

## The four forms of diamond\*

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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

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\*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.

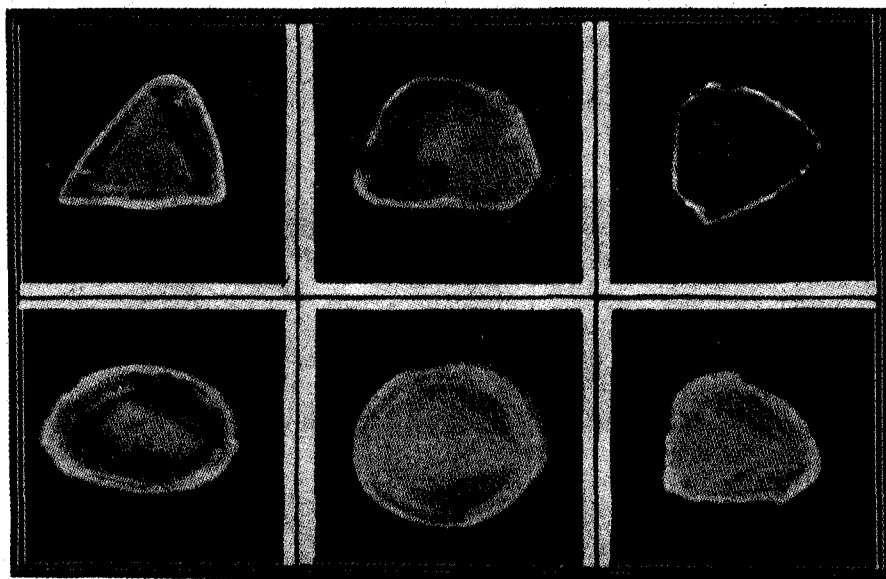


Figure 1. Luminescence patterns in diamond.

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.

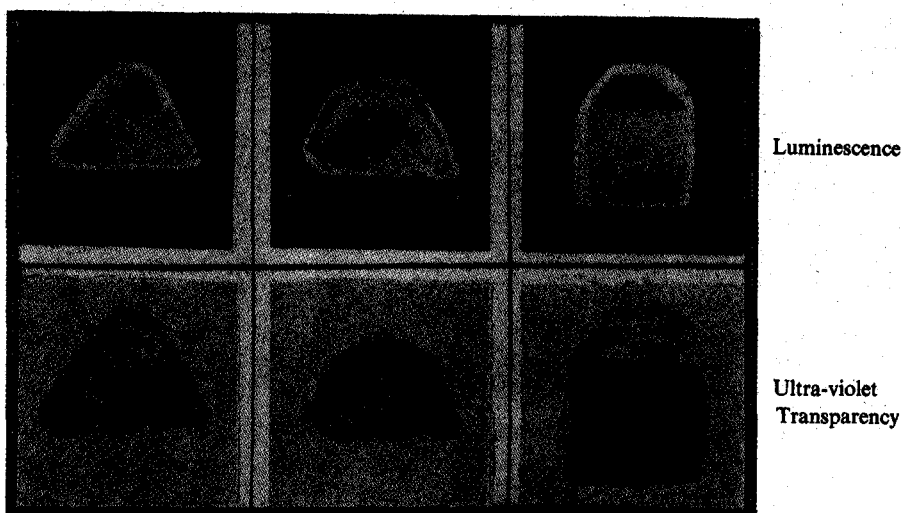


Figure 2. Comparison of luminescence and ultra-violet transparency patterns.

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  $3050 \text{ \AA}$  in weakly blue luminescent diamonds, but progressively extends into the ultra-violet in intensely luminescing diamonds even up to  $2450 \text{ \AA}$ . The non-fluorescent diamonds are ultra-violet transparent, transmitting freely up to  $2250 \text{ \AA}$ , 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  $2360 \text{ \AA}$  in diamonds that show both the 4152 and the 5032 systems.

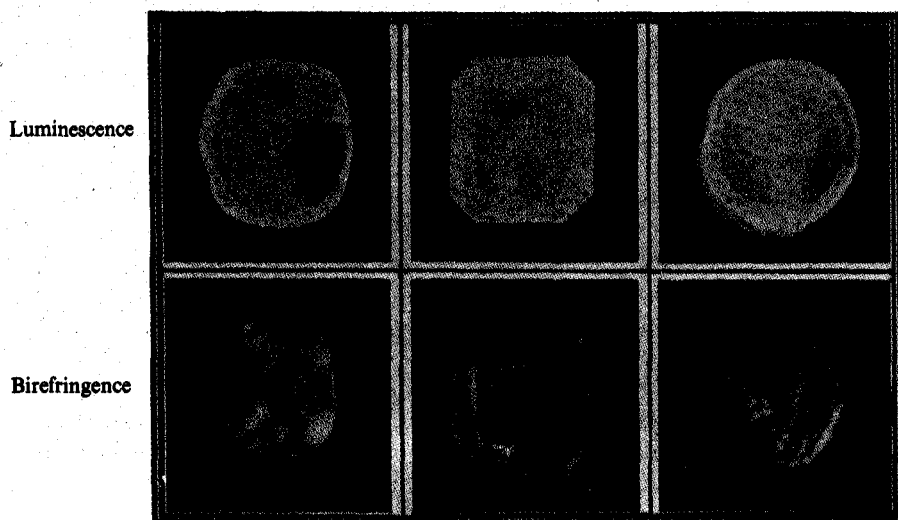


Figure 3. Comparison of luminescence and birefringence patterns.

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.