

THE THEORY OF THE VIBRATIONS AND THE RAMAN SPECTRUM OF THE DIAMOND LATTICE

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SEVERAL investigations by the author on the scattering of light in diamond and on its Raman spectrum have already been reported in earlier publications (Krishnan, 1944, 1945, 1946, 1947 *a, b, c*). The frequency shifts observed in diamond are of three kinds:—(a) the Brillouin shifts in the vicinity of the exciting radiation less intense than (b), the first-order frequency shift of 1332 cm.^{-1} , but both are recorded with short exposures, while (c) the second-order spectrum requires much heavier exposures. Under the high resolution provided by the Hilger E1 quartz spectrograph, the second-order Raman spectrum which is confined to the region of frequency shifts 2665.4 cm.^{-1} and 2015 cm.^{-1} exhibits a set of sharply defined and discrete lines. These results together with those obtained by Ramanathan (1947) by the method of infra-red absorption have been fully and satisfactorily explained on the basis of the new lattice dynamics.

A paper by Helen M. J. Smith (1948), a student of Born, with the same title as the present one has appeared in a recent number of the *Transactions of the Royal Society*, in which she has attempted to work out theoretically the vibration spectrum of the diamond lattice on the basis of the Born theory and to derive its second-order Raman spectrum. She has claimed to have satisfactorily explained the facts reported by the present writer. It is the purpose of this paper to point out that the above claim is not justified.

On the basis of the cyclic postulate, Helen Smith has calculated the second-order vibration spectrum of the diamond lattice. It is a continuous one with 13 branches as shown in the accompanying Fig. 1. From the vibration spectrum she has calculated the intensity distribution in the second-order Raman spectrum involving some arbitrary assumptions. The theoretical curve is reproduced in Fig. 2 *a*.

(1) *The form of the curve.*—In order to fit the theoretical curve with the experimental one, the author arbitrarily assumes that the factors $A(jj)$ must be zero for the branches 4, 5, 7, 8, 9, 11, 12 and 13 (see Fig. 1). This is sufficient to show the artificial character of the procedure adopted by Smith in deriving the theoretical curve.

(2) *The extent of the spectrum in the region of high frequency shifts.*—The theoretical curve extends over a region of frequency shifts 1700 to 2700 cm.^{-1} , i.e., 1000 wavenumbers. The observed second-order spectrum, on the other hand, is restricted to a region of frequency shifts 2176 cm.^{-1} to 2665 cm.^{-1} . Below 2176 cm.^{-1} there is only one faint line at 2015 cm.^{-1} but no continuum of even 1/10th intensity of the 2176 cm.^{-1} line. The extension of the spectrum up to about 1700 cm.^{-1} on the shorter wavelength side, of the type and of comparable intensity as suggested by the theory does not find experimental support.

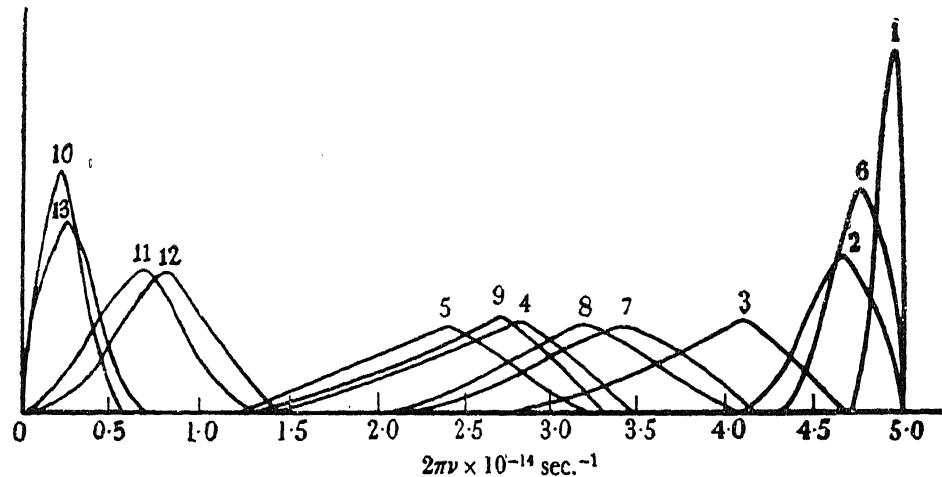


FIG. 1. Frequency density functions $Z^{ij}(\omega)$ taken from Smith's paper.

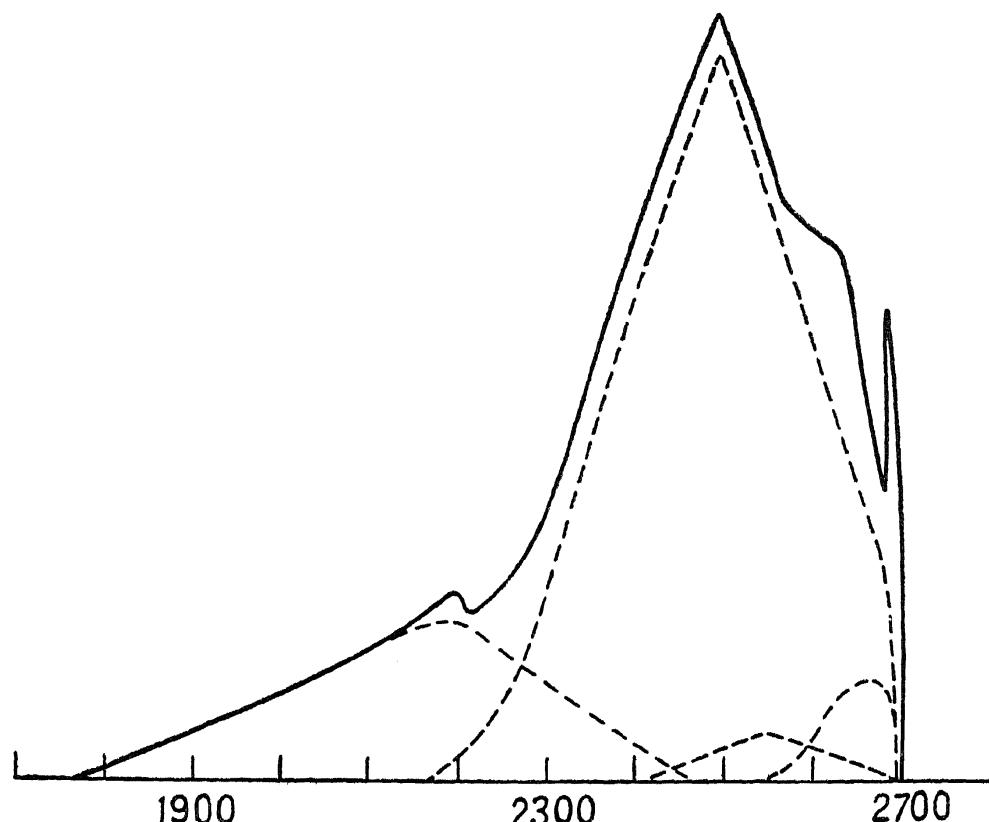


FIG. 2a. The theoretical intensity distribution curve.

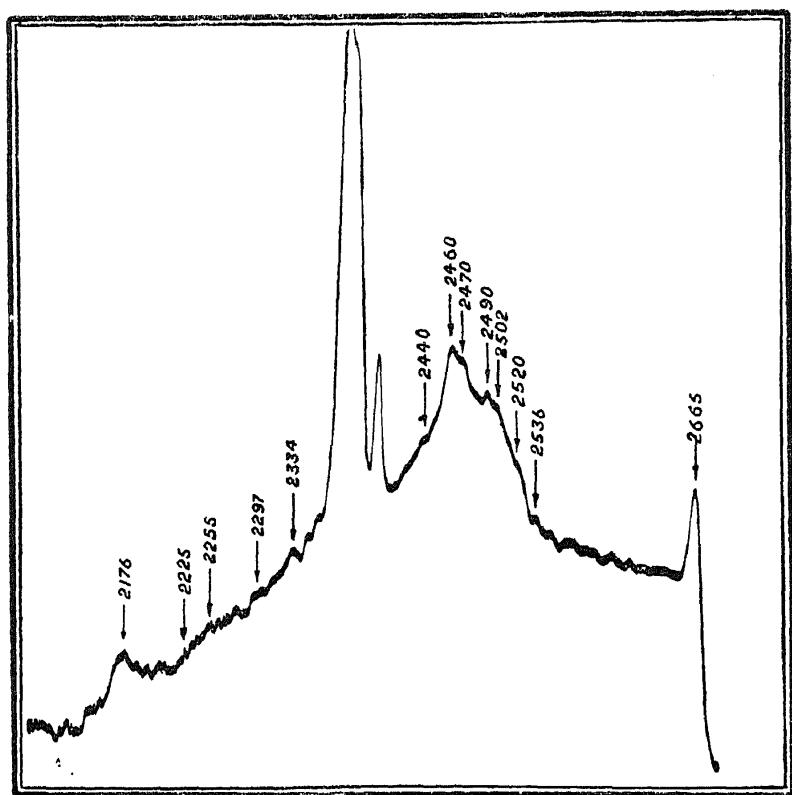


FIG. 2 b. Microphotometer record of the second-order Raman spectrum of diamond taken with large quartz spectrograph.

(3) *The number of lines or peaks.*—The theoretical curve exhibits four maxima, as is to be expected by the superposition of the four branches (1), (2), (3) and (6). Any further refinement in the theoretical calculations cannot give rise to more than four maxima in the region under consideration. The microphotometer record of the observed spectrum shows no less than 12 kinks, each one of them representing a sharply defined line. That these kinks are not due to random fluctuations in intensity as Smith would like to call them, will be obvious to anybody who examines the spectrograms taken under high dispersion and resolution. Even a lightly exposed spectrogram reproduced in Fig. 3 exhibits at least four extremely sharp lines adjacent to the most intense line at 2460 cm.^{-1} The theoretical curve has, instead, only one maximum in this region.

(4) *The high frequency cut-off of the spectrum.*—In the intensity distribution curve calculated on the basis of the Born theory, the peak with the maximum frequency shift, *i.e.*, 2664 cm.^{-1} does not coincide with the end of the spectrum, whereas in the experimental curve the line at $2665\cdot4\text{ cm.}^{-1}$ represents the upper limit of the spectrum. This line is the octave of the fundamental mode of oscillation of the diamond lattice having the highest frequency shift, namely 1332 cm.^{-1} As is to be expected, the octave appears as a sharp line and stands out from the rest of the spectrum. The sharp

peak at 2664 cm.^{-1} of the theoretical curve, on the other hand, appears to have been manufactured by giving suitable intensities to the branches (1) and (6).

(5) *Region of low frequency shifts.*—According to the calculations of Smith, the branch (10) (see Fig. 1) has an intensity comparable to that of the high frequency branches and a maximum at 106 cm.^{-1} . She says that this low frequency band is not observed experimentally as it may be covered by the incident mercury line. Heavily exposed spectrograms taken with efficient filtering of the exciting radiation do not exhibit any low frequency shift line even faintly, much less a band of the type predicted by the Born theory, other than the Brillouin components. Spectrograms reproduced on page 230 of *Nature* (1947, 160) and on Plate X of the *Proceedings of the Indian Academy of Sciences* (1947, 26) will bear testimony to the above statement.

From what has been said above, it is clear that the theoretical intensity curve for the second-order Raman spectrum of diamond is wholly artificial and bears no resemblance whatsoever to the facts. Any theory which wants to hold on its own should be capable of explaining the existence of at least the five sharp intense lines (see Fig. 3), appearing in the second-order spectrum of diamond, not to say anything about the rest. The Born theory as worked out by Smith for the case of diamond, however, is unable to explain them.

In conclusion, the author feels it necessary to refer to some points concerning the theoretical paper by Helen Smith. The experimental results mentioned above were first published in two notes in the correspondence columns of *Nature* in the January 11th and August 16th (1947) issues. In the first note on the "Raman spectrum of diamond under high dispersion", the spectrograms taken with the large quartz spectrograph and exhibiting the true nature of the Raman spectrum of diamond unambiguously were reproduced. Anyone familiar with the elements of spectroscopy would unhesitatingly admit that the characteristic feature of the spectrum as revealed by the reproduced photographs is the appearance of a whole series of sharply defined Raman lines clearly resolved from one another, a fact which does not find any explanation whatsoever on the Born theory. In the second note on the "Second-order Raman spectra of crystals", it was clearly pointed out that in spectrograms heavily exposed under the most perfect experimental conditions, there is not a trace of any scattered radiations having frequency shifts (other than the Brillouin doublets) less than 1332 cm.^{-1} . The two notes mentioned were published long before Prof. Born

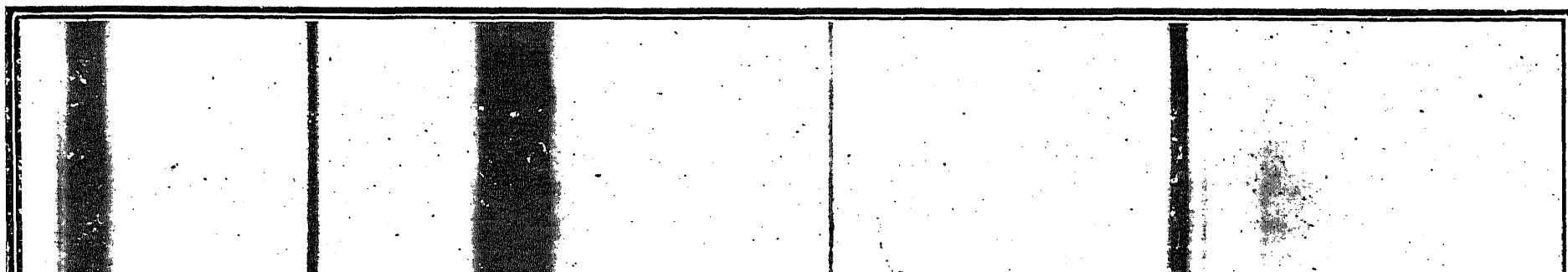


FIG. 3. Lightly exposed photograph of the Raman spectrum of diamond taken with the large quartz spectrograph

communicated the manuscript of Smith's paper to the Royal Society. No reference to them, however, is made in Helen Smith's paper as published.

The detailed paper giving the latest results and a full theoretical discussion appeared in the December (1947) issue of the *Proceedings of the Indian Academy of Sciences*, which would have been received by Prof. Born in the normal course in January or February, 1948. Moreover, the author understands that when Prof. Born presented Smith's theoretical intensity distribution curve during the Bordeaux meeting in April, 1948, he was appraised of the latest experimental results and slides exhibiting them were shown. This took place long before Smith's paper was actually published in the *Transactions of the Royal Society*. It is therefore extremely surprising to find no reference to the author's detailed publication and no attempt to correct the wholly misleading and erroneous statements concerning the experimental facts appearing in Helen Smith's paper.

SUMMARY

The observed features of the Raman spectrum of diamond have briefly been summarised and compared with the theoretical conclusions arrived at by Helen Smith on the basis of Born's postulate of the cyclic lattice. In every respect and especially as regards the form, the extent, the number and sharpness of the lines, the spectrum in the low frequency shift region, etc., the theoretical intensity distribution curve is found to differ widely from what has been observed experimentally. It has been shown that the Born theory as worked out by Smith for the case of diamond is unable to explain the characteristic features of the second-order spectrum of diamond.

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