

# THE SECOND ORDER RAMAN SPECTRUM OF DIAMOND

BY DR. R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

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## 1. INTRODUCTION

THE Raman effect in diamond has been studied by several investigators, viz., Ramaswamy (1930), Robertson and Fox (1930), Bhagavantam (1930), Robertson, Fox and Martin (1934) and Nayar (1941, 1942). They reported the existence of only a single sharp and intense Raman line with a frequency shift of  $1332 \text{ cm.}^{-1}$  corresponding to the triply degenerate vibration of the two Bravais lattices of carbon atoms with respect to each other. Investigations by Robertson, Fox and Martin (1936) on the infra-red absorption spectrum and those by Nayar (1941 *a*, 1942 *a*) and by Miss Mani (1944) on the luminescence and absorption spectra of diamond, however, indicated that the lattice spectrum includes many more vibrations with discrete frequencies besides the one with the frequency shift of  $1332 \text{ cm.}^{-1}$  so far recorded in the Raman spectrum. It was therefore natural to expect that some of these vibrations would manifest themselves as second order Raman lines in an intensely exposed spectrum of diamond. Accordingly, the author (Krishnan, 1944) undertook a re-examination of the Raman effect in diamond. The technique of using the visible and near ultra-violet radiations of the mercury arc as exciter has been exploited to the limits of its utility by the investigators already referred to, and consequently no further useful information regarding the second order spectrum of diamond would be got by employing the same. Using the extremely intense  $2536.5$  mercury resonance radiation from a water-cooled magnet-controlled mercury arc as exciter and diamonds of the ultraviolet transparent type, the author succeeded in recording a spectrum which exhibited besides the intense line with a frequency shift of  $1332 \text{ cm.}^{-1}$ , no fewer than ten Raman lines of comparatively feeble intensity. These constitute the Raman spectrum of the second order in diamond, the appearance of which was predicted on the basis of the Raman dynamics of crystal lattices. In the preliminary investigation the results of which were published in the earlier symposium (Krishnan, 1944), the author had used a quartz spectrograph of small dispersion. Because of this and also due to imperfect reproduction, the second order Raman lines are not

seen clearly resolved from the background either in the spectrogram or in the microphotometric record. Using a Hilger medium quartz spectrograph which had a higher dispersion than the one previously employed, fresh photographs were obtained, the best of which was published in *Nature* (Krishnan, 1945). Here also the reproduction was not quite satisfactory, as the picture was too small to bring out the real nature of the second order Raman spectrum of diamond, viz., a set of sharp lines appearing on a feeble continuum. It was therefore thought desirable to investigate the problem afresh under more favourable conditions. Improved experimental technique and the use of an exceptionally colourless plate of diamond belonging to the ultraviolet transparent type recently acquired by Sir C. V. Raman have enabled the author to record spectra of much greater intensity and much better resolved. The results are presented in this paper.

## 2. EXPERIMENTAL DETAILS AND RESULTS

The catalogue number of the diamond used is N.C. 174. It was in the form of a semicircular disc about one centimetre in diameter and 2 millimetres thick. It was held with its flat faces vertical and facing the most intense portion of a specially designed quartz mercury arc. The arc was run under special conditions so as to emit the resonance radiation with exceptional intensity. The light scattered through the straight edge of the diamond was focussed on the slit of a Hilger (E3) medium quartz spectrograph. The diamond was kept cool with the aid of a fan. The scattering from the specimen was so intense that the principal line could be recorded on the plate with an exposure of five seconds, while an exposure of the order of one hour was sufficient to bring out the essential features of the second order spectrum. Numerous spectrograms were taken with exposures varying from 15 seconds to 15 hours. Kodak B 20 Process Regular plates were used. It is interesting to record the fact that the second order spectrum becomes visible with an exposure of 15 minutes and the anti-Stokes of the principal line  $1332 \text{ cm.}^{-1}$  appears with an exposure of 45 minutes.

A microphotometric record of a moderately exposed spectrogram is reproduced together with the spectrum itself as Fig. 1 (a) and 1 (b) in Plate IV. The microphotometric record of the mercury arc is also included in Fig. 1 (c) for purposes of comparison. The photograph and the microphotometric record reproduced here represent a considerable improvement on the ones published earlier by the author. As is evident from the figures, the second order spectrum of diamond is mainly confined to a region extending to about 300 wave numbers on either side of  $\lambda 2698.9$ . It consists of a series of distinct Raman lines of which at least 7 can be dis-

tinguished without difficulty. Their positions have been marked in Fig. 1 (a). The frequency shifts of these lines have been accurately determined by direct measurements made on the negative. Their values are 2176, 2253, 2299, 2330, 2460, 2502 and 2666  $\text{cm.}^{-1}$ . Three of them, namely the lines at 2176, 2460 and 2666  $\text{cm.}^{-1}$ , stand out prominently in the spectrum. The line at 2460  $\text{cm.}^{-1}$  is the most intense one, while the sharpness of the line at 2666  $\text{cm.}^{-1}$  is comparable with that of a mercury line. The line at 2502  $\text{cm.}^{-1}$  has an appreciable width extending from 2490 to 2514  $\text{cm.}^{-1}$ . This line can be seen clearly separated from the intense line at 2460  $\text{cm.}^{-1}$ . See Fig. 1 (b). The line with the frequency shift 2253  $\text{cm.}^{-1}$  appears to have a finite width. A careful examination of a lightly exposed spectrogram and its microphotometric record has shown that this line is made up of two closely spaced lines with frequency shifts 2245 and 2265  $\text{cm.}^{-1}$ .

Besides the 7 lines described above, the presence of at least 3 other feeble lines with frequency shifts 2190, 2225 and 2430  $\text{cm.}^{-1}$  has been identified by a careful scrutiny of the spectrogram and its microphotometric record. The positions of these lines have also been indicated in Fig. 1 (a). The frequency shifts of the 10 Raman lines belonging to the second order spectrum are listed in Table I, those of the prominent lines being shown in heavy type.

TABLE I  
*Second Order Spectrum of Diamond*

No.	Frequency shifts of the observed Raman lines in $\text{cm.}^{-1}$	Relative intensity	Frequencies of the observed infra-red absorption maxima in $\text{cm.}^{-1}$
1	<b>2176</b>	5	<b>2170</b>
2	2190		2186
3	2225		2217
4	2253	7	2240
5	<b>2299</b>	8	2290
6	2330	9	
7	2430		
8	<b>2460</b>	15	<b>2452</b>
9	<b>2502</b>	13	<b>2506</b>
10	<b>2666</b>	10	<b>2666*</b>

\* Please see remarks in text. The frequencies of the prominent peaks appearing in the infra-red absorption spectrum are also shown in heavy type.

Superposed over the Raman lines there is a feeble continuum which extends from the Raman line 2253  $\text{cm.}^{-1}$  to the line 2666  $\text{cm.}^{-1}$ . It is to be remarked that the line with the frequency shift of 2666  $\text{cm.}^{-1}$  has an individual

existence and is not merely the sharp cut off of the continuum. See Figs. 1 (a) and 1 (b).

The values of the frequency shifts of the second order Raman lines reported earlier by the author were less accurate than the values presented now, as the former had to be evaluated from measurements made on the microphotometric record. In the region between the mercury triplet and  $\lambda$  2675.0 there is a sharp Raman line separated by about 1940 wave numbers from  $\lambda$  2536.5. See Figs. 1 (a) and 1 (b). This was wrongly assigned as a second order Raman line in the paper published in the earlier symposium. It should, however, be assigned as the first order Raman line  $1332 \text{ cm.}^{-1}$  excited by the mercury line  $\lambda$  2576.3. The Raman line at  $\lambda$  2749 seen in Figs. 1 (a) and 1 (b) likewise corresponds to a first order line with the frequency shift  $1332 \text{ cm.}^{-1}$  excited by the mercury line  $\lambda$  2652.

### 3. INTENSITY MEASUREMENTS

In order to estimate the relative intensities of the second order Raman lines as well as the ratios of the intensities of the Stokes, the anti-Stokes and the octave of the principal Raman line  $1332 \text{ cm.}^{-1}$ , the following procedure was adopted. As already mentioned in the last section, a series of photographs of the Raman spectrum of diamond was taken with exposures varying from 15 seconds to 15 hours. Standard developers were used throughout and the time and temperature of development was kept constant. A series of graded intensity marks was obtained on a separate Kodak B 20 plate by photographing the spectrum of a tungsten filament lamp provided with a quartz window with different slit-widths, but keeping the time of exposure constant. A second series of photographs was taken on another plate varying the time of exposure but keeping the slit-width constant. These two negatives were put through the microphotometer. With the aid of the microphotometric records, the density-log intensity and density-log time curves were plotted for the spectral region corresponding to the mean wave-length  $\lambda$  2650. From these curves, the Schwarzschild correction factor appearing in the expression for the photographic density as exponent for time was evaluated. For  $\lambda$  2650 the Schwarzschild factor has the mean value of 0.8.

With the help of the density-log intensity curve and the microphotometric record of a moderately exposed spectrogram of the Raman effect in diamond, the relative intensities of the prominent second order Raman lines were evaluated in the usual way. Taking the intensity of the line  $2666 \text{ cm.}^{-1}$  as 10 arbitrary units, the intensities of the other lines have been calculated and the values are listed in Table I. It is reasonable to assume that the

intensities of the lines 2176, 2460, 2502 and 2666  $\text{cm.}^{-1}$  are not affected to any appreciable extent by the presence of the feeble continuum and hence the values given in Table I may be taken to represent the actual peak intensities of these lines.

With the aid of the microphotometer and using the series of photographs of the Raman spectrum taken with graded exposures, the density-log time curves were plotted for the Stokes line ( $1332 \text{ cm.}^{-1}$ ), the anti-Stokes line ( $-1332 \text{ cm.}^{-1}$ ) and the octave ( $2666 \text{ cm.}^{-1}$ ). The time of exposure required to produce the same density (darkening) on the plate by each one of these lines was read off from the respective density-log time curve. Knowing the values of the exposure time for the three lines, their relative intensities were evaluated using the known value of the Schwarzschild factor. For the 1332 Raman line in diamond, the ratio of the intensities of the Stokes to the anti-Stokes is 575, while that of the fundamental to the octave is 290. In evaluating the former ratio it has been assumed that the density-log intensity curve is the same for the two regions of the spectrum, namely 2625 Å.U. and 2453 Å.U. where the Stokes and anti-Stokes lines fall.

The ratio of the intensity of the Stokes to that of the anti-Stokes line to be expected on the basis of the Boltzmann formula was evaluated taking the temperature of the diamond to be  $27^\circ \text{ C}$ . It is equal to 590 which agrees fairly well with the observed value of 575.

#### 4. INFRA-RED SPECTRUM OF DIAMOND

The infra-red absorption spectrum of diamond was investigated in some detail by Robertson, Fox and Martin (1934). They reported the existence of three distinct regions of absorption in diamonds of the ultra-violet opaque type and two in diamonds of the transparent type. The three groups of absorption which were denoted by letters A, B and C appeared respectively at  $3 \mu$ ,  $4-4.8 \mu$  and  $7-9 \mu$ . They could not detect any difference in the structure of the absorption bands given by the two types of diamond except for the absence of the absorption band C in diamonds of the ultra-violet transparent type. Robertson, Fox and Martin analysed the absorption in the region from  $4-4.8 \mu$  into three separate absorption bands denoted by the letters  $B'$ ,  $B_\alpha$  and  $B_\beta$ . They noticed definite indications of structure in the absorption bands  $B_\alpha$  and  $B_\beta$ . See Fig. 7 reproduced on page 482 of their paper.

Two years later, Robertson, Fox and Martin (1936) carried out further exploration of the fine structure of the absorption bands  $B_\alpha$  and  $B_\beta$  with the aid of a grating. The absorption curve obtained thereby is reproduced in Fig. 1 (a) on page 581 of their second paper. The  $B_\alpha$  band is bounded on

either side by a steep fall in absorption strength and exhibits a very sharp and prominent peak on its longer wavelength edge which forms a characteristic feature of this absorption band. Robertson, Fox and Martin gave the value of  $2170\text{ cm.}^{-1}$  for the frequency of infra-red vibration corresponding to this peak. This peak may be identified in its position with the Raman line  $2176\text{ cm.}^{-1}$  which stands out prominently in the observed second order spectrum.

The principal peak at  $2170\text{ cm.}^{-1}$  is followed by two others, then by a well-defined kink and finally by another peak. The positions of these have been estimated by the author from the curve reproduced by Robertson, Fox and Martin (1936) and their values in wave numbers are 2186, 2217, 2240 and 2290. These are included in Table I. The positions of these peaks and kinks may be identified with those of the observed Raman lines 2190, 2225, 2253 and  $2299\text{ cm.}^{-1}$ . Thus the fine structure of the infra-red absorption band  $B_a$  shows a very striking correspondence with the features observed in the second order spectrum.

Robertson, Fox and Martin (1936) re-examined the absorption band at  $4.1\ \mu$  also with the aid of a grating, but no new details except those already reported by them in their earlier paper were obtained. In the absorption curves of the two types of diamond reproduced in Fig. 7 on page 482 of their paper, the band at  $4.1\ \mu$  exhibits some structure. The existence of two rather broad peaks is easily noticeable in the absorption band of the ultra-violet transparent type of diamond. The positions of these have been estimated by the author. Their frequencies in wave numbers are 2452 and  $2506\text{ cm.}^{-1}$ . Corresponding to these two infra-red absorption maxima, one observes two intense Raman lines with frequency shifts 2460 and  $2502\text{ cm.}^{-1}$  appearing prominently in the second order spectrum.

The absorption curve for diamond of the ultra-violet opaque type shows a peak coinciding with the fundamental Raman frequency of  $1332\text{ cm.}^{-1}$  (K. G. Ramanathan, 1946, see the paper appearing elsewhere in this symposium). The fine structure of the corresponding absorption band in the  $4.1\ \mu$  region has not been investigated. The curve reproduced by Sutherland and Willis (1945), however, shows a precipitous fall of absorption strength beyond the  $4.1\ \mu$ . The point where the slope is greatest has the same frequency as that of the Raman line of frequency shift  $2666\text{ cm.}^{-1}$ .

##### 5. COMPARISON WITH LUMINESCENCE AND ABSORPTION SPECTRA

The luminescence and absorption spectra of diamonds have been studied in great detail by Nayar (1941 *a*, 1942 *a*) and by Miss Mani (1944). Associated with the principal electronic lines at  $\lambda\ 4152$  and  $\lambda\ 5032$  a set of lattice

lines appears at greater wavelengths in fluorescence and at diminished wavelengths in absorption. The most clearly defined and prominent lattice frequencies appearing in luminescence and absorption spectra are in wave numbers 1332, 1251, 1149 and 1088. The Raman lines with frequency shifts 2666, 2502, 2299 and 2176  $\text{cm.}^{-1}$  appearing prominently in the second order spectrum are evidently the octaves of these lattice frequencies.

## 6. CONCLUSION

According to the existing theories of Debye and Born, the vibration spectrum of a crystal is essentially a continuous distribution of frequencies ranging from zero upwards. On this basis, the appearance of only a single sharp and intense line with the frequency shift of 1332  $\text{cm.}^{-1}$  in the Raman spectrum of the first order in diamond is scarcely intelligible. In order to get over this obvious contradiction with the facts, it has been suggested that only the limiting frequencies of the lattice, *viz.*, those having phase-wavelengths large compared with the lattice spacing could appear in the observed Raman spectrum. It is further assumed that the frequencies of the vibrations of shorter phase-wavelengths disappear by reason of the optical interference of the effects due to them arising from different volume elements. There is no experimental justification for such an assumption. Even if it were valid, the second order spectrum of diamond should likewise consist of a single sharp line corresponding to the octave of the limiting frequency of vibration, namely 2664  $\text{cm.}^{-1}$ . What is actually observed is wholly different, *viz.*, a set of Raman lines with discrete frequencies. It is therefore impossible to reconcile the consequences of the Born theory with the experimental facts of the Raman effect in diamond.

The appearance of a set of lines with discrete frequency shifts in the second order spectrum of diamond finds a natural explanation in the new theory of lattice dynamics put forward by Sir C. V. Raman (1943). According to the Raman dynamics the diamond lattice has a small number of fundamental modes of vibration with discrete frequencies. The observed second order lines are the octaves and allowed combinations of some of these fundamental frequencies of oscillation of the diamond lattice.

The author is grateful to Professor Sir C. V. Raman for the loan of the diamond used in the present investigation and for some useful discussions.

## 7. SUMMARY

Using an exceptionally colourless plate of diamond of the ultra-violet transparent type and the  $\lambda$  2536.5 resonance radiation of mercury as exciter, the author has photographed the second order Raman spectrum of diamond

with greatly increased intensity and much better resolved than any recorded hitherto. The spectrum exhibits ten distinct Raman lines with frequency shifts 2176, 2190, 2225, 2253, 2299, 2330, 2430, 2460, 2502 and 2666  $\text{cm.}^{-1}$ . The frequency shifts of the first five lines, in particular, correspond very closely with the positions of a set of five absorption peaks observed by Robertson, Fox and Martin while exploring the absorption band in the region  $4-4.8 \mu$  with the aid of a concave grating of the echelette type. Of the ten observed second order Raman lines, the more intense and prominent ones have been identified as octaves of the prominent lattice frequencies of diamond appearing in the luminescence and absorption spectra. These facts are irreconcilable with the consequences of the Born lattice dynamics. They can, however, be satisfactorily explained on the basis of the Raman dynamics of crystal lattices.

The relative intensities of the second order Raman lines, as well as the ratios of the intensities of the Stokes, the anti-Stokes and the octave of the principal Raman shift of  $1332 \text{ cm.}^{-1}$  have been estimated by photographic photometry.

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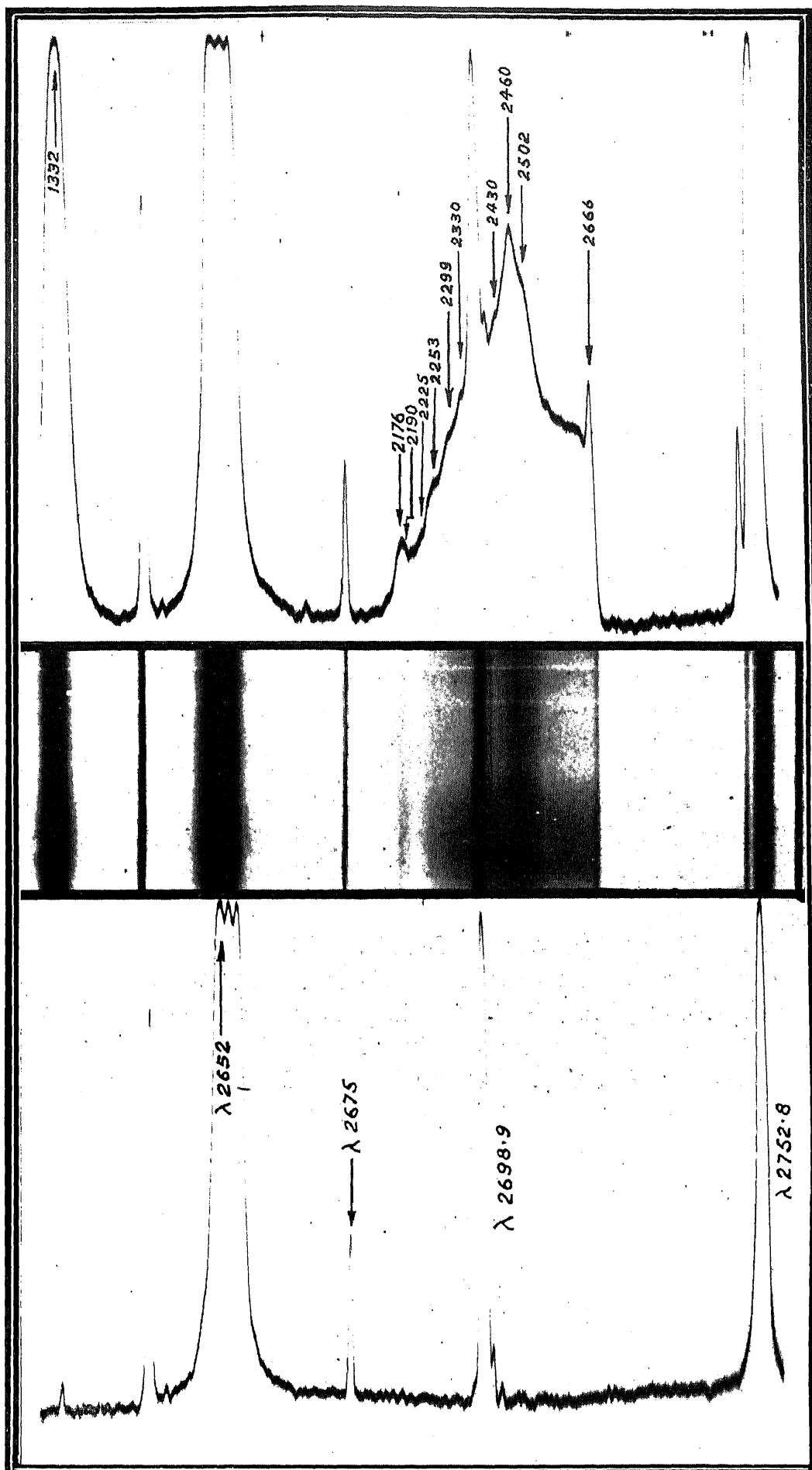


FIG. 1. (a) Microphotometer record of the second order spectrum of diamond.  
(b) The Raman spectrum of the second order in diamond.  
(c) Microphotometer record of the mercury spectrum.