ON THE CRYSTAL SYMMETRY OF DIAMOND AND ITS X-RAY REFLECTIONS

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§1. On the basis of the observed crystal forms of diamond, especially of grooved octahedra, duplex tetrahedra and such other typical twin forms, the earlier crystallographers assigned diamond to the hemimorphic hemihedral or the tetrahedral (Td) class of the cubic system (*vide* Groth, 1895; Liebisch, 1896; Miers, 1902; Hintze, 1904). That this is the case in the majority of diamonds is confirmed by observations of the infra-red absorption of diamond by a number of investigators (Ångstrom, 1892; Julius, 1893; Reinkober, 1911) and particularly by Robertson, Fox and Martin (1934), who found that a majority of diamonds exhibit a strong infra-red absorption in the region of 8μ, while in other diamonds, the absorption is absent. Applying the well-known selection rules for infra-red absorption (Placzek, 1934), it becomes obvious that the former class of diamonds should possess only tetrahedral (Td) symmetry, while the latter should possess the full octahedral (Oh) symmetry of the cubic system (Raman, 1944). An alternative explanation that the infra-red absorption arises from the presence of impurities or of structural imperfections is ruled out by the fact that the diamonds that show the absorption most prominently are precisely those that possess the maximum amount of crystal perfection (Ramachandran, 1944 *b*), while *per contra* diamonds that possess a large mosaic structure are transparent to the infra-red (Hariharan, 1944; Ramachandran, 1944 *a*). To explain these facts regarding infra-red absorption as well as a whole series of other phenomena exhibited by diamond, Sir C. V. Raman (1944) put forward considerations which indicate that there are four possible structures for diamond, two with tetrahedral symmetry and two others with octahedral symmetry, and in doing so remarked that the data regarding the X-ray reflections given by diamond are consistent with the existence of these four forms. In the present paper, this question is considered in a formal and rigorous manner. The consequences of the difference in symmetry of the various structures

are worked out, and are compared with the observed X-ray behaviour of diamond.*

We shall accept the results of X-ray analysis that the diamond structure consists of two interpenetrating face-centred cubic lattices, with the carbon atoms in the basis occupying the positions 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. It may be pointed out that the main facts which led to this structure were the absence of the 200 and the 222 X-ray reflections observed by the earliest investigators (Bragg and Bragg, 1913). We shall accept the structure described above, since it fits in well with the quadrivalence of carbon, a well-known chemical result. The questions to be decided are: (*a*) what the symmetry of the electronic configurations of the individual carbon atoms is, and (*b*) what the relationship between the electronic structures of the two carbon atoms is. In this connection, we have also to discuss the results of later experimenters, who have remarked that the 222 reflection is present feebly, *e.g.*, Bragg, 1921; Ehrenberg, Ewald and Mark, 1928.

§2. On account of the special positions which the carbon atoms occupy in the space-lattice, they should possess a symmetry not lower than that of the point-group Td. For the purpose of the following discussion, we shall take it that they possess that symmetry. This means that if $\rho_1(xyz)$ is the electronic charge density at the point xyz, then it is the same at the following 24 equivalent points:

$$\begin{array}{llllll} xyz\,; & zxy\,; & yzx\,; & yxz\,; & zyx\,; & xzy\,; \\ x\bar{y}\bar{z}\,; & z\bar{x}\bar{y}\,; & y\bar{z}\bar{x}\,; & y\bar{x}\bar{z}\,; & z\bar{y}\bar{x}\,; & x\bar{z}\bar{y}\,; \\ \bar{x}y\bar{z}\,; & \bar{z}xy\,; & \bar{y}z\bar{x}\,; & \bar{y}x\bar{z}\,; & \bar{z}y\bar{x}\,; & \bar{x}z\bar{y}\,; \\ \bar{x}\bar{y}z\,; & \bar{z}\bar{x}y\,; & \bar{y}\bar{z}x\,; & \bar{y}\bar{x}z\,; & \bar{z}\bar{y}x\,; & \bar{x}\bar{z}y\,; \end{array} \qquad (1)$$

This set may be represented by the symbol $\{xyz\}$. Similarly, the electronic charge densities at the points $\frac{1}{4}\frac{1}{4}\frac{1}{4}+\{xyz\}$ are all equal, which may be denoted by $\rho_2(xyz)$. Note that no assumption is made as to the relationship between ρ_1 and ρ_2. For the present, it is supposed that the two carbon atoms are different. It is also to be noted that $\rho(xyz)$ is not necessarily equal to $\rho(\bar{x}\bar{y}\bar{z})$.

We shall now derive an expression for the structure factor for the *hkl* reflection with such a structure. Consider a set of 96 volume elements, each of magnitude dv, surrounding the points $\{xyz\}$, $\{\bar{x}\bar{y}\bar{z}\}$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}+\{xyz\}$

* A preliminary report by the author (1945) appeared in *Nature*, in which some specific points raised by Mrs. Lonsdale (1945) regarding the X-ray behaviour of the various forms of diamond were answered.

and $\frac{1}{4}\frac{1}{4}\frac{1}{4} + (\bar{x}\bar{y}\bar{z})$. Denoting by $\phi(hkl)$ the structure factor corresponding to these volume elements, it can be shown that

$$\phi(hkl) = \{\rho_1(xyz)(A + iB) + \rho_1(\bar{x}\bar{y}\bar{z})(A - iB) + \rho_2(xyz)(A + iB).$$
$$\exp 2\pi i(h + k + l)/4 + \rho_2(\bar{x}\bar{y}\bar{z})(A - iB) \exp 2\pi i(h + k + l)/4\}\, dv, \quad (2)$$

where
$$A = 16 \cos 2\pi \frac{h-k}{4} \cos 2\pi \frac{k-l}{4} \cos 2\pi \frac{l-h}{4}.$$
$$\{\cos 2\pi lz (\cos 2\pi hx \cos 2\pi ky + \cos 2\pi kx \cos 2\pi hy)$$
$$+ \cos 2\pi hz (\cos 2\pi kx \cos 2\pi ly + \cos 2\pi lx \cos 2\pi ky)$$
$$+ \cos 2\pi kz (\cos 2\pi lx \cos 2\pi hy + \cos 2\pi hx \cos 2\pi ly)\} \quad (3)$$

and
$$B = -16 \cos 2\pi \frac{h-k}{4} \cos 2\pi \frac{k-l}{4} \cos 2\pi \frac{l-h}{4}$$
$$\{\sin 2\pi lz (\sin 2\pi hx \sin 2\pi ky + \sin 2\pi kx \sin 2\pi hy)$$
$$+ \sin 2\pi hz (\sin 2\pi kx \sin 2\pi ly + \sin 2\pi lx \sin 2\pi ky)$$
$$+ \sin 2\pi kz (\sin 2\pi lx \sin 2\pi hy + \sin 2\pi hx \sin 2\pi ly)\}. \quad (4)$$

The crystal structure factor $F(hkl)$ can be obtained by integrating $\phi(hkl)$ over the appropriate volume. From the above expressions, the elementary structure factors corresponding to the 200 and the 222 reflections are:

$$\phi(200) = A dv \{\rho_1(xyz) + \rho_1(\bar{x}\bar{y}\bar{z}) - \rho_2(xyz) - \rho_2(\bar{x}\bar{y}\bar{z})\} \quad (5)$$

$$\phi(222) = iB dv \{\rho_1(xyz) - \rho_1(\bar{x}\bar{y}\bar{z}) - \rho_2(xyz) + \rho_2(\bar{x}\bar{y}\bar{z})\} \quad (6)$$

Consequently, the condition that the 200 or the 222 reflection should vanish is that the quantity within the double brackets in Eq. (5) or (6) respectively should be equal to zero.

Let us now consider the circumstances under which the structure possesses octahedral symmetry. This can occur in one of two possible ways: the individual carbon atoms can themselves possess octahedral symmetry, or the two carbon atoms can be tetrahedral, but possess identical configurations with the two tetrahedral atoms pointing in opposite directions. In the latter case, the structure has a centre of symmetry at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, and belongs to the space group O_h^7. The two conditions can algebraically be represented as follows:

$$\left.\begin{aligned} &(a)\quad \rho_1(xyz) = \rho_1(\bar{x}\bar{y}\bar{z});\quad \rho_2(xyz) = \rho_2(\bar{x}\bar{y}\bar{z}) \\ &(b)\quad \rho_1(xyz) = \rho_2(\bar{x}\bar{y}\bar{z});\quad \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(xyz) \end{aligned}\right\} \quad (7)$$

A careful comparison of the conditions for the vanishing of the 200 and the 222 reflections with those for the existence of octahedral symmetry shows that there is really no interrelation between them, though if 7 (*b*) subsists, the 200 reflection automatically vanishes. In other words, from the knowledge that the 200 or the 222 reflection is present or absent, one cannot uniquely conclude that the crystal has tetrahedral or octahedral symmetry and *vice versa*.

§3. It is a fairly well-established experimental fact that the 200 reflection does not appear with diamond. Taking this into consideration, let us consider what restrictions it imposes on the structure. From (5), the condition that 200 should vanish is

$$\rho_1(xyz) + \rho_1(\bar{x}\bar{y}z) = \rho_2(xyz) + \rho_2(\bar{x}\bar{y}\bar{z}), \tag{8}$$

i.e., if we take two points in each of the atoms such that they are equidistant in opposite directions from the centre of the atoms, then the sum of the electronic charge densities at these two points should be the same for both the atoms. From this, it follows that the total charge in spherical shells surrounding the two atoms are equal, provided the radii of the two shells is the same, independent of the magnitude of the radius. This explains why diamond is not a polar substance, and also makes it comprehensible why diamond does not exhibit any appreciable piezo- or pyro-electric properties. However, the condition (8) does not impose any restriction at all on the symmetry of the structure.

We shall now consider the various structures that are possible, subject to the condition (8). In this connection, it will be convenient to use a special nomenclature. It will be seen that if

$$\rho_1(xyz) = \rho_2(\bar{x}\bar{y}z) \text{ and } \rho_1(\bar{x}\bar{y}z) = \rho_2(xyz),$$

then the equation (8) is satisfied. This is identical with (7 *b*), and the structure has a centre of symmetry mid-way between the two atoms. We shall therefore designate it as a symmetric structure. On the other hand, we shall call a structure antisymmetric if

$$\rho_1(xyz) = \rho_2(xyz) \text{ and } \rho_1(\bar{x}\bar{y}z) = \rho_2(\bar{x}\bar{y}\bar{z}). \tag{9}$$

It is obvious that this also satisfies Eq. (8). It is easy to show that the ρ's in Eq. (8) can always be split into a symmetric and an antisymmetric component, and that the manner in which this can be done is unique if the ρ's are known quantities. For let

$$\rho_1(xyz) = \alpha + \beta \quad \text{and } \rho_1(\bar{x}\bar{y}\bar{z}) = \alpha' + \beta', \tag{10}$$

where α and β are respectively the symmetric and the antisymmetric components. Then, by the definitions above,

$$\rho_2(xyz) = \alpha' + \beta \qquad \text{and } \rho_2(\bar{x}\bar{y}\bar{z}) = \alpha + \beta'. \tag{11}$$

The four equations in (10) and (11) form a set of linear equations in the four unknown α, β, α', β' and can therefore be uniquely solved. If, on the other hand, it is only known that the 200 reflection is absent, then all that can be said about the electronic distribution is that it consists of a symmetric component α and an antisymmetric component β, the ratio of α to β being undetermined.

Now, it is evident that if $\beta = \beta' = 0$, *i.e.*, if the antisymmetric component is entirely absent, then the structure possesses octahedral symmetry. But if the β's are finite, however small they might be, then the structure has only tetrahedral symmetry. Since various physical properties of the tetrahedral and octahedral modifications of diamond do not differ notably (as, for example, the lattice spacing, the principal vibrational frequency of 1332 cm.$^{-1}$, etc.), the differences in the electronic configurations must be small. In other words, the tetrahedral symmetry must arise from the presence of a relatively small proportion of an antisymmetric distribution. This would explain why the infra-red absorption observed in tetrahedral diamond is not very strong, a thickness of 1 mm. producing only about 90% absorption (Ramanathan, 1946) in comparison with the practically cent. per cent. absorption of the alkali halides in extremely small thickness of the order of a few microns (Barnes, 1932).

§4. We shall now consider the various possibilities for the 222 reflection, *subject to the condition that the* 200 *reflection vanishes*. From (6), 222 vanishes if

$$\rho_1(xyz) - \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(xyz) - \rho_2(\bar{x}\bar{y}\bar{z}). \tag{12}$$

Combining (12) with (8), the conditions that the 200 and the 222 reflections should simultaneously vanish can be put in the form

$$\rho_1(xyz) = \rho_2(xyz): \quad \rho_1(\bar{x}\bar{y}\bar{z}) = \rho_2(\bar{x}\bar{y}\bar{z}).$$

These are identical with (9), which means that 222 is absent if and only if the structure is completely antisymmetric. On the other hand, a symmetric distribution must necessarily give rise to a finite 222 structure amplitude. These statements however need a qualification. In the special case, in which the individual carbon atoms possess octahedral symmetry, the distinction between the terms symmetric and antisymmetric disappears, since the electronic charge distribution satisfies the conditions for both. The 222 reflection would be absent for this structure.

We are now in a position to discuss the origin of the observed feeble 222 reflection referred to in §1. If we assume that this is a genuine Bragg reflection, then the octahedral diamond should have an electronic distribution of the symmetric type with no antisymmetric component whatsoever. The tetrahedral modification must arise from the presence of a small proportion of an antisymmetric distribution as mentioned in §3. It can be shown that the structure amplitudes for reflections like 400 and 220 for which $h + k + l = 4n$ will be unaffected, while that for 222 will theoretically be different, the difference however being small, since it is proportional to the ratio of the antisymmetric to the symmetric component.

Pisharoty (1941) has suggested that the 222 reflection is purely a modified or quantum reflection. If this is the case, then, in the octahedral diamond, each of the carbon atoms should possess octahedral symmetry. Here also, the tetrahedral modification must arise from the presence of a small proportion of the antisymmetric distribution. The 222 reflection is absent for both, and reflections hkl with $h + k + l = 4n$ are also unaffected.

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Summary

The problem of the symmetry of the diamond structure in relation to its X-ray behaviour is considered in a formal manner. It is shown that the presence or absence of the 200 or the 222 reflection cannot uniquely decide whether the symmetry is tetrahedral or octahedral. The 200 reflection is shown to be absent if the structure is either completely symmetric or antisymmetric with respect to the centre of inversion at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ or if the two distributions are superposed in any arbitrary ratio. The 222 reflection is, however, absent only in the fully antisymmetric case. Making use of these results, the nature of the structures that are possible for the tetrahedral and the octahedral modifications of diamond are discussed.

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