The structure and properties of diamond*

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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
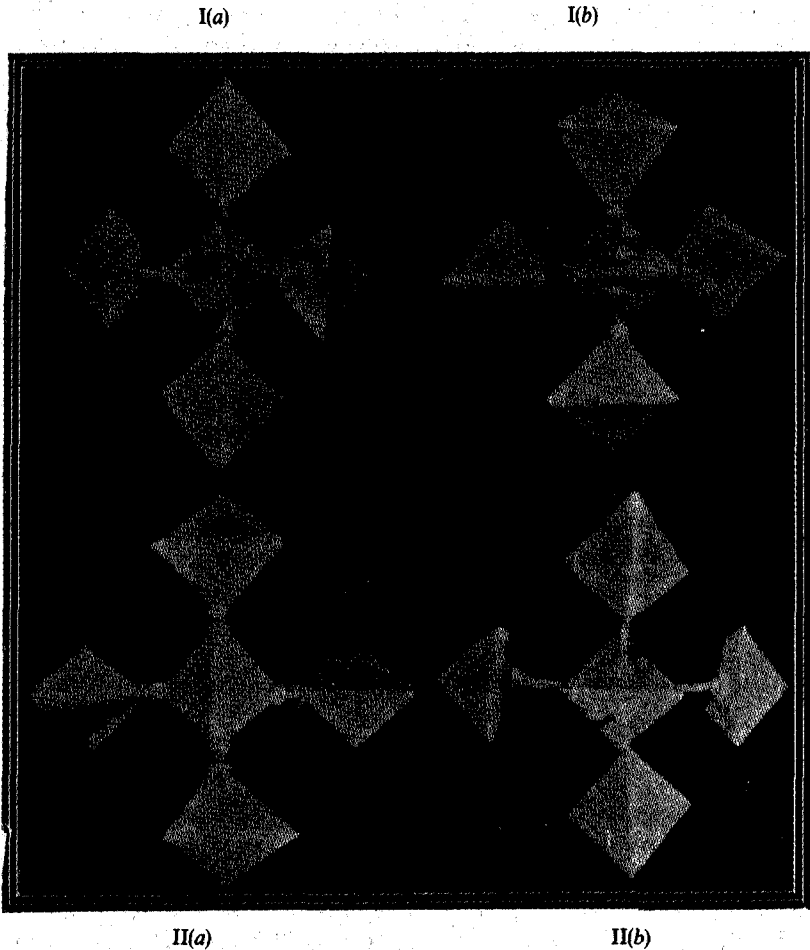

I(a)   I(b)

II(a)   II(b)

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
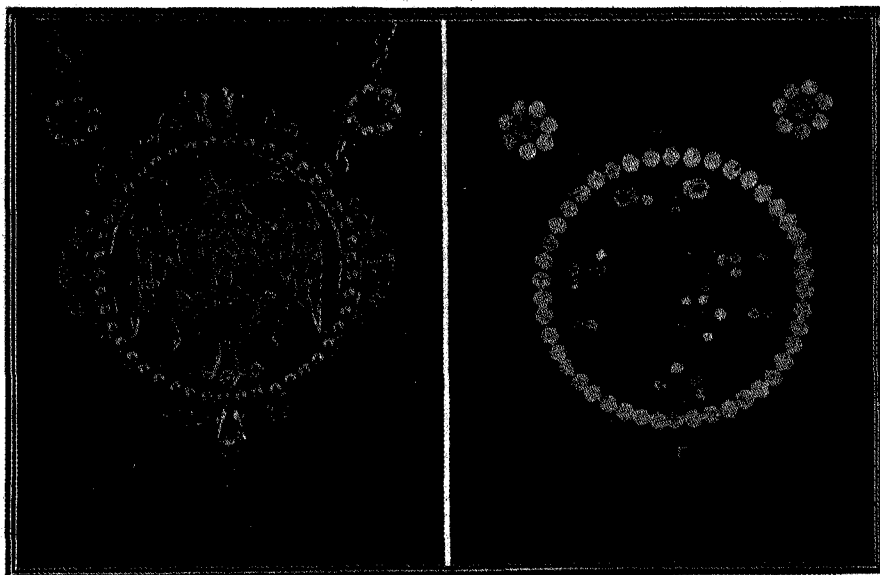

Figure 2. Luminescence of diamonds, pearls and rubies. (Photographs by Mr T M K Nedungadi.)

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.

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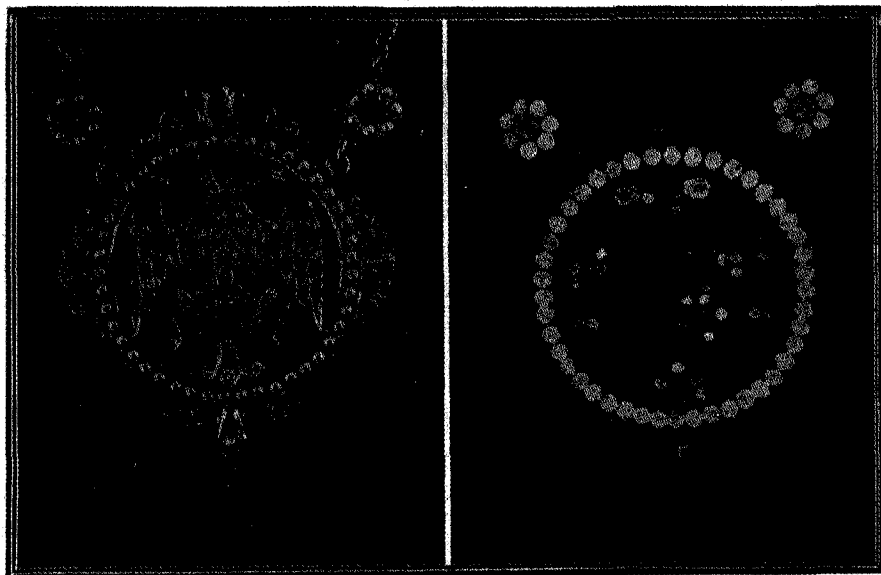

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diamonds. These investigators have found that in spite of the enormous differences mentioned above, the luminescence spectra of all diamonds (irrespective of their origin) are essentially similar and that this is also the case for the associated absorptions 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.
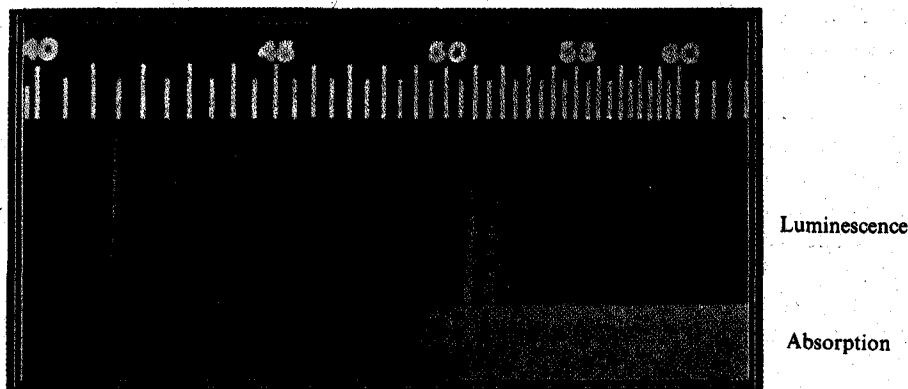

Luminescence

Absorption

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 allotropic 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
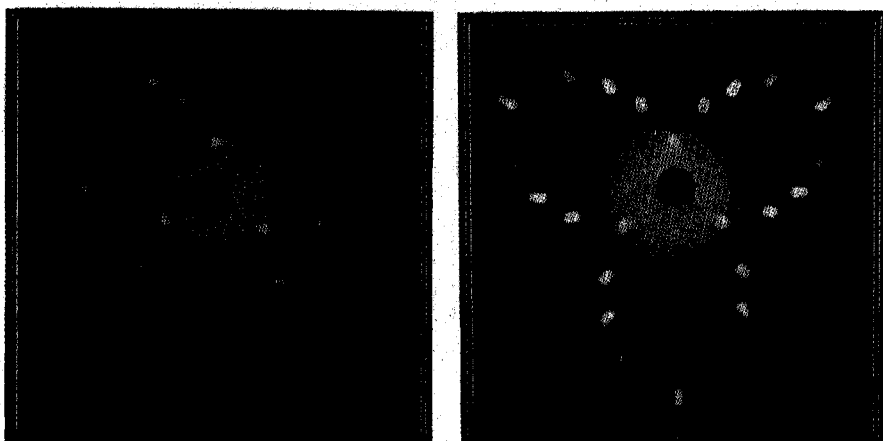
I. Weakly fluorescent tetrahedral diamond   II. Strongly fluorescent tetrahedral diamond

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 8μ. 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.