

THE DIFFRACTION OF X-RAYS BY DIAMOND: PART II

BY SIR C. V. RAMAN

(*Memoir No. 109 of the Raman Research Institute, Bangalore-6*)

Received May 5, 1958

1. INTRODUCTION

FOR various reasons, diamond is the ideal case for a consideration of the consequences following from the ideas set out in Part I of this series of papers regarding the diffraction of X-rays by crystals. Since diamond is a cubic crystal of relatively simple structure, it is possible to determine and describe in purely geometrical terms the modes of vibration of which that structure is capable and with which we are concerned. It can also be shown that these modes have a high frequency, from which again it follows that they would not be thermally excited to any appreciable extent at ordinary temperatures. For the same reason also, it is permissible to ignore the disturbing effects on the phenomena with which we are concerned, of the thermal agitation in the crystal. It accordingly becomes possible to present a very clear picture of the effects which may be expected to present themselves to observation in strongly exposed X-ray diffraction patterns of diamond, on the basis of the theory developed in Part I.

2. THE STRUCTURE OF DIAMOND

Diamond exhibits in its structure a complete justification of Van't Hoff's hypothesis of the tetrahedral carbon atom. That hypothesis was originally put forward on the basis of the known chemical behaviour of carbon. It implies that the four valences which carbon exhibits in its compounds are tetrahedrally disposed in space and are indistinguishable from each other. Why this is so is one of the fundamental problems of theoretical chemistry. According to the spectroscopist's view of atomic structure, the nucleus of the carbon atom is surrounded by six electrons, two of which are in the inner or K-shell and the other four in the outer or L-shell. The latter four electrons again are assigned to two sub-groups, each containing two electrons. In the first sub-group, the electrons are assumed to be in the $2s$ state, while the two electrons in the other sub-group are in the $2p$ state. This situation of the four outer electrons is not in agreement with that indicated by the facts

of chemistry and hence it becomes necessary to modify the description of their states to bring it into line with the known chemical behaviour of carbon. All the four electrons have indeed to be considered as being in states indistinguishable from each other and so orientated that the resulting structure has perfect tetrahedral symmetry. Such a concept is necessary also to fit the picture of the carbon atom into the known facts concerning the structure of diamond. Having only two atoms in each unit cell, diamond nevertheless exhibits cubic symmetry. This situation requires that the nuclei of the carbon atoms occupy certain special positions in the crystal structure, namely, the points at which the four trigonal axes of cubic symmetry intersect each other.

The theory of hybridised orbitals is one of the best known attempts in the direction of describing the electronic state of the carbon atom in such manner as to bring it into line with the hypothesis of Van't Hoff. As full accounts of that theory are to be found in several recent treatises, it is not necessary here to expound it in detail. It is sufficient to mention that the states of the four electrons are assumed in that theory to be representable as a superposition of four hydrogen-like wave-functions which are so chosen that all the four electrons appear in similar states differing only in their orientations, which again exhibit tetrahedral symmetry. In the wave-functions assumed for the purpose, the $2p$ states preponderate, and hence each of the four electrons is implicitly assumed to possess an orbital angular momentum about an axis which coincides in direction with its directed valence. We may remark that for the shell of valence electrons thus constituted to possess true tetrahedral symmetry, it is necessary that the orbital movements of the four electrons about their respective axes should be described in the same sense, that is to say, either all of them in a right-handed sense, or else all of them in a left-handed sense. We are thus led to recognize that there are two possible descriptions of the carbon atom, namely, a dextro-carbon atom and a laevo-carbon atom, which correspond respectively to the two possible senses of the orbital angular momentum of the electrons about the tetrahedral valence directions.

The considerations set forth above have important consequences in relation to the structure and physical properties of diamond. That crystal is usually described as made up of two non-equivalent sets of carbon atoms each located at the points of a face-centred cubic lattice; the two lattices interpenetrate each other in such manner that every carbon atom in one lattice is tetrahedrally surrounded by four others belonging to the other lattice. Accepting this description, it follows that in a truly homogeneous crystal of

diamond, only one out of four possible situations can exist: (i) both lattices are occupied by dextro-carbon atoms, (ii) both lattices are occupied by laevo carbon atoms, (iii) one lattice is occupied by dextro-carbon atoms and other by laevo-carbon atoms, or (iv) the first lattice is occupied by laevo- and the second by dextro-carbon atoms. It is entirely possible that two or three or all four of these possible structures may exist simultaneously in different parts of the same crystal. It is sufficient, however, to consider here only the case of truly homogeneous diamonds the structure of which is exclusively one or another of the four categories set out above.

3. THE VIBRATION SPECTRUM OF DIAMOND

The vibration spectrum of a crystal containing p atomic nuclei in each unit cell consists of $(24p - 3)$ distinct modes with monochromatic frequencies, supplemented by a continuous spectrum which is the residue representing the three omitted degrees of translatory freedom of motion. Since the unit cell of diamond contains 2 atomic nuclei only, we have 45 possible modes of vibration with monochromatic frequencies. The description of these modes and the evaluation of their frequencies have been very fully set out in an earlier memoir published in these *Proceedings*. In two other memoirs again, it has been shown that the heat capacity of diamond over the entire range of temperatures may be quantitatively evaluated in terms of these frequencies. It is therefore unnecessary to traverse the same field again, and indeed in the present paper we are only concerned with the three modes of vibration of highest frequency which may be described as an oscillation of the two lattices of carbon atoms with respect to each other along one or another of the three cubic axes. The free vibrations of the structure in all these three modes have the same frequency, and this is known exactly from spectroscopic studies on the diffusion of monochromatic light in diamond. A sharply defined line with a frequency shift of 1332 cm.^{-1} is recorded in the spectrum of the scattered light, and this frequency is associated with a vibration of the kind described above.

Whether the mode of vibration referred to above would be excited by the passage of X-rays through the crystal depends, as we have seen in Part I, on whether this mode is or is not active in the absorption of infra-red radiation. The circumstances which determine whether a specified mode of vibration in a crystal is active or not in the absorption of infra-red radiation have been considered by various authors and will be found discussed in detail in several recent treatises. It is a well-established rule deduced from theory and confirmed experimentally that if a structure possesses centres of symmetry,

any mode of vibration which manifests itself as a frequency shift in light scattering would be *inactive* in the absorption of infra-red radiation. In the first two sub-species of diamond referred to above, both sets of carbon atoms are dextro-carbon atoms or both laevo-carbon atoms respectively. It is clear that every point midway between a pair of atoms belonging respectively to the two lattices would in these cases be a centre of symmetry. Accordingly, in these two sub-species of diamond, since the mode of vibration with the frequency 1332 cm.^{-1} manifests itself as a frequency in light-scattering, that mode would be *inactive* in infra-red absorption. *Per contra*, in the two other sub-species of diamond where the carbon atoms located at the points of the two lattices are of different species, the points midway between two carbon atoms are *not* centres of symmetry. Hence the rule of mutual exclusion stated above is not applicable in their cases and hence the modes of vibration would be active *both* in the scattering of light and in the absorption of infra-red radiation. In what follows, we shall refer to the first two sub-species of diamond as the Oh I and Oh II types of diamond respectively, and the two other sub-species as Td I and Td II respectively. The use of these symbols has a special significance, *viz.*, that the electronic structure of the first two species of diamond has the full or octahedral symmetry of the cubic system, whereas the electronic structure of the two other species has only the lower or tetrahedral symmetry.

We may conclude this section by a categorical statement of the results indicated by the theory. *In diamonds which belong to the two sub-species Oh I and Oh II, the fundamental vibration of the structure with frequency of 1332 cm.^{-1} would not be active in infra-red absorption and hence the passage of X-rays through the crystal would not excite that vibration and hence would not result in a dynamic reflection.* *Per contra, in diamonds which belong to the two other sub-species Td I and Td II, the said vibration would be active in the absorption of infra-red radiation and hence the passage of X-rays through the crystal would excite those vibrations and give rise to dynamic reflections by the lattice planes in the crystal.*

4. THE PHASE WAVES OF DYNAMIC REFLECTION

We shall proceed to consider the nature of the dynamic reflections which may be expected to manifest themselves in the case of diamonds possessing only the lower or tetrahedral symmetry of electronic structure as the result of the excitation of the infra-red active vibration. As already stated, this vibration is an oscillation of the interpenetrating lattices of carbon atoms (in these cases dissimilar to each other) along one or another of the three cubic axes of the crystal. The atoms belonging to the two lattices appear in distinct but

equidistant layers parallel to the cubic planes. The infra-red activity of the vibration arises from the fact that the electronic structure of the carbon atoms in the alternate layers is not completely identical. Hence, the oscillations of the two lattices with respect to each other results in periodic displacements of electric charge along the direction of vibration. We have three such movements to consider, which are respectively along one or another of the three cubic axes of the crystal. Hence, we have also three sets of phase-waves to consider whose normals are likewise the cubic axes.

The oscillatory movements of electric charge along the cubic axes of the crystal would necessarily also result in periodic movements of the stratifications of electric charge which appear in the crystal in other directions. In considering the question whether these movements would give rise to dynamic reflections by those stratifications, we have to remark that movements *parallel* to any set of stratifications cannot give rise to any dynamic reflections by them; only movements *normal* to the stratifications can give rise to such reflections, and hence if the actual movements are *inclined* to the stratifications, we need consider only the components of the movement along their normals.

Considering for example the (111) planes in a crystal, the three movements respectively along the three cubic axes are equally inclined to those planes, and hence the magnitude of all the three components resolved along the normal to the (111) planes would be diminished to the same extent. Hence, in general, *the (111) planes would give three dynamic reflections* which in appropriate circumstances, may be expected to be of comparable intensities. On the other hand, the (220) planes of the crystal contain one cubic axis and are equally inclined to the other two at angles of 45° . The displacements of electric charge parallel to the first axis and hence also parallel to the plane of the stratifications would not give rise to any dynamic reflection. However, movements along the two other cubic axes would result in a displacement of the stratifications in the (220) planes diminished to equal extents by reason of their inclination to those planes. We conclude that *the (220) planes would give only two dynamic reflections* which in appropriate circumstances would be of equal intensity. Considering again the (400) planes, these contain two of the cubic axes and are normal to the third, it follows for similar reasons that *the (400) planes give only one dynamic reflection*. The fact that the phase-waves are parallel to those planes has a further interesting consequence to which we shall revert later. Finally, we may briefly consider the (311) planes. These planes are equally inclined to two of the cubic axes at small angles and are nearly perpendicular to the third. The dynamic

reflections due to the first two movements may therefore be expected to behave very differently from the third.

5. THE GEOMETRY OF THE DYNAMIC REFLECTIONS

The general method already indicated in Part I enables us to picture the configuration of the dynamic reflections given by the various lattice planes in the crystal. We shall here content ourselves with the consideration of the dynamic reflections associated with the (111), (220), (311) and (400) planes, since these are the four largest spacings in the crystal which also reflect X-rays with notable intensity. The first three cases are represented in Figs. 1, 2 and 3 respectively for settings of the crystal so chosen that the

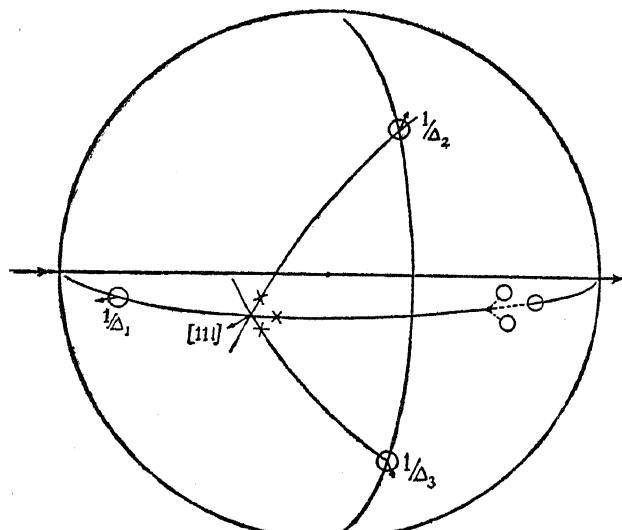


FIG. 1. Dynamic Reflections by the (111) planes.

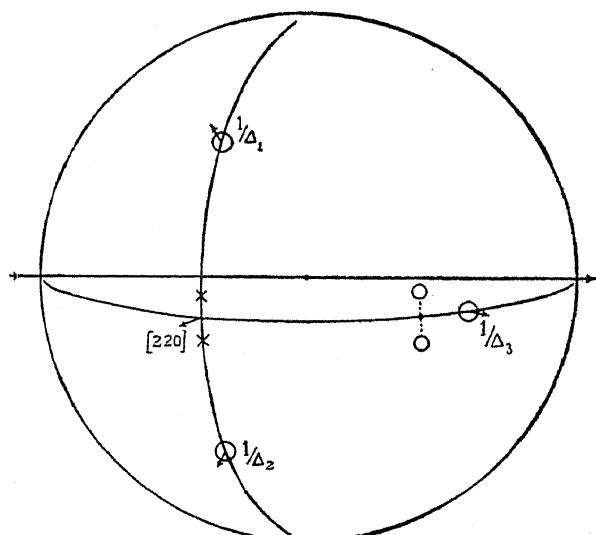


FIG. 2. Dynamic Reflections by the (220) planes.

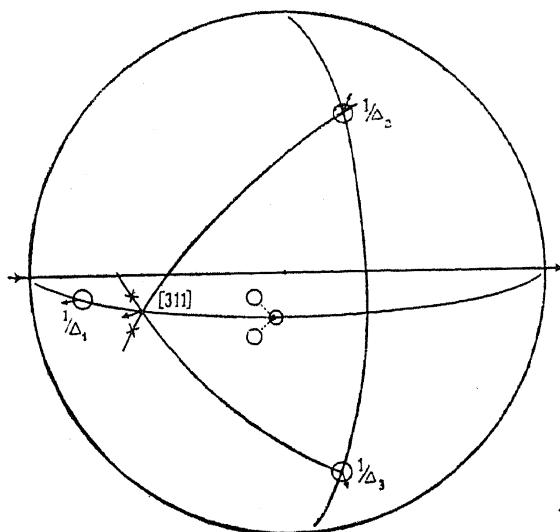


FIG. 3. Dynamic Reflections by the (311) planes.

characteristic features of each case are brought out clearly. The primary X-ray beam is assumed to traverse the crystal horizontally and its direction is indicated by arrows at the points of entry and exit on a sphere. The plane of incidence on the lattice-spacings is also assumed to be horizontal and is indicated by a great circle drawn on the surface of the sphere. The normal to the lattice spacings accordingly appears as a point on the same great circle with an arrow attached to it and directed radially outwards. The three cubic axes of the crystal which are the normals to the phase-waves of dynamic reflection are represented on the sphere in a similar fashion, the points where they appear being determined by the chosen setting of the crystal. Three great circles are also drawn each of which contains one of the phase-wave normals and the normal to the lattice spacings. In each case the setting of the crystal chosen is such that one of the great circles coincides with the plane of incidence. The normals to the three sets of dynamic stratifications would necessarily lie on these three great circles. The positions of the dynamic reflections would be determined by drawing three other great circles, each containing the direction of the incident beam and the normal to the particular dynamic stratification, and marking off on these circles, points such that the angle of reflection is equal to the angle of incidence in the respective planes. The entire procedure is that indicated by the theory of dynamic reflection developed in Part I and contained in the two equations

$$\vec{D} = \vec{d} + \frac{1}{d} \vec{A} \quad (1)$$

$$2D \sin \psi = \lambda \quad (2)$$

For a particular X-ray wavelength determined by the lattice spacings and the angle of incidence of the X-rays on them, we would observe the ordinary or unmodified reflection in the plane of incidence. The direction in which this appears is represented in each of the figures as another point on the equatorial circle. For the same X-ray wavelength, the dynamic reflection or reflections permitted would also appear in the same direction superposed on the ordinary or static reflection. For other X-ray wavelengths, the static reflection ceases to appear but the dynamic reflections would persist, their directions being determinable in the manner already explained. The phase wavelength is infinite for the particular case in which the static and dynamic reflections are superposed. With progressively changing X-ray wavelength, $1/\lambda$ would increase in numerical magnitude and the point on the sphere representing the dynamic stratification would move out in one direction or another along the great circle which defines its path. The construction already indicated would then result in giving positions to the dynamic reflections differing from that in which they were originally coincident. In the particular settings of the crystal which have been chosen for drawing the figures, the dynamic reflection which corresponds to the cubic axis in the plane of incidence would—if it exists at all—appear in the plane of incidence, while the other two would swing out of that plane symmetrically in either side.

For reasons already explained, whereas the (111) planes show *three* dynamic reflections in the setting indicated, the (220) planes show only two reflections: these are displaced laterally, one on either side. The third reflection lying in the plane of incidence though *geometrically* permitted is *physically* excluded by reason of the movement of the stratifications being in their own plane. The case of (400) reflection is of special interest. As explained earlier, only one dynamic reflection is possible in this case and since the phase-waves which give that reflection are parallel to the stratifications themselves, the dynamic reflection for all X-ray wavelengths would appear in the same direction, *viz.*, that indicated by the ordinary law of geometric reflection.

6. SUMMARY

Considerations of the physical nature of the directed valences of the tetrahedral carbon atom lead to the conclusion that there are two possible states of the carbon atom, *viz.*, a dextro-state and a laevo-state corresponding respectively to the two possible senses of the orbital angular momentum of the electrons about their tetrahedral valence directions. From this again it follows that a homogeneous diamond crystal may have an electronic structure which has either the highest or octahedral symmetry or else only the lower

or tetrahedral symmetry of the cubic system. In diamonds having octahedral symmetry, the oscillations of the two carbon atoms with respect to each other would be inactive in the absorption of infra-red radiation, whereas in diamonds of which the electronic configuration has tetrahedral symmetry that vibration would be active in such absorption. From this it follows that only with diamonds of the latter type would the X-rays excite the lattice vibrations and exhibit the dynamic reflections consequent thereon. The vibrations excited and their phase-wave-normals are parallel to the three cubic axes of the crystal. It follows that whereas the (111) planes would exhibit *three* dynamic reflections at any one setting of the crystal, the (220) would exhibit only *two* and the (400) planes only *one*.