The crystal symmetry and structure of diamond

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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 elctronic 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 strucutre 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
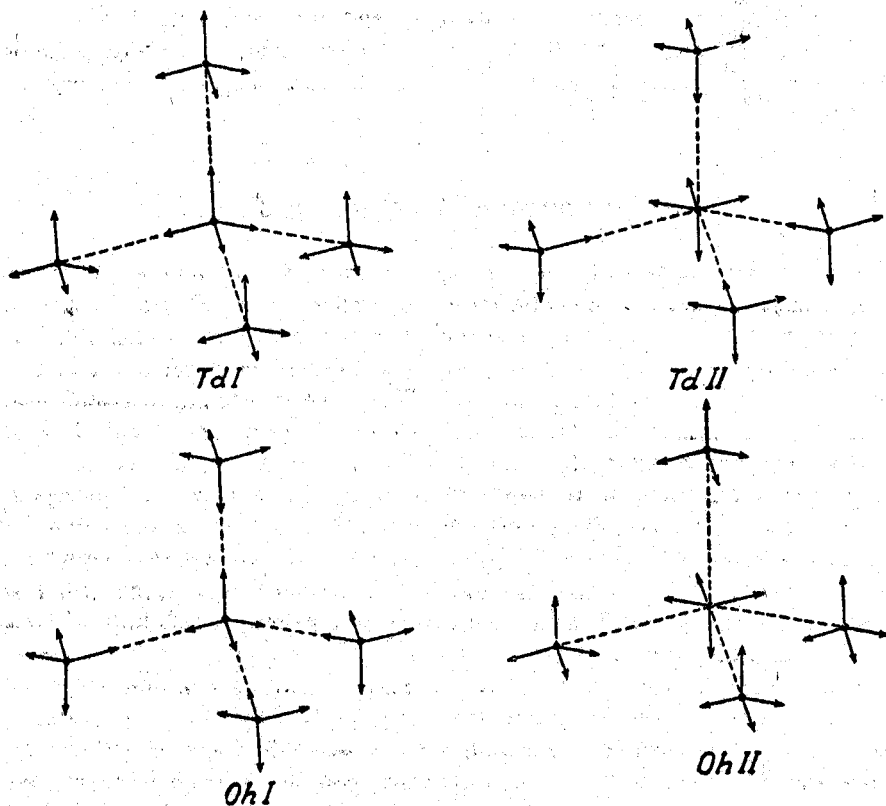

Figure 1. The four possible structures of diamond.

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 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 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 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 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 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 predic-
tions 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.

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