LETTERS TO THE EDITORS

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Infra-Red Absorption Spectrum of Diamond

In the recent Faraday Society discussion on infra-red spectroscopy reported in *Nature* of February 17, 1945, certain comments were made on the work done at this Institute on diamond. The full report of the discussion is now in our hands, and we wish to point out that, contrary to what was stated at the meeting, the experimental data presented by Dr. Sutherland and Mr. Willis¹ are in full accord with what should be expected on the basis of the ideas regarding the structure of diamond and the nature of its lattice spectrum published from this Institute^{2,3}.

If diamond has octahedral symmetry of structure, none of the lattice vibrations could, in the first approximation, appear in infra-red absorption. In the second approximation, when anharmonicity is considered, they would be allowed as octaves and may also appear as combinations. On the other hand, if the structure is tetrahedral, the Raman-active frequency of $1,332\text{ cm}^{-1}$ would be active as a fundamental in the infra-red absorption, while all the other lattice vibrations would, in the first approximation, be inactive. In the second approximation they would, as in the case of octahedral symmetry, be allowed as octaves and may also appear as combinations. The first-order activity of the $1,332$ vibration would also result in all the other lattice frequencies in its vicinity being rendered infra-red active as fundamentals to varying extents.

Reproduced herewith is one of the absorption curves of Sutherland and Willis carefully redrawn on a uniform frequency scale. The peaks marked as 2,500, 2,170 and 2,028, when examined under adequate resolving powers, appear extremely sharp⁴, and their frequencies coincide with the octaves of the fundamental frequencies of diamond at 1,250, 1,088 and $1,013\text{ cm}^{-1}$ revealed by the investigations made at this Institute on the luminescence spectrum and the second-order Raman effect. A striking feature of the experimental data is the precipitous fall of the absorption strength between 1,285 and $1,376\text{ cm}^{-1}$. The centre of this fall coincides exactly with the Raman frequency $1,332\text{ cm}^{-1}$. A similar precipitous

fall of intensity appears at the corresponding positions in the second-order Raman spectrum and in the luminescence spectrum, and there can be no doubt, therefore, that the absorption band arises from the activity of the $1,332$ vibration and is the joint effect of this and the three other fundamental vibrations close to it in frequency which are rendered active by its influence. The correctness of this view is demonstrated by the appearance of a feeble peak at the fundamental frequency $1,013$, while the more prominent peak at $1,105$ undoubtedly represents the fundamental frequency $1,088$ which appears slightly shifted as a result of the steepness of the absorption curve at this point.

We desire also to emphasize two major points which appear to have been overlooked in the discussion. That diamond may be either tetrahedral or octahedral in symmetry is not an *ad hoc* hypothesis. One has only to study the extensive crystallographic literature on diamond and the reports of experienced observers who have had access to suitable material to appreciate the position in this respect correctly. Further, it is an indisputable fact⁵ that the diamonds which show the infra-red absorption in the 8μ region are precisely those which make the nearest approach to ideal crystal perfection, while the diamonds which do not show this absorption band exhibit characteristic irregularities of structure. Hence, the appearance of the absorption band and its absence respectively in the two cases cannot be ascribed to crystal imperfections or other adventitious circumstances, and must be due to a fundamental difference in crystal symmetry.

R. S. KRISHNAN.

K. G. RAMANATHAN.

Physics Department,
Indian Institute of Science,
Bangalore. July 7.

¹ Sutherland and Willis, *Trans. Faraday Soc.*, **41**, 281 (1945).

² Raman, C. V., *Proc. Ind. Acad. Sci.*, **A**, **19**, 189 (1944).

³ Raman, C. V., *Proc. Ind. Acad. Sci.*, **A**, **18**, 237 (1943).

⁴ Robertson, Fox and Martin, *Proc. Roy. Soc.*, **A**, **157**, 579 (1936).

⁵ Raman, C. V., *Current Science*, **12**, 33 (1943).

ONE of the crucial arguments put forward by Raman in support of 'tetrahedral' and 'octahedral' diamonds being associated with the Type I and Type II diamonds of Robertson, and Fox and Martin, was that the tetrahedral form should have a certain fundamental vibration frequency active in infra-red absorption and also in scattering, while for the octahedral form this same frequency should be inactive in absorption. Raman identified this frequency with the well-known scattering line at $1,332\text{ cm}^{-1}$ and claimed that this frequency coincided with the infra-red absorption "between 1350 and 1300 cm^{-1} " on Type I diamonds. One of the purposes of the paper by Willis and myself was to point out that this last was a serious mis-statement of fact, since the principal infra-red absorption maxima in this region of the spectrum lie at $1,286\text{ cm}^{-1}$ and $1,376\text{ cm}^{-1}$, of which the former is much more intense than the latter.

Krishnan and Ramanathan now propose to evade this awkward fact by considering the infra-red frequency to be defined by the position of minimum absorption between the above-mentioned two bands. Why is this particular minimum singled out for preferential treatment? In all the other identifications Krishnan and Ramanathan make, they choose the maximum of absorption to define the infra-red