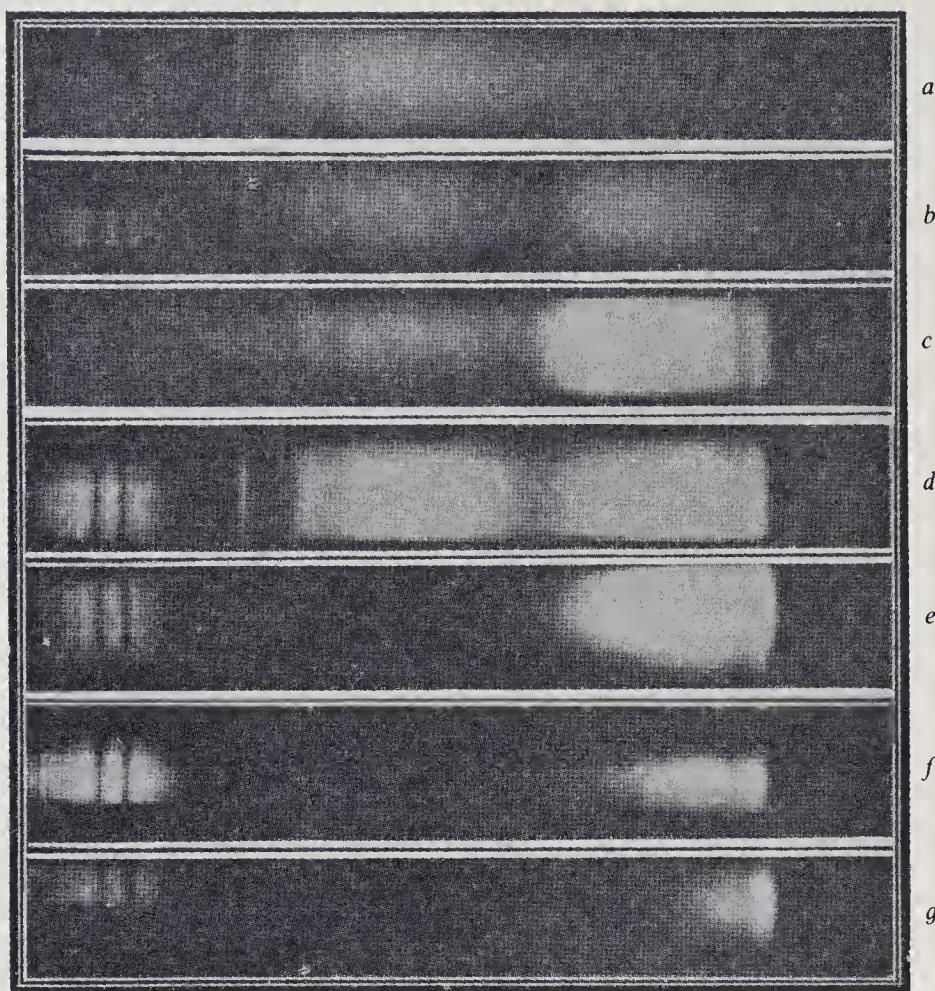
by sunlight filtered through a plate of nickel-oxide glass. The five pictures were recorded respectively with exposures of 5 seconds, 15 seconds, 30 seconds, 120 seconds and 1,800 seconds. Only in the last and most heavily exposed picture is it possible to recognise the original pattern seen by daylight.

Equally noteworthy are the variations in the colour of the luminescence of diamond. While the majority of clear white diamonds show a blue luminescence, others exhibit a greenish-blue, green or greenish-yellow luminescence under ultra-violet irradiation, while a small minority are definitely non-luminescent. In June 1942, the writer had the opportunity of examining a great many diamonds of Indian origin at Panna, and was much impressed by the fact that all the 52 diamonds of the highest quality and of great size in the necklace owned by the Maharaja of Panna were blue-luminescent, though the intensity of such luminescence varied largely. During a visit by the present writer to London in May 1948, the opportunity arose of examining the luminescence of a very large number of diamonds of high grade from the Congo area in their natural form as crystals. The stones had been sorted and arranged in cages in the order of their excellence as judged by their water and freedom from colour. Each cage contained some fifty to sixty crystals. All the diamonds without exception from the first six cages showed a luminescence of blue colour. Examples of green or yellow luminescence were very few even in the cages containing the lower grades, a blue or bluish-green luminescence being by far the commonest effect observed. The similarity between these results and those observed with the Panna diamonds in June 1942 was so striking that one could scarcely doubt that the blue luminescence was a characteristic property of diamond of the first quality.

## 2. Luminescence and absorption spectra

Examination of the spectrum of the light emitted by luminescent diamonds reveals the cause of the variations in its colour. In figure 2 are reproduced a set of seven pictures recorded in some recent studies by Mr A Jayaraman. The first of these pictures is that of a typical blue-luminescent diamond, while the third spectrum is that of a diamond exhibiting an intense green luminescence. These types of emission were those very thoroughly studied by Mr P G N Nayar and Miss Anna Mani respectively. It is evident that the second and fourth spectra in the figure are superpositions in different intensity ratios of the blue and green types of luminescence. The last three spectra in the figure represent other types of luminescence which are less common but are also of great interest. It would seem that they arise from a progressive extinction of the shorter wavelengths in the second or green type of spectrum with a consequent approach of the colour of the luminescence to a pure yellow or orange.

The spectra reproduced in figure 2 were recorded with the diamonds held at room temperatures. Lowering the temperature of the crystal to that of liquid air



**Figure 2.** Luminescence spectra of diamonds.  
(a) Blue, (b) Bluish-green, (c) Green, (d) Bluish-white, (e) Greenish-yellow, (f) Yellow, (g) Orange.

results in the sharpening of the bands, whereby the true character of the spectra stands clearly revealed. Lowering of the temperature has an analogous effect on the corresponding absorption spectra exhibited by the same diamond. Inter-comparison of the emission and absorption by the same diamond at low temperatures reveals the remarkable connections between the two. These features are apparent from figures 3, 4 and 5 reproduced from the papers of Mr P G N Nayar and Anna Mani. In figure 3, the upper of the two spectrograms represents the emission spectrum and the lower the absorption spectrum. The former exhibits the bright lines at  $\lambda 4152$  and  $\lambda 5032$  characteristic of the blue and green types of luminescence respectively. The lower spectrum, on the other hand, exhibits dark lines in absorption at the same wavelengths. It will be seen from the same figure that the emission at  $\lambda 4152$  and  $\lambda 5032$  are accompanied by subsidiary bands towards the longer wavelengths. In absorption, on the other hand, the subsidiary bands appear towards shorter wavelengths. The subsidiary bands in

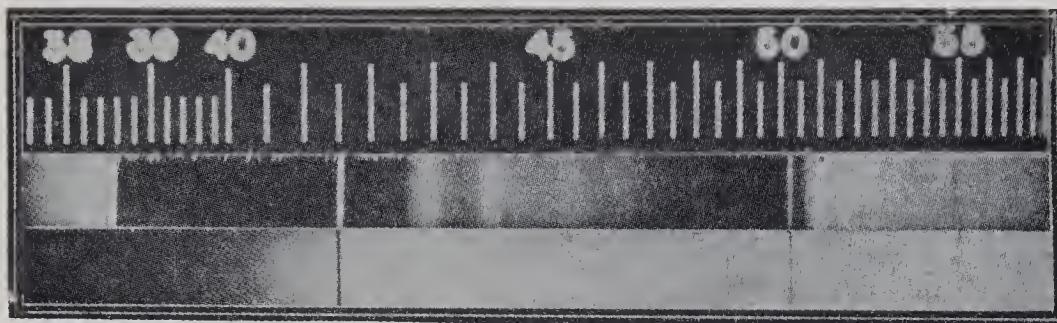


Figure 3. The fluorescence and absorption spectra of diamond.

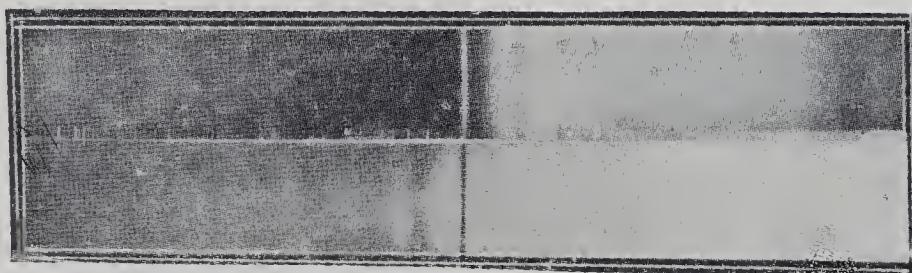


Figure 4. The 5032 system in emission and absorption at liquid air temperature showing mirror image symmetry.

emission and absorption exhibit mirror image symmetry about  $\lambda 4152$  and  $\lambda 5032$  as the case may be, their frequency shifts with respect to these being equal and opposite. This is clearly seen from figure 4 in the case of  $\lambda 5032$  and from figure 5 in the case of  $\lambda 4152$ . In the latter figure, the absorption spectrum has been reversed so as to exhibit the mirror image symmetry about  $\lambda 4152$  line by the coincidence of the dark bands in absorption with the bright bands in emission.

The relationship between the emission and absorption spectra of diamond is also illustrated in a striking manner by studying the effect on the intensity of the luminescence of exciting the same with monochromatic light the wavelength of which can be altered. Anna Mani carried out a series of experiments of this kind and found that the intensity of the blue luminescence passes through a series of maxima and minima when the exciting radiation is on the short wavelength side of  $\lambda 4152$  and is gradually shifted towards that wavelength. It reaches a large maximum when the exciting band coincides with  $\lambda 4152$  and then drops suddenly to a small value when shifted to greater wavelengths. Similar effects in respect of the green luminescence are noticed when the exciting radiation lies on one side or the other of the principal absorption at  $\lambda 5032$  which goes hand in hand with that luminescence. The facts recited show that the absorption and emission centred at  $\lambda 4152$  and  $\lambda 5032$  respectively represent electronic transitions, while the subsidiary bands represent the vibrational transitions of the crystal lattice which are coupled with these electronic transitions.

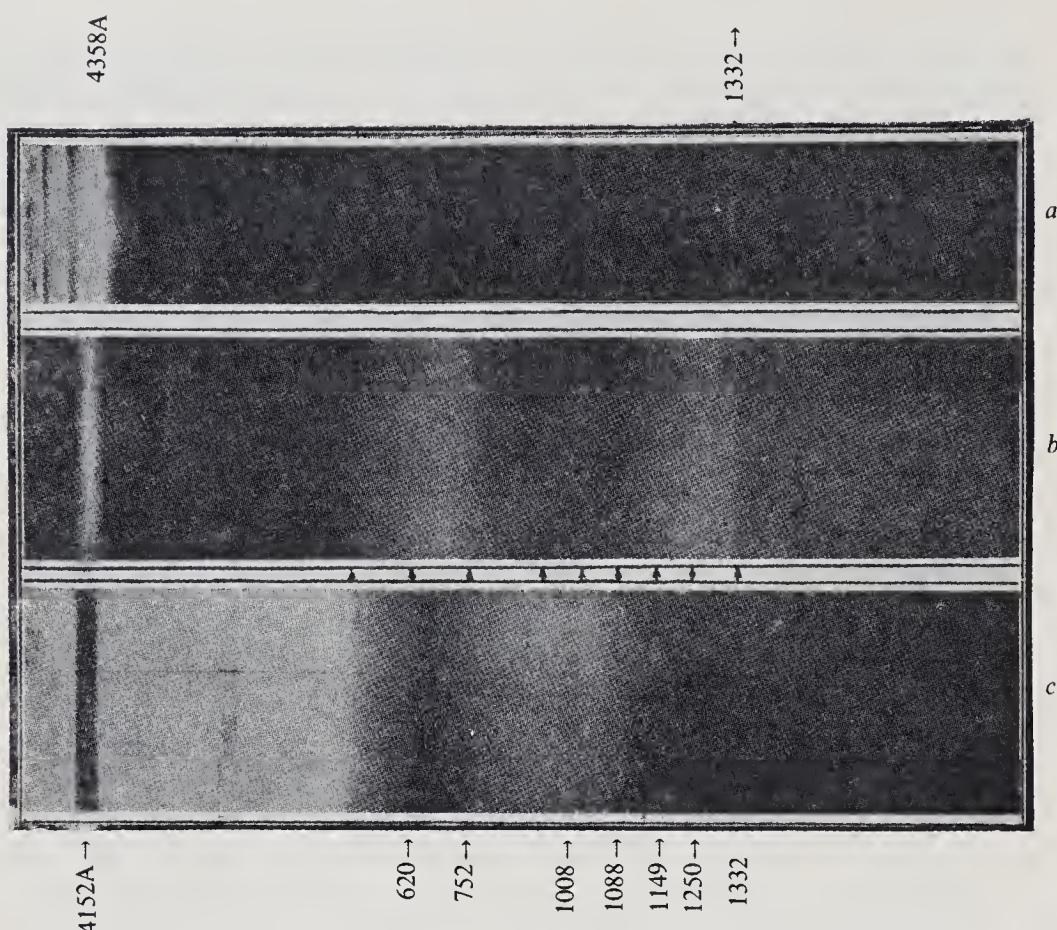


Figure 5. (a) Raman spectrum of diamond, (b) emission spectrum and (c) absorption spectrum (reversed).

### 3. The lattice spectrum of diamond

The foregoing interpretation of the observed facts finds confirmation in the agreement of the frequency differences (positive and negative respectively) derived from the luminescence and absorption spectra with the lattice frequencies in diamond as determined from studies on the scattering of light and on the infrared absorption in the substance. The electronic absorption and emission lines are diffuse at room temperatures and exhibit a readily observable width and structure when it is cooled down to liquid air temperature. This introduces some uncertainties in the lattice frequencies as deduced from the studies on luminescence or the corresponding absorption. Such uncertainties are even greater in the case of the green luminescence, the  $\lambda 5032$  line being diffuse even at liquid air temperature. Nevertheless, the results are sufficiently definite to give us an indication of the nature of the vibration spectrum of the diamond lattice.

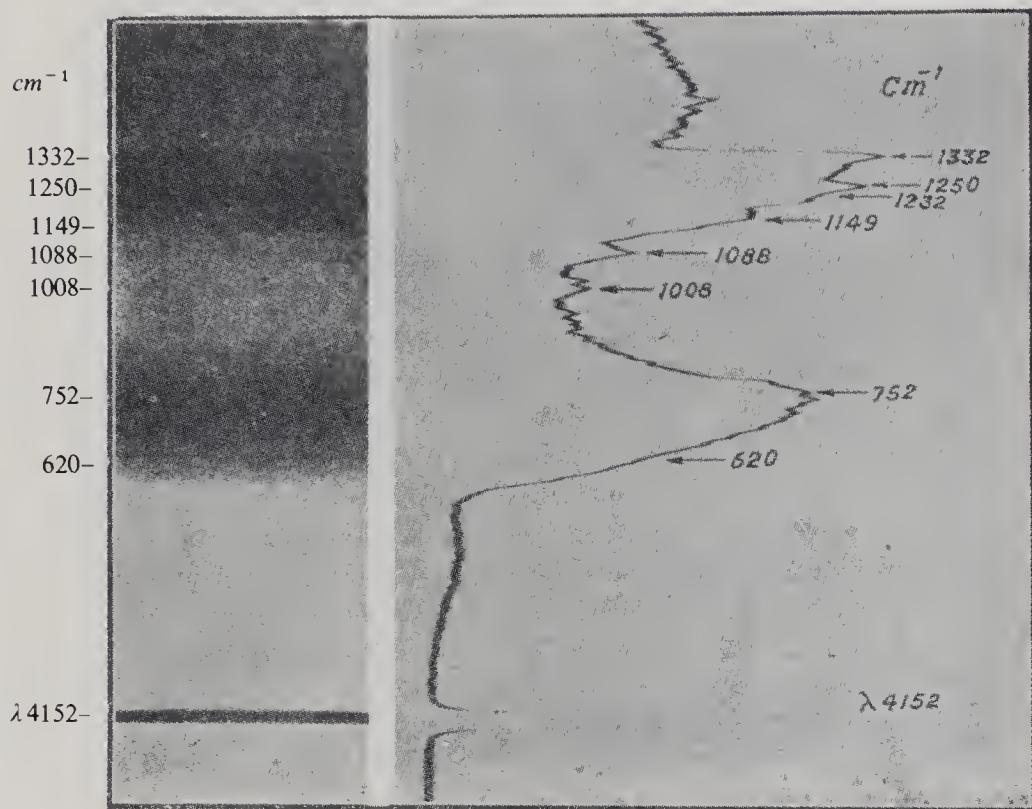


Figure 6. The emission spectrum of blue-luminescent diamond.

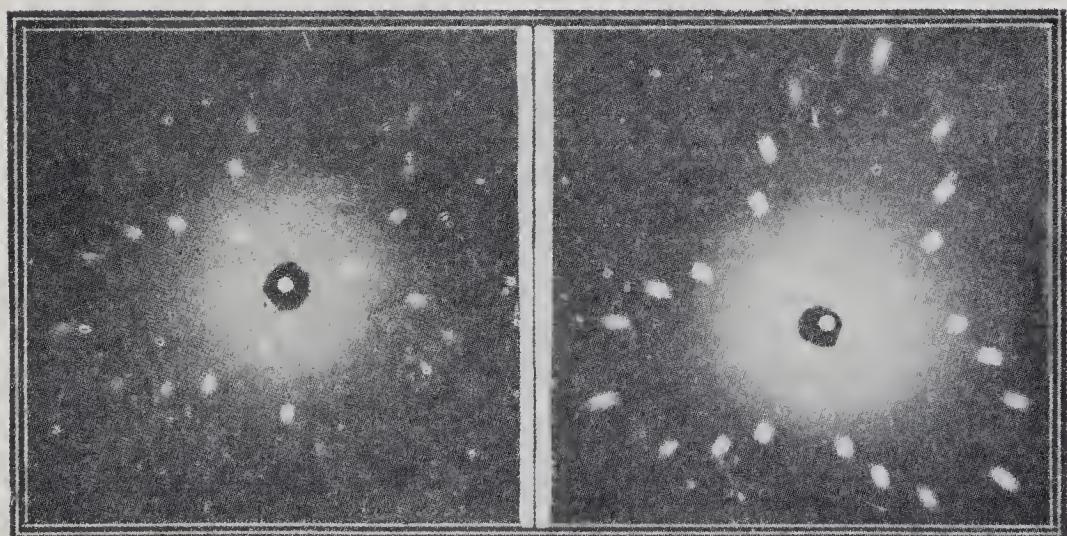


Figure 7. Laue photographs of two blue-fluorescent diamonds.

Particularly remarkable is the appearance in the emission spectrum of blue luminescence, of a series of well-defined bands. These are shown in figure 6 taken from a paper by K G Ramanathan. Their positions are marked in the figure and their sharpness is evident from the accompanying microphotometer record. As already remarked, the finite width of the  $\lambda 4152$  line sets a limit to the sharpness with which the vibrational transitions are recorded. The sharpness is even less satisfactory in the case of the  $\lambda 5032$  line and the accompanying vibrational transitions. Hence, the evidence from the luminescence spectra regarding the discrete character of the lattice vibration spectrum of diamond must be regarded as indicative rather than as demonstrative. The real proof of the discrete line-character of the lattice vibration spectrum of diamond comes from the studies on light-scattering, where the sharpness of the recorded lines is determined by the monochromatism of the incident light which is very high.

The spectroscopic facts set forth above make it clear that in spite of the enormous variations in the intensity and colour of the luminescence of diamond, we are dealing with a well-defined phenomenon namely, certain electronic transitions and associated vibrational transitions, the positions of which do not vary either with the particular specimen or with the locality of its origin. What varies is the intensity of these transitions. Thus, we are naturally led to infer that the luminescence is a phenomenon characteristic of the diamond itself, and that the variations observed arise from corresponding variations in the fine structure of the crystal. This conclusion is powerfully reinforced by X-ray studies especially those made and reported in various papers by Dr G N Ramachandran. It is found that there is a precise quantitative correlation between the strength of the blue luminescence exhibited by diamonds with the intensity of the X-ray reflections, both of the Laue and the Bragg types, given by their crystal planes. This is illustrated for the Laue reflections in figure 7. The two photographs reproduced were recorded with equal exposure, with two diamonds of equal thickness but differing in the intensities of their blue luminescence. It is seen that the Laue reflections of the two diamonds differ greatly in their intensity. Dr G N Ramachandran has also shown that the angular divergence of the Bragg reflection given by the diamond with monochromatic X-rays is least for faintly blue-luminescent diamonds and increases with the intensity of that type of luminescence. In other words, the former represent the nearest approach to an ideally perfect crystal structure.

## The luminescence of diamond—II

SIR C V RAMAN

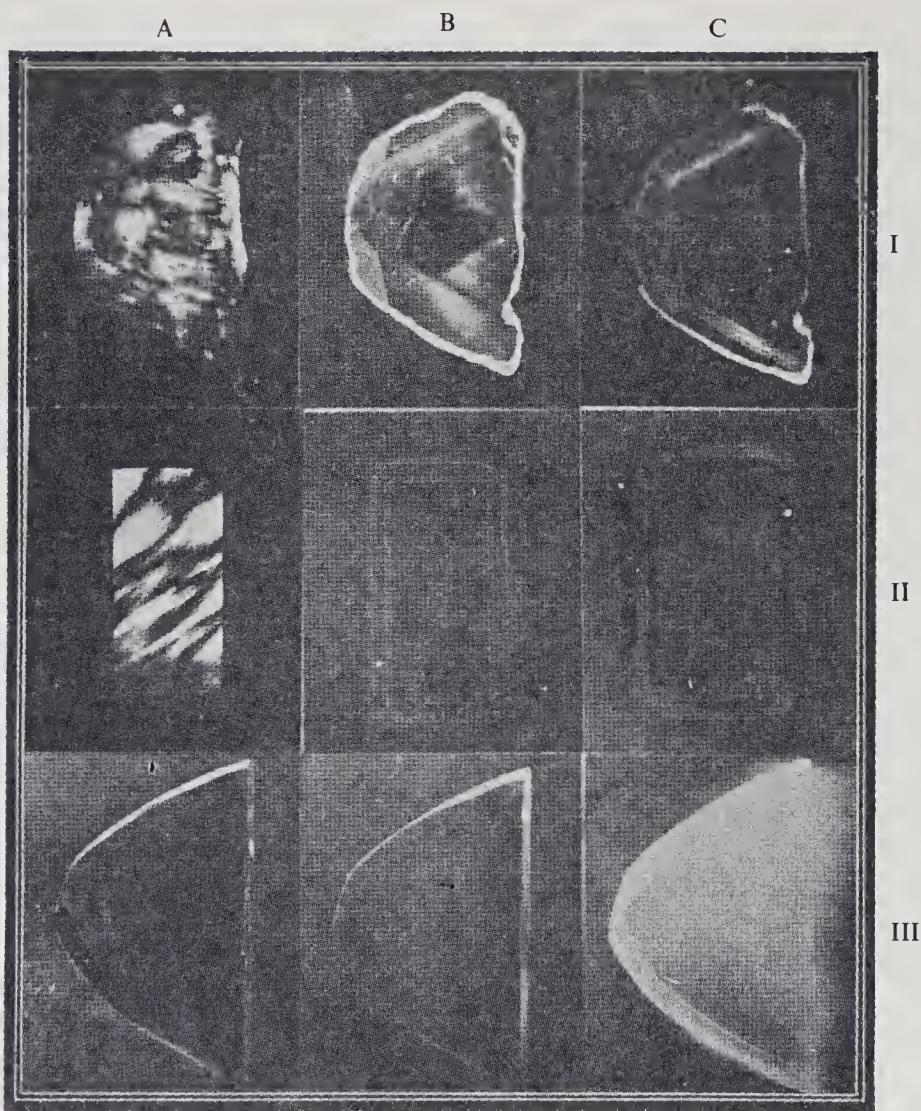
### 1. Luminescence and crystal structure

The spectral character of the visible luminescence excited in diamond by irradiation with long-wave ultra-violet light was described and illustrated in an earlier article of this series, and the remarkable diversity of behaviour displayed by different specimens of diamond in these circumstances was duly stressed. Why this should be so is a problem which might well have remained unsolved, had it been an isolated issue. At our early stage of the Bangalore investigations, however, it became apparent that luminescence was only one of a whole group of physical properties of diamond which exhibit large variations, and that these are interrelated with each other. A detailed study of the situation was made possible by the circumstance that the collection of material included a large number of polished cleavage plates of diamond—a form which is exceptionally well-suited for such investigations. It will suffice here to mention four series of studies made with these plates which covered the following topics: (a) the absorption in diamond of ultra-violet radiation of wavelengths between  $\lambda 2000$  and  $\lambda 3000$ ; (b) the absorption of infra-red radiation of wavelengths between  $6 \mu$  and  $12 \mu$ ; (c) its structural birefringence; and (d) the intensity of X-ray reflections by the lattice planes of the crystal.

That physical properties so different in their nature as those stated above exhibit variations correlated with each other and with luminescence is by itself an indication that a common cause underlies all the variations. Of particular importance in this connection was the discovery that a good many of the plates exhibited luminescence of varying colour and intensity over their area, showing geometric patterns with a configuration related to the structure of the crystal. This suggested investigations by appropriate methods of the other properties listed above, and the result emerged that the cleavage plates which showed geometric patterns of luminescence also exhibited patterns of ultra-violet transparency, patterns of infra-red transmission, patterns of structural birefringence and patterns of X-ray reflection intensity; the geometric features of all these patterns bore a recognizable relationship with each other. The evidence for the structural origin of the whole group of effects was thereby greatly strengthened.

It is proposed in this article to present the experimental facts briefly summarised above, in somewhat greater detail. Of particular significance and

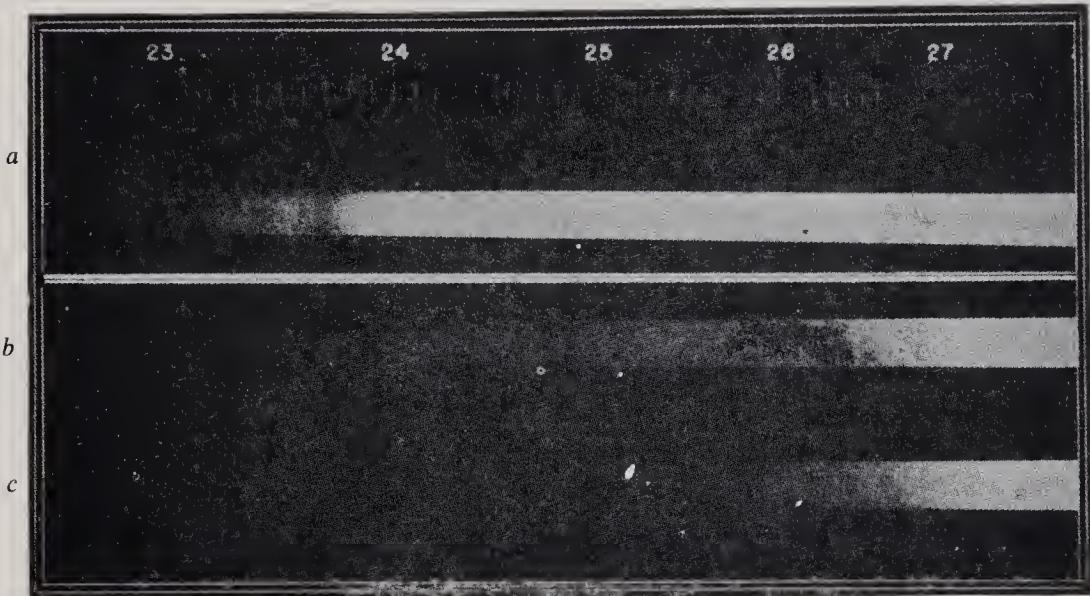
importance is the relationship between luminescence and birefringence in diamond. The technique of photographing their patterns so as to exhibit the relationship between them has recently been greatly improved, and a whole series of new photographs by Mr A Jayaraman were reproduced with a paper which appeared in the *Proceedings of the Indian Academy of Sciences* for August 1950. Other photographs taken with the same apparatus illustrate the present article (figures 1 and 6 below).



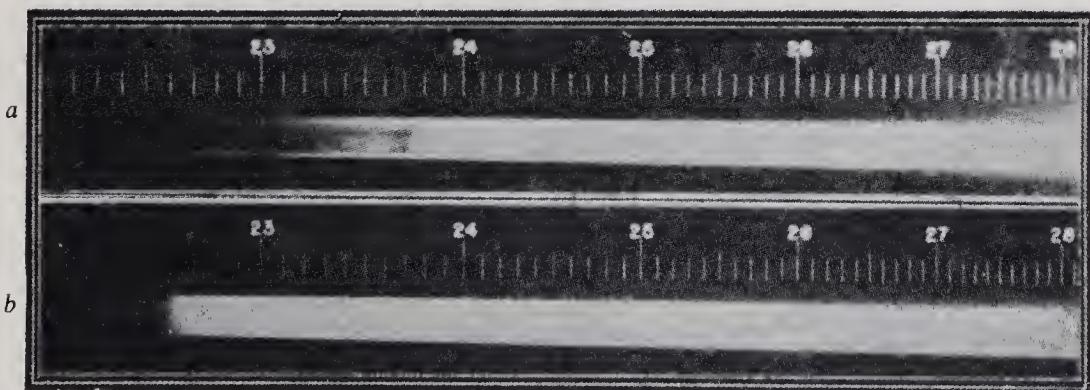
**Figure 1.** Luminescence and birefringence patterns of three representative diamonds. (A) Birefringence, (B) Green luminescence and (C) Blue luminescence.

## 2. The luminescence patterns

In order to observe or photograph its luminescence, the diamond is placed on a piece of black glass and irradiated by a beam of sunlight filtered through a plate of Wood's glass and focussed on the specimen. Viewing the diamond through a blue filter, one isolates the part of the luminescence which arises from the electronic transition at  $\lambda 4152$  and its associated vibrational transitions. Similarly, viewing the diamond through a filter which has a cut-off for wavelengths shorter than  $\lambda 5400$ , the blue part of the luminescence is extinguished, while the luminescence



**Figure 2.** Ultra-violet absorption in blue-fluorescent diamond of different thicknesses.  
(a) 0.15 mm, (b) 0.30 mm and (c) 0.37 mm (after K G Ramanathan).



**Figure 3.** Ultra-violet absorption in (a) green-fluorescent diamond and (b) non-fluorescent diamond  
(after K G Ramanathan).

arising from the electronic line at  $\lambda$  5036 and its associated vibrational transitions can be seen, though with considerably reduced intensity.

Over a hundred cleavage plates of diamond included in the Bangalore collection have been studied in the manner described. They are found to fall into three groups. *Firstly*, we have a group which exhibits "blue" luminescence. This is more or less perfectly uniform in intensity over the area of the plate, while observations through the appropriate filter show the "green" luminescence to be either weak or wholly absent. *Secondly*, we have a group which exhibits neither the blue nor the green luminescence with observable intensity. Such diamonds may, therefore, be classed as *non-fluorescent*. *Thirdly*, we have a group comprising the majority of our specimens. These exhibit geometric luminescence patterns, the nature of which varies greatly from specimen to specimen. In some diamonds, part of the area is non-fluorescent while the rest exhibits the "blue" luminescence usually accompanied by a weak green luminescence, as shown by observation through the filter. There are, however, many specimens in which the presence of both types of luminescence is evident even without the aid of the filter. Viewed through the filter which cuts out the blue luminescence, the "green" luminescence becomes apparent as parallel bands of a greenish-yellow colour traversing the plate in different directions. The assistance of the filter enables such bands to be detected in areas which show only blue luminescence without such aid.

We may summarise the position by the statement that some diamonds are non-luminescent, others exhibit only blue luminescence, while a third class exhibits a more complex behaviour in which the appearance of both the blue and green types of luminescence with varying relative intensities is a characteristic feature. The facts observed suggest that this third category of specimens may be described as being a "mixture" of the first two kinds of diamond, namely, the non-fluorescent and blue-fluorescent ones. Their juxtaposition is evident in some specimens on a simple inspection of their luminescence patterns. In other specimens, especially those showing the green luminescence prominently, the mixture appears to be on a finer scale.

### 3. Patterns of ultra-violet transparency

A simple technique was developed for the study of the transparency of cleavage plates of diamond to the ultra-violet radiations of the mercury arc in quartz. The most intense part, viz., the resonance radiation of wavelength  $\lambda$  2537 is separated from the rest by the use of a dispersing assembly composed of a quartz prism and a pair of quartz lenses. The radiation thus isolated falls on the cleavage plate of diamond which is held attached to a thin sheet of canary-yellow or uranium glass. The fluorescence excited in the latter in the parts screened by the diamond reveals whether any of the incident radiation is transmitted by the latter. The parts that are opaque to the radiation appear dark in the fluorescent glass. Those that are

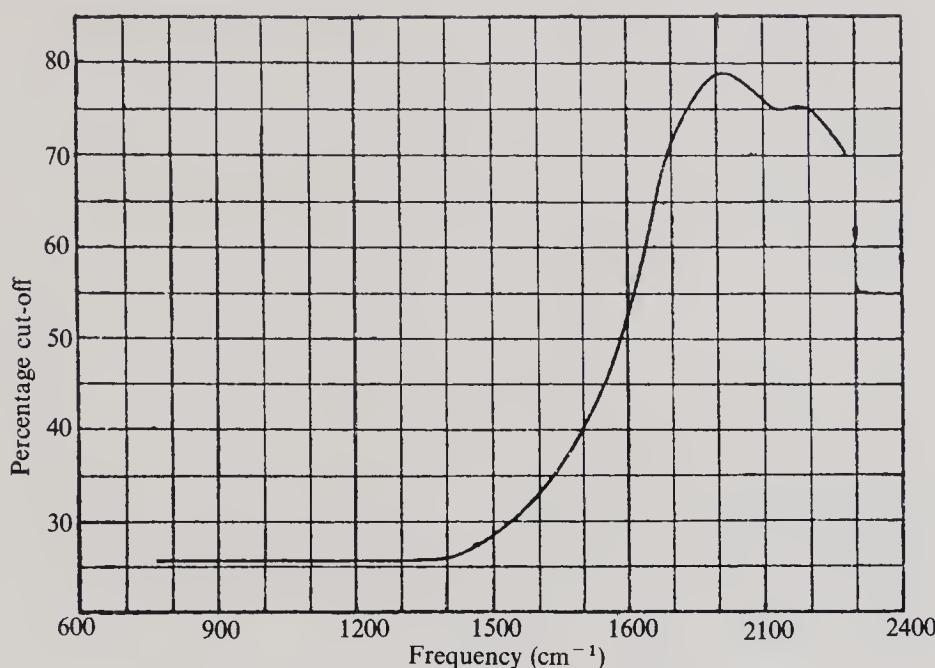


Figure 4. Infra-red transmission by non-fluorescent diamond.

transparent show the full intensity, while partial transparency is indicated by a diminished brightness of fluorescence.

Observations made by this technique reveal the correlation which exists between the ultra-violet transparency of a diamond to the  $\lambda 2537$  radiation and the luminescence excited in it by ultra-violet radiation of much greater wavelengths. Non-fluorescent diamonds are completely transparent to the  $\lambda 2537$  radiation. Diamonds which fluoresce blue with weak or moderate intensity are opaque to the same radiation. "Mixed" diamonds which are in part non-luminescent and in part blue-luminescent show these parts as respectively transparent and opaque to the  $\lambda 2537$  radiation. The diamonds which are green-fluorescent exhibit a marked transmission, which is however distinctly inferior to that of non-fluorescent diamond. Strongly blue-luminescent diamonds show a weak but nevertheless observable transmission of the  $\lambda 2537$  radiation.

It is obvious that the terms transparency and opacity used above can have a precise meaning only if the thickness of the plate and its percentage of transmission are specified. The investigations made reveal that while all diamonds show a complete cut-off for wavelengths less than  $\lambda 2250$ , it is possible by reducing the thickness sufficiently to observe a transmission down to that limit even in the case of diamonds which in thick layers are opaque beyond  $\lambda 3000$ . This effect is illustrated in figure 2 for a diamond of the blue luminescent type.

#### 4. Patterns of infra-red transmission

Investigations reveal a precise correlation between the transparency of diamond to infra-red radiation in the  $8\ \mu$  region of wavelength and its behaviour in respect of luminescence. When appropriate corrections are made for reflection at their surfaces, non-luminescent diamonds are found to be completely transparent to infra-red radiation of wavelength  $8\ \mu$ , while diamonds which are blue-fluorescent with weak or moderate intensity show a strong absorption in that region. The absorption is, however, distinctly less for diamonds which exhibit an intense blue luminescence. Diamonds which exhibit a green luminescence have only a weak absorption in the  $8\ \mu$  region and indeed approach the non-fluorescent diamonds in their behaviour. It should be remarked that all diamonds irrespective of their behaviour in luminescence show an absorption in the infra-red region between  $7\ \mu$  and  $4\ \mu$ . This is a second-order absorption due to the octaves and combinations of the characteristic frequencies of the crystal lattice.

#### 5. Patterns of structural birefringence

We are not here concerned with the accidental birefringence due to visible flaws or inclusions in diamond, but will consider only the birefringence having a structural origin observed in plates which appear otherwise faultless. The effect, if present, is readily observed when the plate is held between crossed polaroids and viewed against a bright source of light. Since the optical effects arising from a local stress extend far beyond the point of its application, while, on the other hand, luminescence is an essentially localised phenomenon, we cannot expect a perfect

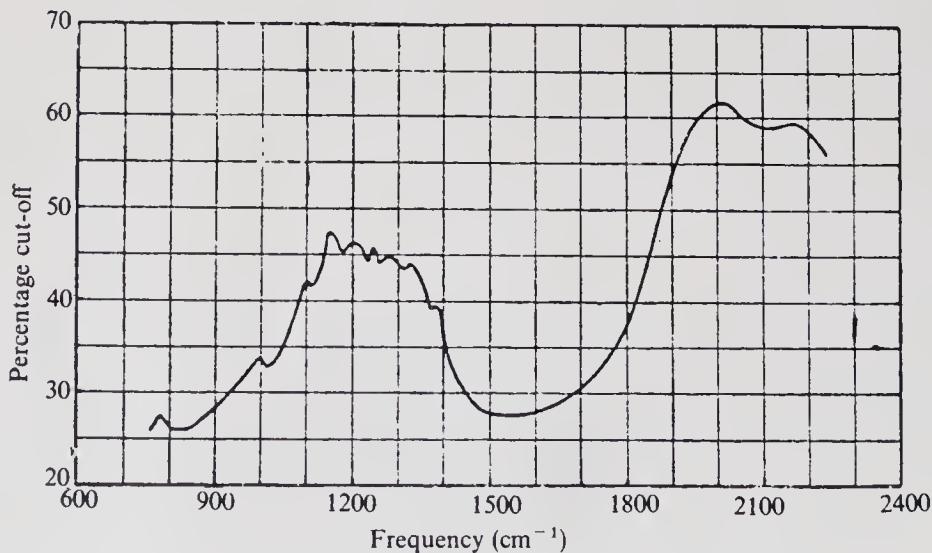


Figure 5. Infra-red transmission by green fluorescent diamond.

correspondence between the luminescence and birefringence patterns. Nevertheless, the effects observed, especially in plates of small thickness, are sufficiently striking to carry conviction. The numerous specimens available for the study enable a complete correlation to be established.

The diamond plates in the collection may be divided into three categories. *Firstly*, we have a group, which exhibits little or no birefringence and makes a near approach to the perfect optical isotropy to be expected in a cubic crystal. Such diamonds invariably exhibit "blue" luminescence, its intensity being more or less perfectly uniform over the area of the specimen. *Secondly*, we have a group of diamonds which exhibit a characteristic type of lamellar birefringence: fine

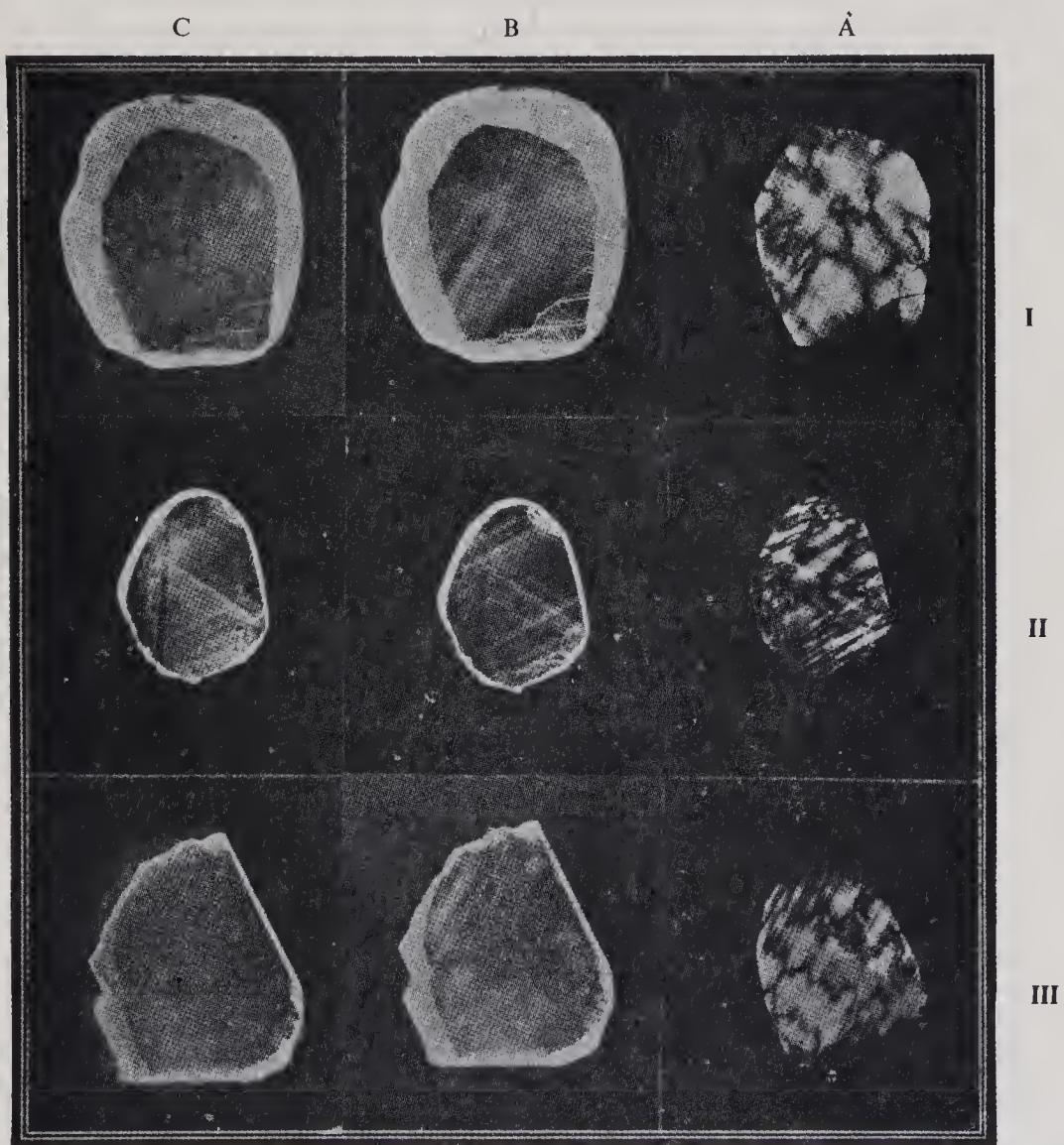


Figure 6. Luminescence and birefringence patterns. (A) Birefringence, (B) green luminescence and (C) blue luminescence.

streaks are seen running parallel to the octahedral or the dodecahedral planes of the crystal, the alternate layers exhibiting positive and negative birefringence as determined with the aid of a Babinet compensator. Diamonds which exhibit this type of birefringence over their entire area are invariably *non-luminescent*. Thirdly, we have a group of diamonds in which the birefringence is a more complex character, varying from specimen to specimen. In some specimens, extensive areas are observed where the birefringence is of the type characteristic of non-fluorescent diamonds, while in other areas the birefringence is weak or absent as in the case of "blue" luminescent diamonds. More common are the specimens in which broad bands of birefringence run parallel to each other over the area of the plate. The presence of such bands in birefringence goes hand in hand with the appearance of green or greenish-yellow bands of luminescence as already described.

Figures 1 and 6 above have been reproduced from photographs taken recently by Mr A Jayaraman and illustrate the foregoing remarks. The three photographs marked III in figure 1 illustrate a typical case of a blue-fluorescent diamond exhibiting no birefringence and no green luminescence. The three pictures marked II in the same figure represents a typical non-fluorescent diamond giving neither blue nor green luminescence but exhibiting a streaky birefringence. The three pictures marked I in the figure are photographs of a diamond which exhibits both green and blue bands of luminescence over a greater part of the area, but has a central area which is non-fluorescent. The birefringence of the plate exhibits a banded structure having a recognisable relationship to the features observed in luminescence. This is better seen in figure 6 which reproduces the patterns of blue and green luminescence and birefringence of three typical diamonds of the third or mixed category. In figure 6(I), the striking feature is the appearance of broad bands of yellow luminescence traversing the crystal. These run parallel to the broad bands of birefringence seen cutting across numerous fine streaks of the kind seen in non-luminescent diamond which appear in a different direction. A careful study of figures 6(II) and 6(III) will repay the reader for his trouble. They form excellent illustrations of the relations between luminescence and birefringence described in the foregoing pages.

## 6. Patterns of X-ray reflection intensity

The method of recording these patterns—also called X-ray topographs—is in principle simple and has been described in detail in the papers by Dr G N Ramachandran on the subject. It makes use of white X-rays diverging from a pin hole to obtain the Laue reflections from the full area of the cleavage plate. The reflections recorded may be either from the internal or the surface crystallographic planes, the technique necessary to obtain a undistorted picture of the

crystal being different in two cases. Clear photographs can only be obtained with relatively thin plates.

The features observed in the X-ray topographs are very revealing. It is found that the weakly-blue luminescent areas make a near approach to the ideally perfect crystal structure and give the weakest Laue reflections. A greater intensity of blue luminescence results in a corresponding increase in the intensity of X-ray reflection. On the other hand, areas which are non-luminescent give extremely intense X-ray reflections. The reason for this is presumably the lamellar structure of the diamond which is evident also in the birefringence. It is found that the bands of greenish-yellow luminescence crossing the areas of blue luminescence are represented in the X-ray topographs by very bright streaks. This observation supports the inference that the "green" luminescence is a consequence of the admixture on a fine scale of the blue-luminescent and the non-luminescent types of diamond.

## The luminescence of diamond—III

SIR C V RAMAN

### 1. The electronic emission spectra

As was remarked in the first article of the series, the emission band at  $\lambda 4156$  discovered by C Ramaswamy in the year 1930 plays the leading role in the blue luminescence of diamond, while the band at  $\lambda 5038$  studied later by Dr Nayar and by Miss Mani plays an analogous role in respect of the green luminescence. These bands sharpen when the diamond is held at liquid air temperature and shift to  $\lambda 4152$  and  $\lambda 5032$  respectively. The  $\lambda 4152$  emission also then appears resolved into a doublet, the width and separation of the components varying considerably with the specimen under study. In particular, the doublet is narrow for the diamonds which exhibit the blue luminescence feebly, a circumstance which is favourable for a satisfactory resolution of the associated vibrational spectrum into its discrete components. Absorption bands are also observed at  $\lambda 4152$  and  $\lambda 5032$  in the spectrum of white light transmitted by the respective diamonds, the strength of such absorption varying *pari passu* with the intensity of the corresponding emission. Hence, one is justified in ascribing them to electronic transitions in the crystal lattice. Where there is an apparent lack of correspondence between the strength of the absorption and of the emission, there is evidence for the existence of self-reversal or other cause affecting the emission intensity.

The investigations of Dr Nayar and of Miss Mani have also shown that  $\lambda 4152$  and  $\lambda 5032$  are by no means the only electronic transitions recorded in the luminescence spectra, though these stand out by reason of their special intensity and their association with vibrational transitions in the lattice. Lines appearing strongly both in emission and absorption have been observed at  $\lambda 4189$ ,  $4197$ ,  $4206$ ,  $4907$ ,  $4959$  and  $5359$ . A fairly strong line at  $\lambda 5758$  and numerous others which are less intense have also been recorded in the emission spectra of various diamonds but have not so far been detected in absorption. The electronic emission lines may be divided broadly into two groups, viz., those that appear along with the emission at  $\lambda 4152$  and the rest with that at  $\lambda 5032$ . They are observed respectively with the diamonds exhibiting these two types of luminescence.

The electronic line at  $\lambda 4156$  present in the blue luminescence spectrum sharpens and increases in peak intensity when the diamond is cooled down. *Per*

*contra*, it decreases in peak intensity when the diamond is heated up, until finally at  $350^{\circ}\text{C}$  it merges into a continuous background and ceases to be visible. Its integrated intensity has been investigated by Chandrasekharan and found to remain unaltered over a wide range of temperature. Miss Mani's investigations have shown that the other electronic lines likewise shift towards smaller wavelengths and sharpen when the diamond is cooled down to liquid air temperature. The shift in wave numbers in the various cases is found to be of the same order of magnitude and roughly proportional to the respective frequencies.

## 2. The electronic absorption spectra

The refractive indices of diamond fit very well into a dispersion formula containing two terms, the major term indicating an absorption at  $\lambda 1060$ , and the minor term with an absorption wavelength at  $\lambda 1750$ . The actually observed absorption in the ultra-violet, however, extends further towards greater wavelengths. Diamonds of the non-luminescent type show a complete cut-off for wavelengths less than  $\lambda 2250$ , while the best specimens of this class exhibit a complete transparency in the visible and near ultra-violet regions of the spectrum. Diamonds which exhibit luminescence, however, show a different behaviour. When the thickness of the plate is reduced sufficiently, the observed transmission extends down to  $\lambda 2250$ . There is, however, a strong absorption at greater wavelengths, and indeed with the largest thicknesses, a complete cut-off is

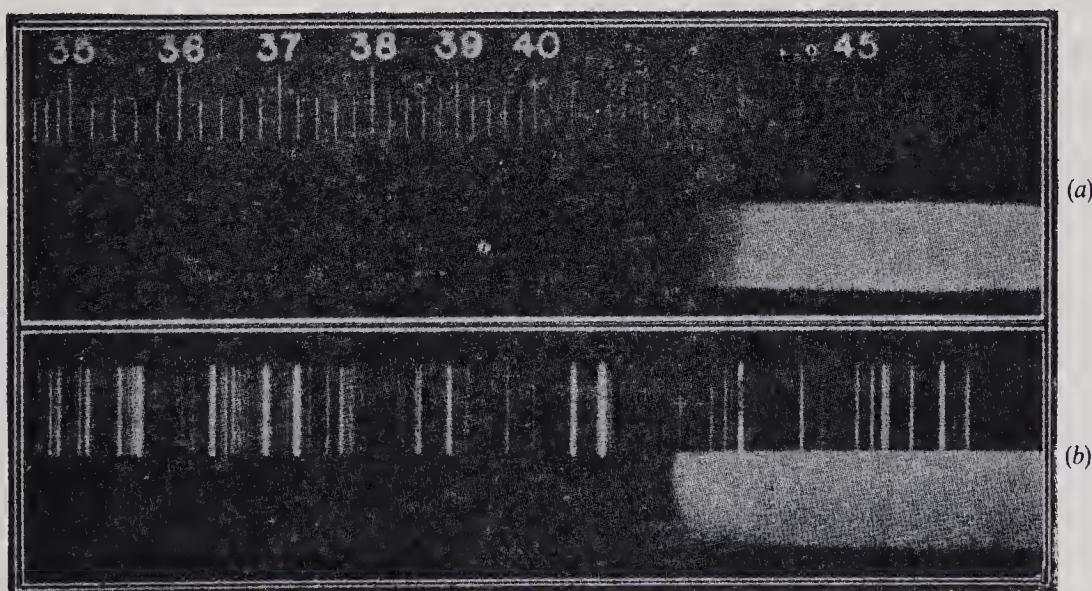


Figure 1. Absorption of visible light by thick diamond. (a) At room temperature, (b) At liquid air temperature.

observed extending to  $\lambda 4152$ , and feebler absorption bands are noticed at even greater wavelengths. These features are exhibited in figures 1 and 2 taken from a paper by K G Ramanathan.

In moderate thicknesses, however, blue-luminescent diamonds transmit wavelengths greater than  $\lambda 3000$  quite freely with the exception of certain absorption lines noticed in the region between  $\lambda 3500$  and  $\lambda 3000$ , and the vibrational bands associated with the  $\lambda 4152$  electronic transition.

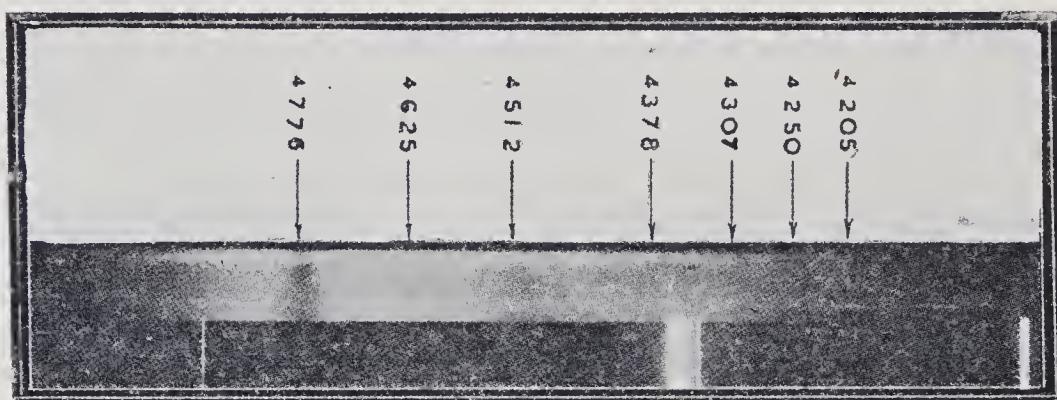


Figure 2. Absorption of visible light by thick diamond under high dispersion.

Some 25 such absorption lines of the first kind can be seen in figure 3 which is reproduced from a paper by Dr Nayar. To record them successfully, it is necessary to hold the diamond at liquid air temperature and to adjust the thickness of diamond traversed as well as the photographic exposure suitably.

Ordinarily, a diamond of the blue-luminescent class should be less than a millimeter thick to show any transmission for wavelengths less than  $\lambda 3000$ . Very thin diamonds of the same variety exhibit a series of sharply-defined absorption lines in the wavelength region between  $\lambda 2370$  and  $\lambda 2240$ . These are shown in figure 4 reproduced from a paper by K G Ramanathan.

It is noteworthy that a precisely similar set of absorption lines is observed also in the ultra-violet transmission of green-luminescent diamond, but can then be seen with moderate thicknesses of the material.

It should be emphasised that the absorption spectra exhibited in figures 3 and 4 stand on a different footing from those mentioned in the preceding section and those shown in figures 1 and 2. They do not appear as emission lines, and their strength is not directly related to the intensity of luminescence. Indeed, the absorption lines seen in the vicinity of  $\lambda 3000$  become weak and diffuse and the transparency extends further into the ultra-violet in the case of strongly blue-luminescent diamonds, as was first observed by Sunanda Bai.

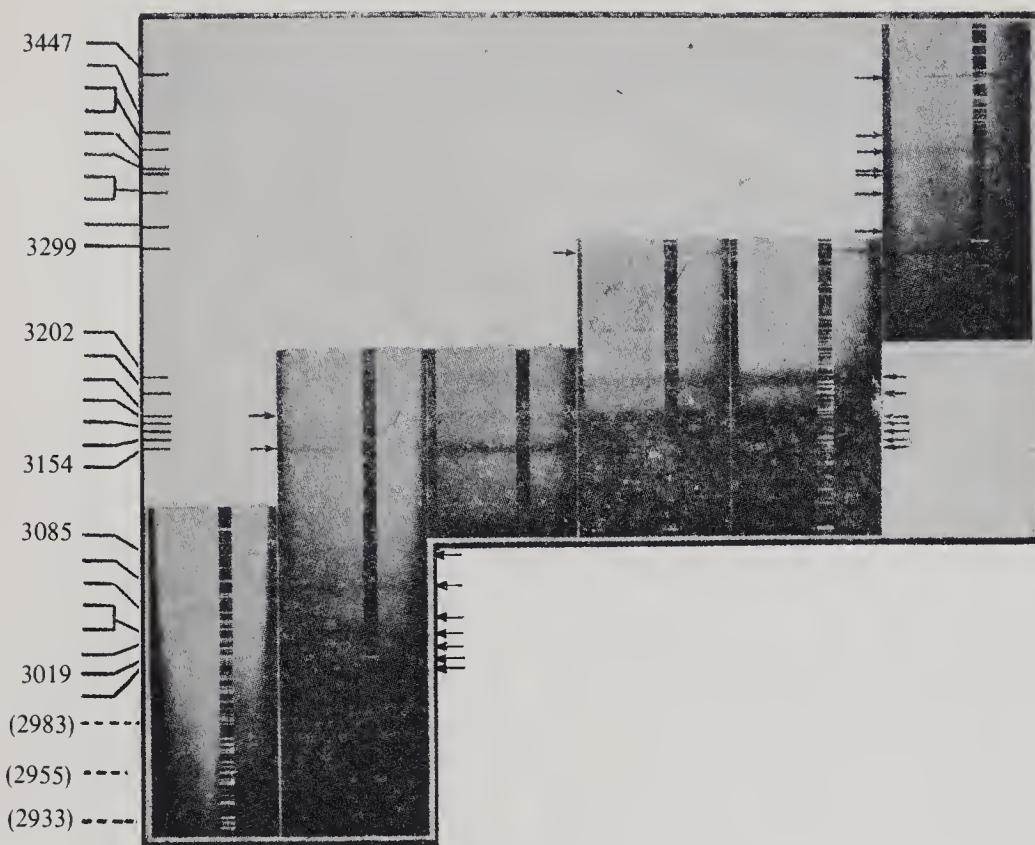


Figure 3. Absorption lines in the ultra-violet.

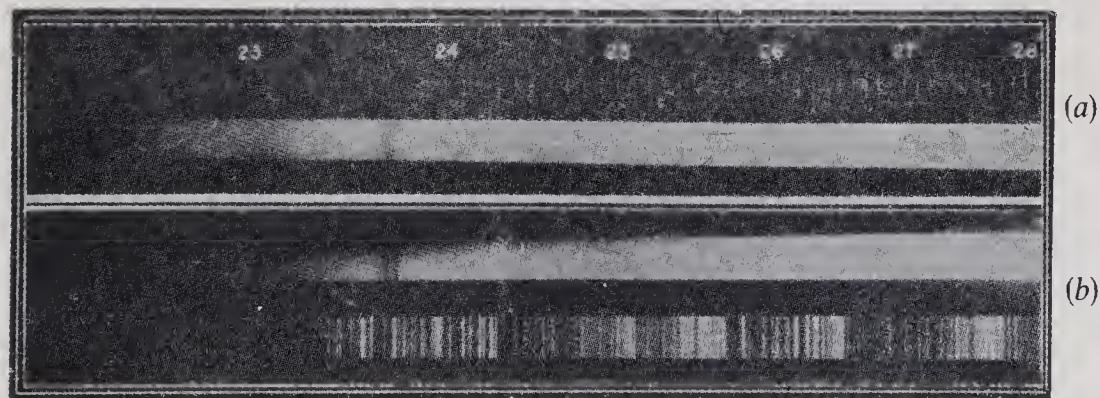


Figure 4. Ultra-violet absorption spectrum of thin blue-fluorescent diamond. (a) At room temperature and (b) liquid air temperature.

### 3. The infra-red activity of diamond

Polished cleavage plates are particularly suitable for quantitative studies on infra-red absorption. The results obtained by K G Ramanathan with a whole series of such plates are highly significant in relation to our present subject. No important differences are observed as between different diamonds in the infra-red activity in the spectral region between 1400 and  $2800\text{ cm}^{-1}$  which covers the octaves and combinations of the fundamental vibration frequencies. There are, however, great differences in behaviour in the spectral region between 700 and  $1400\text{ cm}^{-1}$  which covers the first-order vibration frequencies. The diamonds which are non-luminescent are completely transparent in the latter region. On the other hand, the non-birefringent and weakly blue-luminescent diamonds show a strong activity in the latter region, and the absorption-curves exhibit a series of peaks exhibiting a resolution of the vibration spectrum into distinct components (see figure 5). Green-luminescent diamonds show an intermediate behaviour, such as would result from passage successively through two plates of appropriate thickness belonging respectively to the active and non-active types (see figure 6). Strongly blue-luminescent diamonds are found to exhibit an infra-red activity which is distinctly less than in the case of diamonds with a weak luminescence. The character of the absorption-curve also shows minor variations accompanying the changes in the colour and intensity of the luminescence.

The diamonds which show the first-order infra-red activity most strongly are those which make the nearest approach to ideal perfection of crystal structure as shown by their freedom from birefringence and their X-ray behaviour. *Per contra*, the diamonds which do not show the first-order activity are those which exhibit the largest departure from ideality as indicated by such tests. In these circumstances, it is clearly not possible to ascribe the infra-red activity exhibited by the

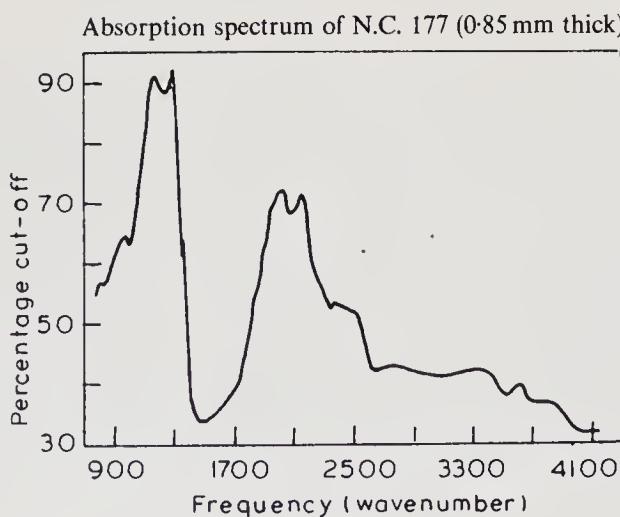


Figure 5. Infra-red absorption spectrum of blue-fluorescent diamond.

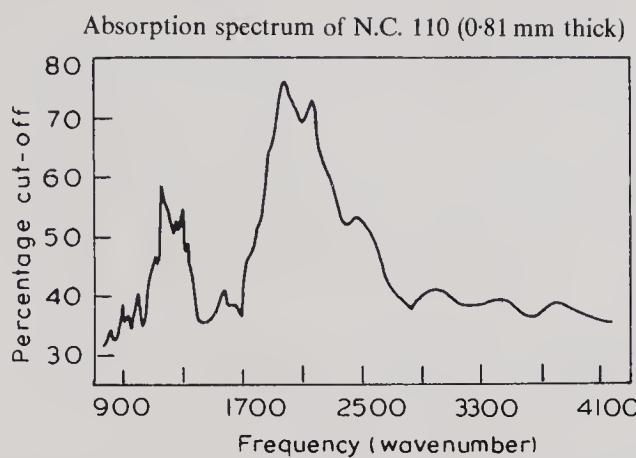


Figure 6. Infra-red absorption spectrum of green-fluorescent diamond.

former class of diamonds to structural imperfections or other accidental circumstances. We are, in fact, compelled to recognize that the difference in behaviour connotes a fundamental difference in crystal structure. The nature of such difference follows from well-established spectroscopic principles, according to which the absence or presence of first-order infra-red activity in a crystal of the cubic class depends on whether the structure of the crystal does or does not possess centres of symmetry. In other words, the observed behaviour in respect of infra-red activity indicates that the electronic structure of the non-luminescent diamond has the highest or Oh type of symmetry, while the electronic structure of the blue-luminescent diamonds possesses only the lower or Td type of symmetry.

#### 4. The origin of the luminescence

The experimental facts already described do not permit us to accept the belief formerly entertained that the luminescence of diamond arises from the presence of chemical impurities. They also serve to exclude the alternative hypothesis that the luminescence is activated by extraneous impurities. As early as 1941, Dr Nayar suggested that the origin of the blue luminescence studied by him should be sought for in the departure of the crystal structure from ideal perfection. While this suggestion contains an element of truth, the results of subsequent investigations with a wider range of material show that it is not by itself sufficient to cover the facts. It does not, for instance, explain why diamonds which, as judged by optical and X-ray tests, show structural imperfections of the crystal in the highest degree, are precisely those which are non-luminescent. Neither does it account for the green type of luminescence and for the relationship between luminescence and birefringence which has been so clearly established. We are thus forced to look a little deeper to reach a clear understanding of the array of facts revealed by the Bangalore investigations.

## The luminescence of diamond—IV

SIR C V RAMAN

### 1. Structure and crystal symmetry of diamond

The clue to an understanding of the luminescence of diamond is to be sought for in the relationship between the spectroscopic properties of the material on the one hand and its crystal structure on the other. Of fundamental importance in this respect is a result which emerged from the Bangalore investigations, namely, that the diamonds which are the most perfect as indicated by their freedom from birefringence and by the low intensity and extreme sharpness of their X-ray reflections are those which most prominently exhibit the infra-red absorption of the first-order between  $7\ \mu$  and  $14\ \mu$ , and the series of sharply-defined absorption lines in the ultra-violet spectrum between  $\lambda 2250$  and  $\lambda 3500$ . *Per contra*, the diamonds which do not manifest either the infra-red or the ultra-violet absorption in these regions are those which exhibit the maximum of imperfections in their crystal structure, as indicated by the birefringence which they display and the intense and diffuse X-ray reflections which they give. These facts preclude us from ascribing the activity in infra-red and ultra-violet absorption present in one case and absent in the other to irregularities in crystal structure, and compel us to recognise that there is, in fact, a fundamental difference in structure between the two varieties of diamond. Spectroscopic theory enables us to specify the nature of such difference. If the electronic structure of diamond possesses centres of symmetry located at the points midway between every pair of neighbouring carbon atoms in the crystal lattice, the diamond would necessarily be infra-red inactive in the first-order vibration spectrum. But, if on the other hand, such centres of symmetry are absent, the diamond would necessarily exhibit an infra-red activity of the first-order. Such a fundamental difference in electronic structure may be expected also to manifest itself in a notable difference in respect of ultra-violet absorption, as is indeed actually observed.

Thus, spectroscopic theory leads us to recognise the existence of two varieties in the crystal structure of diamond possessing respectively tetrahedral and octahedral symmetry. It may be remarked that the infra-red activity present in one case and absent in the other is very feeble compared with the infra-red activity of crystals having a heteropolar constitution. It is also necessary to point out that the lower symmetry of the infra-red active diamond, whatever may be its origin, would not necessarily involve either piezo-electric or pyro-electric activity. The

feebleness of the infra-red activity is itself also an indication that the differences in structure between the tetrahedral and octahedral varieties when expressed in quantitative measure are very small. It is, therefore, not surprising that the two varieties of diamond make a very close approach to each other in many of their physical properties. Such similarity has another important consequence. Since both structures belong to the cubic system, we should expect that their appearance side by side in the same specimen of diamond should be a very frequent occurrence. That this is indeed actually the case is shown by the frequency with which patterns of ultra-violet transparency are observed in cleavage plates of diamond, as already mentioned in an earlier article of the series. These patterns always exhibit a geometric character, the boundaries of separation between the opaque and transparent regions running parallel to the octahedral or dodecahedral planes in the crystal lattice. This is ocular evidence that we are concerned with a real difference in structure between the areas under consideration.

## 2. The crystal forms of diamond

It is well known that crystals of the tetrahedral class in the cubic system frequently exhibit interpenetration twinning, as the result of which their external forms imitate or mimic octahedral symmetry. It follows that such interpenetration of the positive and negative tetrahedral forms should be commonly observable in crystals of diamond. This is fully borne out by experience. Indeed, from the very beginnings of crystallographic science, it had been noticed by mineralogists that the evidence presented by the crystal forms of diamond very definitely placed this substance in the tetrahedral class and indicated a strong disposition on its part to imitate octahedral symmetry by interpenetration twinning.

Figure 1 reproduces photographs of nine crystals from the Bangalore collection which illustrate the tendency of diamond to exhibit pseudo-octahedral forms as the result of internal twinning. Five of the diamonds, viz., A I, A II, C I, C II and C III are from Panna in Central India and have the rounded forms with smooth lustrous faces characteristic of the finest diamonds from that locality. They also show a feature which is highly characteristic of diamonds with curved surfaces, namely a pattern of sharp ridges which run along the six reflection planes of tetrahedral symmetry and divide the external area into 24 triangular areas (see for instance, A II, which is nearly a spherical diamond). A I, which is octahedral in its general shape, exhibits six sharp vertices where four ridges meet, while at each of its eight face-centres, six ridges meet; but the edges characteristic of a real octahedron are missing, being replaced by smoothly curved surfaces. On the other hand, the diamonds pictured in C I, C II and C III, have forms in which the features characteristic of a hexakis-tetrahedron may be readily recognised, C I

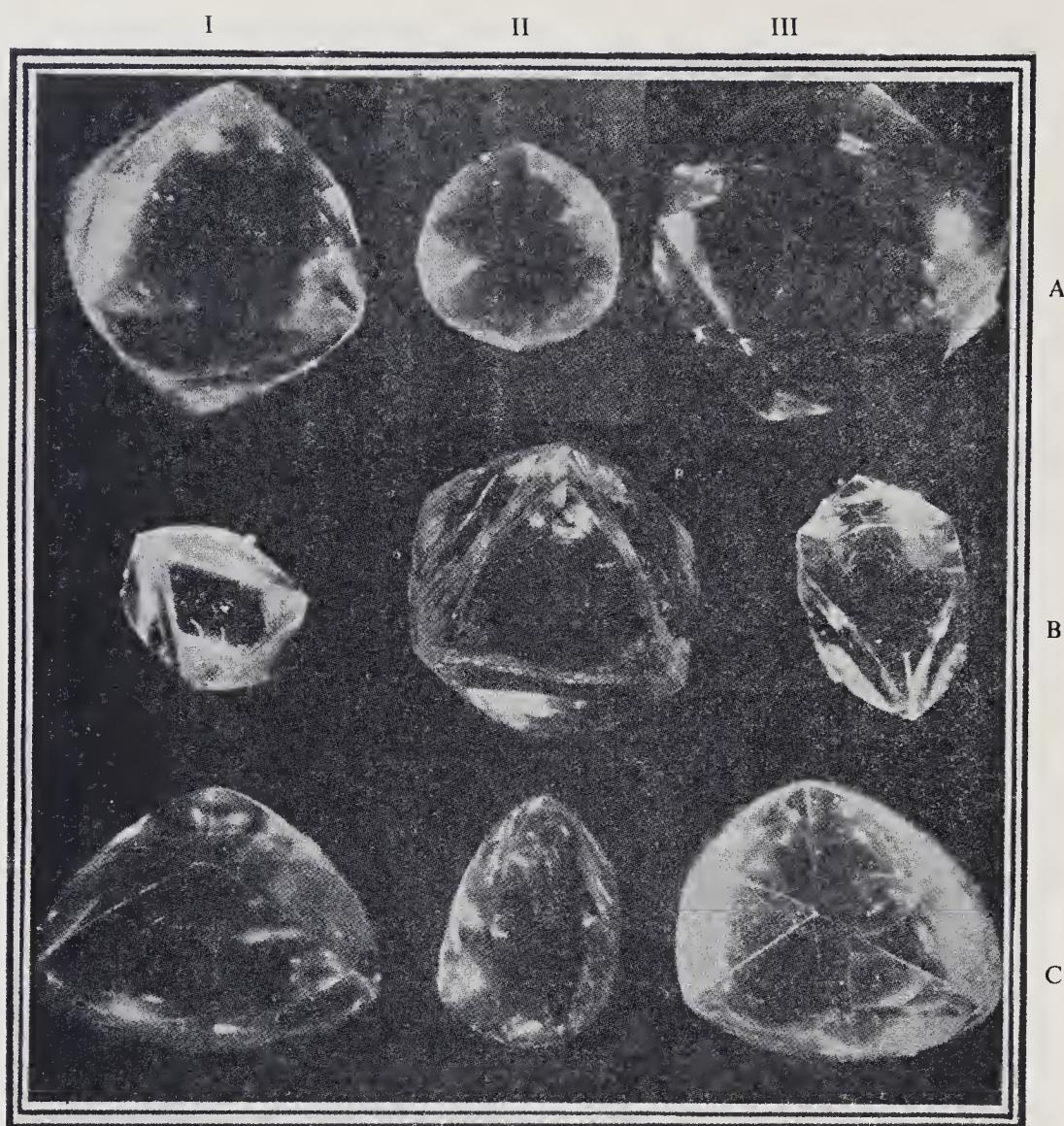


Figure 1. Photographs of diamond crystals.

being the best example in this respect in the collection. The three diamonds reproduced as B I, B II, B III illustrate another typical form of diamond, viz., octahedra with plane faces and grooved edges. B II (the central picture in figure 1) is a particularly fine example of this class from South Africa. It exhibits sharply-defined re-entrant edges which limit the faces of the octahedron and give them a hexagonal instead of a triangular outline. The form is very clearly a consequence of the interpenetration twinning of positive and negative hexakis-tetrahedra.

### 3. The origin of the blue luminescence

The existence of interpenetration twinning in the tetrahedral type of diamond which is demonstrated by the study of its crystal forms allows us to offer an intelligible explanation of the observed association of blue luminescence with this particular variety of diamond. Every boundary within the crystal at which the positive and negative tetrahedral structures meet is a discontinuity in the crystal structure. The finer the subdivision of the entire volume of the crystal between the two interpenetrating structures, the more numerous would be the possible centres of luminescence brought into existence thereby. The interpenetration of the positive and negative tetrahedral forms thus furnishes a mechanism for the production of luminescence centres in greater or less number and, therefore also for a highly variable intensity of emission as between different specimens or within the volume of any given diamond, as is actually observed.

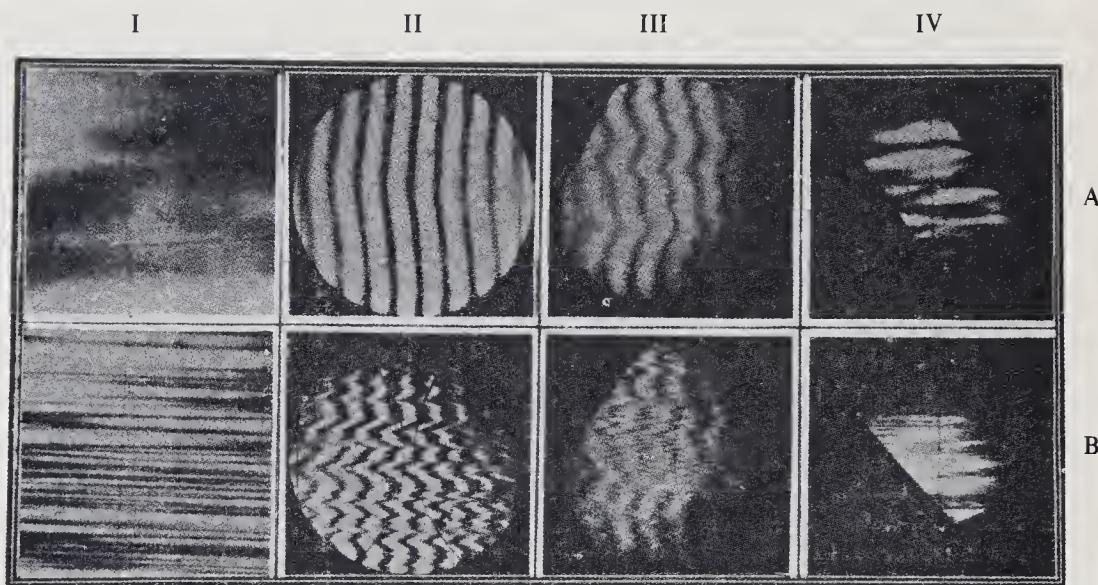
If the blue luminescence arises in the manner stated above, it follows that an increased intensity of luminescence would necessarily mean an increase in the lack of perfect homogeneity in the lattice structure of the crystal. In other words, the more intense the luminescence which a diamond displays, the less perfect would it be as a crystal. This consequence was actually foreseen by the present writer before X-ray studies confirmed its reality. In particular, an investigation by Dr G N Ramachandran established the existence of a quantitative relationship between fluorescence intensity and the characters of the X-ray reflections by the lattice planes of the crystal, viz., their intensity and their angular range.

A further consequence of the idea that interpenetration of the positive and negative tetrahedral forms is the origin of the blue luminescence may also be pointed out. If the subdivision of the crystal by such interpenetration is carried far enough, we should expect the behaviour of the diamond to be noticeably altered as the result of the juxtaposition of the oppositely directed tetrahedral structures at their boundaries of separation. In particular, a diamond which exhibits an intense blue luminescence may be expected to differ noticeably in its behaviour in respect of infra-red and ultra-violet absorption from a diamond which shows only a weak luminescence. This, again, has actually been observed. One finds a distinct weakening of the infra-red activity characteristic of the tetrahedral type of structure in the more strongly blue-luminescent diamonds; simultaneously, the sharp absorption lines in the ultra-violet between  $\lambda 2250$  and  $\lambda 3500$  tend to become weaker and the diamond as a whole becomes more transparent to that region of the spectrum.

### 4. The origin of the green luminescence

One need not be surprised that the diamonds having an octahedral symmetry of structure are not luminescent under ultra-violet irradiation. For, they are

transparent to radiations of wavelength greater than  $\lambda 2250$ , and if there is no absorption, there can be no re-emission. The origin of the birefringence exhibited by such diamonds becomes clear when a cleavage plate of the same is examined under a polarising microscope provided with a Federov stage. It is then found that the birefringence is due to a lamellar structure running parallel to the octahedral or dodecahedral planes in the crystal. The use of Babinet compensator in addition reveals that the lamellae present in the diamond are alternately under tension and compression. It thereby becomes evident that the birefringence arises from the co-existence in the same specimen of two sub-species both having octahedral structures but of slightly different lattice spacings (see figure 2).



**Figure 2.** Birefringence of diamond as seen in the polarising microscope on the Federov stage. A as viewed normally, and B as viewed under tilt; I and IV without compensator, and II and III with it.

As already remarked, intergrowths of the octahedral and tetrahedral species of diamond are exceedingly common. Cleavage plates in which there are such intergrowths invariably exhibit birefringence. They also exhibit bands of green luminescence. It is evident that when diamond of the non-luminescent or octahedral type and of the blue-luminescent or tetrahedral type are present side by side in the same specimen, the boundaries between them would represent discontinuities of crystal structure. Since absorption of ultra-violet radiation can occur in the vicinity of such boundaries, there is clearly a possibility of their functioning as centres of luminescence. There is ample experimental evidence to show that the green type of luminescence arises in this way. In the first place, one can understand on this basis why both the blue and green types of luminescence usually appear together, though in varying ratios of intensity. One can also understand why the green luminescence exhibits a banded structure and why

there is a perfect correspondence between such structure and the birefringence pattern observed in the same diamonds. Then again, it is found that when a cleavage plate of diamond showing the banded green luminescence is tilted one way or another, the birefringence and luminescence bands both sharpen in one position and both become diffuse in the other position, showing that they have a common orientation in the crystal. See figure 3 in which A and B represent the same cleavage plate photographed in two different directions relative to its surface. I represents the green luminescence bands and II the birefringence.

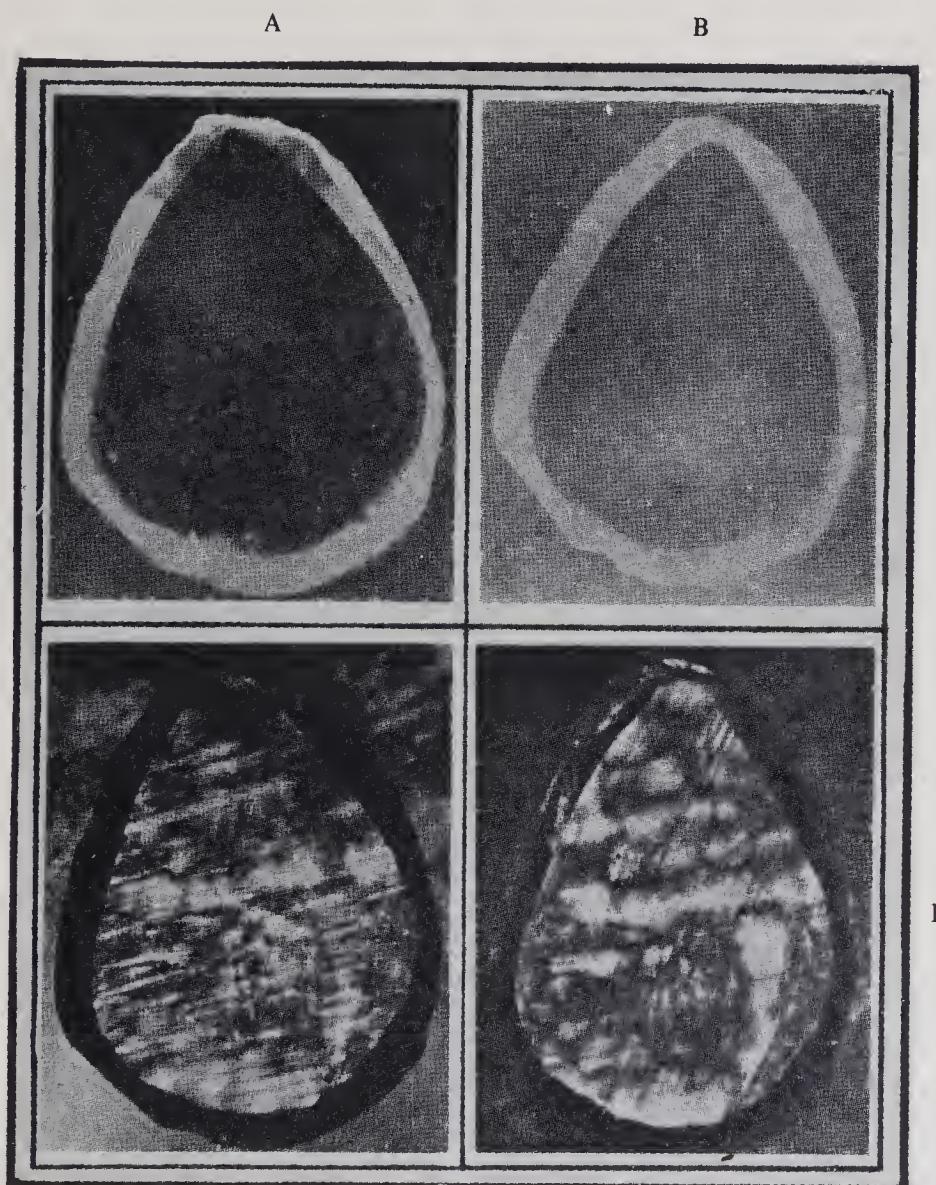


Figure 3. Showing effect of tilting on birefringence and luminescence.

From measurements of the tilt of the plate necessary to give the maximum sharpness to the bands, it is readily shown that we are concerned with layers running parallel to the octahedral or dodecahedral planes in the crystal, thus affording support to the hypothesis that both the green luminescence and birefringence arise from local variations in crystal structure. We may further remark that the explanation given above for the origin of green luminescence is supported by the observation that the patterns of ultra-violet transparency exhibit a close correspondence with such luminescence. The X-ray topographs also show a great intensity of X-ray reflection along the bands of green luminescence.

### 5. Concluding remarks

The foregoing account of the subject has been confined to statements of fact and to interpretations of the same based on well-established principles and therefore of a compelling nature. There are other aspects of the subject which are of interest but being of a somewhat speculative character have not been touched upon here. For instance, what is the exact nature of the difference in the electronic structures exhibiting respectively tetrahedral and octahedral symmetry? Why are there two sub-species of octahedral symmetry, as is evident from the lamellar structure and birefringence of non-luminescent diamond? We have also not dealt with various other important issues which arise from the facts under consideration. What is the scheme of electronic energy levels in diamond which give rise to the observed emission and absorptions spectra? Why are the transitions between them allowed in some cases and forbidden in others? Unless we are in a position to answer such questions, we cannot claim to have fully understood either the structure of diamond or the many fascinating phenomena which it displays.

## The diamond\*

SIR C V RAMAN

Memoir No. 86 from the Raman Research Institute, Bangalore-6

Received September 5, 1956

### 1. Introduction

The many remarkable properties which diamond exhibits, taken in conjunction with the simplicity of its crystal structure and composition, make it a substance of quite exceptional interest to the physicist. In the hope that investigations made with it would result in significant contributions to knowledge, a collection of some five hundred diamonds was built up in the course of years and used by the present author and his collaborators in an extensive series of researches. It would not be possible in this lecture to survey all the topics investigated. We shall confine ourselves to the consideration of some results which have emerged from our studies and which are of fundamental significance for the physics of the solid state.

In his paper of 1907 introducing the quantum theory of specific heats, Einstein made use of the experimental data for the variation with temperature of the specific heat of diamond which had been discovered by earlier investigators to demonstrate the correctness of the basic ideas set out in his paper. The expression for the thermal energy of crystals as a function of temperature derived by Einstein in that paper was a logical deduction from his hypothesis that the structural units comprised in the crystal and capable of mechanical vibration obey the quantum rule, in other words, that their energy can only increase or diminish by quanta proportional to the frequency of vibration. Einstein did not however, deal with the question of how the modes and frequencies of vibration under consideration could be evaluated in the general case. In my address to the Lindau Conference this year, I showed how this basic problem can be handled rigorously and a solution obtained which reconciles the results of classical dynamics with the fundamental notions of the quantum theory and the principles of

---

\*A lecture delivered at the Federal Polytechnic Institute in Zurich and at the Universities of Freiburg and Bonn early in July 1956, following the address on "The physics of crystals" given at Lindau in June, 1956. The latter address has been published in these *Proceedings* (Memoir No. 85 of the Institute), but the present memoir may be read independently of the same.

thermodynamics. Diamond is exceptionally well-suited for a test of the correctness of the theoretical approach set out in that address, since the necessary calculations are readily made and the experiments necessary to check the consequences of the theory are also feasible. It is the purpose of this lecture to show how perfectly the theory and the results of experiment are in accord with each other. For the sake of ready intelligibility, the subject will be dealt with from first principles.

## 2. The characteristic vibrations of linear lattices

We shall commence by considering a few simple models of which the behaviour may serve to illustrate the principles underlying the general theory. The simplest of such models is a stretched string loaded by a series of equidistant particles of identical mass along its length. It is immediately obvious that a mode of oscillation is possible on such a string in which the successive particles have the same amplitude but opposite phases of vibration. Such an oscillation is pictured in figure 1(a). It has all the characters of a normal mode of vibration and possesses a specific frequency which can therefore be regarded as characteristic of the system. We may next consider the case in which the particles on the string are equidistant but have alternately two different masses. It can be seen that such a system would have *three* possible modes of normal vibration with different frequencies. These modes are represented in figure 1(b), (c) and (d) respectively. In figure 1(b), successive particles of equal mass have identical amplitudes and oscillate in the same phase, while in figure 1(c) and (d), they have the same amplitudes but opposite phases, the situation thus being analogous to that pictured in figure 1(a).

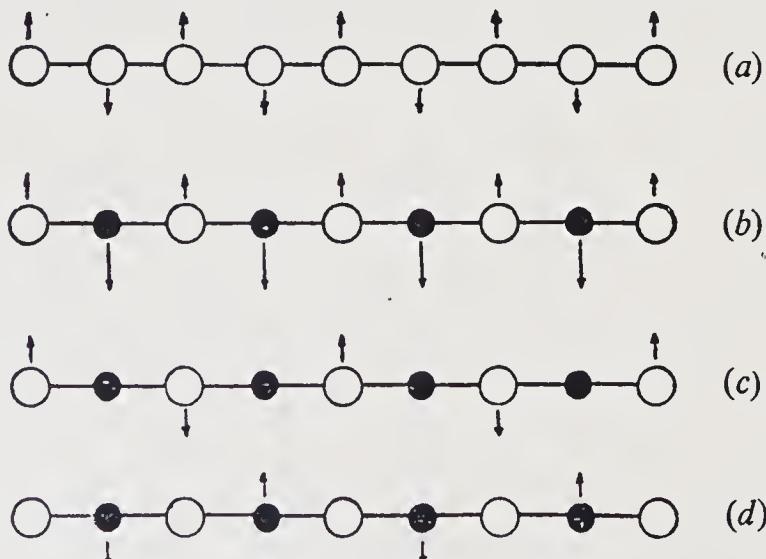


Figure 1. The characteristic vibrations of linear lattices.

The foregoing results can readily be generalized. It can be proved that a periodic linear lattice with  $p$  particles in each unit of its structure would have  $(2p - 1)$  normal modes and frequencies of vibration; in  $(p - 1)$  of these modes, the amplitudes and phases of vibration of the corresponding particles in the successive units are the same, while in the  $p$  other modes, they have the same amplitudes but opposite phases. It can also be shown analytically that any initial disturbance set up locally on such a linear lattice would resolve itself quickly into a summation of the  $(2p - 1)$  characteristic modes of oscillation with their respective frequencies.

### 3. The normal vibrations of crystal structures

The basic principle of crystal architecture is that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes in two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following an unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed. Since these two alternatives are possible for a unit translation along each of the three axes of the lattice, we have  $2 \times 2 \times 2$  or 8 possible situations. In each of these situations, the equations of motion of the  $p$

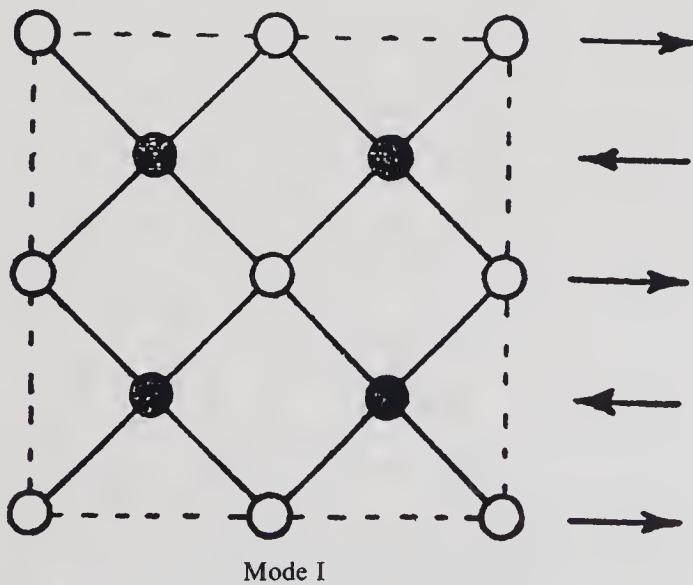


Figure 2. Diamond: the principal mode of oscillation.

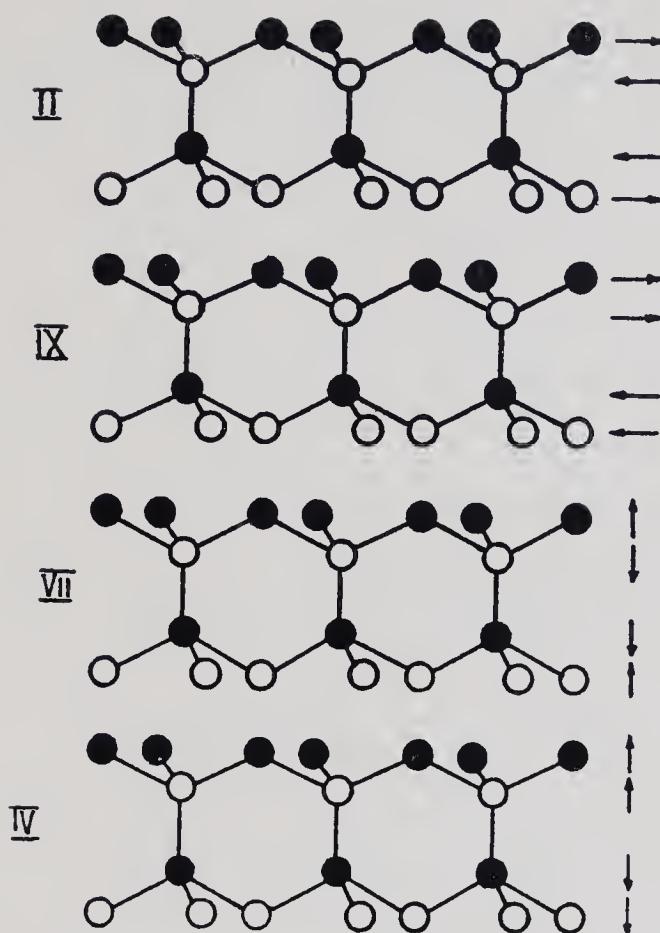
atoms contained in the unit cell of the structure can be written down and completely solved, giving us  $3p$  solutions. Thus in all we have  $24p$  solutions. ( $3p - 3$ ) of these solutions represent normal modes of vibration of the first kind,  $21p$  solutions represent normal modes of the second kind and the 3 remaining solutions represent the simple translations of the unit cell of the structure.

The general principles set forth above enable us to describe in simple geometric terms, the normal modes of vibration of the atoms located at the points of a Bravais lattice for each of the known fourteen species. In the general case when  $p = 1$ , we have 21 distinct normal modes and frequencies of vibration, besides the three translations. But, if the lattice possesses some elements of symmetry, the number of distinct frequencies would be notably reduced. We shall consider here the case of the face-centred cubic lattice. The primitive translations in such a lattice may be taken as the lines joining a cube corner with the centres of the three cube faces meeting at that corner. Applying the symmetry operations of the point group  $O_h$  to which the lattice belongs and considering the 8 possible combinations of the phases of atomic vibration; the 21 modes of vibration which thereby result can be grouped together and described as follows: (I) a vibration of the alternate octahedral planes of atoms with opposite phases normally to themselves (degeneracy 4); (II) the same but transversely to the planes (degeneracy 8); (III) the vibrations of the cubic planes of atoms normally to themselves (degeneracy 3); (IV) the same but with the vibrations tangentially to the planes (degeneracy 6). The same results can be very simply deduced by inspection of a model exhibiting the unit rhombohedral cells in a face-centred cubic lattice.

#### 4. The vibrations of the diamond structure

The structure of diamond may be described as an interpenetration of two face-centred cubic lattices of carbon atoms, each atom in one lattice being linked to its four nearest neighbours in the other lattice by tetrahedrally directed valence bonds. This situation is diagrammatically represented in figure 2 by a projection of the cubic cell on a plane normal to the cubic axis. (No attempt is made to show the different planes in which the atoms lie.)

The normal modes of vibration of the atoms in the diamond structure may be very simply derived from those for a simple face-centred lattice listed above by taking into account the phases of the motion of the atoms in the two lattices which may be either the same or opposite. The nine possible modes of vibration thus derived are depicted in figures 2, 3 and 4. The principal mode which is depicted in figure 2 is a translatory movement of the two lattices in opposite phases. This is triply degenerate and can occur along anyone of the three cubic axes, as indicated by the arrows in the figure. Figure 3 shows the diamond structure viewed in a direction normal to a trigonal axis of symmetry and exhibits the octahedral layers of atoms. The normal and tangential movements of these



**Figure 3.** Diamond: normal and tangential oscillations of the octahedral layers.

planes in the two possible relative phases give us four modes of vibration; the directions of movement of the atomic planes are indicated by arrows in the figures. Figure 4 shows the structure of diamond as viewed in a direction slightly inclined to a face diagonal and exhibits the cubic layers of atoms. The directions of movement of these layers in the four possible modes are likewise indicated by arrows in the figure.

Very simple considerations enable us to arrange the nine normal modes of vibration of the diamond structure in the descending order of their frequencies as indicated by the Roman numerals entered against them in figures 2, 3 and 4. The triply degenerate oscillation of the two interpenetrating lattices against each other shown in figure 2 would evidently have the highest frequency of all, since the movement involves variation of all the four bond lengths and all the six bond angles at each carbon atom; the restoring forces brought into play would therefore be the maximum possible. It is likewise evident that the mode marked

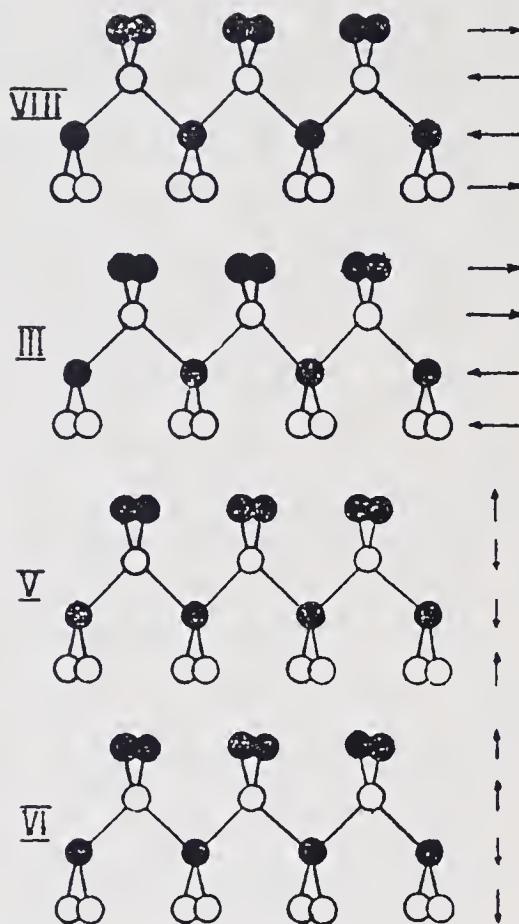


Figure 4. Diamond: normal and tangential oscillations of the cubic layers.

IX in figure 3 would have the lowest frequency of all and the mode marked VIII in figure 4 would be the next lowest. For, in neither of these modes is there any variation of the bond lengths; in mode IX, only two bond angles vary and in mode VII only four bond angles, the rest of them remaining unaltered. *Per contra*, the same modes but with the relative phases of motion of the adjacent layers reversed, viz., mode II shown in figure 3 and mode III shown in figure 4 may be expected to have high frequencies which follow that of mode I in the order indicated. It remains to determine the sequence of the frequencies of the four remaining modes. It is obvious that the modes marked V and VI in figure 4 would have identical frequencies; for in these modes, the cubic layers which move normally to themselves, in other words along the cubic axis, are equidistant. Finally, we remark that the modes marked IV and VII in figure 3 may be expected to have frequencies respectively higher and lower than the common frequency of modes V and VI, though the differences would not be large. In mode IV, the oscillation involves the maximum stretching of one bond out of the four in the successive layers of the structure, the three others remaining invariable, while the mode VII,

the bond along which the motion takes place remains of invariable length, while the three other bonds inclined at a large angle to the direction of movement are tilted periodically. The restoring forces acting in the direction of movement may be expected to be distinctly greater in the former case than in the latter.

### 5. Numerical evaluation of the frequencies

Exact formulae are readily derived for the eight distinct frequencies of vibration in terms of the force constants expressing the interactions between each carbon atom and the surrounding ones. The equations of motion from which these formulae are derived take a very simple form by reason of the fact that the relative displacements of the atoms are either zero or else are twice the value of the absolute displacement of each atom. The force-constants are most conveniently defined in terms of the components of the relative displacements and the forces of interaction resolved along the three cubic axes and considering their ratios. The symmetry of the structure results in a very considerable diminution in the number of distinct force-constants: it is found that two constants express the interactions with the four nearest neighbours, five others the interactions with the twelve next nearest neighbours, and five more the interactions with the twelve more distant neighbours. However, on writing down the equations of motion, it emerges that only three of the five force-constants for the next nearest neighbours actually appear in them and that the five force-constants for the twelve more distant neighbours also appear in the equations as sums of which there are only two. Accordingly, if we restrict ourselves to the interactions with the twenty-eight nearest neighbours of any given atom, we have only seven force-constants to deal with.

The seven force-constants referred to above will be denoted by  $\alpha$ ,  $\beta$  for the first four atoms;  $\theta$ ,  $\phi$ ,  $\psi$  for the next twelve and  $k$  and  $\chi$  for the twelve atoms still further out. By way of explanation, it may be stated that the force-constant  $\alpha$  refers to the case in which the force and displacement are both along the same cubic axis, while  $\beta$  refers to the case in which they are mutually perpendicular. The constant  $\theta$  refers to the case in which the force and displacement are parallel to each other but are both perpendicular to the line joining the atoms which is a face-diagonal of the cube;  $\phi$  and  $\psi$  refer to the cases in which the component forces and displacements both lie in the same plane as this diagonal, but the force and displacement are parallel to each other for  $\phi$  and perpendicular for  $\psi$ . The constant  $k$  refers to the cases in which the components of force and displacement are parallel to each other while  $\chi$  refers to the cases in which they are mutually perpendicular.  $k$  and  $\chi$  both represent the joint effect of a whole set of twelve atoms. Table 1 shows the eight frequencies of vibration arranged in the sequence already explained which will be found entered in the first column. The second column shows the degeneracy of each of these modes. The total of the figures shown in this

**Table 1.** Evaluation of frequencies.

Mode No.	Degeneracy	Complete formula $4\pi^2 v^2 c^2 m =$	$\alpha, \beta$ only	$\alpha, \beta, \theta,$ $\phi, \psi$ only	$\alpha, \beta, \theta,$ $\phi, \psi,$ $k, \chi$
I	3	$4\alpha + 12k$	1332	1332	1332
II	8	$3\alpha + \beta + 2\theta + 4\phi - 2\psi + 3k$ - $3\chi$	1250	1285	1250
III	6	$2\alpha + 2\beta + 4\theta + 4\phi + 6k$ + $6\chi$	1162	1232	1239
IV	4	$\alpha + 2\beta + 2\theta + 4\phi + 4\psi + 9k$ - $6\chi$	952	1099	1149
V & VI	3 + 3	$2\alpha + 8\phi + 6k$	942	1088	1088
VII	4	$3\alpha - 2\beta + 2\theta + 4\phi + 4\psi$ + $3k + 6\chi$	931	1068	1008
VIII	6	$2\alpha - 2\beta + 4\theta + 4\phi + 6k$ - $6\chi$	651	752	740
IX	8	$\alpha - \beta + 2\theta + 4\phi - 2\psi + 9k$ + $3\chi$	460	538	621

**Table 2.** Values of force-constants used.

Force-constants	Table 1, column 4	Table 1, column 5	Table 1, column 6
$\alpha$	$3.135 \times 10^5$ dynes/cm	$3.135 \times 10^5$ dynes/cm	$2.78 \times 10^5$ dynes/cm
$\beta$	$1.637 \times$ "	$1.682 \times$ "	$1.746 \times$ "
$\theta$		$0.012 \times$ "	$0.010 \times$ "
$\phi$		$0.262 \times$ "	$0.262 \times$ "
$\psi$		$0.240 \times$ "	$0.228 \times$ "
$k$			$0.12 \times$ "
$\chi$			$0.00 \times$ "

column amounts to forty-five as is to be expected. The third column shows the operative force-constants in each case in terms of the seven force-constants, viz.,  $\alpha, \beta$  for the first group;  $\theta, \phi, \psi$  for the second group;  $k$  and  $\chi$  for the third group. In the fourth, fifth and sixth columns are given respectively the values of the frequencies calculated with only the first two constants, then with only five and finally with all the seven. The values of the constants in each case have been so chosen as to give the same frequency for the principal mode. They are given in table 2.

It will be remarked from tables 1 and 2 that even with only two force-constants we obtain a rough approximation to all the frequencies and that with five constants we get a fair approximation to the values calculated with all seven constants shown in the last column of table 1. It will also be seen from table 2 that the force-constants fall off rapidly in magnitude as we proceed to the more distant neighbours. The magnitudes of the force-constants in each group are also related

to each other in the manner that could have been expected a priori from their respective definitions as given above.

## 6. The scattering of light in diamond

Spectrograms of the light scattered by diamond when illuminated by the light of a mercury arc lamp exhibit, for each of the monochromatic radiations of the incident light, a single sharp line with a frequency shift of  $1332 \text{ cm}^{-1}$  which may be identified with the highest of the frequencies listed in table 1. But no lines appear with frequency shifts other than that mentioned. This is readily understood, since in all the modes except that of the highest frequency, the atomic oscillations have opposite phases in the successive layers, and hence the effects arising at these layers cancel each other out. Overtones and combinations of the frequencies of all the normal modes are, however, permitted to appear as frequency shifts in light-scattering, thereby making the existence of these modes open to observation. That diamond would exhibit this type of light-scattering was theoretically predicted, following which experimental studies undertaken by Dr R S Krishnan confirmed the expectations.

The second-order spectrum of light-scattering is of extremely low intensity, and one has necessarily to use diamonds of small size for the experiments. Further, it is necessary to record the spectrum under high dispersion to enable its features to be adequately exhibited. These difficulties are successfully overcome by the aid of the extremely intense  $\lambda 2537$  radiations emitted by a quartz water-cooled mercury arc when it is set between the poles of an electro-magnet. It is necessary, of course, to employ diamonds which are transparent to the ultra-violet region of the spectrum. In these circumstances, it is also essential to use mercury vapour as a filter inside the spectrograph to absorb the intense  $\lambda 2537$  radiations before they reach the photographic plate, and thus prevent its fogging.

Spectrograms obtained in the manner explained are reproduced as figure 1 in plates I and II respectively. The spectrum in plate I was recorded with a medium-sized spectrograph and that in plate II with a larger instrument of higher resolving power. A microphotometer record of the spectrum obtained with the smaller instrument is reproduced in juxtaposition with the spectrum itself as figure 2 in plate I, below which has been placed the spectrum of the mercury arc alone as a comparison. Figure 2 in plate II reproduces the microphotometer record of the second-order spectrum obtained with the larger instrument and below it the spectrum itself to admit of ready comparison with the features seen in it.

The features visually observed in the spectra and confirmed by inspection of their microphotometric records are diagrammatically represented in figure 5 below, the measured frequency shift being indicated against each feature.

Very conspicuous is the sharply defined peak of intensity terminating the

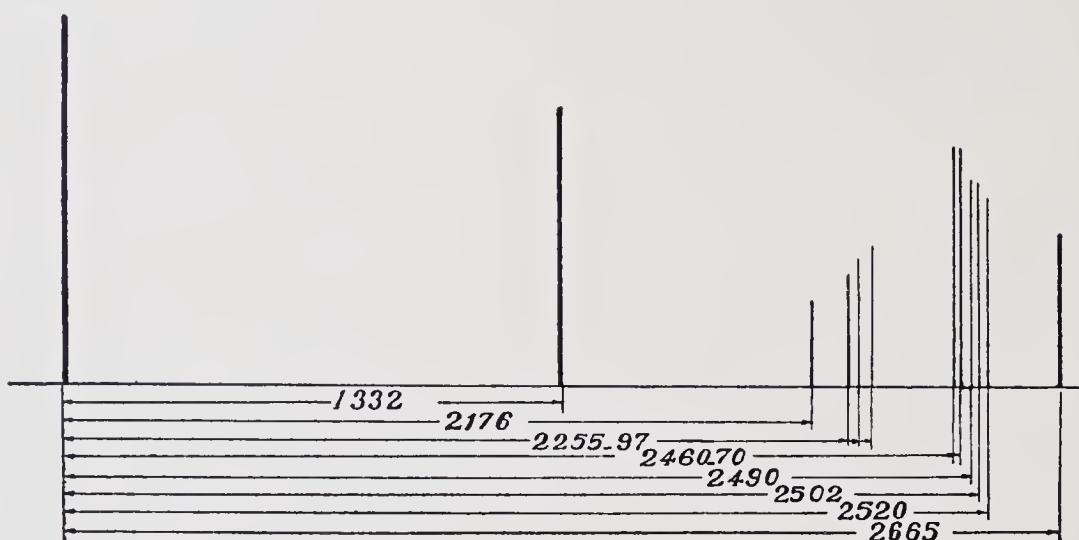


Figure 5. Frequency shifts in light-scattering.

second-order spectrum and exhibiting a frequency shift of  $2665\text{ cm}^{-1}$ . This is clearly to be identified as the octave of the principal mode of vibration having a frequency shift of  $1332\text{ cm}^{-1}$ : its measured spectral width of 8 wave numbers is also approximately double the spectral width of that frequency shift at room temperature.

Very conspicuous also in the microphotometer records is the sharply defined peak of intensity with a frequency shift of  $2176\text{ cm}^{-1}$ . This is clearly the octave of the common frequency  $1088\text{ cm}^{-1}$  of modes V and VI listed in table 1.

Of much greater intensity than either of the peaks mentioned above is that which can be recognised both in the spectra and in the microphotometer records as a clearly resolved pair of lines whose frequency shifts are 2460 and  $2470\text{ cm}^{-1}$  respectively. The calculated frequency of the octave of mode III in table 1 is  $2478\text{ cm}^{-1}$  and this is sufficiently close to the position of the doublet to justify our identifying the latter with it.

Close to the doublet but clearly separated from it appear a group of rather diffuse lines whose frequency shifts are 2490, 2502 and 2520 respectively. The mean of these three shifts is 2504 and we may therefore identify the triplet of lines as being the octave of mode III in table 1 whose calculated value is  $2500\text{ cm}^{-1}$ .

Finally, we have a group of rather inconspicuous maxima, of which the most evident is one with frequency shift of  $2255\text{ cm}^{-1}$  followed by a series of others with larger frequency shifts. The octave of mode IV the frequency of which is  $2298\text{ cm}^{-1}$  lies within this range.

## 7. Some concluding remarks

Spectroscopic investigation of the scattering of light in diamond thus decisively confirms the theoretical result that its structure possesses a discrete set of normal modes of vibration with well-defined frequencies forming a sequence as indicated in table 1. Various details revealed by the study, viz., the great differences in the relative intensities with which the various modes appear and the spectral splitting which some of them exhibit are also readily explicable.

The non-appearance of modes VIII and IX as frequency shifts even in the second-order scattering is not surprising. In these modes of vibration, neighbouring atoms of carbon do not approach or recede from each other but move laterally. Hence, no very sensible variations in the optical polarisability of the structural units are to be expected. *Per contra*, the approach and recession of neighbouring carbon atoms is very conspicuous in modes I, II and III and the appearance of the octaves of these modes with notable intensities is therefore in accord with expectation. That modes II and III appear even more strongly than mode I is clearly a consequence of their degeneracies being 8 and 6 respectively as compared with the degeneracy 3 of mode I. The strength with which the peak at  $2176\text{ cm}^{-1}$  is recorded is likewise explicable as due to the superposition of the effect of six modes having a common frequency.

That a second-order spectrum of light-scattering is at all observable becomes intelligible when it is recalled that the oscillators which are set in vibration and diffuse the incident radiation with a diminished frequency are the structural elements in the crystal. These are of extremely small dimensions and contain relatively few atoms. Hence, the absorption by them of a quantum of energy would result in vibrations of which the amplitude cannot be considered as infinitesimally small in relation to the interatomic distances. It follows that the periodic variation of optical properties resulting from the vibration would exhibit anharmonicity. Frequency shifts corresponding to overtones and combinations of the frequencies of the normal modes can therefore appear in the scattered light. The mechanical anharmonicity associated with vibrations of finite amplitude may likewise result in the splitting up of energy levels which in the harmonic oscillator approximation can be considered as identical.

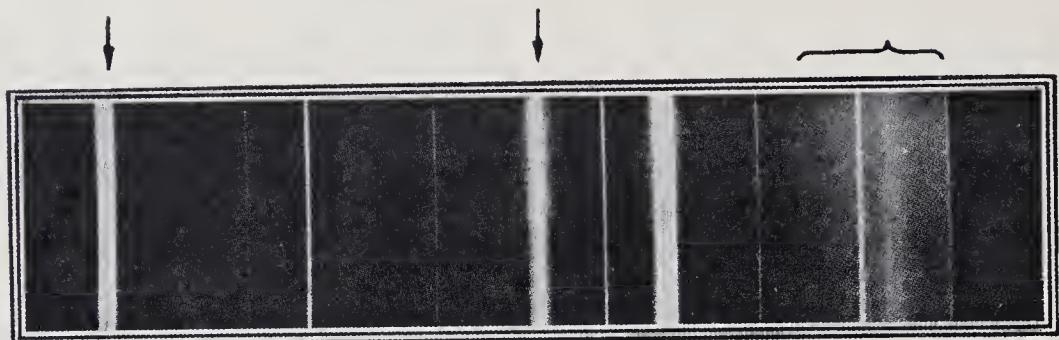


Figure 1

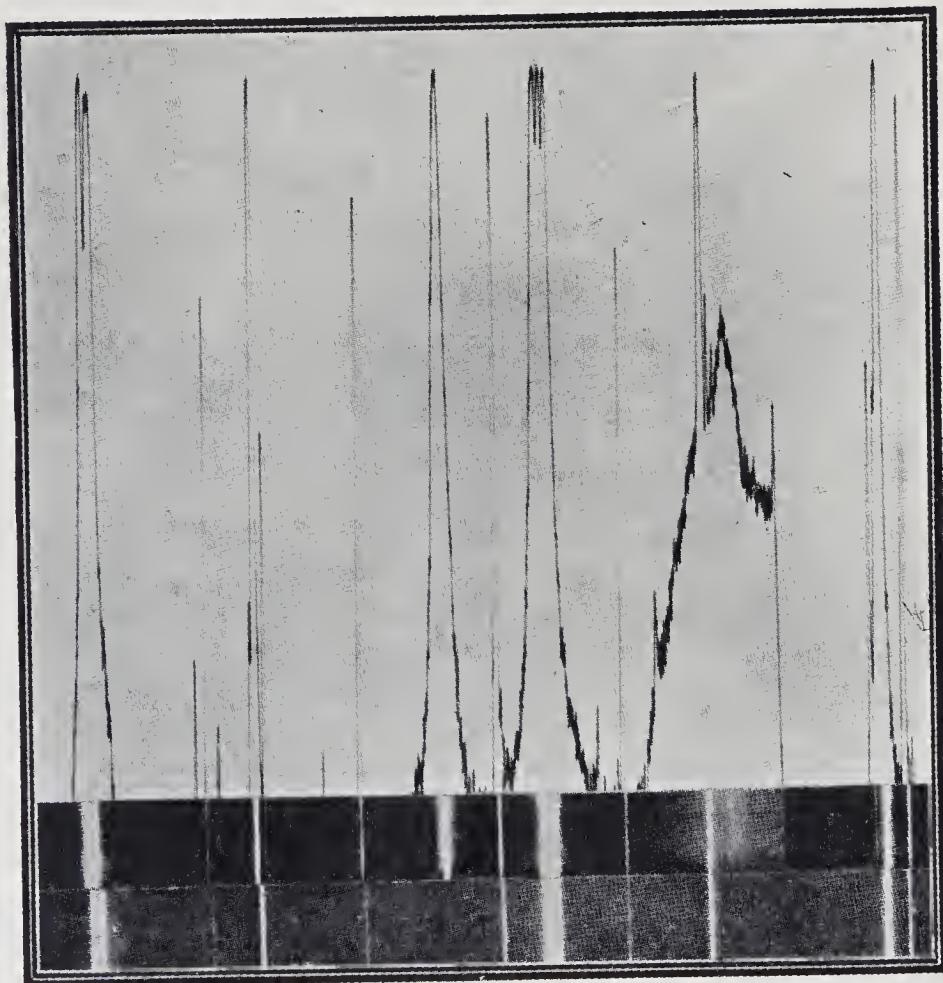


Figure 2

Scattering of light in diamond: medium spectrograph.

Plate I



Figure 1

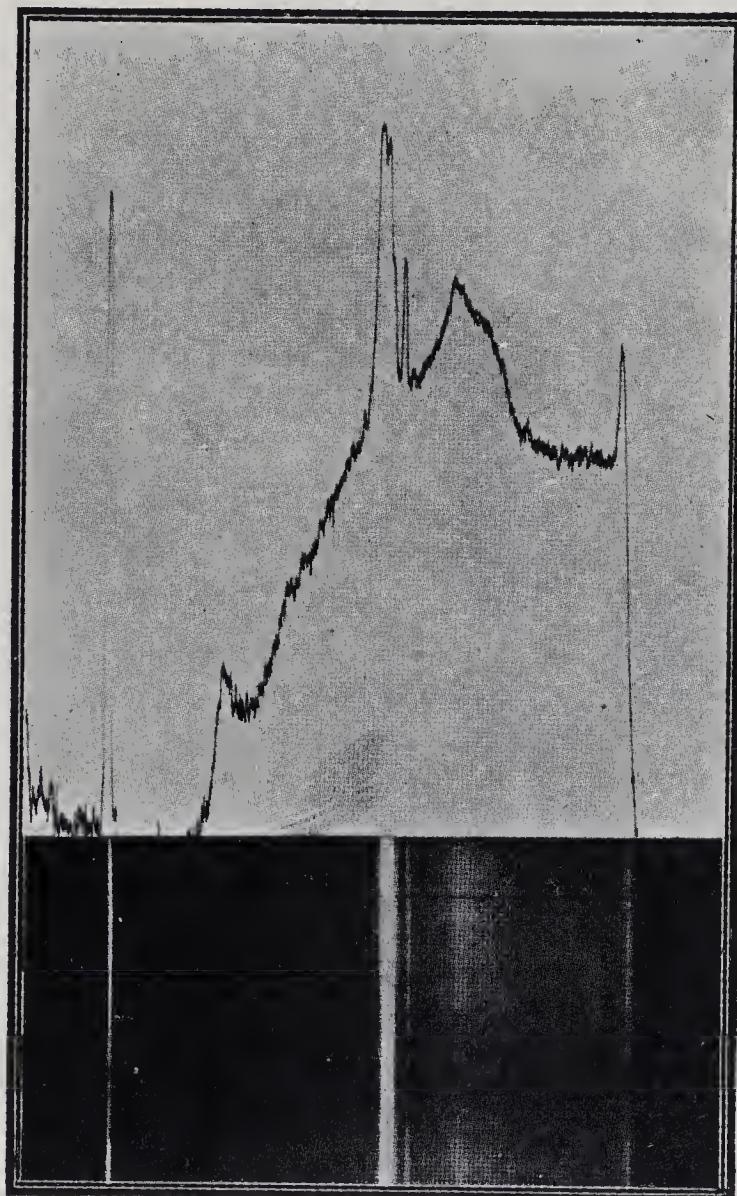


Figure 2

Scattering of light in diamond: large spectrograph.

# The tetrahedral carbon atom and the structure of diamond\*

SIR C V RAMAN

Memoir No. 104 from the Raman Research Institute, Bangalore-6

## 1. Introduction

My address to the Academy this year concerns itself with the element carbon and its chemical behaviour. The importance of this subject hardly needs to be stressed. Indeed, the amazing power which the atoms of carbon display of combining with themselves and with other atoms to form an immense variety of distinct compounds is one of the marvels of nature. It is perhaps part of the secret of life itself.

The science of chemistry made a great step forwards when it was realised that the structure of a chemical molecule can only be properly described in terms of the configuration in three-dimensional space of the atoms of which it is composed. This approach to chemical problems made its debut in the year 1874 when Van'T Hoff put forward his famous hypothesis of the tetrahedral carbon atom. What that description of the carbon atom really signifies, the physical and chemical evidence on which our belief in its validity is based and the explanation of the chemical behaviour of carbon in terms of the ultimate structure of its atom are the topics which we shall proceed to consider. The ideas which emerge from the discussion will then be applied to an elucidation of the crystal structure of diamond and the explanation of the properties of that remarkable substance.

## 2. The four valences of carbon

The simplest molecules exhibiting the disposition in space of the valences of the carbon atom are those in which an atom of carbon combines with four similar atoms or similar groups of atoms. This situation exists, for example, in the cases of methane ( $\text{CH}_4$ ), deuteromethane ( $\text{CD}_4$ ), carbon tetrafluoride ( $\text{CF}_4$ ), carbon tetrachloride ( $\text{CCl}_4$ ), carbon tetrabromide ( $\text{CBr}_4$ ), tetramethyl methane [ $\text{C}(\text{CH}_3)_4$ ] and so forth. In all these cases, the atoms or atomic groups which

\* Presidential Address to the Indian Academy of Sciences at the Tirupati Meeting on the 28th December, 1957.

combine with the carbon atom are found to be disposed in space with perfect tetrahedral symmetry round it. This is most convincingly shown by the study of the vibration spectra of these molecules. A molecule composed of five atoms would in general exhibit nine modes of free vibration. On the other hand, the five-atom groups listed above exhibit only four fundamental frequencies of vibration. Such a reduction would follow as a necessary consequence of the molecule possessing perfect tetrahedral symmetry. It is therefore to be regarded as demonstrating that the atoms in these molecules are located at the vertices of a regular tetrahedron with the carbon atom itself at its centre.

The vibration spectra of molecules in which an atom of carbon combines with three atoms of one kind and a fourth of a different kind show that in every such case, they have six fundamental vibration frequencies and no more. As examples of this behaviour may be listed the molecules of  $DCH_3$ ,  $HCD_3$ ,  $HCF_3$ ,  $FCH_3$ ,  $HCCl_3$ ,  $DCCl_3$ ,  $FCCl_3$ ,  $CICH_3$ ,  $CICD_3$ ,  $BrCH_3$ ,  $BrCD_3$  and  $ICH_3$ . Dynamical theory shows that a five-atom group possessing a triad axis of symmetry would exhibit only six distinct frequencies instead of nine. The observed facts are thus a clear proof that the molecules listed do possess such a symmetry. On the other hand, molecules containing carbon combining with two atoms of one kind and two atoms of another kind should exhibit all the nine modes of vibration, and this is in agreement with experience.

The symmetry of form of the molecules in each of the cases referred to above can also be inferred from the numbers respectively of polarised and depolarised lines observed as frequency shifts in the spectra of light-scattering. Here again, the experimental facts confirm the tetrahedral character of the atomic grouping around the central carbon atom.

Studies on the vibration spectra of various molecules of the kind quoted above also furnish us with a convincing proof of the non-existence of the several isomers which may be expected to be forthcoming if the four valences of carbon were not equivalent. For, the vibration frequencies of the molecules would be influenced by the atomic configurations and each isomer would therefore have its own set of vibration frequencies. As the characteristic frequencies reveal themselves as well-defined lines in the spectrum, multiplication of the number of observed frequencies would follow as a consequence of the existence of more than one form of the molecule. As no such effect is observed in the numerous cases which have been studied, we are justified in inferring that such isomers do not exist.

A question of great importance which arises in regard to molecules in which an atom of carbon is joined to four others which are not all the same is whether their joins with it make equal angles with each other as is to be expected if the valences were directed along the axes of a regular tetrahedron. This question can only be answered if methods for precise determination of the atomic configurations were available. Two such methods have been employed for the determination of the atomic configurations in molecules, namely, X-ray diffraction and electron diffraction. Both of these methods involve recondite theoretical considerations

besides complicated calculations. The results derived from them must therefore be considered as subject to some measure of uncertainty and this has to be borne in mind in assessing the significance of the reported results. Pauling, in his book *On the nature of the chemical bond* (second edition, 1940, table 14-I) gives a list of sixteen carbon compounds of varying degrees of complexity whose molecular structure has been investigated by electron diffraction methods. The table of results gives the bond angle subtended at the carbon atom for eight different species of bonds, namely, C—C—C, C—C—Cl, C—C—Br, F—C—F, Cl—C—Cl, Br—C—Br, F—C—Cl and N—C—N. In five of these cases, namely, C—C—Br, C—C—Cl, F—C—F, F—C—Cl and N—C—N the angles are indistinguishable from the tetrahedral angle of  $109^{\circ} 28'$ , while in the three other cases, namely, Cl—C—Cl, C—C—C and Br—C—Br the reported bond angles exceed the tetrahedral angles by a degree or two; but this difference cannot be regarded as significant since the reported experimental uncertainties are of the same order of magnitude.

We may sum up the conclusions which may be legitimately drawn from the facts of experiment cited above as follows: *When an atom of carbon combines with four others, the four valences are directed along the four axes of a regular tetrahedron but are otherwise indistinguishable from each other.*

### 3. The atomic structure of carbon

The interpretation which has to be placed on the results stated above becomes clear when we take note of the position of carbon in a list of the chemical elements arranged in the order of atomic numbers, that is to say, according to the magnitude of charge on the nucleus of the atom or the number of the electrons outside the nucleus. In such a list, the chemically inert gas helium occupies the second position, and the chemically inert neon occupies the tenth, while carbon with its six electrons occupies a position midway between them. Likewise, silicon which in several respects exhibits a chemical behaviour similar to carbon and has fourteen electrons stands midway between the inert gases neon and argon which have respectively ten and eighteen electrons outside their atomic nuclei. This is an example of the periodicity in chemical behaviour which makes itself evident when the elements are listed in the order of their atomic numbers. Such periodicity finds its explanation in certain general features manifested in the building up of the atoms, viz., the arrangement of the extra-nuclear electrons in a series of shells denoted respectively as K, L, M, etc. When the K shell is complete with its two electrons, we have the inert gas helium; when the L shell is also complete with its eight additional electrons, we have the inert gas neon; when a further eight electrons have been put into the M shell, we have the inert gas argon. Thus it is clear that the quadrivalence of carbon arises from the fact that it has four electrons in the L shell, just half the full quota of eight electrons needed to

complete that shell. Further, since the valences are directed along the four axes of a regular tetrahedron, we are evidently concerned here with a state of the atom in which the four electrons in the L shell by reason of their interactions with each other and with the force field of the charged core of the atom constitute a system which is electrically neutral but exhibits perfect tetrahedral symmetry. This system may therefore be rightly designated as the tetrahedral carbon atom. It can combine with four other atoms or groups of atoms to form molecules, but does not depart sensibly from its tetrahedral symmetry of structure as the result of such combination.

We have now to ask ourselves what precisely are the circumstances which favour the formation of the tetrahedral quartet of electrons referred to above. It is well known that helium, neon and argon besides being chemically inert are also diamagnetic in their behaviour. The explanation given for the latter circumstance is that in the building up of the electronic clouds, the magnetic moments arising from the inherent spins of the electrons as well as those, if any, arising from their orbital movements around the nucleus mutually cancel each other out. The same circumstance is also responsible for the chemical inertness of these gases. For this to happen in the L shell of an atom we require eight electrons, but since there are only four present in the L shell of carbon, the same situation cannot arise in its case. But the question does arise as to how the angular momenta associated with the orbital motion and the inherent spins of the four electrons are disposed. If the configuration resulting from the mutual interactions of the four electrons is to possess full tetrahedral symmetry, it is clearly necessary that the resultant angular momenta associated with each of the four electrons considered individually should be equal and that further, these momenta should set themselves respectively along the four axes of a regular tetrahedron. The total angular momentum of the quartet and hence also its magnetic moment would vanish in these circumstances, and hence *the quartet of electrons must be considered as diamagnetic. But it would not be chemically inert since the cancellation is a result of the tetrahedral setting of the individual angular momenta and not of their internal pairing off.*

An interesting consequence of the foregoing ideas should be here referred to. The angular momentum of an electron and hence also the magnetic moment associated with it is a vector and hence must be regarded as having both a direction and a sign. As already remarked, the directions in the present case are along the four axes of a regular tetrahedron, and if the quartet is to possess tetrahedral symmetry, all the four vectors concerned should have the same sense. Hence, they should all be directed either outwards or inwards from the core of the atom. Thus we have two distinct possible states of the tetrahedral carbon atom which we might designate as the  $\alpha$  and the  $\beta$  states respectively. These do not differ from each other except in the sense of the angular momenta of the individual electrons, these being directed respectively outwards or inwards from the charged core of the atom in the two cases.

#### 4. The crystal structure of diamond

Diamond furnishes a perfect illustration of Van'T Hoff's hypothesis of the tetrahedral carbon atom. For, X-ray analysis discloses its structure to consist of two sets of carbon atoms, each carbon atom in one set being chemically linked with perfect tetrahedral symmetry to four carbon atoms belonging to the other set and *vice versa*. The joins of the carbon atom in each set with the four others in the second set are all parallel to each other and to the four body-diagonals of a cube. Hence diamond exhibits the symmetry belonging to a crystal of the cubic class. Considering this situation in the light of the remarks made in the preceding section, it follows that diamond is a crystal whose properties would not be uniquely decided by the crystal structure alone as determined by the methods of X-ray analysis. Diamond consists of two interpenetrating lattices of carbon atoms. In an ideal crystal all the atoms belonging to one lattice should be the same, but as there are two possible types of tetrahedral carbon atom, it follows that an ideal diamond may belong to any one of four types, namely,  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$ , and  $\beta\beta$ . There is no reason to expect that these four types of diamond would exhibit any significant differences in such properties as lattice spacings, or the energy of formation, or the atomic vibration frequencies and so forth. But we should expect observable differences of a less obvious kind arising from the fact that the  $\alpha\alpha$  and  $\beta\beta$  types of diamond would possess a perfect octahedral symmetry in their crystal structure, whereas the two other types  $\alpha\beta$  and  $\beta\alpha$  would exhibit only the lower or tetrahedral symmetry.

Thus our present approach to the basic problems of organic chemistry leads to a natural and intelligible explanation of the fact that some diamonds exhibit infra-red absorption in the region of wavelengths about  $8 \mu$  including the characteristic lattice frequencies of vibration, while other diamonds do not exhibit this absorption. The diamonds which exhibit such absorption are those whose structure is of the  $\alpha\beta$  or  $\beta\alpha$  type, while those that do not are those whose structure is of the  $\alpha\alpha$  or  $\beta\beta$  type. Considerations of the same nature would also account for the differences exhibited by diamond in respect of other properties including especially the presence or absence of absorption of light in the near ultra-violet, which as is well known accompany the presence or absence of infra-red absorption in the  $8 \mu$  region. We shall not enter into these questions here in detail but shall content ourselves with making two further remarks. The difference between the diamonds exhibiting octahedral and tetrahedral symmetry respectively cannot be expected to manifest itself in any difference in piezo-electric behaviour. The other remark is to recall the fact long known to mineralogists that the external forms of the diamond crystals found in nature more often than not indicate the lower or tetrahedral symmetry instead of the higher or octahedral one. This fact ceases to be surprising in the light of the considerations set forth above.

### 5. The theory of hybrid bond orbitals

We cannot avoid making some reference here to the attempts that have been made to explain the directed valences of the carbon atom in terms of ideas based on the Schrodinger solution of the wave-equation for the hydrogen atom. The theory of hybrid bond orbitals, as it is called, can be summarised as follows: The solution of the hydrogen problem by the Schrodinger method yields a series of solutions ( $s, p, d$  etc.) which indicate the possible distributions of electron density around the nucleus. The wave-function  $s$  indicates a distribution of electron density spherically symmetrical round the nucleus, where there are three wave-functions denoted by  $p_x$ ,  $p_y$  and  $p_z$  respectively which represent density distributions whose maximum extensions are respectively along the  $x$ ,  $y$  and  $z$  axes in both directions. All these wave-functions represent the same energy and hence it is possible to construct linear combinations of them so as to produce new wave-functions which are orthogonal to each other. By giving equal weights to the wave-functions  $p_x$ ,  $p_y$  and  $p_z$  but different signs in different cases and adding the  $s$  wave-function, it is possible to obtain four wave-functions which are tetrahedrally symmetric with respect to the nucleus. The four orbitals thus derived are put forward as a representation of the directed valences of a carbon atom.

Several criticisms of a fundamental nature regarding the theory thus briefly summarised may be put forward. The first objection is that we are not concerned here with a hydrogen atom having a single electron but with a carbon atom having two inner and four outer electrons; the interactions of these with each other and with the atomic nucleus are of the very essence of the problem but they are left out of consideration in the theory. A second objection is that the theory does not explicitly consider the spin of the electrons, though they play a fundamental role in the theory of atomic structure. Apart from these difficulties, one is also confronted with the fact that we have an infinite number of possible  $sp^3$  hybrids and the question may well be asked why the particular set which gives four orbitals indicative of a tetrahedral orientation of the valences should be chosen out of them all. The fundamental feature of the quadrivalence of carbon is that the tetrahedral disposition of the valences is maintained even when the four atoms with which the combination occurs differ from each other enormously, as for example, hydrogen, carbon, nitrogen, fluorine, bromine, chlorine and iodine—to mention no others. *It is this circumstance which indicates that the determining factor which gives rise to the tetrahedral configuration of the valences is not the energy of formation of the bond or bonds, but is an inherent property of the carbon atom itself.* In other words, it is to be found in the mutual interactions between the quartet of electrons which compel them to set themselves in a uniquely determined tetrahedral configuration.

## 6. Summary

The experimental evidence derived from the study of the vibration spectra of molecules and of their electron diffraction patterns shows unequivocally that the four valences directed outwards from a carbon atom are parallel to the four axes of a regular tetrahedron. That this disposition is maintained even when the four atoms combining with the carbon atom differ enormously from each other indicates that we are concerned here with an intrinsic property of the carbon atom, namely, that the quartet of electrons in the L shell as a result of their mutual interactions can set themselves so as to constitute a structure possessing perfect tetrahedral symmetry. Such a structure would be diamagnetic but not chemically inert, since the individual angular momenta cancel out as a result of the tetrahedral setting and not as a consequence of the internal pairing off as in the inert gas molecules.

It follows from these considerations that there are two possible states of the carbon atom and hence also four possible forms of diamond, which may be designated as  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$  and  $\beta\beta$  respectively. The first and the last would have true octahedral symmetry, while the second and the third would have the lower or tetrahedral symmetry. The differences in physical behaviour exhibited by even ideal diamonds in various respects, including especially their infra-red absorption spectra, thus receive a natural and intelligible explanation.

## **Index to Co-authors**

### **Volume IV**

- Jayaraman A 228, 248, 265, 335, 346, 394, 415,  
452, 475, 487, 497, 512, 642  
Krishnamurti D 158, 278, 292, 303, 310, 318, 363,  
377, 383  
Rajagopalan V S 175, 201
- Ramaseshan S 599  
Ramdas A K 406, 501  
Rendall G R 587  
Srinivasan T K 248

## **Subject Index**

### **Volume IV**

- Absorption spectrum—diamond 538  
Agate—iridescence 394–401  
Alabaster 507  
Allotropic forms of diamond 540, 631  
Amethyst—nature of 469–486  
Amorphous solids—birefringence 436–444  
Astronomy research in India 65–72  
Atmosphere of the earth 95  
Atomic vibration of diamond 627
- Birds—plumage colours 101–107  
Birefringence  
    amorphous solids 436–444  
    crystal spheres 460–468  
    diamond 533, 555, 587–598
- Calcite—iridescence 406–412  
Crystal forms of diamond 532, 599–625  
Crystallography of diamond 542  
Crystal symmetry of diamond 558–566, 626
- Diamond  
    absorption spectrum 538  
    accidental birefringence 533  
    allotropic forms 540  
    allotropic modification 631  
    atomic vibration 627  
    birefringence 555  
    birefringence patterns 587–598  
    crystal forms 532, 599–625  
    crystallography 542  
    crystal symmetry 558–566, 626
- electronic spectrum 630  
fluorescence 534  
four forms of 551  
genesis 636  
infra-red absorption 543, 629  
lattice spectrum 537  
luminescence 544, 553–555, 567–585, 633,  
642, 659–688  
photo-conductivity 549  
scattering of light 534  
tetrahedral carbon atom 702  
ultra-violet absorption 554  
X-ray phenomena 546  
X-ray reflections 535
- Eastern Europe—science in 77–90  
Electronic spectrum of diamond 630
- Faraday—a tribute 59  
Faraday effect—centenary 63  
Feldspars  
    diffusion haloes 265–277  
    iridescence 222–247, 265–277  
Fluorite 525–530  
Fluorspar—luminescence 518–524  
Fourier series—discontinuities 11
- Genesis of diamond 636  
Glass  
    ancient decomposed 201–213  
    iridescence of 175–200

- laminar structure 445–450  
 plate 445–450  
 stratified media 202  
**Gypsum**  
 polycrystalline form 501–517  
 X-ray studies of 512–521  
**Hertz**—theory of impact 20–36  
**Hyalite** 335  
**Impact**—at minimal velocities 20–58  
**Infra-red absorption** of diamond 543, 629  
**Iridescence**  
 agate 394–401  
 calcite 406–412  
 feldspar 222–247, 265–277  
 glass (ancient, decomposed) 175–200  
 jadeite 415–418  
 labradorite 228–247  
 moonstone 248–264  
 opal 335–362  
 pearls 363–388  
 potassium chlorate 278–335  
 quartz 420–428  
 shells 108–173  
**Jet streams** 91  
**Kinematical theory** 7  
**Labradorite**—iridescence 228–247  
**Lattice spectrum**—diamond 537  
**Luminescence**  
 birefringence and ultra-violet transparency  
     in diamond 642–658  
 diamond 544, 553–555, 567–585, 633, 642,  
     659–688  
**Moonstones**—iridescence optical behaviour  
     248–264  
**Newton**—history of optics 63  
**Opal**—iridescence 335–362  
**Pearls**  
 chromatic halo 383  
 iridescence 363–388  
 optical behaviour 363–388  
 whispering gallery effect 367  
**Percussion figures**  
 in crystals 41–58  
 isotropic solids 26  
 optical study of 37–40  
**Photo-conductivity**—diamond 549  
**Potassium chlorate**—iridescence 278–335  
**Quartz**  
 amethyst 452–459  
 crypto crystalline 487–496  
 fibrous 497  
 iridescent 420–425  
 iridescent agate 490–492  
 pleochroism 452–459  
 smoky 451  
**Satin-spar** 508  
**Scattering of light**—diamond 534  
**Shells**  
 iridescence 108–173  
 optical behaviour 158–173  
 photographs of 114–118, 134–139, 151–157  
**Silica**—natural 427  
 optical anisotropy 426–433  
 structural birefringence 432  
 vitreous 426–433  
**Surface tension**  
 curvature method 1  
 liquids 1–5  
**Ultra-violet absorption**—diamond 554  
**Viscosity of liquids** 15–19  
 pressure variation 18  
 temperature variation 18  
**X-ray phenomena**—diamond 546  
**X-ray reflections**—diamond 535  
**Zonal winds** 91

## Name Index

### Volume IV

- Achyutan 636  
Alling 229  
Anderson B W 241, 649  
Angstrom K 561  
Anna Mani 57, 544, 553, 556, 578, 630, 643,  
    661, 662, 663, 676, 677  
Archimedes 63, 68  
Aryabhatta 65  
Asperger S 85, 86  
  
Badarov 83  
Baini Prashad 113, 132  
Balkrishna 531  
Bancroft W D 104  
Banerjee Kedareswar 20, 38  
Banerji 20  
Becquerel H 75  
Becquerel J 60, 75, 76  
Belic 85  
Belov 79  
Bender F 175  
Berl F 175  
Bhagavantam S 60, 534, 535, 568  
Bhaskaracharya 65, 68  
Bhatnagar S S 62  
Bianu 84  
Biscoe J Z 415  
Boggild O B 109, 110, 111, 112, 113, 228, 236,  
    237, 250, 265  
Bohr Niels 69, 71  
Boltzmann L 15  
Bonn 369  
Born M 534, 535, 537, 547, 548  
Bose D M 62  
Boutan L 109  
Boyle Robert 567  
Bradley 66, 68  
Bragg W H 559  
Bragg W L 559, 579  
Brahmagupta 65  
Brauns R 512  
Brewster Sir David 108, 120, 175, 201, 203,  
    204, 212  
Buerger M J 338  
  
Cairo 303  
Carslaw 11  
Chandrasekhar S 68, 72, 480, 677  
Chandrasekharan V 636  
Chao 230, 231, 260, 261  
Chapman 16  
Chellam E V 541  
Chidambaram 61  
Chinchalkar S W 61  
Clayton 427  
Clement 108  
Coeling 201  
Copernicus 69  
Cotton A 201  
Crelle 30  
  
Dana E S A 599  
Darwin C G 76  
Dayal Bisheshwar 556  
Debye P 534, 535, 537  
Dutt Adair 426  
Dwyer E P 338  
  
Einstein Albert 68  
Emil Ott 338  
Euler 303  
  
Faraday Michael 59, 60, 73, 74, 75  
Federov 638  
Fersmann 647  
Ford K L 175  
Fox J J 549, 561, 562, 566, 573, 577, 590, 591  
Fraunhofer 66, 68  
Fricke 303  
Fuchs S 40  
  
Galileo G 63, 534  
Gavrila 83  
Ghosh J C 62  
Ghosh P N 128  
Glaser 61  
Goldschmidt V Z 599, 647  
Grailich 406

- Groth P 558, 647, 599  
 Gudden B F A 549  
 Guillot M Marcel 175, 201, 212  
 Gyulai Z 82
- Haas F 109, 112  
 Hale 66, 68  
 Hall T P 5  
 Hamburger 20  
 Hariharan P S 546, 556, 579  
 Harnack A 11  
 Heaton Noel 175  
 Helle Schicht 108  
 Helmholtz H V 7, 10, 24  
 Hertz P 20, 21, 26, 28, 29, 33, 34, 37, 40, 41,  
     59, 73  
 Hintze C 228, 415, 497, 512, 558, 599  
 Hirschwald J 599  
 Hodgkinson 21  
 Hooke Robert 64  
 Hornell J 110  
 Horvath Janos 82  
 Hubble 66, 69  
 Hugel G 175  
 Hulubei 83  
 Huygens Christian 63, 64, 406
- Inuzuke 230, 260
- Janossy L 81  
 Jaroslav Heyrovsky 78  
 Jay A H 339  
 Jayaraman A 222, 248, 265, 273, 319, 346, 347,  
     365, 425, 469, 471, 475, 487, 488, 491, 498,  
     659, 661, 668, 674  
 Joffe 79  
 John A 568  
 John A Brashear 65  
 John M V 569  
 Jones F T 491  
 Julis 561
- Kapitza P 79  
 Kasanin 85  
 Kathavate Y V 166  
 Kayser 567, 569  
 Kelvin Lord 1  
 Kennelly 20  
 Kepler 66, 68, 69  
 Kirk 647  
 Kriger-Menzel 7, 10
- Krishnamurthy L S 241  
 Krishnamurti D 303, 310, 363, 379, 383, 386,  
     409  
 Krishnan K S 60, 62, 432  
 Krishnan R S 426, 547, 555, 556, 579, 592,  
     628, 629, 697  
 Kundt 74
- Ladenburg 60  
 Lady Raman 77  
 Lafay 20  
 Lamb H 30, 31, 32  
 Laplace 68  
 Larmor Sir Joseph 59, 61, 75  
 Laszlo Szalay 81  
 Laubengayer A W 175  
 Leduc 108  
 Leela M 477  
 Leipzig 369  
 Lenard 63  
 Leonardo da Vinci 63, 77  
 Levin I 338  
 Liesegang 108  
 Liebisch 558, 587  
 Lindemann F 11  
 Lippmann 119  
 Lockyer 66, 68  
 Lonsdale 547, 548  
 Lord Rayleigh 20, 30, 104, 108, 119, 123, 209,  
     237, 293, 297, 303, 406, 424, 426, 430, 431,  
     451  
 Lorentz H A 59
- Mahadevan C 241  
 Martin A E 561, 566, 573, 577, 590, 591, 599  
 Mascart 406  
 Mason C W 104  
 Maxwell C 59, 73  
 Mecke R 525  
 Mellor D P 338  
 Mendeljeff 79  
 Mervin H E 415  
 Miers H A 599  
 Mikhailov 80  
 Milojevic 85  
 Moriyasu S 175  
 Muthuswamy T N 241, 265  
 Mylius F 175
- Nagendra Nath N S 447, 543  
 Nayar P G N 531, 533, 534, 539, 544, 545,

- 556, 569, 578, 580, 588, 630, 643, 659, 661,  
662, 676, 678, 681  
**Nedungadi T M K** 544  
**Nesmeyanov** 79  
**Newton Isaac** 63, 64, 68, 69  
**Nieuwenkamp** 339  
**Nilakantan P** 536  
**Northrup** 20  
**Osthoff** 406  
**Othmar** 647  
**Padmanaban J** 48, 433, 439, 449, 460  
**Paic** 86, 87, 89  
**Pancharatnam S** 455, 471, 475  
**Pant D D** 549  
**Paranjpye R P** 132  
**Pattabhiramayya P** 132, 150  
**Paul Grodzinski** 649  
**Pauling** 704  
**Perkin W H** 76  
**Pfund A H** 108  
**Pichamuthu C S** 241, 476, 497, 498  
**Placzek G** 561  
**Pliva Josef** 78  
**Plyler E K** 525  
**Pochettino** 21  
**Pochhammer** 30  
**Pockels** 406  
**Pohl P** 549  
**Popovic** 85  
**Preston H B** 110  
**Pringsheim E** 568  
**Punnyasoma G L** 262  
**Pupil M** 201, 212  
**Pythagoras** 63  
**Rajagopalan V S** 160, 201, 364, 365  
**Ramachandran G N** 163, 282, 283, 303, 354,  
448, 542, 556, 579, 580, 590, 627, 633, 636,  
645, 646, 666, 674, 685  
**Ramachandra Rao S** 61  
**Ramanathan K G** 628, 630, 647, 648, 666, 669,  
678, 680  
**Ramaseshan S** 557, 601, 606, 616, 631, 636,  
647  
**Ramaswamy C** 562, 676  
**Rama Swamy S** 160, 363, 365  
**Ramdas A K** 512  
**Ramdas L A** 303  
**Ranganadham S P** 62  
**Rao H Srinivasa** 113, 132  
**Rao I R** 128, 129, 175, 177  
**Raps** 7, 10  
**Ray B B** 104  
**Reinkober** 561  
**Rendall G R** 554, 574, 575, 636, 643  
**Riviere** 108  
**Robertson R** 549, 561, 562, 566, 573, 577, 590,  
591  
**Romer** 66, 68  
**Sadebeck A Z** 599  
**Sastri Rao Saheb T P Bhaskara** 72  
**Savic** 85  
**Schmidt W J** 109, 111, 112, 113, 127, 132, 369  
**Schneebeli** 20  
**Schoenflies** 638  
**Sears J E** 29  
**Sigamony A** 557  
**Singh Bawa Kanwal** 439  
**Sinor K P** 532, 533, 571, 587, 599  
**Sircar Mahendra Lal** 59  
**Sircar S C** 62  
**Skobelcyn** 79  
**Smare** 230, 261  
**Sohncke** 638  
**Spencer L J** 257, 272, 349, 426, 427  
**Srinivasan T K** 222, 241, 265, 273, 331  
**Stephenson A** 7  
**Stevin** 63  
**Stokes G G** 303  
**Strutt R J (see Lord Rayleigh)** 451  
**Subramanian R V** 303, 536  
**Sunanda Bai K** 548, 554, 573, 591, 630, 678  
**Supek** 86  
**Sur N K** 128  
**Sutton J R** 542, 558, 564, 599  
**Szalay** 82  
**Szigeti G** 82  
**Tabata K** 175  
**Taylor** 229, 230, 231, 260, 261  
**Tei-Ichi Ito** 230, 248, 261, 265, 272  
**Titeica** 83  
**Thosar B V** 261  
**Tito Marshal** 85  
**Tutton A E H** 559, 599  
**Tyndall J** 104, 268, 451  
**Vaidyanathan V I** 61  
**Van der Veen** 559

- Varahamihira 65  
Venkatasubbaraman A 28, 34  
Venkateswaran C S 113, 132, 150, 541  
Vincent 21  
Voltz T H 175  
Vredenburg E W 532  
  
Warren B E 415  
Washington H S 415  
Watson E R 76  
  
Weber W 531  
Weiss 599  
Wood R W 303  
Wyckoff R W G 339, 415  
  
Yavar Jung Nawab Ali 84  
Yegami K 175  
Yoder H S 415  
  
Zeeman 75

## List of papers published from C V Raman's laboratory

### Volume IV

#### A. Miscellaneous I

1. Ghosh R N, 1921, Some new illustrations of optical theory by ripple motion, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 155
2. Seshagiri Rao K, 1921, Theory of impact on elastic plates, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 165
3. Narayan A L and Subrahmanyam G, 1922, On the surface tension of soap solutions for different concentrations, *Philos. Mag.*, **43** 663
4. Roy B B, 1922, Optical analogue of the whispering gallery effect, *Cal. Math. Soc. Bull.*, **12** 225
5. Ramanathan K R, 1923, On the visual and photographic albedo of the earth, *Astrophys. J.*, **57** 177
6. Bhargava S and Ghosh R N, 1924, On the elastic impact of a pianoforte hammer, *Philos. Mag.*, **47** 1141
7. Ghosh R N, 1924, Pianoforte string struck by an elastic hammer, *Phys. Rev.*, **24** 456
8. Barkat Ali, 1925–26, Surface tension of water, benzene, methyl and ethyl alcohols, *Proc. Indian Assoc. Cultiv. Sci.*, **9** 155
9. Ghosh R N and Dey J N, 1925–26, Experimental study of the elastic impact of pianoforte hammer, *Proc. Indian Assoc. Cultiv. Sci.*, **9** 193
10. Das P, 1925–26, On the pressure exerted by an elastic hammer impinging on a pianoforte string, *Proc. Indian Assoc. Cultiv. Sci.*, **9** 297
11. Ramdas L A, 1926, On the origin of movements of camphor on water and allied phenomena, *Indian J. Phys.*, **1** 1
12. Banerjee K, 1926, On the permanent deformation produced by contact of solids, *Indian J. Phys.*, **1** 59
13. Das P, 1926, On the impact of an elastic hammer on a pianoforte string, *Indian J. Phys.*, **1** 75
14. Ghosh P N, Banerji D and Datta S K, 1926, Determination of surface-tension by the method of ripples, *Philos. Mag.*, **1** 1252
15. Das P, 1927, Theory of the elastic pianoforte hammer, *Proc. R. Soc. London*, **A40** 29
16. Venkateswaran S, 1927, Compressibilities of aqueous solutions of some fatty acids, *J. Phys. Chem.*, **31** 1521
17. Das P and Datta S K, 1928, On the acoustic of strings struck by a hard hammer, *Philos. Mag.*, **6** 479
18. Banerji D and Ganguli R, 1929, On the duration of contact between the pianoforte strings and hard hammer, *Philos. Mag.*, **7** 345
19. Ghosh R N, 1930, On the elastic impact of pianoforte hammer, *Philos. Mag.*, **9** 1174
20. Venkatarama Iyer M P, 1930, The température variation of the viscosity of liquids and its theoretical significance, *Indian J. Phys.*, **5** 371
21. Ghosh M M, 1932, Experimental study of the duration of contact of an elastic hammer striking a damped pianoforte string, *Proc. Indian Assoc. Cultiv. Sci.*, **7** 365
22. Venkataraman S, 1933, Measurement of viscosity by oscillating columns, *Proc. Indian Assoc. Cultiv. Sci.*, **8** 25
23. Ghosh R N and Mohammad H G, 1935, On the kinks on impact diagrams of struck strings, *Philos. Mag.*, **19** 260

### B. The colour and optics of minerals

24. Ray B B, 1922, The colours of colloids in relation to the size of the dispersed particles, *Proc. Indian Assoc. Cultiv. Sci.*, **7** 221
25. Ramdas L A, 1923, Colours of chlorate of potash, *Proc. Indian Assoc. Cultiv. Sci.*, **8** 231
26. Ramanathan K R, 1923, On the colour of sea, *Philos. Mag.*, **46** 543
27. Venkateswaran S, 1927, Compressibilities of aqueous solutions of some fatty acids, *J. Phys. Chem.*, **31** 1521
28. Sirkar S C, 1930, On the Laue photographs of iridescent crystals of potassium chlorate, *Indian J. Phys.*, **5** 337
29. Rama Swamy S, 1935, X-ray analysis of the structure of iridescent shells, *Proc. Indian Acad. Sci., A1* 871
30. Pisharoty P R, 1935, Laminar diffraction and the Becke phenomenon, *Proc. Indian Acad. Sci., A2* 14
31. Rama Swamy S, 1935, X-ray analysis of the structure of iridescent shells Part II. The Haliotidae, *Proc. Indian Acad. Sci., A2* 345
32. Nilakantan P, 1936, Magnetic anisotropy of naturally occurring substances I. mother-of-pearl, *Proc. Indian Acad. Sci., A2* 621
33. Nilakantan P, 1937, X-ray studies of wood, lignin and wood-cellulose, *Proc. Indian Acad. Sci., A5* 166
34. Srinivasan P S, 1937, The elastic properties of mother-of-pearl, *Proc. Indian Acad. Sci., A5* 463
35. Nilakantan P, 1937, Magnetic anisotropy of naturally occurring substances III. Wood and its constituents, *Proc. Indian Acad. Sci., A7* 38
36. Thosar B V, 1945, Crystalline sheen of moonstones, *Philos. Mag.*, **36** p. 719
37. Ramdas A K, 1952, The infra-red absorption spectrum of potassium chlorate crystals: Part I, *Proc. Indian Acad. Sci., A35* 249
38. Ramdas A K, 1952, The infra-red absorption spectrum of potassium chlorate crystals: Part II, *Proc. Indian Acad. Sci., A36* 55
39. Ramdas A K, 1954, Some illustrations of the optical behaviour of iridescent calcite, *Proc. Indian Acad. Sci., A40* 217
40. Mahadevan C, 1926–27, Pleochroic haloes in cordierite, *Indian J. Phys.*, **4** 444
41. Sur N K, 1923, Scattering of light by smoky quartz, *Proc. Indian Assoc. Cultiv. Sci.*, **8** 271
42. Mahadevan C, 1929, X-ray study of vitrain and durain and their constituents, *Indian J. Phys.*, **4** 79
43. Paramasivan S, 1929, Anomalous diamagnetism of graphite, *Indian J. Phys.*, **4** 141
44. Mahadevan C, 1929, Further X-ray studies of carbonaceous and bituminous materials, *Proc. Indian Assoc. Cultiv. Sci.*, **4** 457
45. Mahadevan C, 1929, Constitution of coal, *Proc. Inst. Chem. India*,
46. Krishnan M S and Mahadevan P C, 1930, Pleochroic "giant" haloes in cordierite, *Proc. Indian Assoc. Cultiv. Sci.*, **5** 669
47. Mahadevan C, 1930, X-ray studies of natural and fossil resins, *Indian J. Phys.*, **5** 345
48. Mahadevan C, 1930, X-ray study of vitrains, *Indian J. Phys.*, **5** 525
49. Ranganathan S, 1931, X-ray diffraction studies of calculi, *Indian J. Phys.*, **6** 433
50. Krishnan M S and Mahadevan C, 1932, Giant pleochroic haloes, *Nature (London)* **129** 135
51. Mahadevan C, 1933, Investigations on peaty lignites and anthracitic coals, *Indian J. Phys.*, **8** 259
52. Krishnan K S, 1934, Magnetic anisotropy of graphite, *Nature (London)* **133** 174
53. Rajagopalan V S, 1936, On the structure and optical characters of the nacre in iridescent shell—Part I, *Proc. Indian Acad. Sci., A3* 572
54. Rama Swamy S and Srinivasa Iyengar K Y, 1937, X-ray analysis of the structure of fibrous modification of tourmaline, *Proc. Indian Acad. Sci., A5* 419
55. Oke B Y, 1938, The electro-static forces and elasticity constants, *Proc. Indian Acad. Sci., A7* 265

56. Nilakantan P, 1938, Magnetic anisotropy and pleochroism of biotite mica, *Proc. Indian Acad. Sci.*, **A8** 39
57. Sigamony A, 1944, The magnetic susceptibility and anisotropy of carborundum, *Proc. Indian Acad. Sci.*, **A19** 377–380
58. Sigamony A, 1944, The magnetic behaviour of tektite, *Proc. Indian Acad. Sci.*, **A20** 15–17
59. Sigamony A, 1944, The magnetic properties of a tourmaline and epidote, *Proc. Indian Acad. Sci.*, **A20** 200–203
60. Sigamony A, 1944, Magnetic behaviour of iron-pyrites, *Proc. Indian Acad. Sci.*, **A20** 204–210
61. Sigamony A, 1944, Magnetic properties of augite, *Proc. Indian Acad. Sci.*, **A20** 261
62. Ramaseshan S, 1945, Mahadevite—A new species of mica, *Proc. Indian Acad. Sci.*, **A22** 177
63. Ramaseshan S, 1947, The magnetic properties of iron-pyrites, *Proc. Indian Acad. Sci.*, **A25** 201–207
64. Krishnamurti D, 1955, Raman spectra of borax, kernite and colemanite, *Proc. Indian Acad. Sci.*, **A41** 7
65. Jayaraman A, 1959, X-ray study of the structure of moonstones, *Proc. Indian Acad. Sci.*, **A50** 349

### C. The diamond

66. Ramaswamy C, 1930, The Raman effect in diamond, *Proc. Indian Assoc. Cultiv. Sci.*, **5** 97
67. Ramaswamy C, 1930, Raman effect in diamond, *Nature (London)*, **125** 704
68. Bhagavantam S, 1930, Relation of Raman effect to crystal structure and properties of diamond, *Proc. Indian Assoc. Cultiv. Sci.*, **5** 169
69. Bhagavantam S, 1930, Further studies on the Raman spectrum of diamond, *Proc. Indian Assoc. Cultiv. Sci.*, **5** 573
70. Bhagavantam S, 1930, Raman effect, fluorescence and colour of diamonds, *Nature (London)* **126** 168
71. Nagendra Nath N S, 1934, The normal vibrations of molecules having tetrahedral-symmetry, *Indian J. Phys.*, **8** 581
72. Nagendra Nath N S, 1934, The normal vibrations of molecules having octahedral symmetry, *Proc. Indian Acad. Sci.*, **A1** 250–260
73. Nagendra Nath N S, 1934, The dynamical theory of the diamond lattice, *Proc. Indian Acad. Sci.*, **A1** 333
74. Nagendra Nath N S, 1935, The dynamical theory of the diamond lattice: Part II. The elastic constants of diamond, *Proc. Indian Acad. Sci.*, **A1** 841
75. Nagendra Nath N S, 1935, The dynamical theory of the diamond lattice: Part III. The diamond-graphite transformation, *Proc. Indian Acad. Sci.*, **A2** 143
76. Pisharoty P R, 1940, The Young's modulus of diamond, *Proc. Indian Acad. Sci.*, **A12** 208–211
77. Nayar P G N, 1941, Temperature variation of the Raman frequency of diamond, *Proc. Indian Acad. Sci.*, **A13** 284
78. Nayar P G N, 1941, Luminescence, absorption and scattering of light in diamonds: Part I. Fluorescence, *Proc. Indian Acad. Sci.*, **A13** 483
79. Nayar P G N, 1941, Luminescence, absorption and scattering of light in diamond: Part II. Phosphorescence, *Proc. Indian Acad. Sci.*, **A13** 534
80. Nayar P G N, 1941, Luminescence, absorption and scattering of light in diamonds, Part III. Absorption, *Proc. Indian Acad. Sci.*, **A14** 1
81. Pisharoty P R, 1941, On the geometry of the quantum reflection of X-rays in diamond, *Proc. Indian Acad. Sci.*, **A14** 56
82. Pisharoty P R, 1941, A quantum theoretical explanation of the appearance of forbidden X-ray reflections in diamond, *Proc. Indian Acad. Sci.*, **A14** 377

83. Pisharoty P R, 1941, The absolute intensity of the Raman X-ray reflections in diamond, *Proc. Indian Acad. Sci.*, **A14** 434
84. Pisharoty P R and Subrahmanian R V, 1941, On the multiple spots and streamers exhibited by the (iii) dynamic reflections in diamond, *Proc. Indian Acad. Sci.*, **A14** 439
85. Anand V B, 1941, The thermal energy of crystalline solids: Diamond, *Proc. Indian Acad. Sci.*, **A14** 484
86. Nayar P G N, 1942, The lattice and electronic spectrum of diamond, *Proc. Indian Acad. Sci.*, **A15** 293
87. Nayar P G N, 1942, The luminescence, absorption and scattering of light in diamond Part IV. Raman effect, *Proc. Indian Acad. Sci.*, **A15** 310
88. Chelam E V, 1943, The normal vibrations in some typical cubic crystals, *Proc. Indian Acad. Sci.*, **A18** 257–265
89. Ramachandran G N, 1943, Modes of atomic vibration in the fourteen Bravais lattices, *Proc. Indian Acad. Sci.*, **A18** 266–282
90. Krishnan R S, 1943, Raman spectra of crystals and their interpretation, *Proc. Indian Acad. Sci.*, **A18** 298
91. Pant D D, 1943, Luminescence spectra and vibrations in crystal lattices, *Proc. Indian Acad. Sci.*, **A18** 309–326
92. Chelam E V, 1943, The frequency spectrum of the diamond lattice, *Proc. Indian Acad. Sci.*, **A18** 334–340
93. Ramachandran G N, 1943, Modes of vibrations of the hexagonal close-packed lattice, *Proc. Indian Acad. Sci.*, **A18** 341–344
94. Nagendra Nath N S, 1943, Dynamics of real crystals, *Nature (London)* **151** 196
95. Krishnan R S, 1944, The Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, **A19** 216
96. Dayal B, 1944, The lattice spectrum and specific heat of diamond, *Proc. Indian Acad. Sci.*, **A19** 224
97. Anna Mani, 1944, The fluorescence and absorption spectra of diamond in the visible region, *Proc. Indian Acad. Sci.*, **A19** 231–252
98. Sunanda Bai K, 1944, The ultra-violet absorption spectrum of diamond, *Proc. Indian Acad. Sci.*, **A19** 253–260
99. Hariharan P S, 1944, Intensity of X-ray reflection by diamond, *Proc. Indian Acad. Sci.*, **A19** 261–264
100. Sunanda Bai K, 1944, Luminescence patterns in diamond, *Proc. Indian Acad. Sci.*, **A19** 274–279
101. Ramachandran G N, 1944, X-ray topographs of diamond, *Proc. Indian Acad. Sci.*, **A19** 280
102. Rendall G R, 1944, Ultra-violet transparency patterns in diamond, *Proc. Indian Acad. Sci.*, **A19** 293–297
103. Krishnan R S, 1944, Experimental evidence for the existence of the four possible structures of diamond, *Proc. Indian Acad. Sci.*, **A19** 298
104. Ramachandran G N, 1944, X-ray reflection and the structure of diamond, *Proc. Indian Acad. Sci.*, **A19** 304
105. Sigamony A, 1944, Magnetic susceptibility of diamond, *Proc. Indian Acad. Sci.*, **A19** 310–314
106. Pant D D, 1944, The photoconductivity of diamonds: Part I. Experimental results, *Proc. Indian Acad. Sci.*, **A19** 315–324
107. Pant D D, 1944, The photoconductivity of diamond Part II. Theoretical considerations, *Proc. Indian Acad. Sci.*, **A19** 325–333
108. Ramaseshan S, 1944, The crystal forms of the panna diamonds, *Proc. Indian Acad. Sci.*, **A19** 334
109. Saksena B D, 1944, The thermal expansion of diamond, *Proc. Indian Acad. Sci.*, **A20** 92–99
110. Anna Mani, 1944, Polarisation of Raman scattering and of fluorescence in diamond, *Proc. Indian Acad. Sci.*, **A20** 117
111. Bhagavantam S, 1944, Normal oscillations of the  $T_d$  class diamond structure, *Proc. Indian Acad. Sci.*, **A20** 122.

112. Anna Mani, 1944, Spectroscopic study of luminescence patterns in diamond, *Proc. Indian Acad. Sci.*, **A20** 155–162
113. Dayal B, 1944, The theory of the thermal expansion of diamond, *Proc. Indian Acad. Sci.*, **A20** 187
114. Ramachandran G N, 1944, The angular divergence of the X-ray reflections by diamond, *Proc. Indian Acad. Sci.*, **A20** 245–256
115. Anna Mani, 1944, Fluorescence and absorption patterns in diamonds at low temperatures, *Proc. Indian Acad. Sci.*, **A20** 323–328
116. Krishnan R S, 1944, Thermal expansion of diamond, *Nature (London)*, **154** 486
117. Anna Mani, 1945, Excitation curves of luminescence in diamond, *Proc. Indian Acad. Sci.*, **A21** 280
118. Krishnan R S, 1945, Raman spectrum of diamond, *Nature (London)*, **155** 171
119. Ramanathan K G, 1945, Infra-red spectrum of diamond, *Nature (London)*, **156** 23
120. Ramachandran G N, 1945, Crystal structure of diamond, *Nature (London)*, **156** 83
121. Krishnan R S, 1946, The second order Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, **A24** 25
122. Krishnan R S, 1946, Thermal expansion of diamond, *Proc. Indian Acad. Sci.*, **A24** 33–44
123. Krishnan R S, 1946, Temperature variations of the Raman frequencies in diamond, *Proc. Indian Acad. Sci.*, **A24** 45
124. Ramachandran G N, 1946, On the crystal symmetry of diamond and its X-ray reflections, *Proc. Indian Acad. Sci.*, **A24** 58–64
125. Ramachandran G N, 1946, On the nature and origin of laminations observed in diamond, *Proc. Indian Acad. Sci.*, **A24** 65–80
126. Ramachandran G N, 1946, The luminescence of diamond excited by X-ray radiation, *Proc. Indian Acad. Sci.*, **A24** 81–94
127. Ramachandran G N, 1946, X-ray topographs of diamond: Part II, *Proc. Indian Acad. Sci.*, **A24** 95–103
128. Ramaseshan S, 1946, The Faraday effect in diamond, *Proc. Indian Acad. Sci.*, **A24** 104–113
129. Ramaseshan S, 1946, The cleavage properties of diamond, *Proc. Indian Acad. Sci.*, **A24** 114–121
130. Ramaseshan S, 1946, A theory of the crystal forms of diamond, *Proc. Indian Acad. Sci.*, **A24** 122–129
131. Ramanathan K G, 1946, Variations in the absorption of infra-red radiation by diamond, *Proc. Indian Acad. Sci.*, **A24** 130
132. Ramanathan K G, 1946, The absorption of ultra-violet radiation by diamond, *Proc. Indian Acad. Sci.*, **A24** 137
133. Ramanathan K G, 1946, The absorption spectrum of diamond in the visible region, *Proc. Indian Acad. Sci.*, **A24** 145
134. Ramanathan K G, 1946, The infra-red absorption spectrum of diamond, *Proc. Indian Acad. Sci.*, **A24** 150–161
135. Achyuthan K, 1946, Local variations in the photoconductivity of diamond, *Proc. Indian Acad. Sci.*, **A24** 162–167
136. Rendall G R, 1946, Geometric patterns of fluorescence in diamond, *Proc. Indian Acad. Sci.*, **A24** 168–175
137. Ramachandran G N and Chandrasekharan V, 1946, Luminescence as "forbidden" electronic transitions in diamond, *Proc. Indian Acad. Sci.*, **A24** 176
138. Chandrasekharan V, 1946, Phosphorescence patterns in diamond, *Proc. Indian Acad. Sci.*, **A24** 182–185
139. Chandrasekharan V, 1946, The thermoluminescence of diamond, *Proc. Indian Acad. Sci.*, **A24** 187–192
140. Chandrasekharan V, 1946, The phosphorescence of diamond, *Proc. Indian Acad. Sci.*, **A24** 193
141. Krishnan R S and Ramanathan K G, 1946, Infra-red absorption spectrum of diamond, *Nature (London)*, **157** 582

142. Krishnan R S, 1947, Raman spectrum of diamond under high resolution, *Nature (London)*, **159** 60, 266
143. Krishnan R S, 1947, Thermal scattering of light in diamond, *Nature (London)*, **159** 740
144. Ramachandran G N, 1947, Photoelastic constants of diamond, *Proc. Indian Acad. Sci.*, **A25** 208–220
145. Krishnan R S, 1947, The scattering of light in diamond and its Raman spectrum, *Proc. Indian Acad. Sci.*, **A26** 399
146. Ramanathan K G, 1947, The infra-red absorption spectrum of diamond and its variations, *Proc. Indian Acad. Sci.*, **A26** 469
147. Ramanathan K G, 1947, The emission and absorption spectra of luminescent diamond, *Proc. Indian Acad. Sci.*, **A26** 479–480
148. Achyuthan K, 1948, Directional variations of the photoconductivity in diamond, *Proc. Indian Acad. Sci.*, **A27** 171–176
149. Chandrasekharan V, 1948, Fluorescence and phosphorescence of diamond at different temperatures, *Proc. Indian Acad. Sci.*, **A27** 316–320
150. Ramachandra Rao S, 1948, Sir C V Raman on his sixtieth birthday, *Proc. Indian Acad. Sci.*, **A28** 253
151. Madhava Rao B S, 1948, Sir C V Raman as physicist and teacher, *Proc. Indian Acad. Sci.*, **A28** 254
152. Krishnan R S, 1948, Sir C V Raman and crystal physics, *Proc. Indian Acad. Sci.*, **A28** 258
153. Krishnan R S, 1948, The theory of vibrations and the Raman spectrum of the diamond lattice, *Proc. Indian Acad. Sci.*, **A28** 307
154. Ramanathan K G, 1948, Theoretical evaluation of the acoustic wave-velocities in diamond, *Proc. Indian Acad. Sci.*, **A28** 370
155. Krishnan R S and Chandrasekharan V, 1950, Thermal scattering of light in crystals: Part I. Quartz, *Proc. Indian Acad. Sci.*, **A31** 427
156. Krishnan R S and Narayanan P S, 1950, Intensity ratio of the Raman lines in diamond, *Proc. Indian Acad. Sci.*, **A32** 352
157. Chandrasekharan V, 1950, Thermal scattering of light in crystals: Part II. Diamond, *Proc. Indian Acad. Sci.*, **A32** 379
158. Chandrasekharan V, 1951, Thermal scattering of light in crystals: Part III. Theory of birefringent crystals, *Proc. Indian Acad. Sci.*, **A33** 183
159. Krishnamurti D, 1951, Evaluation of the elastic constants of diamond from its Raman frequencies, *Proc. Indian Acad. Sci.*, **A33** 325
160. Narayanan P S, 1951, The distribution of intensity in the Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, **A34** 1
161. Krishnamurti P, 1951, Evaluation of the specific heat of diamond from its Raman frequencies, *Proc. Indian Acad. Sci.*, **A34** 121
162. Krishnamurti D, 1954, The Raman spectrum of diamond, *Proc. Indian Acad. Sci.*, **A40** 211
163. Jayaraman A, 1960, The luminescence spectra of diamond, *Proc. Indian Acad. Sci.*, **A52** 189

#### D. Miscellaneous II (General)

164. Seshagiri Rao K, 1920, The magneto-crystalline properties of Indian braumites, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 87
165. Ray B B, 1920, The free and forced convection from heated cylinders in air, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 95
166. Pramanic S C, 1922, An optical study of free and forced convection from thin heated wires in air, *Proc. Indian Assoc. Cultiv. Sci.*, **7** 115
167. Banerji D, 1922, On the chronographic determination of acceleration of gravity, *Proc. Indian Assoc. Cultiv. Sci.*, **8** 51

168. Krishnaiyar N C, 1923, On the fluorescence of didymium in glass, *Proc. Indian Assoc. Cultiv. Sci.*, **8** 217
169. Narayan A L, Gunnaiya M A and Rao K R, 1924, Absorption and dispersion of thallium vapours, *Proc. R. Soc. London*, **A106** 596
170. Subrahmanian G and Gunnaiya D, 1924, On curvature of the spectral lines in a prism spectroscope, *Philos. Mag.*, **48** 896
171. Ramanathan K R, 1925–26, The polarisation of resonance radiation and the duration of excited state, *Proc. Indian Assoc. Cultiv. Sci.*, **9** 93
172. Sur N K and Ghosh R N, 1925, On absorption spectrum of potassium vapour at high temperatures, *Philos. Mag.*, **49** 60
173. Krishnan K S, 1926, Are gaseous molecules orientated in a magnetic field?, *Indian J. Phys.*, **1** 35
174. Vaidyanathan V I, 1926, On the magnetic susceptibilities of gases at low pressures, *Indian J. Phys.*, **1** 183
175. Sur N K and Majumdar K, 1926, On the absorption spectra of aluminium and cobalt, *Philos. Mag.*, **1** 451
176. Sur N K, 1926, On the water-spark absorption spectrum of iron, *Philos. Mag.*, **1** 433, 704
177. Sur N K, 1926, On the arc spectrum of lead, *Philos. Mag.*, **2** 633
178. Ramanathan K R, 1927, On fluctuations of dielectric constants in liquids and theories of molecular scattering of light, *Indian J. Phys.*, **1** 413
179. Sur N K, 1927, On the origin of terms of the spectrum of cobalt, *Philos. Mag.*, **4** 36
180. Vaidyanathan V I, 1927, On the magnetic susceptibilities of vapours of organic liquids, *Phys. Rev.*, **30** 512
181. Rao K R and Narayan A L, 1928, On series in the spark spectra of germanium, *Proc. R. Soc. London*, **A119** 607
182. Vaidyanathan V I, 1928, On the relation of diamagnetic susceptibility in the liquid and vapour states, *Indian J. Phys.*, **2** 135
183. Sreenivasiah B N, 1928, Crystal structure of paranitrotoluene, *Indian J. Phys.*, **2** 151
184. Krishnamurthi P, 1928, The relation between chemical constitution and X-ray diffraction in liquids: Part I, *Indian J. Phys.*, **2** 355
185. Vaidyanathan V I, 1928, On the magnetic susceptibilities of ozonides, *Indian J. Phys.*, **2** 421
186. Ramdas L A, 1928, The spectrum of potassium excited during its spontaneous combustion with chlorine, *Proc. Indian Assoc. Cultiv. Sci.*, **3** 31
187. Vaidyanathan V I, 1928, On the magnetic susceptibilities of ozone, *Indian J. Phys.*, **3** 151
188. Vaidyanathan V I, 1928, On diamagnetism and structure of ethylene, *Indian J. Phys.*, **3** 165
189. Mahanti P C and Sen Gupta D N, 1928, Electric moment and its relation to chemical constitution, *Proc. Indian Assoc. Cultiv. Sci.*, **3** 181
190. Sirkar S C, 1928, The electrical moment of methylchloride, ethylchloride, and chloroform, *Indian J. Phys.*, **3** 197
191. Sirkar S C, 1928, The Kerr effect in viscous liquids due to radio frequency oscillating field, *Indian J. Phys.*, **3** 409
192. Ray B B, 1928, X-ray absorption limits and the distribution of electrons round the atom, *Proc. Indian Assoc. Cultiv. Sci.*, **3** 477
193. Vaidyanathan V I, 1928, On the diamagnetic susceptibilities of gases at low pressures, *Philos. Mag.*, **5** 380
194. Bhagavantam S, 1929, Structure of some organic crystals, *Proc. Inst. Chem. India*
195. Rao K R, 1929, The arc spectrum of germanium, *Proc. R. Soc. London*, **A124** 465
196. Rao K R, 1929, Regularities in the arc spectrum of arsenic, *Proc. R. Soc. London*, **A125** 238
197. Chandrasekhar S, 1929, Generalised form of new statistics, *Phys. Rev.*, **34** 1204
198. Ray B B and Majumdar R G, 1929, Critical potentials of light elements for simultaneous transition, *Nature (London)*, **123** 49
199. Ray B B and Mahanti P C, 1929, Fine structure absorption edges in metals, *Nature (London)*, **123** 528

200. Ghosh P N and Mahanti P C, 1929, The heterodyne null method of measuring dielectric constant, *Nature (London)*, **124** 13
201. Banerji K, 1930, Orientation of the molecules in naphthalene and anthracene crystals, *Proc. Indian Assoc. Cultiv. Sci.*, **5** 557
202. Banerji K, 1930, Structure of naphthalene and anthracene, *Nature (London)*, **125** 456
203. Vaidyanathan V I, 1930, Influence of chemical colloidisation on the anomalous diamagnetism of bismuth and antimony, *Nature (London)*, **125** 672
204. Banerji S K, 1930, Electric field of overhead thunder clouds, *Nature (London)*, **125** 729
205. Ray B B, 1930, Scattering of X-rays by bound electrons, *Nature (London)*, **125** 746
206. Bhagavantam S, 1930, The magnetic and optical properties of the benzene ring and aromatic compounds, *Proc. R. Soc. London*, **A126** 143
207. Lunt R W and Govinda Rau M A, 1930, The variation of the dielectric constant of some organic liquids with frequency in the range 1 to  $10^3$  kilocycles, *Proc. R. Soc. London*, **A126** 213
208. Vaidyanathan V I, 1930, Anomalous diamagnetic and crystal structure, *Indian J. Phys.*, **5** 501
209. Banerji D and Ganguli R, 1931, On the distribution of space-potential in high-frequency glow discharge, *Philos. Mag.*, **11** 410
210. Ramachandra Rao S, 1931, Magnetic susceptibilities of liquid mixtures, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 241
211. Ranganadham S P, 1931, Magnetic susceptibilities of liquid mixtures, *Indian J. Phys.*, **6** 421
212. Ranganathan S, 1931, A note on the scattering of light in urines, *Proc. Indian Assoc. Cultiv. Sci.*, **6** 463
213. Vaidhyanathan V I and Balwanth Singh, 1931, Magnetism of colloidal gold, *Nature (London)*, **128** 87
214. Ramachandra Rao S, 1931, Diamagnetism and the colloidal state, *Nature (London)*, **128** 153
215. Ramdas L A and Venkiteswaran P, 1931, Spectrum of glow-worm, *Nature (London)*, **128** 726
216. Ramachandra Rao S and Sivaramakrishnan G, 1931, Diamagnetism of liquid mixtures, *Nature (London)*, **128** 872
217. Ranganadham S P, 1931, Diamagnetism of liquid mixtures, *Nature (London)*, **128** 975
218. Rao K R, 1931, The third spark spectrum of arsenic (As IV), *Proc. R. Soc. London*, **A134** 604
219. Bhagavantam S, 1932, Electric polarisability and diamagnetic susceptibility of molecules, *Indian J. Phys.*, **7** 617
220. Vaidyanathan V I and Puri B S, 1932, Magnetism of precipitates of colloidal silver, *Nature (London)*, **129** 170
221. Dixit K R, 1933, On an investigation of the orientations in thin evaporated metallic films by the method of electron diffraction, *Philos. Mag.*, **16** 1049
222. Ramachandra Rao S, 1933, Ferromagnetism of nickel colloids, *Phys. Rev.*, **44** 850
223. Govinda Rau M A and Narayanaswamy B N, 1934, The effect of the solvent in dipole moment measurements: the moment of ethylene bromide, *Proc. Indian Acad. Sci.*, **A1** 14
224. Narasimhaih G, 1934, The refractivity of liquid mixtures, *Proc. Indian Acad. Sci.*, **A1** 34–38
225. Venkatachala Iyengar K, 1934, On the validity of the Raman–Banerjee analysis of the pianoforte hammer problem, *Proc. Indian Acad. Sci.*, **A1** 60
226. Subbaramaiya D S, 1934, Dielectric constants of liquids and liquid mixtures, *Proc. Indian Acad. Sci.*, **A1** 355
227. Govinda Rau M A, 1935, Theory of the solvent effect in dipole moment measurements, *Proc. Indian Acad. Sci.*, **A1** 498
228. Bhatt N B, 1935, High frequency spectrum of mercury vapour, *Proc. Indian Acad. Sci.*, **A1** 891
229. Govinda Rau M A and Satyanarayana Rao S, 1935, On the dipole moment of tetralin, *Proc. Indian Acad. Sci.*, **A2** 232
230. Vaidya W M, 1935, The flame spectra of some aromatic compounds, *Proc. Indian Acad. Sci.*, **A2** 352
231. Ramaswamy K L, 1935, Dielectric coefficients of volatile compounds of fluorine and boron–carbon tetrafluoride, nitrogen trifluoride, fluoroform, carbon-nitrogen compound of fluorine

- $(CF_3N)_2$  boron hexahydride and nitrogenous boron hydride  $B_3N_3H_6$ , *Proc. Indian Acad. Sci.*, **A2** 364
232. Ramaswamy K L, 1935, Refractive indices and dispersion of volatile compounds of fluorine and boron. Carbon tetrafluoride, nitrogen trifluoride, fluoroform, carbon-nitrogen compound of fluorine  $(CF_3N)_2$ , boron hexahydride and nitrogenous boronhydride  $B_3N_3H_6$ , *Proc. Indian Acad. Sci.*, **A2** 630
233. Max Born, 1936, Unitary theory of field and matter I. Classical treatment charge particle with magnetic rest moment, *Proc. Indian Acad. Sci.*, **A3** 8
234. Max Born and Nagendra Nath N S, 1936, The neutrino theory of light, *Proc. Indian Acad. Sci.*, **A3** 318
235. Ramaswamy K L, 1936, Dielectric coefficients of gases and vapours: substituted methanes and ethane, cyclopropane, ethylene oxide and benzene, *Proc. Indian Acad. Sci.*, **A4** 108
236. Madhava Rao B S, 1936, Ring singularity in Born's unitary theory-I, *Proc. Indian Acad. Sci.*, **A4** 355
237. Madhava Rao B S, 1936, A theorem on action functions in Born's field theory, *Proc. Indian Acad. Sci.*, **A4** 377
238. Nilakantan P, 1936, The magnetic anisotropy of rhombic sulphur, *Proc. Indian Acad. Sci.*, **A4** 419
239. Rama Swamy S, 1936, The structure of thin metallic films, *Proc. Indian Acad. Sci.*, **A4** 656
240. Krishnan R S, 1936, X-ray diffraction and electrolytic dissociation—I sulphuric acid and sulphates, *Proc. Indian Acad. Sci.*, **A4** 661
241. Ramaswamy K L, 1936, Refractive indices and dispersions of gases and vapours—substituted methanes and ethane, cyclopropane, ethylene oxide and benzene, *Proc. Indian Acad. Sci.*, **A4** 675
242. Govinda Rau M A, 1936, The dipole moment and structure of pyrones 2–6 dimethyl-gamma-pyrone, xanthone and coumarin, *Proc. Indian Acad. Sci.*, **A4** 687
243. Madhava Rao B S, 1937, On the fine structure of the Balmer lines, *Proc. Indian Acad. Sci.*, **A5** 56
244. Govinda Rau M A and Anantanarayanan N, 1937, The dipole moment and structure of some cyclic anhydrides: Phthalic succinic and citraconic anhydrides, *Proc. Indian Acad. Sci.*, **A5** 185
245. Padmanabhan R, 1937, The fluorescence of acetone vapour, *Proc. Indian Acad. Sci.*, **A5** 594
246. Vaidya W M, 1937, The flame spectra of some aliphatic halides—Part I. Methyl iodide, *Proc. Indian Acad. Sci.*, **A6** 122
247. Ramaswamy K L, 1937, Dielectric polarisation and form of the carbon dioxide molecule, *Curr. Sci.*, **6** 153
248. Ramaswamy K L, 1937, Dielectric polarisation and the form of the carbon dioxide molecule, *Proc. Indian Acad. Sci.*, **A6** 301
249. Nilakantan P, 1937, Temperature variation of magnetic anisotropy of organic crystals, *Nature (London)*, **140** 29
250. Nagendra Nath N S, 1937, Beta decay as due to a neutrino shower, *Nature (London)*, **140** 278
251. Oke B Y, 1938, The electro-static forces and elasticity constants, *Proc. Indian Acad. Sci.*, **A7** 265
252. Madhava Rao B S, 1938, Question of invariance in the neutrino theory of light, *Proc. Indian Acad. Sci.*, **A7** 293–295
253. Madhava Rao B S, 1938, Prefatory note to the special number, *Proc. Indian Acad. Sci.*, **A8** 249–250
254. Srinivasan P S, 1940, Ultra-violet irradiation of rubber, *Proc. Indian Acad. Sci.*, **A10** 186
255. Subrahmanian R V, 1941, The spectral character of the reflection by a regularly stratified medium—Part I., *Proc. Indian Acad. Sci.*, **A13** 467
256. Sarabhai Vikram, 1942, The time distribution of cosmic rays, *Proc. Indian Acad. Sci.*, **A15** 89
257. Chelam E V, 1942, Application of tensor analysis to molecular anisotropy, *Proc. Indian Acad. Sci.*, **A15** 190–194
258. Satynarayana B S, 1942, The fluorescence of uranyl compounds and the Raman spectrum of the uranyl ion, *Proc. Indian Acad. Sci.*, **A15** 414

259. Ramachandran G N, 1942, Reflection of light by a periodically stratified medium, *Proc. Indian Acad. Sci.*, **A16** 336
260. Ramachandran G N, 1943, Fluctuations of light intensity in coronae formed by diffraction, *Proc. Indian Acad. Sci.*, **A18** 190
261. Ramachandran G N, 1944, A new derivation of the Darwin–Prins formula of X-ray reflection, *Proc. Indian Acad. Sci.*, **A20** 100
262. Kathavate Y V, 1945, The diffraction of light by an assembly of opaque circular disks, *Proc. Indian Acad. Sci.*, **A21** 233
263. Pant D D, 1945, Some studies in the spectra of single uranyl halides and other uranyl salts, *Proc. Indian Acad. Sci.*, **A22** 95
264. Chandrasekhar S, 1953, Theoretical interpretation of the optical activity of quartz, *Proc. Indian Acad. Sci.*, **A37** 468
265. Jayaraman A, 1953, The structure and optical behaviour of chalcedony, *Proc. Indian Acad. Sci.*, **A38** 441
266. Pancharatnam S, 1954, On the pleochroism of amethyst quartz and its absorption spectra, *Proc. Indian Acad. Sci.*, **A40** 196
267. Jayaraman A, 1957, Optical properties and unit cell parameters of nickel nitrate hexahydrate, *Proc. Indian Acad. Sci.*, **A45** 263
268. Viswanathan K S, 1958, Anharmonicity of vibration in molecules, *Proc. Indian Acad. Sci.*, **A47** 85
269. Jayaraman A, 1958, Reciprocal lattice photography, *Proc. Indian Acad. Sci.*, **A47** 142
270. Jayaraman A, 1958, Unit cell parameters, space-group and optical properties of cobalt nitrate hexahydrate, *Proc. Indian Acad. Sci.*, **A47** 147
271. Viswanathan K S, 1959, The relativistic theory of chemical binding, *Proc. Indian Acad. Sci.*, **A50** 1
272. Viswanathan K S, 1960, The Dirac equation for many-electron systems, *Proc. Indian Acad. Sci.*, **A52** 35
273. Viswanathan K S, 1961, The correlated Hartree–Fock equations and the generalized density matrices, *Proc. Indian Acad. Sci.*, **A53** 169

## **Author index of papers from C V Raman's laboratory**

### **Volume IV**

(The numbers against the names indicate the serial number in the list of papers)

- Achyuthan K 135, 148  
Anand V B 85  
Anantanarayanan N 244  
Anna Mani 97, 110, 112, 115, 117
- Balwant Singh 213  
Banerjee D 167  
Banerjee K 12  
Banerji D 14, 18, 209  
Banerji K 201, 202  
Banerji S K 204  
Barkat Ali 8  
Bhagavantam S 68, 69, 70, 111, 194, 206, 219  
Bhargava S 6  
Bhatt N V 228  
Born Max 233, 234
- Chandrasekhar S 197, 264  
Chandrasekharan V 137, 138, 139, 140, 149,  
155, 157, 158  
Chelam E V 88, 92, 257
- Das P 10, 13, 15, 17  
Datta S K 14, 17  
Dayal Bisheshwar 96, 113  
Dey J N 9  
Dixit K R 221
- Ganguli R 18, 209  
Ghosh M M 21  
Ghosh P N 14, 200  
Ghosh R N 1, 6, 7, 9, 19, 23, 172  
Govinda Rau M A 207, 223, 227, 229, 242,  
244  
Gunnaiya D 170  
Gunnaiya M A 169
- Hariharan P S 99
- Jayaraman A 65, 163, 265, 267, 269, 270
- Kathavate Y V 263  
Krishnaiyar N C 168  
Krishnamurti D 64, 159, 162  
Krishnamurti P 162  
Krishnan K S 52, 173  
Krishnan M S 46, 50, 52  
Krishnan R S 90, 95, 103, 116, 118, 121, 122,  
123, 141, 142, 143, 145, 152, 153, 155, 156,  
240
- Lunt R W 207
- Madhava Rao B S 151, 236, 237, 243, 252, 253  
Mahadevan C 40, 42, 44, 45, 46, 47, 48, 50, 51  
Mahadevan P C 46  
Mahanti P C 189, 199, 200  
Majumdar K 175  
Majumdar R G 198  
Mohammad Hoji Ghulam 23
- Narasimhaih G 223  
Narayan A L 3, 169, 181  
Narayanan P S 156, 160  
Narayanaswamy B N 223  
Nath N S Nagendra 71, 72, 73, 74, 75, 94, 234,  
250  
Nayar P G N 77, 78, 79, 80, 86, 87  
Nilakantan P 32, 33, 35, 56, 238, 249
- Oke B Y 55, 251
- Padmanabhan R 245  
Pancharatnam S 266  
Pant D D 91, 106, 107, 263  
Paramasivan S 43  
Pisharoty P Rama 30, 76, 81, 82, 83, 84  
Pramanic S C 166  
Puri B S 220
- Rajagopalan V S 53

- Ramachandran G N 89, 93, 101, 104, 114, 120, 124, 125, 126, 127, 137, 144, 259, 260, 261  
Ramachandra Rao S 150, 210, 214, 216, 222  
Ramanathan K G 119, 131, 132, 133, 134, 141, 146, 147, 154  
Ramanathan K R 5, 26, 171, 178  
Ramaseshan S 62, 63, 108, 128, 129, 130  
Ramaswamy C 66, 67  
Ramaswamy K L 231, 232, 235, 241, 247, 248  
Rama Swamy S 29, 31, 54, 239  
Ramdas A K 37, 38, 39  
Ramdas L A 11, 25, 186, 215  
Ranganadham S P 211, 217  
Ranganathan S 49, 212  
Rao K R 169, 181, 195, 196, 218  
Ray B B 24, 165, 192, 198, 199, 205  
Rendall G R 102, 136  
Roy B B 4  
  
Sakseña B D 109  
Sarabhai Vikram 256  
Satyanarayana B S 258  
Satyanarayana Rao S 229  
  
Sen Gupta D N 189  
Seshagiri Rao K 2, 164  
Sigamony A 57, 58, 59, 60, 61, 105  
Sirkar S C 28, 190, 191  
Sreenivasiah B N 183  
Srinivasa Iyengar K Y 54  
Srinivasan P S 34, 254  
Subbaramaiya D S 226  
Subrahmanian R V 255  
Subrahmanyam G 3, 171  
Sunanda Bai K 98, 100  
Sur N K 41, 172, 175, 176, 177, 179  
  
Thosar B V 36  
  
Vaidya W M 230, 246  
Vaidyanathan V I 174, 180, 182, 185, 187, 188, 193, 203, 208, 213, 220  
Venkatachala Iyengar K 225  
Venkatarama Iyer M P 20  
Venkataraman S 22  
Venkateswaran S 16, 27  
Viswanathan K S 268, 271, 272, 273

# Consolidated list of C V Raman's scientific papers

## Volumes I–VI

### Volume I. Scattering of Light

1. THE DOPPLER EFFECT IN THE MOLECULAR SCATTERING OF RADIATION [1919 *Nature (London)* **103** 165]
2. ON THE TRANSMISSION COLOURS OF SULPHUR SUSPENSIONS [1921 *Proc. R. Soc. London A* **100** 102; with B B Ray]
3. A METHOD OF IMPROVING VISIBILITY OF DISTANT OBJECTS [1921 *Nature (London)* **108** 242]
4. THE COLOUR OF THE SEA [1921 *Nature (London)* **108** 367]
5. THE MOLECULAR SCATTERING OF LIGHT IN LIQUIDS AND SOLIDS [1921 *Nature (London)* **108** 402]
6. ON THE MOLECULAR SCATTERING OF LIGHT IN WATER AND THE COLOUR OF THE SEA [1922 *Proc. R. Soc. London A* **101** 64]
7. OPTICAL OBSERVATIONS OF THE THERMAL AGITATION OF THE ATOMS IN CRYSTALS [1922 *Nature (London)* **109** 42]
8. ANISOTROPY OF MOLECULES [1922 *Nature (London)* **109** 75]
9. MOLECULAR STRUCTURE OF AMORPHOUS SOLIDS [1922 *Nature (London)* **109** 138]
10. MOLECULAR DIFFRACTION OF LIGHT [1922 The Calcutta University Press 103 pages]
11. DIFFRACTION BY MOLECULAR CLUSTERS AND THE QUANTUM STRUCTURE OF LIGHT [1922 *Nature (London)* **109** 444]
12. MOLECULAR AELOTROPY IN LIQUIDS [1922 *Nature (London)* **110** 11]
13. OPALESCENCE PHENOMENA IN LIQUID MIXTURES [1922 *Nature (London)* **110** 77]
14. TRANSPARENCY OF LIQUIDS AND COLOUR OF THE SEA [1922 *Nature (London)* **110** 280]
15. THERMAL OPALESCENCE IN CRYSTALS AND THE COLOUR OF ICE IN GLACIERS [1923 *Nature (London)* **111** 13]
16. ON THE MOLECULAR SCATTERING OF LIGHT IN DENSE VAPOURS AND GASES [1923 *Philos. Mag.* **45** 113; with K R Ramanathan]
17. ON THE MOLECULAR SCATTERING AND EXTINCTION OF LIGHT IN LIQUIDS AND THE DETERMINATION OF THE AVOGADRO CONSTANT [1923 *Philos. Mag.* **45** 625; with K Seshagiri Rao]
18. THE MOLECULAR SCATTERING OF LIGHT IN LIQUID MIXTURES [1923 *Philos. Mag.* **45** 213; with K R Ramanathan]
19. ON THE POLARIZATION OF THE LIGHT SCATTERED BY GASES AND VAPOURS [1923 *Philos. Mag.* **46** 426; with K Seshagiri Rao]
20. THE MOLECULAR SCATTERING OF LIGHT IN CARBON DIOXIDE AT HIGH PRESSURES [1923 *Proc. R. Soc. London A* **104** 357; with K R Ramanathan]
21. THE SCATTERING OF LIGHT BY ANISOTROPIC MOLECULES [1923 *Nature (London)* **112** 165]
22. THE STRUCTURE OF MOLECULES IN RELATION TO THEIR OPTICAL ANISOTROPY [1924 *Nature (London)* **114** 49]
23. THE SCATTERING OF LIGHT BY LIQUID AND SOLID SURFACES [1923 *Nature (London)* **112** 281]
24. RELATION OF TYNDALL EFFECT TO OSMOTIC PRESSURE IN COLLOIDAL SOLUTIONS [1927 *Indian J. Phys.* **2** 1]
25. THE SCATTERING OF X-RAYS IN LIQUIDS [1923 *Nature (London)* **111** 185]
26. THE NATURE OF THE LIQUID STATE [1923 *Nature (London)* **111** 428]

27. THE DIFFRACTION OF X-RAYS IN LIQUIDS, LIQUID MIXTURES, SOLUTIONS, FLUID CRYSTALS AND AMORPHOUS SOLIDS [1923 *Proc. Indian Assoc. Cultiv. Sci.* **8** 127; with K R Ramanathan]
28. ON THE MEAN DISTANCE BETWEEN NEIGHBOURING MOLECULES IN A FLUID [1924 *Philos. Mag.* **47** 671]
29. THE SCATTERING OF LIGHT BY LIQUID BOUNDARIES AND ITS RELATION TO SURFACE TENSION—PART I [1925 *Proc. R. Soc. London* **A108** 561; with L A Ramdas]
30. THE SCATTERING OF LIGHT BY LIQUID BOUNDARIES AND ITS RELATION TO SURFACE TENSION—PART II [1925 *Proc. R. Soc. London* **A109** 150; with L A Ramdas]
31. THE SCATTERING OF LIGHT BY LIQUID BOUNDARIES AND ITS RELATION TO SURFACE TENSION—PART III [1925 *Proc. R. Soc. London* **A109** 272; with L A Ramdas]
32. DIE ZERSTREUUNG DES LICHTES DURCH DIELEKTRISCHE KÜGELN (*German*) [1925 *Z. Phys* **33** 870]
33. ON THE THICKNESS OF THE OPTICAL TRANSITION LAYER IN LIQUID SURFACES [1927 *Philos. Mag.* **3** 220; with L A Ramdas]
34. THE BIREFRINGENCE OF CRYSTALLINE CARBONATES, NITRATES AND SULPHATES [1926 *Nature (London)* **118** 264]
35. THE ELECTRICAL POLARITY OF MOLECULES [1926 *Nature (London)* **118** 302; with K S Krishnan]
36. MAGNETIC DOUBLE-REFRACTION IN LIQUIDS, PART I: BENZENE AND ITS DERIVATIVES [1927 *Proc. R. Soc. London* **A113** 511; with K S Krishnan]
37. ELECTRIC DOUBLE-REFRACTION IN RELATION TO THE POLARITY AND OPTICAL ANISOTROPY OF MOLECULES, PART I: GASES AND VAPOURS [1927 *Philos. Mag.* **3** 713; with K S Krishnan]
38. ELECTRIC DOUBLE-REFRACTION IN RELATION TO THE POLARITY AND OPTICAL ANISOTROPY OF MOLECULES, PART II: LIQUIDS [1927 *Philos. Mag.* **3** 724; with K S Krishnan]
39. DISAPPEARANCE AND REVERSAL OF THE KERR EFFECT [1928 *Nature (London)* **121** 794; with S C Sirkar]
40. OPTIQUE—LA CONSTANTE DE BIREFRINGENCE MAGNETIQUE DU BENZENE (*French*) [1927 *C. R. Acad. Sci. Paris* **184** 449; with K S Krishnan]
41. MAGNETIC DOUBLE REFRACTION [1927 *Nature (London)* **119** 528; with I Ramakrishna Rao]
42. THE MAGNETIC ANISOTROPY OF CRYSTALLINE NITRATES AND CARBONATES [1927 *Proc. R. Soc. London* **A115** 549; with K S Krishnan]
43. A THEORY OF ELECTRIC AND MAGNETIC BIREFRINGENCE IN LIQUIDS [1927 *Proc. R. Soc. London* **A117** 1; with K S Krishnan]
44. A THEORY OF THE OPTICAL AND ELECTRICAL PROPERTIES OF LIQUIDS [1928 *Proc. R. Soc. London* **A117** 589; with K S Krishnan]
45. THE MAXWELL EFFECT IN LIQUIDS [1927 *Nature (London)* **120** 726; with K S Krishnan]
46. A THEORY OF THE BIREFRINGENCE INDUCED BY FLOW IN LIQUIDS [1928 *Philos. Mag.* **5** 769; with K S Krishnan]
47. THE SCATTERING OF LIGHT IN AMORPHOUS SOLIDS [1927 *J. Opt. Soc. Am.* **15** 185]
48. THE MOLECULAR SCATTERING OF LIGHT IN A BINARY LIQUID MIXTURE [1927 *Philos. Mag.* **4** 447]
49. A THEORY OF LIGHT-SCATTERING IN LIQUIDS [1929 *Philos. Mag.* **5** 498; with K S Krishnan]
50. THE THEORY OF LIGHT-SCATTERING IN LIQUIDS [1929 *Philos. Mag.* **7** 160]
51. OPTICAL BEHAVIOUR OF PROTEIN SOLUTIONS [1927 *Nature (London)* **120** 158]
52. X-RAY DIFFRACTION IN LIQUIDS [1927 *Nature (London)* **119** 601; with C M Sogani]
53. X-RAY DIFFRACTION IN LIQUIDS [1927 *Nature (London)* **120** 514; with C M Sogani]
54. THERMAL DEGENERATION OF THE X-RAY HALOES IN LIQUIDS [1927 *Nature (London)* **120** 770]
55. A CRITICAL-ABSORPTION PHOTOMETER FOR THE STUDY OF THE COMPTON EFFECT [1928 *Proc. R. Soc. London* **A119** 526; with C M Sogani]

56. THERMODYNAMICS, WAVE-THEORY AND THE COMPTON EFFECT [1927 *Nature (London)* **120** 950]
57. A CLASSICAL DERIVATION OF THE COMPTON EFFECT [1928 *Indian J. Phys.* **3** 357]
58. A NEW TYPE OF SECONDARY RADIATION [1928 *Nature (London)* **121** 501; with K S Krishnan]
59. A CHANGE OF WAVELENGTH IN LIGHT-SCATTERING [1928 *Nature (London)* **121** 619]
60. A NEW RADIATION [1928 *Indian J. Phys.* **2** 387]
61. THE OPTICAL ANALOGUE OF THE COMPTON EFFECT [1928 *Nature (London)* **121** 711; with K S Krishnan]
62. A NEW CLASS OF SPECTRA DUE TO SECONDARY RADIATION, PART I [1928 *Indian J. Phys.* **2** 399; with K S Krishnan]
63. THE NEGATIVE ABSORPTION OF RADIATION [1928 *Nature (London)* **122** 12; with K S Krishnan]
64. POLARIZATION OF SCATTERED LIGHT-QUANTA [1928 *Nature (London)* **122** 169; with K S Krishnan]
65. MOLECULAR SPECTRA IN THE EXTREME INFRARED [1928 *Nature (London)* **122** 278; with K S Krishnan]
66. THE PRODUCTION OF NEW RADIATIONS BY LIGHT SCATTERING—PART I [1929 *Proc. R. Soc. London A* **122** 23; with K S Krishnan]
67. ROTATION OF MOLECULES INDUCED BY LIGHT [1928 *Nature (London)* **122** 882; with K S Krishnan]
68. INVESTIGATIONS OF THE SCATTERING OF LIGHT [1929 *Nature (London)* **123** 50]
69. THE RAMAN EFFECT: INVESTIGATION OF MOLECULAR STRUCTURE BY LIGHT SCATTERING [1929 *Trans. Faraday Soc.* **25** 781]
70. THE MOLECULAR SCATTERING OF LIGHT, NOBEL LECTURE DELIVERED AT STOCKHOLM, 11th December 1930
71. COLOUR AND OPTICAL ANISOTROPY OF ORGANIC COMPOUNDS [1929 *Nature (London)* **123** 494]
72. MAGNETIC BEHAVIOUR OF ORGANIC CRYSTALS [1929 *Nature (London)* **123** 605]
73. THE RELATION BETWEEN COLOUR AND MOLECULAR STRUCTURE IN ORGANIC COMPOUNDS [1929 *Indian J. Phys.* **4** 57; with S Bhagavantam]
74. DIAMAGNETISM AND CRYSTAL STRUCTURE [1929 *Nature (London)* **123** 945]
75. A NEW X-RAY EFFECT [1929 *Nature (London)* **124** 53; with P Krishnamurti]
76. ANOMALOUS DIAMAGNETISM [1929 *Nature (London)* **124** 412]
77. DIAMAGNETISM AND MOLECULAR STRUCTURE [1930 *Proc. Phys. Soc.* **42** 309]
78. A NEW TYPE OF MAGNETIC BIREFRINGENCE [1931 *Nature (London)* **128** 758; with S W Chinchalkar]
79. ATOMS AND MOLECULES AS FITZGERALD OSCILLATORS [1931 *Nature (London)* **128** 795]
80. EVIDENCE FOR THE SPIN OF THE PHOTON FROM LIGHT-SCATTERING [1931 *Nature (London)* **128** 114; with S Bhagavantam]
81. THE ANGULAR MOMENTUM OF LIGHT [1931 *Nature (London)* **128** 545]
82. EXPERIMENTAL PROOF OF THE SPIN OF THE PHOTON [1931 *Indian J. Phys.* **6** 353; with S Bhagavantam]
83. EXPERIMENTAL PROOF OF THE SPIN OF THE PHOTON [1932 *Nature (London)* **129** 22; with S Bhagavantam]
84. DOPPLER EFFECT IN LIGHT-SCATTERING [1931 *Nature (London)* **128** 636]
85. NATURE OF THE THERMAL AGITATION IN LIQUIDS [1935 *Nature (London)* **135** 761; with B V Raghavendra Rao]
86. ACOUSTIC SPECTRUM OF LIQUIDS [1937 *Nature (London)* **139** 584; with B V Raghavendra Rao]
87. LIGHT SCATTERING AND FLUID VISCOSITY [1938 *Nature (London)* **141** 242; with B V Raghavendra Rao]
88. NEW METHODS IN THE STUDY OF LIGHT SCATTERING, PART I: BASIC IDEAS [1941 *Proc. Indian Acad. Sci. A* **14** 228]

89. DETERMINATION OF THE ADIABATIC PIEZO-OPTIC COEFFICIENT OF LIQUIDS [1939 *Proc. R. Soc. London A171* 137; with K S Venkataraman]
90. SPECTROSCOPIC INVESTIGATION OF THE SOLID AND LIQUID STATES [1942 *Curr. Sci.* 11 225]
91. THE NATURE OF THE LIQUID STATE [1942 *Curr. Sci.* 11 303]
92. THE  $\alpha - \beta$  TRANSFORMATION OF QUARTZ [1940 *Nature (London)* 145 147; with T M K Nedangadi]
93. LATTICE OSCILLATIONS IN CRYSTALS [1939 *Nature (London)* 143 679; with T M K Nedungadi]
94. SCATTERING OF LIGHT IN CRYSTALS [1945 *Nature (London)* 155 396]

## Volume II. Acoustics

### 1. Vibrations and Wave Motions

95. THE SMALL MOTION AT THE NODES OF A VIBRATING STRING [1909 *Nature (London)* 82 9]
96. THE MAINTENANCE OF FORCED OSCILLATIONS OF A NEW TYPE (1909 *Nature (London)* 82 156)
97. THE MAINTENANCE OF FORCED OSCILLATIONS [1910 *Nature (London)* 82 428]
98. PHOTOGRAPHS OF VIBRATION CURVES [1911 *Philos. Mag.* 21 615]
99. REMARKS ON A PAPER BY J S STOKES ON "SOME CURIOUS PHENOMENA OBSERVED IN CONNECTION WITH MELDE'S EXPERIMENT" [1911 *Phys. Rev.* 32 307]
100. THE SMALL MOTION AT THE NODES OF A VIBRATING STRING [1911 *Phys. Rev.* 32 309]
101. THE MAINTENANCE OF FORCED OSCILLATIONS OF A NEW TYPE [1912 *Philos. Mag.* 24 513]
102. SOME REMARKABLE CASES OF RESONANCE [1912 *Phys. Rev.* 35 449]
103. EXPERIMENTAL INVESTIGATIONS ON THE MAINTENANCE OF VIBRATIONS [1912 *Bull. Indian Assoc. Cultiv. Sci.* 6, 1]
104. SOME ACOUSTICAL OBSERVATIONS [1913 *Bull. Indian Assoc. Cultiv. Sci.* 8 17]
105. THE MAINTENANCE OF VIBRATIONS [1914 *Phys. Rev.* 4 12]
106. ON MOTION IN A PERIODIC FIELD OF FORCE [1914 *Bull. Indian Assoc. Cultiv. Sci.* 11 25]
107. ON MOTION IN A PERIODIC FIELD OF FORCE [1915 *Philos. Mag.* 29 15]
108. THE MAINTENANCE OF VIBRATIONS BY A PERIODIC FIELD OF FORCE [1917 *Philos. Mag.* 34 129; with A Dey]
109. ON THE MAINTENANCE OF COMBINATIONAL VIBRATIONS BY TWO SIMPLE HARMONIC FORCES [1915 *Phys. Rev.* 5 1]
110. ON DISCONTINUOUS WAVE-MOTION, Part I [1916 *Philos. Mag.* 31 47; with S Appaswamaiyar]
111. ON DISCONTINUOUS WAVE-MOTION, Part II [1917 *Philos. Mag.* 33 203; with A Dey]
112. ON DISCONTINUOUS WAVE-MOTION, Part III [1917 *Philos. Mag.* 33 352; with A Dey]
113. AN EXPERIMENTAL METHOD FOR THE PRODUCTION OF VIBRATIONS [1919 *Phys. Rev.* 14 446]
114. A NEW METHOD FOR THE ABSOLUTE DETERMINATION OF FREQUENCY [1919 *Proc. R. Soc. London A95* 533; with A Dey]
115. WHISPERING GALLERY PHENOMENA AT ST. PAUL'S CATHEDRAL [1921 *Nature (London)* 108 42; with G A Sutherland]

116. ON THE WHISPERING GALLERY PHENOMENON [1922 *Proc. R. Soc. London* A100 424; with G A Sutherland]
117. ON WHISPERING GALLERIES [1922 *Bull. Indian Assoc. Cultiv. Sci.* 7 159]
118. ON THE SOUNDS OF SPLASHES [1920 *Philos. Mag.* 39 145; with A Dey]
119. THE NATURE OF VOWEL SOUNDS [1921 *Nature (London)* 107 332]

## 2. Musical Instruments—The Violin and the Pianoforte

120. THE DYNAMICAL THEORY OF THE MOTION OF BOWED STRINGS [1914 *Bull. Indian Assoc. Cultiv. Sci.* 11 43]
121. ON THE “WOLF-NOTE” OF THE VIOLIN AND ’CELLO [1916 *Nature (London)* 97 362]
122. ON THE “WOLF NOTE” IN THE BOWED STRINGED INSTRUMENTS [1916 *Philos. Mag.* 32 391]
123. ON THE ALTERATIONS OF TONE PRODUCED BY A VIOLIN “MUTE” [1917 *Nature (London)* 100 84]
124. ON THE “WOLF-NOTE” IN BOWED STRINGED INSTRUMENTS [1918 *Philos. Mag.* 35 493]
125. THE “WOLF-NOTE” IN PIZZICATO PLAYING [1918 *Nature (London)* 101 264]
126. ON THE MECHANICAL THEORY OF THE VIBRATIONS OF BOWED STRINGS AND OF MUSICAL INSTRUMENTS OF THE VIOLIN FAMILY, WITH EXPERIMENTAL VERIFICATION OF THE RESULTS—Part I [1918 *Bull. Indian Assoc. Cultiv. Sci.* 15 1]
127. ON THE PARTIAL TONES OF BOWED STRINGED INSTRUMENTS [1919 *Philos. Mag.* 38 573]
128. THE KINEMATICS OF BOWED STRINGS [1919 *J. Dept. of Sci., Univ. Calcutta* 1 15]
129. ON A MECHANICAL VIOLIN-PLAYER FOR ACOUSTICAL EXPERIMENTS [1920 *Philos. Mag.* 39 535]
130. EXPERIMENTS WITH MECHANICALLY-PLAYED VIOLINS [1920 *Proc. Indian Assoc. Cultiv. Sci.* 6 19]
131. THE THEORY OF THE CYCLICAL VIBRATIONS OF A BOWED STRING [1918 *Bull. Indian Assoc. Cultiv. Sci.* 5 1]
132. THE SUBJECTIVE ANALYSIS OF MUSICAL TONES [1926 *Nature (London)* 117 450]
133. ON KAUFMANN’S THEORY OF THE IMPACT OF THE PIANOFORTE HAMMER [1920 *Proc. R. Soc. London* A97 99; with B Banerji]

## 3. Musical Instruments of India

134. ‘THE ECTARA’, [1909 *J. Indian Math. Club* 170]
135. OSCILLATIONS OF THE STRETCHED STRINGS [1910 *J. Indian Math. Club* 14]
136. MUSICAL DRUMS WITH HARMONIC OVERTONES [1920 *Nature (London)*, 104 500; with S Kumar]
137. THE INDIAN MUSICAL DRUMS [1935 *Proc. Indian Acad. Sci. A1* 179]
138. ON SOME INDIAN STRINGED INSTRUMENTS [1921 *Proc. Indian Assoc. Cultiv. Sci.* 7 29]
139. THE ACOUSTICAL KNOWLEDGE OF THE ANCIENT HINDUS, Asutosh Mookerjee Silver Jubilee Volume, (Calcutta: University Press)[1922 2 179]

## 4. Monograph

140. MUSICAL INSTRUMENTS AND THEIR TONES [1927 *Handb. Phys.* 8 354]

## 5. Ultrasonics

141. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART I [1936 *Proc. Indian Acad. Sci. A* 2 406; with N S Nagendra Nath]
142. THE DIFFRACTION OF LIGHT BY SOUND WAVES OF HIGH FREQUENCY: PART II [1936 *Proc. Indian Acad. Sci. A* 2 413; with N S Nagendra Nath]
143. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART III, DOPPLER EFFECT AND COHERENCE PHENOMENA [1936 *Proc. Indian Acad. Sci. A* 3 75; with N S Nagendra Nath]
144. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART IV, GENERALISED THEORY [1936 *Proc. Indian Acad. Sci. A* 3 119; with N S Nagendra Nath]
145. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART V. GENERAL CONSIDERATIONS—OBLIQUE INCIDENCE AND AMPLITUDE CHANGES [1936 *Proc. Indian Acad. Sci. A* 3 459; with N S Nagendra Nath]
146. DIFFRACTION OF LIGHT BY ULTRASONIC WAVES [1936 *Nature (London)* 138 616; with N S Nagendra Nath]
147. NATURE OF THE THERMAL AGITATION IN LIQUIDS [1935 *Nature (London)* 135 761; with B V Raghavendra Rao]
148. ACOUSTIC SPECTRUM OF LIQUIDS [1937 *Nature (London)* 139 584; with B V Raghavendra Rao]
149. LIGHT SCATTERING AND FLUID VISCOSITY [1938 *Nature (London)* 141 242; with B V Raghavendra Rao]

## Volume III. Optics

150. UNSYMMETRICAL DIFFRACTION-BANDS DUE TO A RECTANGULAR APERTURE [1906 *Philos. Mag.* 12 494]
151. NEWTON'S RINGS IN POLARISED LIGHT [1907 *Nature (London)* 76 637]
152. SECONDARY WAVES OF LIGHT [1908 *Nature (London)* 78 55]
153. HISTORICAL NOTE ON THE DISCOVERY OF THE ULMRAMICROSCOPIC METHOD [1909 *Philos. Mag.* 17 495]
154. THE EXPERIMENTAL STUDY OF HUYGENS'S SECONDARY WAVES [1909 *Philos. Mag.* 17 204]
155. THE PHOTOMETRIC MEASUREMENT OF THE OBLIQUITY FACTOR OF DIFFRACTION [1909 *Nature (London)* 82 69]
156. THE PHOTOMETRIC MEASUREMENT OF THE OBLIQUITY FACTOR OF DIFFRACTION [1911 *Philos. Mag.* 21 618]
157. ON INTERMITTENT VISION [1915 *Philos. Mag.* 30 701]
158. THE COLOURS OF THE STRIAE IN MICA [1918 *Nature (London)* 102 205; with P N Ghosh]
159. ON THE DIFFRACTION FIGURES DUE TO AN ELLIPTIC APERTURE [1919 *Phys. Rev.* 13 259]
160. THE SCATTERING OF LIGHT IN THE REFRACTIVE MEDIA OF THE EYE [1919 *Philos. Mag.* 38 568]
161. THE "RADIANT" SPECTRUM [1921 *Nature (London)* 108 12]
162. THE "RADIANT" SPECTRUM [1922 *Nature (London)* 109 175]
163. ON THE PHENOMENON OF THE "RADIANT SPECTRUM" OBSERVED BY SIR DAVID BREWSTER [1922 *Philos. Mag.* 43 357]
164. ON THE COLOURS OF MIXED PLATES—PART I [1921 *Philos. Mag.* 41 338; with B Banerji]
165. ON THE COLOURS OF MIXED PLATES—PART II [1921 *Philos. Mag.* 41 860; with B Banerji]

166. ON THE COLOURS OF MIXED PLATES—PART III [1921 *Philos. Mag.* **42** 679; with K Seshagiri Rao]
167. ON QUETELET'S RINGS AND OTHER ALLIED PHENOMENA [1921 *Philos. Mag.* **42** 826; with G L Datta]
168. THE COLOURS OF BREATHED-ON PLATES [1921 *Nature (London)* **107** 714]
169. THE COLOURS OF TEMPERED STEEL [1922 *Nature (London)* **109** 105]
170. A METHOD OF IMPROVING VISIBILITY OF DISTANT OBJECTS [1921 *Nature (London)* **108** 242]
171. THE SPECTRUM OF NEUTRAL HELIUM [1922 *Nature (London)* **110** 700]
172. ON THE SPECTRUM OF NEUTRAL HELIUM—PART I [1923 *Astrophys. J.* **57** 243; with A S Ganesan]
173. ON THE SPECTRUM OF NEUTRAL HELIUM—PART II [1924 *Astrophys. J.* **59** 61; with A S Ganesan]
174. ANOMALOUS DISPERSION AND MULTIPLET LINES IN SPECTRA [1925 *Nature (London)* **115** 946; with S K Datta]
175. ON EINSTEIN'S ABERRATION EXPERIMENT [1922 *Astrophys. J.* **56** 29]
176. EINSTEIN'S ABERRATION EXPERIMENT [1922 *Nature (London)* **109** 477]
177. ON THE CONVECTION OF LIGHT (FIZEAU EFFECT) IN MOVING GASES [1922 *Philos. Mag.* **43** 447; with N K Sethi]
178. CONICAL REFRACTION IN BIAXIAL CRYSTALS [1921 *Nature (London)* **107** 747]
179. ON A NEW OPTICAL PROPERTY OF BIAXIAL CRYSTALS [1922 *Philos. Mag.* **43** 510; with V S Tamman]
180. THE EFFECT OF DISPERSION ON THE INTERFERENCE FIGURES OF CRYSTALS [1924 *Nature (London)* **113** 127]
181. THE OPTICAL PROPERTIES OF AMETHYST QUARTZ [1925 *Trans. Opt. Soc. London* **26** 289; with K Banerji]
182. ON BREWSTER'S BANDS—PART I [1925 *Trans. Opt. Soc. Am* **26** 51; with S K Datta]
183. ON THE DIFFRACTION OF LIGHT BY SPHERICAL OBSTACLES [1926 *Proc. Phys. Soc. London* **38** 350; with K S Krishnan]
184. ON THE NATURE OF THE DISTURBANCE IN THE SECOND MEDIUM IN TOTAL REFLECTION [1925 *Philos. Mag.* **50** 812]
185. ON THE TOTAL REFLECTION OF LIGHT [1926 *Proc. Indian Assoc. Cultiv. Sci.* **9** 271]
186. HUYGENS'S PRINCIPLE AND THE PHENOMENA OF TOTAL REFLECTION [1927 *Trans. Opt. Soc. London* **28** 149]
187. THE DIFFRACTION OF LIGHT BY METALLIC SCREENS [1927 *Proc. R. Soc. London A* **116** 254; with K S Krishnan]
188. DIFFRACTION OF LIGHT BY A TRANSPARENT LAMINA [1927 *Proc. Phys. Soc. London* **39** 453; with I Ramakrishna Rao]
189. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART I [1936 *Proc. Indian Acad. Sci. A* **2** 406; with N S Nagendra Nath]
190. THE DIFFRACTION OF LIGHT BY SOUND WAVES OF HIGH FREQUENCY: PART II [1936 *Proc. Indian Acad. Sci. A* **2** 413; with N S Nagendra Nath]
191. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART III, DOPPLER EFFECT AND COHERENCE PHENOMENA [1936 *Proc. Indian Acad. Sci. A* **3** 75; with N S Nagendra Nath]
192. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART IV, GENERALISED THEORY [1936 *Proc. Indian Acad. Sci. A* **3** 119; with N S Nagendra Nath]
193. THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART V, GENERAL CONSIDERATIONS—OBLIQUE INCIDENCE AND AMPLITUDE CHANGES [1936 *Proc. Indian Acad. Sci. A* **3** 459; with N S Nagendra Nath]
194. DIFFRACTION OF LIGHT BY ULTRASONIC WAVES [1936 *Nature (London)* **138** 616; with N S Nagendra Nath]

195. ON THE WAVE-LIKE CHARACTER OF PERIODIC PRECIPITATES [1939 *Proc. Indian Acad. Sci.* **A9** 455; with K Subba Ramaiah]
196. INTERFERENCE PATTERNS WITH LIESEGANG RINGS [1938 *Nature (London)* **142** 355; with K Subba Ramaiah]
197. HAIDINGER'S RINGS IN CURVED PLATES [1939 *J. Opt. Soc. Am.* **29** 413; with V S Rajagopalan]
198. HAIDINGER'S RINGS IN SOAP BUBBLES [1939 *Proc. Indian Acad. Sci.* **A10** 317; with V S Rajagopalan]
199. CONICAL REFRACTION IN NAPHTHALENE CRYSTALS [1941 *Proc. Indian Acad. Sci.* **A14** 221; with V S Rajagopalan and T M K Nedungadi]
200. CONICAL REFRACTION IN NAPHTHALENE CRYSTALS [1941 *Nature (London)* **147** 268; with V S Rajagopalan and T M K Nedungadi]
201. THE PHENOMENA OF CONICAL REFRACTION [1942 *Curr. Sci.* **11** 44]
202. THE THEORY OF THE CHRISTIANSEN EXPERIMENT [1949 *Proc. Indian Acad. Sci.* **A29** 381]
203. THE CHRISTIANSEN EXPERIMENT WITH SPHERICAL PARTICLES [1949 *Proc. Indian Acad. Sci.* **A30** 211; with S Ramaseshan]
204. DIFFRACTION OF LIGHT BY TRANSPARENT SPHERES AND SPHEROIDS: THE FRESNEL PATTERNS [1949 *Proc. Indian Acad. Sci.* **A30** 277; with S Ramaseshan]
205. THE CHRISTIANSEN EXPERIMENT [1953 *Curr. Sci.* **22** 31; with M R Bhat]
206. THE STRUCTURE AND OPTICAL BEHAVIOUR OF SOME NATURAL AND SYNTHETIC FIBRES [1954 *Proc. Indian Acad. Sci.* **A39** 109; with M R Bhat]
207. THE THEORY OF THE PROPAGATION OF LIGHT IN POLYCRYSTALLINE MEDIA [1955 *Proc. Indian Acad. Sci.* **A41** 37; with K S Viswanathan]
208. A GENERALIZED THEORY OF THE CHRISTIANSEN EXPERIMENT [1955 *Proc. Indian Acad. Sci.* **A41** 55; with K S Viswanathan]
209. THE CHRISTIANSEN EXPERIMENT WITH BIREFRINGENT POWDERS [1955 *Proc. Indian Acad. Sci.* **A41** 61; with M R Bhat]
210. THE OPTICAL BEHAVIOUR OF POLYCRYSTALLINE SOLIDS [1957 *J. Madras Univ.* **B27** 1]
211. CHRISTIAAN HUYGENS'S AND THE WAVE THEORY OF LIGHT [1959 *Proc. Indian Acad. Sci.* **A49** 185]
212. THE PRINCIPLE OF HUYGENS'S AND DIFFRACTION OF LIGHT [1959 *Curr. Sci.* **28** 267]
213. THE OPTICS OF MIRAGES [1959 *Proc. Indian Acad. Sci.* **A49** 251; with S Pancharatnam]
214. THE SCINTILLATION OF THE STARS [1964 *Curr. Sci.* **33** 355]
215. LECTURES ON PHYSICAL OPTICS, PART I [1959 Indian Academy of Sciences, Bangalore]

## Volume IV

### 1. Miscellaneous Papers

216. THE CURVATURE METHOD OF DETERMINING THE SURFACE TENSION OF LIQUIDS [1907 *Philos. Mag.* **14** 591]
217. SOME NEW METHODS IN KINEMATICAL THEORY [1912–13 *Bull. Calcutta Math. Soc.* **4** 1]
218. ON THE SUMMATION OF CERTAIN FOURIER SERIES INVOLVING DISCONTINUITIES [1913–14 *Bull. Calcutta. Math. Soc.* **5** 5]
219. THE VISCOSITY OF LIQUIDS [1923 *Nature (London)* **111** 600]

220. A THEORY OF THE VISCOSITY OF LIQUIDS [1923 *Nature (London)* 111 532]  
 221. THE PHOTOGRAPHIC STUDY OF IMPACT AT MINIMAL VELOCITIES [1918 *Phys. Rev.* 12 442]  
 222. PERCUSSION FIGURES IN ISOTROPIC SOLIDS [1919 *Nature (London)* 104 113]  
 223. ON SOME APPLICATIONS OF HERTZ'S THEORY OF IMPACT [1920 *Phys. Rev.* 15 277]  
 224. THE OPTICAL STUDY OF PERCUSSION FIGURES [1926 *J. Opt. Soc. Am.* 12 387]  
 225. PERCUSSION FIGURES IN CRYSTALS [1958 *Proc. Indian Acad. Sci. A*48 307]  
 226. PERCUSSION FIGURES IN CRYSTALS [1959 *Curr. Sci.* 28 1]  
 227. INDIA'S DEBT TO FARADAY [1931 *Nature (London)* 128 362]  
 228. NEWTON AND THE HISTORY OF OPTICS [1942 *Curr. Sci.* 11 453]  
 229. ASTRONOMICAL RESEARCH IN INDIA: I [1943 *Curr. Sci.* 12 197]  
 230. ASTRONOMICAL RESEARCH IN INDIA: II [1943 *Curr. Sci.* 12 289]  
 231. ASTRONOMICAL RESEARCH IN INDIA: III [1943 *Curr. Sci.* 12 313]  
 232. CENTENARY OF THE FARADAY EFFECT [1945 *Curr. Sci.* 14 281]  
 233. SCIENCE IN EASTERN EUROPE: I [1958 *Curr. Sci.* 27 371]  
 234. SCIENCE IN EASTERN EUROPE: II [1958 *Curr. Sci.* 27 421]  
 235. ZONAL WINDS AND JET STREAMS IN THE ATMOSPHERE [1967 *Curr. Sci.* 36 593]  
 236. THE ATMOSPHERE OF THE EARTH [1968 *Curr. Sci.* 37 151]

## 2. Colour

237. THE ORIGIN OF THE COLOURS IN THE PLUMAGE OF THE BIRDS [1934 *Proc. Indian Acad. Sci. A*1 1]  
 238. ON IRIDESCENT SHELLS, PART I. INTRODUCTORY [1934 *Proc. Indian Acad. Sci. A*1 567]  
 239. ON IRIDESCENT SHELLS—PART II. COLOURS OF LAMINAR DIFFRACTION [1934 *Proc. Indian Acad. Sci. A*1 574]  
 240. ON IRIDESCENT SHELLS—PART III. BODY-COLOURS AND DIFFUSION-HALOES [1934 *Proc. Indian Acad. Sci. A*1 859]  
 241. THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT SHELLS [1954 *Proc. Indian Acad. Sci. A*39 1; with D Krishnamurti]  
 242. THE STRUCTURE AND OPTICAL CHARACTERS OF IRIDESCENT GLASS [1939 *Proc. Indian Acad. Sci. A*9 371; with V S Rajagopalan]  
 243. COLOURS OF STRATIFIED MEDIA I: ANCIENT DECOMPOSED GLASS [1940 *Proc. Indian Acad. Sci. A*11 469; with V S Rajagopalan]  
 244. THE IRIDESCENT FELDSPARS [1950 *Curr. Sci.* A19 301]  
 245. THE STRUCTURE OF LABRADORITE AND THE ORIGIN OF ITS IRIDESCENCE [1950 *Proc. Indian Acad. Sci. A*32 1; with A Jayaraman]  
 246. THE STRUCTURE AND THE OPTICAL BEHAVIOUR OF THE CEYLON MOONSTONES [1950 *Proc. Indian Acad. Sci. A*32 123; with A Jayaraman and T K Srinivasan]  
 247. THE DIFFUSION HALOES OF THE IRIDESCENT FELDSPARS [1953 *Proc. Indian Acad. Sci. A*37 1; with A Jayaraman]  
 248. ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS—PART I. ITS SPECTRAL CHARACTERS [1952 *Proc. Indian Acad. Sci. A*36 315; with D Krishnamurti]  
 249. ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS—PART II. POLARISATION EFFECTS [1952 *Proc. Indian Acad. Sci. A*36 321; with D Krishnamurti]  
 250. ON THE IRIDESCENCE OF POTASSIUM CHLORATE CRYSTALS—PART III. SOME GENERAL OBSERVATIONS [1952 *Proc. Indian Acad. Sci. A*36 330; with D Krishnamurti]

251. ON THE POLARISATION AND SPECTRAL CHARACTER OF THE IRIDESCEENCE OF POTASSIUM CHLORATE CRYSTALS [1952 *Proc. Indian Acad. Sci.* **A36** 419; with D Krishnamurti]
252. THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT CRYSTALS OF POTASSIUM CHLORATE [1953 *Proc. Indian Acad. Sci.* **A38** 261; with D Krishnamurti]
253. THE STRUCTURE OF OPAL AND THE ORIGIN OF ITS IRIDESCEENCE [1953 *Proc. Indian Acad. Sci.* **A38** 101; with A Jayaraman]
254. THE STRUCTURE OF OPTICAL BEHAVIOUR OF IRIDESCENT OPAL [1953 *Proc. Indian Acad. Sci.* **A38** 343; with A Jayaraman]
255. THE STRUCTURE AND OPTICAL BEHAVIOUR OF PEARLS [1954 *Proc. Indian Acad. Sci.* **A39** 215; with D Krishnamurti]
256. OPTICS OF THE PEARL [1954 *Curr. Sci.* **23** 173; with D Krishnamurti]
257. ON THE CHROMATIC DIFFUSION HALO AND OTHER OPTICAL EFFECTS EXHIBITED BY PEARLS [1954 *Proc. Indian Acad. Sci.* **A39** 265; with D Krishnamurti]
258. THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT AGATE [1953 *Proc. Indian Acad. Sci.* **A38** 199; with A Jayaraman]
259. THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT CALCITE [1954 *Proc. Indian Acad. Sci.* **A40** 1; with A K Ramdas]
260. THE STRUCTURE AND OPTICAL BEHAVIOUR OF JADEITE [1955 *Proc. Indian Acad. Sci.* **A41** 117; with A Jayaraman]
261. CRYSTALS OF QUARTZ WITH IRIDESCENT FACES [1950 *Proc. Indian Acad. Sci.* **A31** 275]

### 3. Optics of Minerals

262. THE OPTICAL ANISOTROPY AND HETEROGENEITY OF VITREOUS SILICA [1950 *Proc. Indian Acad. Sci.* **A31** 141]
263. STRUCTURAL BIREFRINGENCE IN AMORPHOUS SOLIDS [1950 *Proc. Indian Acad. Sci.* **A31** 207]
264. THE LAMELLAR STRUCTURE AND BIREFRINGENCE OF PLATE GLASS [1950 *Proc. Indian Acad. Sci.* **A31** 359]
265. THE SMOKY QUARTZ [1921 *Nature (London)* **108** 81]
266. THE STRUCTURE OF AMETHYST QUARTZ AND THE ORIGIN OF ITS PLEOCHROISM [1954 *Proc. Indian Acad. Sci.* **A40** 189; with A Jayaraman]
267. THE BIREFRINGENCE PATTERNS OF CRYSTAL SPHERES [1956 *Proc. Indian Acad. Sci.* **A43** 1]
268. AMETHYST—ITS NATURE AND ORIGIN [1954 *Curr. Sci.* **23** 379]
269. ON THE STRUCTURE OF AMETHYST AND ITS GENESIS IN NATURE [1954 *Proc. Indian Acad. Sci.* **A40** 221; with A Jayaraman]
270. ON THE OPTICAL BEHAVIOUR OF CRYPTO-CRYSTALLINE QUARTZ [1954 *Proc. Indian Acad. Sci.* **A41** 1; with A Jayaraman]
271. X-RAY STUDY OF FIBROUS QUARTZ [1954 *Proc. Indian Acad. Sci.* **A40** 107; with A Jayaraman]
272. ON THE POLYCRYSTALLINE FORMS OF GYPSUM AND THEIR OPTICAL BEHAVIOUR [1954 *Proc. Indian Acad. Sci.* **A39** 153; with A K Ramdas]
273. X-RAY STUDIES ON POLYCRYSTALLINE GYPSUM [1954 *Proc. Indian Acad. Sci.* **A40** 57; with A Jayaraman]
274. THE LUMINESCENCE OF FLUORSPAR [1962 *Curr. Sci.* **31** 361]
275. THE TWO SPECIES OF FLUORITE [1962 *Curr. Sci.* **31** 445]

#### 4. Diamond

276. THE PHYSICS OF THE DIAMOND [1942 *Curr. Sci.* 11 261]
277. THE STRUCTURE AND PROPERTIES OF DIAMOND [1943 *Curr. Sci.* 12 33]
278. THE FOUR FORMS OF DIAMOND [1944 *Curr. Sci.* 13 145]
279. THE CRYSTAL SYMMETRY AND STRUCTURE OF DIAMOND [1944 *Proc. Indian Acad. Sci.* A19 189]
280. THE NATURE AND ORIGIN OF THE LUMINESCENCE OF DIAMOND [1944 *Proc. Indian Acad. Sci.* A19 199]
281. BIREFRINGENCE PATTERNS IN DIAMONDS [1944 *Proc. Indian Acad. Sci.* A19 265; with G R Rendall]
282. THE CRYSTAL FORMS OF DIAMOND AND THEIR SIGNIFICANCE [1946 *Proc. Indian Acad. Sci.* A24 1; with S Ramaseshan]
283. THE DIAMOND AND ITS TEACHINGS [1946 *Curr. Sci.* 15 205]
284. NEW CONCEPTS OF CRYSTAL STRUCTURE [1946 *Curr. Sci.* 15 329]
285. THE LUMINESCENCE OF DIAMOND AND ITS RELATION TO CRYSTAL STRUCTURE [1950 *Proc. Indian Acad. Sci.* A32 65; with A Jayaraman]
286. THE LUMINESCENCE OF DIAMOND—I [1950 *Curr. Sci.* 19 357]
287. THE LUMINESCENCE OF DIAMOND—II [1951 *Curr. Sci.* 20 1]
288. THE LUMINESCENCE OF DIAMOND—III [1951 *Curr. Sci.* 20 27]
289. THE LUMINESCENCE OF DIAMOND—IV [1951 *Curr. Sci.* 20 55]
290. THE DIAMOND [1956 *Proc. Indian Acad. Sci.* A44 99]
291. THE TETRAHEDRAL CARBON ATOM AND THE STRUCTURE OF DIAMOND [1957 *Proc. Indian Acad. Sci.* A46 391]

### Volume V. Crystal Physics

#### 1. Diffuse X-ray Reflections

292. A NEW X-RAY EFFECT [1940 *Curr. Sci.* 9 165; with P Nilakantan]
293. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART I. THEORETICAL DISCUSSION [1940 *Proc. Indian Acad. Sci.* A11 379; with P Nilakantan]
294. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART II. THE CASE OF DIAMOND [1940 *Proc. Indian Acad. Sci.* A11 389; with P Nilakantan]
295. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART III. THE CASE OF SODIUM NITRATE [1940 *Proc. Indian Acad. Sci.* A11 398; with P Nilakantan]
296. QUANTUM THEORY OF X-RAY REFLECTION AND SCATTERING PART I. GEOMETRIC RELATIONS [1940 *Proc. Indian Acad. Sci.* A12 83; with N S Nagendra Nath]
297. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART IV. ROCK SALT [1940 *Proc. Indian Acad. Sci.* A12 141; with P Nilakantan]
298. THE TWO TYPES OF X-RAY REFLECTION IN CRYSTALS [1940 *Proc. Indian Acad. Sci.* A12 427]
299. CRYSTALS AND PHOTONS [1941 *Proc. Indian Acad. Sci.* A13 1]
300. THE QUANTUM THEORY OF X-RAY REFLECTION: BASIC IDEAS [1941 *Proc. Indian Acad. Sci.* A14 317]
301. QUANTUM THEORY OF X-RAY REFLECTION: MATHEMATICAL FORMULATION [1941 *Proc. Indian Acad. Sci.* A14 332]

- 302. QUANTUM THEORY OF X-RAY REFLECTION: EXPERIMENTAL CONFIRMATION [1941 *Proc. Indian Acad. Sci.* **A14** 356; with P Nilakantan]
- 303. DYNAMIC X-RAY REFLECTIONS IN CRYSTALS [1948 *Curr. Sci.* **17** 65]
- 304. X-RAYS AND CRYSTALS [1955 *Curr. Sci.* **24** 395]
- 305. NEW CONCEPTS OF THE SOLID STATE [1942 *Proc. Indian Acad. Sci.* **A15** 65]

## 2. Dynamics of Crystal Lattices

- 306. THE VIBRATION SPECTRUM OF A CRYSTAL LATTICE [1943 *Proc. Indian Acad. Sci.* **A18** 237]
- 307. NEW PATHS IN CRYSTAL PHYSICS [1947 *Curr. Sci.* **16** 67]
- 308. THE VIBRATION SPECTRA OF CRYSTALS PART I. BASIC THEORY [1947 *Proc. Indian Acad. Sci.* **A26** 339]
- 309. THE VIBRATION SPECTRA OF CRYSTALS PART II. THE CASE OF DIAMOND [1947 *Proc. Indian Acad. Sci.* **A26** 356]
- 310. THE VIBRATION SPECTRA OF CRYSTALS PART III. ROCK SALT [1947 *Proc. Indian Acad. Sci.* **A26** 370]
- 311. THE VIBRATION SPECTRA OF CRYSTALS PART IV. MAGNESIUM OXIDE [1947 *Proc. Indian Acad. Sci.* **A26** 383]
- 312. THE VIBRATION SPECTRA OF CRYSTALS PART V. LITHIUM AND SODIUM FLUORIDES [1947 *Proc. Indian Acad. Sci.* **A26** 391]
- 313. THE VIBRATION SPECTRA OF CRYSTALS PART VI. SYLVINE [1947 *Proc. Indian Acad. Sci.* **A26** 396]
- 314. THE INFRA-RED SPECTRUM [1947 *Curr. Sci.* **16** 359]
- 315. THE EIGENVIBRATIONS OF CRYSTAL STRUCTURES [1948 *Curr. Sci.* **17** 1]
- 316. THE SCATTERING OF LIGHT IN CRYSTALS AND THE NATURE OF THEIR VIBRATION SPECTRA [1951 *Proc. Indian Acad. Sci.* **A34** 61]
- 317. THE VIBRATION SPECTRA OF CRYSTALS AND THE THEORY OF THEIR SPECIFIC HEATS [1951 *Proc. Indian Acad. Sci.* **A34** 141]

## 3. Elasticity of Crystals

- 318. THE ELASTICITY OF CRYSTALS [1955 *Curr. Sci.* **24** 325]
- 319. THE ELASTIC BEHAVIOUR OF ISOTROPIC SOLIDS [1955 *Proc. Indian Acad. Sci.* **A42** 1; with K S Viswanathan]
- 320. ON THE THEORY OF THE ELASTICITY OF CRYSTALS [1955 *Proc. Indian Acad. Sci.* **A42** 51; with K S Viswanathan]
- 321. EVALUATION OF THE FOUR ELASTIC CONSTANTS OF SOME CUBIC CRYSTALS [1955 *Proc. Indian Acad. Sci.* **A42** 111; with D Krishnamurti]

## 4. Vibrational and Thermal Energy of Crystals

- 322. THE NATURE OF THE THERMAL AGITATION IN CRYSTALS [1955 *Proc. Indian Acad. Sci.* **A42** 163]
- 323. THE THERMAL ENERGY OF CRYSTALS [1955 *Curr. Sci.* **24** 357]
- 324. QUANTUM THEORY AND CRYSTAL PHYSICS [1956 *Curr. Sci.* **25** 377]

325. THE PHYSICS OF CRYSTALS [1956 *Proc. Indian Acad. Sci.* A43 327]
326. THE SPECIFIC HEATS OF CRYSTALS: PART I. GENERAL THEORY [1956 *Proc. Indian Acad. Sci.* A44 153]
327. THE SPECIFIC HEATS OF CRYSTALS: PART II. THE CASE OF DIAMOND [1956 *Proc. Indian Acad. Sci.* A44 160]
328. THE SPECIFIC HEATS OF CRYSTALS: PART III. ANALYSIS OF THE EXPERIMENTAL DATA [1956 *Proc. Indian Acad. Sci.* A44 367]
329. THE HEAT CAPACITY OF DIAMOND BETWEEN 0–1000° K [1957 *Proc. Indian Acad. Sci.* A46 323]
330. THE DIFFRACTION OF X-RAYS BY DIAMOND: PART I [1958 *Proc. Indian Acad. Sci.* A47 263]
331. THE DIFFRACTION OF X-RAYS BY DIAMOND: PART II [1958 *Proc. Indian Acad. Sci.* A47 335]
332. THE DIFFRACTION OF X-RAYS BY DIAMOND: PART III [1958 *Proc. Indian Acad. Sci.* A48 1]
333. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART I. MATERIALS AND METHODS [1962 *Proc. Indian Acad. Sci.* A55 1]
334. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART II. A GENERAL SURVEY OF THE RESULTS [1962 *Proc. Indian Acad. Sci.* A55 5]
335. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART III. THE PERFECT DIAMONDS AND THEIR SPECTRAL BEHAVIOUR [1962 *Proc. Indian Acad. Sci.* A55 10]
336. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART IV. THE NON-LUMINESCENT DIAMONDS [1962 *Proc. Indian Acad. Sci.* A55 14]
337. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART V. THE COMPOSITE DIAMONDS [1962 *Proc. Indian Acad. Sci.* A55 20]
338. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART VI. THE FREE VIBRATIONS OF THE STRUCTURE [1962 *Proc. Indian Acad. Sci.* A55 24]
339. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART VII. THE CHARACTERISTIC FREQUENCIES [1962 *Proc. Indian Acad. Sci.* A55 30]
340. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART VIII. DYNAMICAL THEORY [1962 *Proc. Indian Acad. Sci.* A55 36]
341. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART IX. THE ACTIVITY OF THE NORMAL MODES [1962 *Proc. Indian Acad. Sci.* A55 42]
342. THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE PART X. EVALUATION OF THE SPECIFIC HEAT [1962 *Proc. Indian Acad. Sci.* A55 49]
343. THE INFRA-RED BEHAVIOUR OF DIAMOND [1962 *Curr. Sci.* 31 403]
344. THE DIAMOND: ITS STRUCTURE AND PROPERTIES [1968 *Proc. Indian Acad. Sci.* A67 231]
345. QUANTUM THEORY AND CRYSTAL PHYSICS [1956 *Proc. Indian Acad. Sci.* A44 361]
346. THE SPECIFIC HEATS OF CRYSTALLINE SOLIDS: PART I. [1957 *Curr. Sci.* 26 195]
347. THE SPECIFIC HEATS OF CRYSTALLINE SOLIDS: PART II. [1957 *Curr. Sci.* 26 231]
348. THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS PART I. ANALYSIS OF THE EXPERIMENTAL DATA [1957 *Proc. Indian Acad. Sci.* A45 1]
349. THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS PART II. APPROXIMATE THEORETICAL EVALUATION [1957 *Proc. Indian Acad. Sci.* A45 7]
350. THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS PART III. THE CHARACTERISTIC FREQUENCIES [1957 *Proc. Indian Acad. Sci.* A45 59]
351. THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS PART IV. THE RESIDUAL SPECTRUM [1957 *Proc. Indian Acad. Sci.* A45 139]
352. THE SPECIFIC HEATS OF CRYSTALS AND THE FALLACY OF THE THEORIES OF DEBYE AND BORN [1957 *Proc. Indian Acad. Sci.* A45 273]

- THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRARED ABSORPTION SPECTRUM [1961 *Proc. Indian Acad. Sci.* A54]
353. PART I. THE RESULTS OF EXPERIMENTAL STUDY 205  
 354. PART III. DYNAMICAL THEORY 223  
 355. PART III. COMPARISON OF THEORY AND EXPERIMENT 233  
 356. PART IV. EVALUATION OF ITS SPECIFIC HEAT 244
- THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT [1961 *Proc. Indian Acad. Sci.* A54]
357. PART I. THE STRUCTURE AND ITS FREE VIBRATIONS 253  
 358. PART II. ITS INFRA-RED ACTIVITY 266  
 359. PART III. THE SPECTRUM OF LIGHT SCATTERING 281  
 360. PART IV. SPECIFIC HEAT AND SPECTRAL FREQUENCIES 294
361. THE VIBRATION SPECTRUM OF LITHIUM FLUORIDE AND THE EVALUATION OF ITS SPECIFIC HEAT [1962 *Proc. Indian Acad. Sci.* A55 131]
- THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR [1962 *Proc. Indian Acad. Sci.* A56]
362. PART I. INTRODUCTION 1  
 363. PART II. THE FREE MODES OF ATOMIC VIBRATION 6  
 364. PART III. THE INTERATOMIC FORCES 11  
 365. PART IV. THE EQUATIONS OF MOTION 15  
 366. PART V. THE EVALUATION OF THE FREQUENCIES 20  
 367. PART VI. THE ATOMIC VIBRATION SPECTRA 25  
 368. PART VII. EVALUATION OF THE SPECIFIC HEATS 30  
 369. PART VIII. THEIR INFRA-RED ACTIVITY 34  
 370. PART IX. SPECTRAL SHIFTS IN LIGHT SCATTERING 40  
 371. PART X. THE LITHIUM SALTS 45  
 372. PART XI. THE SODIUM SALTS 52  
 373. PART XII. THE POTASSIUM AND RUBIDIUM SALTS 60  
 374. THE INFRA-RED BEHAVIOUR OF SODIUM FLUORIDE [1962 *Proc. Indian Acad. Sci.* A56 223]  
 375. THE INFRARED BEHAVIOUR OF THE ALKALI HALIDES [1963 *Curr. Sci.* 32 1]
- THE DYNAMICS OF THE FLUORITE STRUCTURE AND ITS INFRA-RED BEHAVIOUR [1962 *Proc. Indian Acad. Sci.* A56]
376. PART I. INTRODUCTION 291  
 377. PART II. THE FREE MODES OF VIBRATION 294  
 378. PART III. ACTIVITY OF THE NORMAL MODES 301  
 379. PART IV. THE SPECTROPHOTOMETER RECORDS 304
380. SPECTROSCOPIC EVALUATION OF THE SPECIFIC HEATS OF POTASSIUM BROMIDE [1963 *Proc. Indian Acad. Sci.* A57 1]

## Volume VI. Colour and its Perception

### 1. Light, Colour and Vision

381. LIGHT, COLOUR AND VISION [1959 *Curr. Sci.* 28 429]  
 382. ON THE SENSATIONS OF COLOUR AND THE NATURE OF THE VISUAL MECHANISM [1960 *Curr. Sci.* 29 1]  
 383. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART I: THE MECHANISM OF PERCEPTION [1960 *Proc. Indian Acad. Sci.* A52 255]

384. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART II. THE VISUAL PIGMENTS [1960 *Proc. Indian Acad. Sci.* A52 267]
385. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART III. THE CAROTENOID PIGMENT [1960 *Proc. Indian Acad. Sci.* A52 281]
386. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART IV. FERROHEMЕ AND FERRIHEMЕ [1960 *Proc. Indian Acad. Sci.* A52 292]
387. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART V. THE COLOUR OF TRIANGLE [1960 *Proc. Indian Acad. Sci.* A52 305]
388. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART VI. DEFECTIVE COLOUR VISION [1960 *Proc. Indian Acad. Sci.* A52 314]
389. THE PERCEPTION OF LIGHT AND COLOUR AND THE PHYSIOLOGY OF VISION, PART VII. GENERAL SUMMARY [1960 *Proc. Indian Acad. Sci.* A52 324]
390. THE ROLE OF THE RETINA IN VISION [1962 *Curr. Sci.* 31 315]
391. LIGHT, COLOUR AND VISION [1962 *Curr. Sci.* 31 489]
392. FLORAL COLOURS AND THEIR SPECTRAL COMPOSITION [1963 *Curr. Sci.* 32 147]
393. THE VISUAL PIGMENTS AND THEIR LOCATION IN THE RETINA [1963 *Curr. Sci.* 32 389]
394. FLORAL COLOURS AND THE PHYSIOLOGY OF VISION [1963 *Curr. Sci.* 32 293]
395. THE TRICHROMATIC HYPOTHESIS [1963 *Curr. Sci.* 32 245]
396. VISUAL ACUITY AND ITS VARIATIONS [1963 *Curr. Sci.* 32 531]
397. THE COLOURS OF GEMSTONES [1963 *Curr. Sci.* 32 437]
398. THE GREEN COLOUR OF VEGETATION [1963 *Curr. Sci.* 32 341]

## 2. Visual Perception of Colour

- FLORAL COLOURS AND THE PHYSIOLOGY OF VISION [1963 *Proc. Indian Acad. Sci.* A58]
399. PART I. INTRODUCTORY 57
400. PART II. THE GREEN COLOUR OF LEAVES 62
401. PART III. THE SPECTRUM OF THE MORNING GLORY 67
402. PART IV. THE QUEEN OF FLOWERS 70
403. PART V. THE BLUE OF THE JACARANDA 73
404. PART VI. COMPARATIVE STUDY OF THREE CASES 76
405. PART VII. THE ASTER AND ITS VARIED COLOURS 81
406. PART VIII. THE SPECTRA OF ROSES 84
407. PART IX. HIBISCUS AND BOUGAINVILLEA 87
408. PART X. FLOWERS EXHIBITING BAND SPECTRA 92
409. PART XI. A REVIEW OF THE RESULTS 96
410. PART XII. SOME CONCLUDING REMARKS 106
411. THE VISUAL SYNTHESIS OF COLOUR [1964 *Curr. Sci.* 33 97]
412. FLUCTUATIONS OF LUMINOSITY IN VISUAL FIELDS [1964 *Curr. Sci.* 33 65]
413. STARS, NEBULAE AND THE PHYSIOLOGY OF VISION [1964 *Curr. Sci.* 33 293]
- THE NEW PHYSIOLOGY OF VISION [1964 *Proc. Indian Acad. Sci.*]
414. PART I. INTRODUCTORY [60 139]
415. PART II. VISUAL SENSATIONS AND THE NATURE OF LIGHT [60 143]
416. PART III. CORPUSCLES OF LIGHT AND THE PERCEPTION OF LUMINOSITY [60 211]

417. PART IV. CORPUSCLES OF LIGHT AND THE PERCEPTION OF FORM [60 287]
418. PART V. CORPUSCLES OF LIGHT AND THE PERCEPTION OF COLOUR [60 292]
419. PART VI. VISION IN DIM LIGHT [60 369]
420. PART VII. THE PERCEPTION OF COLOUR IN DIM LIGHT [60 375]
421. PART VIII. THE PERCEPTION OF POLARISED LIGHT [1965 61 1]
422. PART IX. THE STRUCTURE OF THE FOVEA [61 7]
423. PART X. THE MAJOR VISUAL PIGMENTS [61 57]
424. PART XI. THE CAROTENOID PIGMENTS [61 65]
425. PART XII. CHROMATIC SENSATIONS AT HIGH LUMINOSITIES [61 129]
426. PART XIII. BLUE, INDIGO AND VIOLET IN THE SPECTRUM [63 133]
427. PART XIV. THE RED END OF THE SPECTRUM [61 187]
428. PART XV. THE CHROMATIC RESPONSE OF THE RETINA [61 193]
429. PART XVI. FURTHER STUDIES OF THE RETINAL RESPONSES [61 267]
430. PART XVII. LOCATION OF VISUAL PIGMENTS IN THE RETINA [61 335]
431. PART XVIII. THE VISUAL SYNTHESIS OF COLOUR [*Proc. Indian Acad. Sci.* 62 1]
432. PART XIX. PERCEPTION OF COLOUR AND THE TRICHROMATIC HYPOTHESIS [62 10]
433. PART XX. SUPERPOSITION AND MASKING OF COLOURS [62 67]
434. PART XXI. THE GREEN COLOUR OF VEGETATION [62 73]
435. PART XXII. THE COLOURS OF FLOWERS [62 125]
436. PART XXIII. THE COLOURS OF THE ROSES [62 133]
437. PART XXIV. FLORAL PIGMENTS AND THE PERCEPTION OF COLOUR [62 177]
438. PART XXV. THE COLOURS OF NATURAL AND SYNTHETIC GEMSTONES [62 183]
439. PART XXVI. STRUCTURAL COLOURS [62 237]
440. PART XXVII. THE COLOURS OF INTERFERENCE [62 243]
441. PART XXVIII. OBSERVATION WITH A NEODYMIUM FILTER [62 307]
442. PART XXIX. THE REPRODUCTION OF COLOUR [62 310]
443. PART XXX. THE PHOTOMECHANICAL REPRODUCTION OF COLOUR [1966 63 1]
444. PART XXXI. THE INTEGRATION OF COLOUR BY THE RETINA [63 5]
445. PART XXXII. DEFECTS IN COLOUR VISION [63 65]
446. PART XXXIII. THE TESTING OF COLOUR VISION [63 71]
447. PART XXXIV. THE NATURE AND ORIGIN OF DEFECTS IN COLOUR VISION [63 133]
448. PART XXXV. THE FAINTEST OBSERVABLE SPECTRUM [63 138]
449. PART XXXVI. THE POSTULATED DUALITY OF THE RETINA [63 207]
450. PART XXXVII. THE SPECTRUM OF THE NIGHT-SKY [63 213]
451. PART XXXVIII. THE ADAPTATION OF VISION TO DIM LIGHT [63 263]
452. PART XXXIX. DALTONIAN COLOUR VISION [63 267]
453. PART XL. THE COLOURS OF IOLITE [63 321]
454. PART XLI. PHOTOGRAPHY IN COLOUR [63 325]
455. PART XLII. FURTHER OBSERVATIONS WITH THE NEODYMIUM FILTER [63 329]
456. PART XLIII. THE COLOURS OF FLUORSPAR [63 333]

**3. Floral colours**

- 457. FLORAL COLOURS AND THEIR ORIGIN [1969 *Curr. Sci.* **38** 179]
- 458. THE FLORACHROMES: THEIR CONSTITUTION AND OPTICAL BEHAVIOUR [1969 *Curr. Sci.* **38** 451]
- 459. THE COLOURS OF ROSES [1969 *Curr. Sci.* **38** 503]
- 460. SPECTROPHOTOMETRY OF FLORAL EXTRACTS [1969 *Curr. Sci.* **38** 527]
- 461. BLUE DELPHINIUMS AND THE PURPLE BIGNONIA [1969 *Curr. Sci.* **38** 553]
- 462. THE VARIED COLOURS OF VERBENA [1969 *Curr. Sci.* **38** 579]
- 463. THE PELARGONIUMS [1970 *Curr. Sci.* **39** 1]
- 464. THE RED OLEANDER AND THE PURPLE PETRIA [1970 *Curr. Sci.* **39** 25]

**4. Monograph—Physiology of Vision**

- 465. THE PHYSIOLOGY OF VISION, Indian Academy of Sciences, Bangalore [1968 p. 1-164]







Twenty papers deal with miscellaneous topics in which Raman was interested from time to time. His phenomenological theory of viscosity which was so useful to the polymer chemist, his classic studies of impact between two bodies and his pioneering work on the mechanism of the fracture of solids are all dealt with in this volume.

ISBN 81-85324-04-2

