

## Allotropic Modifications of Diamond

THE relationships which exist between the structural symmetry of a molecule and its spectroscopic behaviour have been fully worked out by Placzek<sup>1</sup>. One result of his theory is that if a molecule has the symmetry of the crystallographic point-group *Oh*, the activity of its vibrations in infra-red absorption and in light-scattering are mutually exclusive. On the other hand, if the molecular symmetry is that of the point-group *T<sub>d</sub>*, every vibration of the triply degenerate class must appear both in light-scattering and in infra-red absorption, or else be absent in both.

Placzek's theory is applicable, *mutatis mutandis*, to the spectroscopic behaviour of crystals in respect of their fundamental lattice vibrations. The consequences of it mentioned above afford a straightforward explanation of the remarkable fact that, while all diamonds exhibit in light-scattering an intense line with a spectral frequency shift of about 1,332 wave numbers, the corresponding infra-red absorption appears only in some diamonds, but not in others. This difference in spectroscopic behaviour is, in fact, a complete demonstration of the existence of allotropic modifications of diamond and shows further that the forms more commonly met with showing the infra-red absorption have only tetrahedral symmetry of structure, while the less common variety, in which the absorption is absent, has the full symmetry of the cubic system.

The crystallographers of the nineteenth century (for example, Groth<sup>2</sup> and Miers<sup>3</sup>) who, on the basis of the observed crystal forms, assigned to diamond the lower or tetrahedral symmetry, recognized it as a necessary consequence that two variants of it, namely, the positive and negative tetrahedral forms, must exist, and explained the comparative rarity of forms clearly exhibiting the lower symmetry as the result of their interpenetration. Apart from the crystallographic evidence which supports this explanation, there is an array of experimental facts concerning diamond established by my work and that of my collaborators<sup>4</sup>, which proves that such an interpenetration does really exist in diamonds having tetrahedral symmetry of structure. The evidence can be summarized in the statement that while the characteristic infra-red absorption goes hand in hand with various other physical properties, for example, blue luminescence, ultra-violet opacity, feeble but sharply defined classical X-ray reflexions and small photo-conductivity, all these properties themselves are highly variable, and that such variations are perfectly correlated with each other. The inter-

penetration of the positive and negative tetrahedral structures in different degrees and the resulting variations of structure afford a natural interpretation of these facts.

The existence of two sub-classes *Oh* I and *Oh* II in the octahedral division is also indicated by the highly characteristic laminated structure parallel to the octahedral planes which is characteristic of this type of diamond, and which readily reveals itself under the polarizing microscope. The observed structures cannot be explained on the basis merely of a random irregularity or mosaicity of the crystal lattice. Indeed, the high intensity of X-ray reflexions characteristic of this type of diamond is definitely associated with its laminated structure, as has been clearly demonstrated by the X-ray topographs of Mr. G. N. Ramachandran<sup>5</sup>. Finally, it should be remarked that the appearance of geometric patterns in cleavage plates of diamond exhibiting the local variations in the various physical properties mentioned above is a convincing ocular demonstration of the fact that we are really dealing with distinct allotropic forms of diamond, as also with the consequences of their interpenetration and/or intertwinning.

The above statement of the case is by way of reply to Mrs. Lonsdale's letter published in *Nature* of February 3 last. She does not discuss the array of facts brought forward in the symposium but 'challenges' what she refers to as a 'speculation' on the basis of certain minor aspects of the X-ray behaviour of diamond, which are not really fundamental to the issues under consideration. Mrs. Lonsdale believes that the specific points mentioned by her controvert the main thesis established by the work of my collaborators and myself; this is not so. As the present letter, however, is already of sufficient length, a detailed examination of those points must be reserved for a separate communication.

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<sup>1</sup> Placzek, G., "Handbuch der Radiologie", Part 2, p. 297, table 9 (2nd Edit., 1934).

<sup>2</sup> Groth, P., "Physikalische Kristallographie" (Leipzig, 1895), 575.

<sup>3</sup> Miers, H. A., "Mineralogy" (Macmillan, 1902), 282.

<sup>4</sup> Raman, C. V., and collaborators, *Proc. Ind. Acad. Sci.*, A, 19, 189 (1944).

<sup>5</sup> Ramachandran, G. N., *Proc. Ind. Acad. Sci.*, A, 19, 280 (1944).