LETTERS TO THE EDITORS

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Elastic Constants of Diamond

IN 1914 I published a paper[1] on the lattice theory of diamond in which I obtained expressions for the elastic constants of this crystal in terms of two atomic force constants, one corresponding to the valency bond between next neighbour atoms, the other to the tetrahedral angle between the directions of these valencies.

As there are three elastic constants, C_{11}, C_{12}, C_{44}, this theory leads to an identity between them, namely,

$$\frac{4c_{11}\,(c_{11}-c_{44})}{(c_{11}+c_{12})^2} = 1. \qquad . \quad . \quad . \qquad (1)$$

At that time, no measurements of the elastic constants were available; apart from the compressibility, the characteristic temperature Θ of Debye was known, which is a complicated function of the atomic constants, but turned out to be useless for a reliable determination of them.

Lately, Prof. S. Bhagavantam and collaborators have developed a new method for measuring elastic constants of crystals[2] and have applied it successfully to many crystals. Their results for diamond are:

$$c_{11} = 9{\cdot}5 \times 10^{12} : c_{12} = 3{\cdot}9 \times 10^{12} : \quad c_{44} = 4{\cdot}3 \times 10^{12} \text{ dynes/sq. cm.} \qquad (2)$$

If these numbers are substituted into the identity (1), one finds for the expression on the left-hand side the value 1·10 instead of 1·00. The agreement seems fair enough to be considered a confirmation of the theory developed thirty-two years ago.

Yet there is a discrepancy of about 10 per cent, and the question arises whether this can be improved by taking into account the second neighbours of each atom. The theory was extended in that direction by N. S. Nagendra Nath[3] in 1934, who introduced a third constant representing the action of the second neighbours, regarded as central force. My collaborator, Miss H. M. J. Smith, has reconsidered the whole theory from a general point of view which I have described in my report on "Crystal Dynamics and X-Ray Scattering"[4]. This method consists in constructing the 'dynamical matrix' for each neighbour of a given atom in the cell and reducing it to its simplest form by applying the symmetry operations of the lattice. The result contains two parameters α, β for the first neighbours, and three parameters λ, μ, ν for the second neighbours. As the total number of these parameters (five) is larger than the number of elastic constants (three) no relation between the latter can be expected. If, following Nagendra Nath, the action of the second neighbours is represented by central forces, one has $\lambda = 0$ and $\mu = \nu$, so that only three parameters remain, α, β, μ; there is still no identity between the elastic constants.

But optical investigations supply other data. The infra-red absorption spectrum and the Raman effect have been studied[5,6]. These spectra are highly complicated and their interpretation is controversial. But there is one outstanding feature of which only one explanation seems possible: the strongest Raman line $\nu_0 = 1{,}332$ cm.$^{-1}$ corresponds to the limiting vibration of the lattice where the two face-centred simple lattices oscillate against one another as rigid frames. The four constants c_{11}, c_{12}, c_{44}, ν_0, can be expressed in terms of the three parameters α, β, μ; therefore, one has one identity, namely,

$$\frac{8 \cdot \frac{m}{2a} \cdot 4\pi^2c^2\nu_0{}^2 \left(\frac{m}{2a} \cdot 4\pi^2c^2\nu_0{}^2 + 8c_{11} - 16c_{44}\right)}{\left(3 \cdot \frac{m}{2a} \cdot 4\pi^2c^2\nu_0{}^2 - 8c_{11} + 16c_{12}\right)^2} = 1, \qquad . \quad . \quad . \quad . \qquad (3)$$

where m is mass of carbon atom, and $2a$ is lattice constant. If here the experimental values (2) are inserted, one obtains for the left-hand side 1·4 instead of 1·0. The agreement is less satisfactory than that obtained with the simple formula (1) based on first neighbours only.

Bhagavantam has compared his measurements with Nagendra Nath's theory in a different way. He has used definite interpretations of some weaker Raman lines, following Raman's general theory of lattice vibrations, and determined the three force constants in terms of the frequencies of these lines. Calculating the elastic constants with these data, he obtains almost perfect agreement.

This result is deceptive. In the first place, Nagendra Nath's formulæ as used by Bhagavantam are not correct; he has neglected a term which, in fact, is not small. Secondly, Raman's theory of lattice vibrations is untenable, and the interpretation of the observed lines therefore arbitrary. The excellent agreement is therefore accidental. Our identity (3), on the other hand, is independent of the doubtful interpretation of the second-order Raman spectrum. The fact that it is not satisfied by Bhagavantam's measurement may be due either to experimental errors, or to the assumption that the forces of the second neighbours are central, or finally to neglecting the forces of more distant neighbours. I am inclined to prefer the first alternative; for a small change of c_{44}, namely, $c_{44} = 5{\cdot}0 \times 10^{12}$ instead of $c_{44} = 4{\cdot}3 \times 10^{12}$ dynes/cm.^{2}, puts the identity (3) right.

The question of the infra-red absorption and the secondary Raman spectrum is under investigation (by Miss Smith). We have obviously to do with a spectrum of the same kind as in rock-salt, an explanation of which we have recently given[7]; it is the superposition of numerous bands each corresponding to a combination of two of the frequency branches of the elastic spectrum. A careful study of this problem for diamond will throw light on the much disputed difference between the two types of diamonds found by Robertson, Fox and Martin[8].

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Feb. 25.

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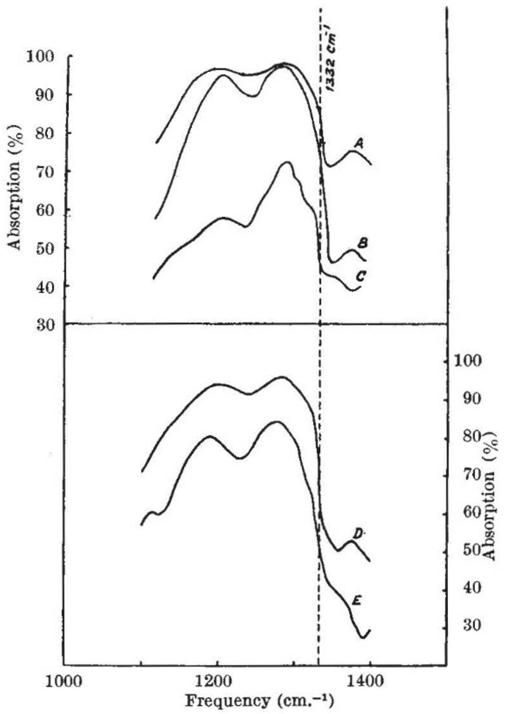
Infra-Red Absorption Spectrum of Diamond

IN his comments appended to our note on the above subject appearing in *Nature* of January 12, Dr. Sutherland ascribes to us the statement that the "principal infra-red frequency of diamond has been defined as the position of minimum absorption". This is not what we said, neither does it represent the actual facts of the case. The true position is that pointed out by Sir C. V. Raman[2], namely, that in the 8 μ band of diamond, the infra-red absorption coefficient rises very steeply in passing through the fundamental vibration frequency of the lattice, namely, 1332 cm.$^{-1}$. The accompanying absorption curves (A), (B), (C) and (D), carefully redrawn on a wave-number scale from the experimental results published by British observers[3,4], demonstrate that this is the actual situation. A similar feature appears also in the infra-red emission spectrum (Curve E) of diamond[3]. The 1332 cm.$^{-1}$ frequency is indicated by the vertical line which, it will be seen, in each case cuts through the curve at or near the point where it is steepest. There can be no doubt, therefore, that the absorption associated with that frequency is an integral part of the 8 μ band and that this latter has its primary origin in the infra-red activity of the fundamental lattice vibration. There remains no need for us to comment on the rest of Dr. Sutherland's note.



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[3] Robertson, Fox and Martin, *Proc. Roy. Soc.*, A, **157**, 579 (1936).

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THE wording used by Krishnan and Ramanathan was "the centre of this fall (i.e. between the absorption maxima at 1285 and 1376 cm.$^{-1}$) coincides with the Raman frequency at 1332 cm.$^{-1}$". Not unnaturally I took this to mean the minimum of absorption between these two