

EXPERIMENTAL EVIDENCE FOR THE EXISTENCE OF THE FOUR POSSIBLE STRUCTURES OF DIAMOND

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1. Introduction

IN the introductory paper of this symposium, Sir C. V. Raman has set out the theoretical considerations which indicate that the crystal structure of diamond has four possible forms. Two of these (Td I and Td II) have only tetrahedral symmetry, while the other two (Oh I and Oh II) have the full symmetry of the cubic system. These considerations receive support from the known spectroscopic behaviour of diamond, as also from the observed crystallographic facts. The fundamental oscillation of the two interpenetrating lattices of carbon atoms with respect to each other should be active in the infra-red absorption in the tetrahedral varieties of diamond, since these do not possess a centre of symmetry. On the other hand, this vibration should be infra-red inactive in the octahedral types of diamond, since these possess a centre of symmetry. The well-known fact that an intense infra-red absorption in the neighbourhood of 7.5μ (corresponding to the lattice frequency of 1332 wavenumbers) is exhibited by some diamonds, while such absorption is absent in others, thus receives a natural explanation.

Accepting the conclusion indicated by the infra-red absorption data and the observed crystal forms that diamond may have either tetrahedral or octahedral symmetry, it is difficult to resist the further implication of the theory that there are two variants under each class. It is obviously of great importance to obtain convincing experimental evidence for the physical existence of all the four forms postulated. Since *prima facie*, all the four types should have closely similar properties, such evidence must be sought in measurements where the highest degree of precision is possible, *viz.*, in X-ray and in spectroscopic data. It is the object of this paper to present such evidence.

2. The Two Tetrahedral Structures

It is obvious that the two tetrahedral types of diamond, namely, the positive and the negative forms, are physically identical and only geometrically

different. Hence, they should possess precisely the same crystal spacing and lattice vibration frequency, and therefore apparently be indistinguishable from each other. If, however, both forms co-exist in one and the same specimen of diamond, this would give rise to a heterogeneity, and variations in the physical properties should arise depending upon the extent of their interpenetration. The spectroscopic studies of Nayar (1941), (Miss) Mani (1944) and Mrs. Sunanda Bai (1944) on the absorption and the luminescence spectra of diamonds show clearly the existence of such large variations. These may be regarded as fairly convincing evidence for the existence of the interpenetration and consequent variations in structure.

A clearer and more direct proof is, however, forthcoming from X-ray studies. The interpenetration of the positive and negative tetrahedral structures and consequent heterogeneity should evidently manifest itself in increased intensity of X-ray reflections from the lattice planes of the crystal. This conclusion was experimentally tested out by the author as early as May 1942. The diffraction of X-rays in a few typical diamonds of the tetrahedral variety exhibiting luminescence in varying degrees, was studied both by the Laue and by the Bragg methods, in the latter case with oscillating crystals. It was found that there was a direct correlation between the intensities of X-ray reflections and of luminescence of the diamond. The diamond exhibiting the blue luminescence with the least observable intensity were also the diamonds which gave the least intensities of X-ray reflections, showing thereby that these diamonds approached more closely to the ideal homogeneous structure. The strongly blue fluorescent diamonds gave rise to intense Laue and Bragg reflections, suggesting thereby that these specimens had a heterogeneous or mosaic structure arising from the interpenetration of the two tetrahedral types. These observations of the author have later been confirmed and extended by Hariharan (1944) and Ramachandran (1944).

3. The Two Octahedral Structures

Unlike the two forms of the tetrahedral type, the possible forms of the octahedral type, namely, Oh I and Oh II should be physically different from one another. Consequently, whenever interpenetration of the two octahedral forms occurs, the specimen exhibits a lamellar structure parallel to one or more of the cleavage planes of the crystal. Such specimens of diamond often show a streaky birefringence. Because of their physical difference, it is reasonable to expect the two octahedral forms of diamond structure to show a small but measurable difference in crystal spacing. The direct way of testing out the above conclusion would consist in an accurate determination of the lattice spacing in two perfectly homogeneous specimens

belonging to the Oh I and Oh II types respectively and comparing the values thus obtained. There is, however, ample evidence to show that the two structures do not ordinarily occur apart from each other, but that they co-exist in the same specimen, endowing it with a finely laminated structure. Such a structure may be expected to show periodic variations in crystal spacing detectable by appropriate methods. Indeed, the fact that diamonds of this type show characteristic birefringence patterns exhibiting their laminated structure may itself be regarded as a proof that the alternate layers in it do not have an identical crystal spacing. For, if the lattice spacings were the same throughout, there is no *prima facie* reason why any birefringence should arise.

From the large collection of diamonds of this kind in the possession of Sir C. V. Raman, diamond D209 which showed a well-defined streaky birefringence between crossed polaroids was selected for the present investigation. The geometric character of the birefringence pattern and its periodic disappearance as the crystal is rotated between the crossed polaroids, indicated that this sample would be an ideal one for the purpose of the present test. The diamond (an octahedral cleavage plate) was mounted on a goniometer with its faces vertical. The X-rays from a copper target after passing through an extremely fine vertical slit (5 mm. \times 0.4 mm.) were allowed to fall on the crystal nearly at the Bragg angle for the surface reflection. The crystal was oscillated through a small angle about this position and the resulting Bragg reflection from the front surface of the crystal was recorded on a photographic film. The film was kept normal to the diffracted beam at a distance of about 40 cm. from the crystal. A typical oscillation photograph obtained is reproduced in Fig. 1 (b) in the accompanying plate. The reflections due to the Cu $K\alpha_1$, and Cu $K\alpha_2$ radiations are seen well resolved in the photograph; the intense one corresponds to Cu $K\alpha_1$. It will be noticed that these Bragg reflections instead of being linear in shape and of uniform intensity are wavy in nature and also show a periodic variation of intensity. The most intense portions are bent towards the direct beam and hence correspond to smaller values of θ , while the less intense portions are bent away from the direct beam. If the crystal were perfectly homogeneous through the section where the X-rays were incident, the Bragg reflections would give rise to a linear and true image of the slit. As the crystal used was heterogeneous with periodic variation in crystal spacing, the Bragg reflections would show a corresponding waviness. From a measurement of the amplitudes of the waviness and the average separation of the $K\alpha_1$ and $K\alpha_2$ reflections, the difference in crystal spacing has been estimated. It is found that the difference is of the order of 5 parts in 10,000. The inter-

penetration of one octahedral form into the other has not only caused a periodic variation in the crystal spacing, but also given rise to a mosaicity, as is evident from the increase in intensity of Bragg reflections from these layers.

Oscillation photographs were also taken for various settings of the same crystal and the Bragg reflection in every case showed the wavy character. The distribution of the intense and weak spots was different in each case. A typical oscillation photograph for a different setting of the crystal is reproduced in Fig. 1 (c) in Plate. XXVIII. The experiment was repeated with a second diamond (D45 in Sir C. V. Raman's collection) which was only very feebly fluorescent and belonged to the tetrahedral type. The oscillation photograph is reproduced in Fig. 1 (d). As is to be expected, the Bragg reflection from D45 does not exhibit any wavy character. The reflected image is quite linear and of uniform intensity.

Very recently, Mrs. Lonsdale (1944) has carried out measurements of the crystal spacing in a large number of diamonds. She found no variation in the spacing greater than 2 parts in 10,000 in the various specimens examined by her. Very few diamonds which were transparent to the ultra-violet were included in her list. As already mentioned, however, the transparent variety of diamond usually occurs as a mixture of the two octahedral structures. Hence what Mrs. Lonsdale measured was the mean of the spacings of the two octahedral structures and her observations leave the question of the difference between the Oh I and Oh II spacings with which we are here concerned entirely untouched. It should be remarked that the success attained in the present investigation is largely due to the choice of the specimen in which the spacings of the laminations were sufficiently great to exhibit the waviness of the Bragg reflections. Specimens in which the laminations are very fine would obviously fail to show the effect.

4. *The Spectroscopic Evidence*

As has already been pointed out earlier in the paper, the two octahedral structures are physically different. It is therefore reasonable to suppose that the frequency of the fundamental lattice oscillation would be different for the two structures. The expected variation in lattice frequency would probably be of the same order of magnitude as the variation in the crystal spacing, namely, about 5 parts in 10,000. Even such a small difference in lattice frequency should, however, be sufficient to give rise to an observable broadening of the fundamental Raman line in the case of a diamond containing a mixture of the two forms. The experiment was carried out as follows :—

The Raman spectrum of diamond D227 (which belonged to the octahedral variety) was photographed through a Hilger E_1 quartz spectrograph using as fine a slit as possible. The 2536 resonance radiations of a water-cooled quartz mercury arc were used for exciting the Raman line. Visual observation of the recorded spectrum showed that the 1332 line had a finite breadth greater than that of any of the mercury lines of comparable intensity. This was confirmed by taking a microphotometric record of the spectrum. The microphotometric records of the mercury triplet at 2655.1, 2653.7 and 2652.0 A.U. and that of the Raman line are reproduced in Figs. 2 *a*, *b*, *c*, and *d* respectively in the accompanying Plate. The mercury line at 2655.1 A.U. has nearly the same intensity as the 1332 Raman line, whereas the width of the Raman line is a little more than one and a half times that of the mercury line. The difference in width between the two is approximately one wavenumber. This is of the same order of magnitude in relation to 1332 as the observed difference in lattice spacings. Thus, the spectroscopic data also lend support to the view that there are two different structures in the octahedral type of diamond, though, no doubt, the observed width of the Raman line is, in part, due to the finite width of the 2536 line itself.

As the two tetrahedral forms of diamond are physically identical, their lattice vibrations should have identical frequencies but different from that of either of the octahedral forms. It is conceivable, however, that the *mean* lattice frequency of the octahedral types might be the same as that of the tetrahedral variety. In order to test these points, the Raman spectra of two diamonds D36 and D227 (the former of the tetrahedral type, while the latter of the octahedral type) were photographed side by side through a Fuess spectrograph using a Hartmann diaphragm. The spectrogram is reproduced in Fig. 1*a* in Plate XXVIII. The top picture represents the Raman spectrum of D227, while the bottom picture represents the Raman spectrum of D36. As far as can be made out, there is no difference in the frequency shifts and the Raman line appears in exactly the same position for the two diamonds. An enlarged picture of the 1332 Raman line excited by the 4046 radiation with suitable adjustment of the background intensity is reproduced in Fig. 1*e*. The upper portion of the figure represents the spectrum in D36, while the lower portion represents the spectrum in D227. The Raman line in D227 appears to be definitely broader than the corresponding line in D36, in agreement with the general considerations indicated above.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for suggesting the problem and for valuable discussions during the progress of the investigation.

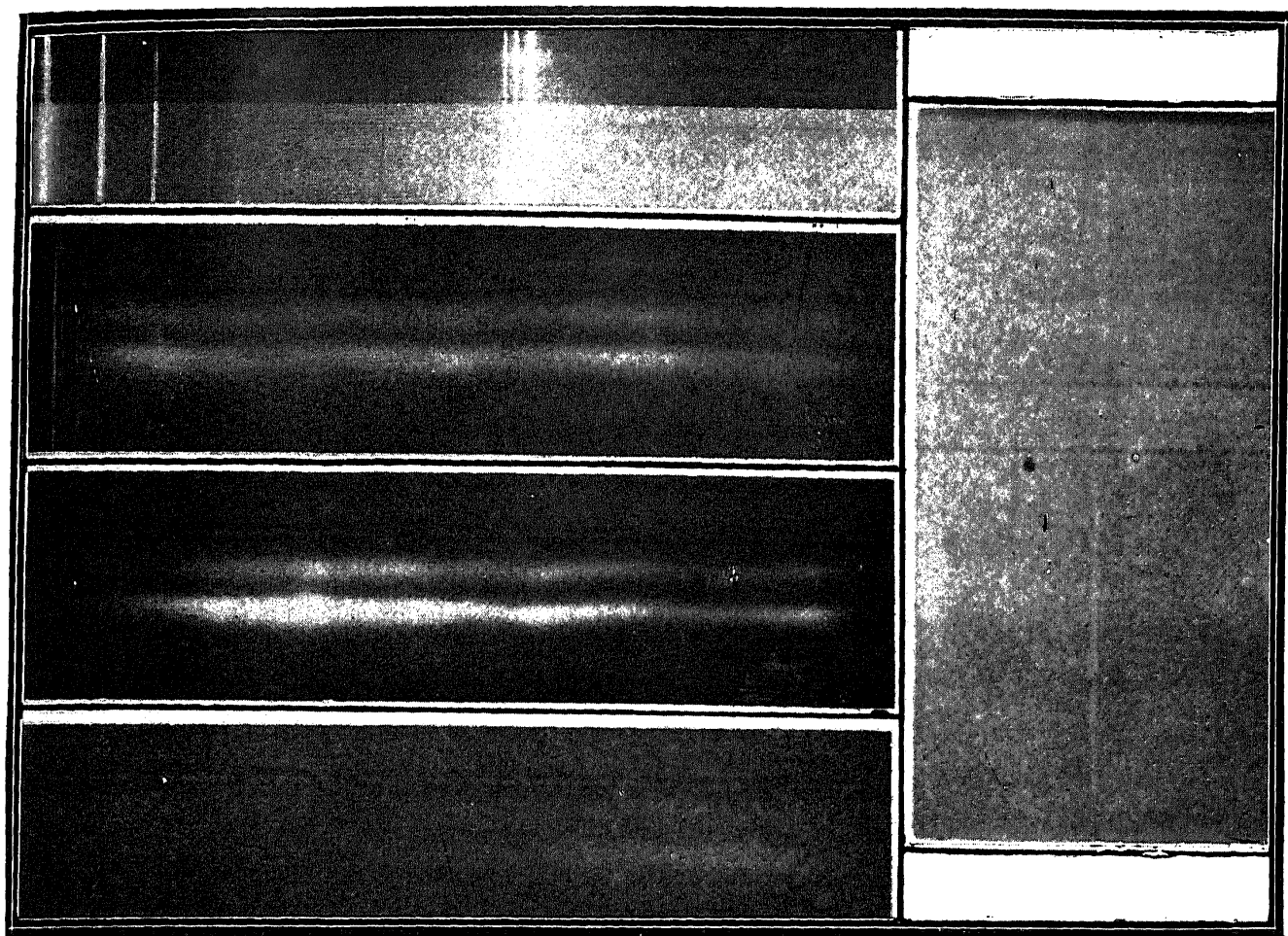
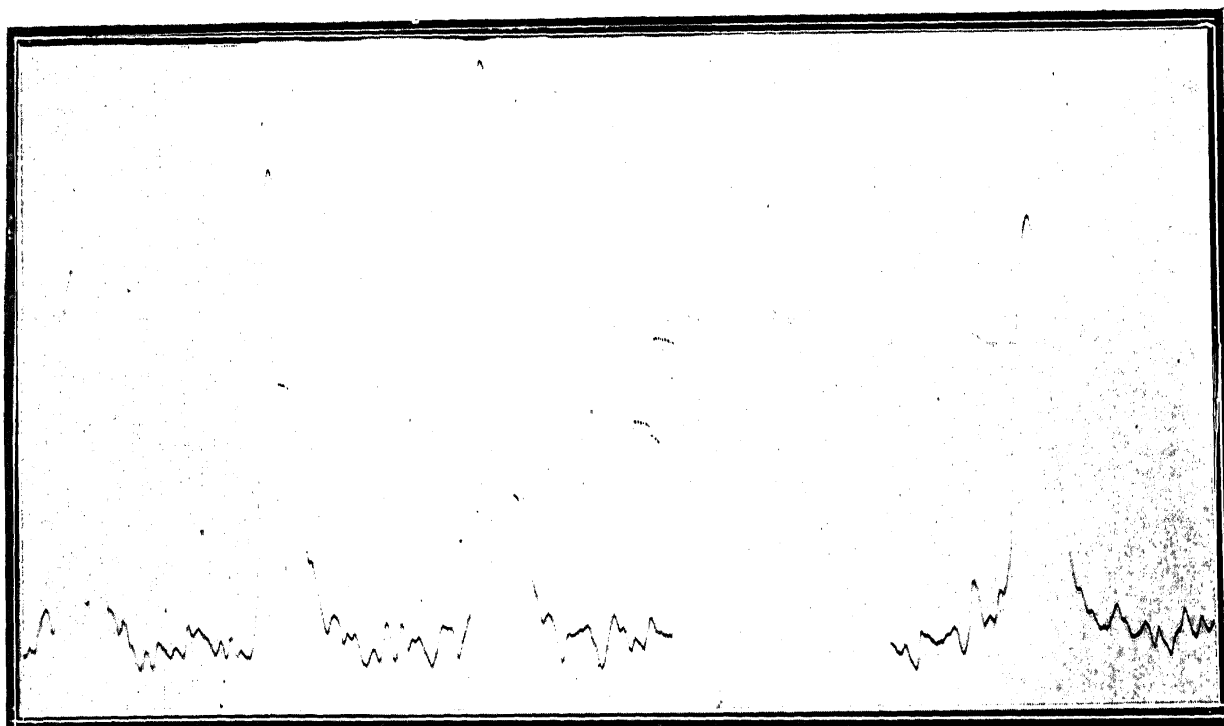


FIG. 1



5. *Summary*

Experimental evidence has been obtained for the existence of the four possible structures of diamond from X-ray and spectroscopic studies. The co-existence of the two variants of the tetrahedral structure in one and the same specimen and the heterogeneity arising therefrom have been confirmed from the observed increased intensities of X-ray reflections in such diamonds. Using the oscillating crystal method and a diamond in which the two structures of the octahedral type co-exist in adjacent layers of the crystal, it is observed that the Bragg reflections exhibit a waviness such as should be observed if there be a difference in the crystal spacings of the alternate layers. The observed difference in crystal spacings thus deduced is of the order of 5 parts in 10,000. The Raman line corresponding to the fundamental lattice vibration shows a definite width in the case of the octahedral type of diamond which agrees at least, in the order of magnitude, with the expected difference in the vibration frequencies of the two octahedral structures.

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