

## 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

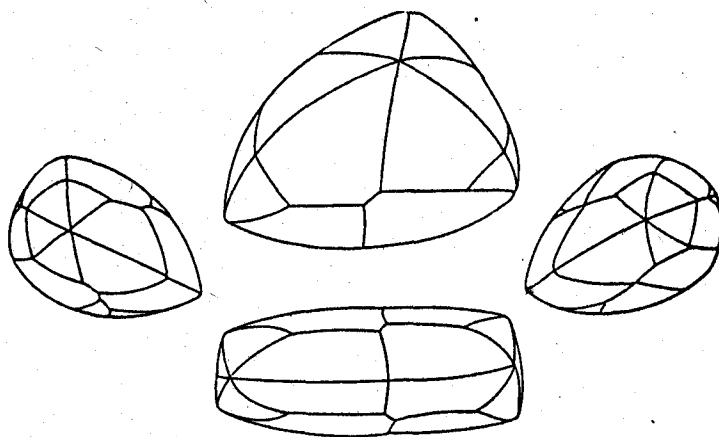


Figure 1. Four views of a tetrahedroid diamond.

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 microphotogram 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

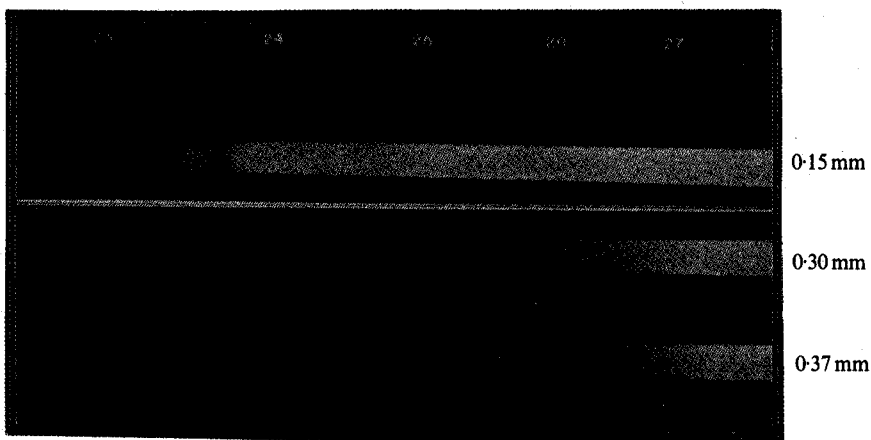


Figure 3. Ultra-violet transparency of thin diamonds.

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 frequently 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

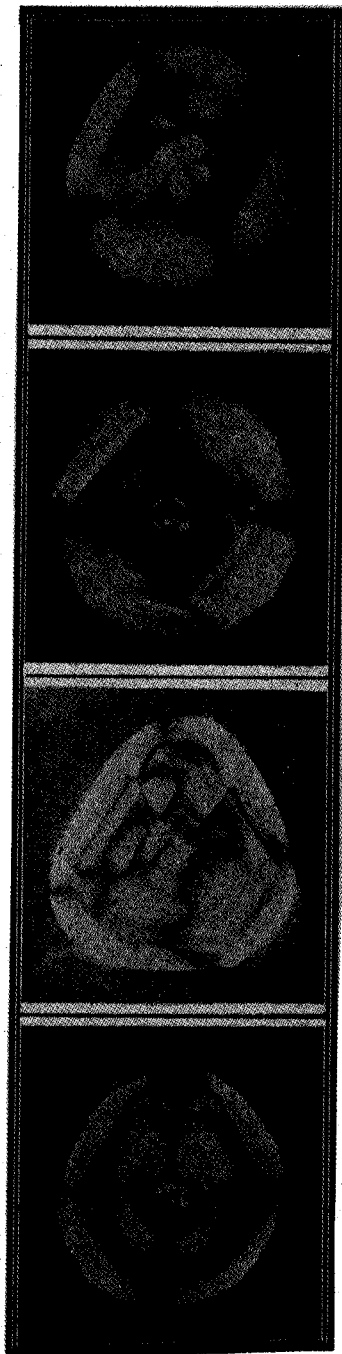


Figure 4. Birefringence patterns in diamond.



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.

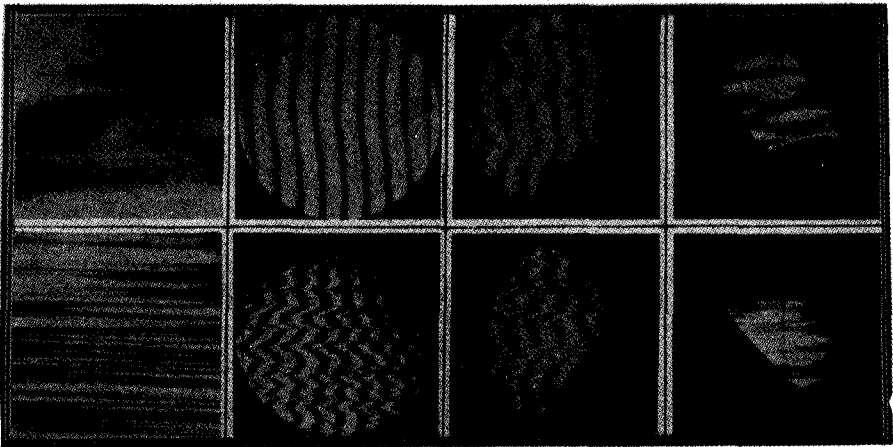


Figure 5. Birefringence in diamond observed with Federov stage and Babinet compensator (octahedral diamond).

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

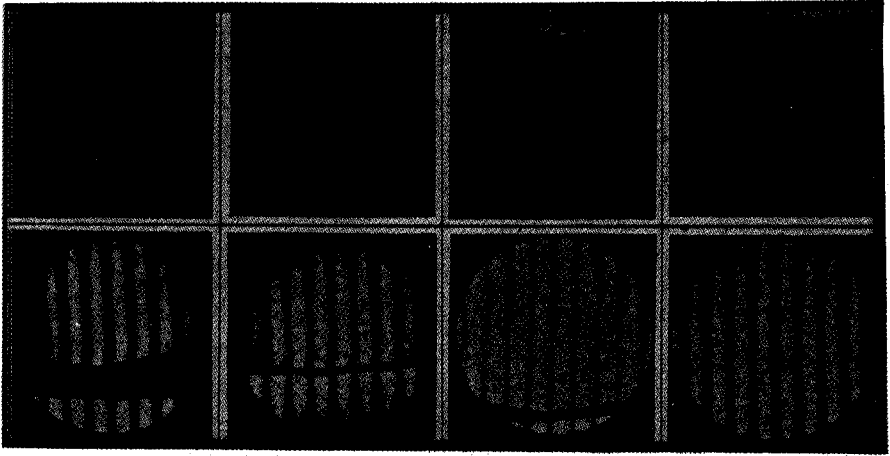


Figure 6. Birefringence observed with Federov stage and Babinet compensator, showing intruding octahedral layer in tetrahedral diamond.

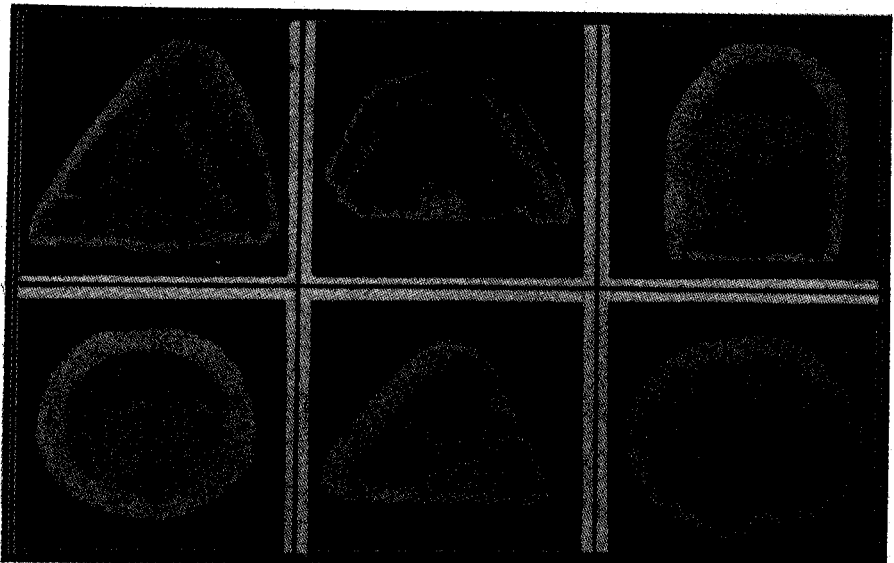
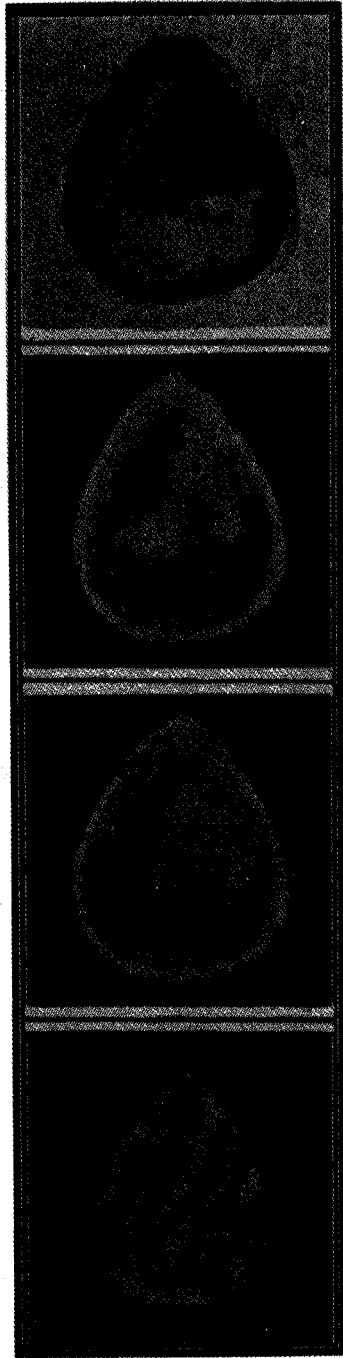


Figure 7. X-ray luminescence patterns.



**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 in 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.

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