THE RAMAN SPECTRUM OF DIAMOND

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1. Introduction

THE Raman spectrum of diamond was first studied by Ramaswamy (1930) who noticed that it exhibits a single sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ Bhagavantam (1930) who examined a number of diamonds reported $1331 \cdot 9 \pm 0 \cdot 3$ as the averaged value of the frequency shift. Subsequently Robertson, Fox and Martin (1934), who examined four diamonds which exhibited the $8\,\mu$ infra-red absorption and five others which did not, gave $1332 \cdot 2$ cm.$^{-1}$ at 20° C. as the frequency shift. Nayar (1941) who undertook the study of a number of diamonds and investigated the temperature variation of the frequency records a value of $1332 \cdot 1$ cm.$^{-1}$ at room temperature, this diminishing slowly at first but more rapidly later to $1316 \cdot 4$ cm.$^{-1}$ at 1130° K.

The lattice dynamics developed by Raman (1943) indicates that the vibration spectrum of diamond should consist of eight frequencies of which only the first and highest representing the vibration of the two inter-penetrating face-centred cubic lattices against each other, should manifest itself both as a fundamental and as an octave in the Raman Effect, whereas all the other frequencies can only appear in the second order Raman spectrum as overtones and combinations. The extensive series of investigations carried out by R. S. Krishnan (1946, 1947) and P. S. Narayanan (1951) have furnished a very complete verification of the predictions of this theory. R. S. Krishnan's investigations have also shown that, hand in hand with the change of the first order frequency shift with rise in temperature, its spectral half width also increases from $1 \cdot 7$ cm.$^{-1}$ at 300° K. to $3 \cdot 6$ cm.$^{-1}$ at 970° K.

Diamonds are known to exhibit wide variations in their optical behaviour, notably in respect of their transparency in the infra-red and ultra-violet regions of the spectrum and in the intensity and colour of the luminescence (if any) which they display. They also exhibit a great diversity in their X-ray behaviour as well, as was shown by Hariharan (1944), Krishnan (1944) and especially by G. N. Ramachandran (1944, 1946).

TABLE I

No.	Description of the specimen	Optical behaviour	Measured value of frequency in cm.$^{-1}$	Remarks
1	Irregular polycrystalline lump of bort	Translucent and feebly blue luminescent	1331·6	
2	Cube of bort with a waxy appearance	No detectable luminescence	1332·0	Faintly recorded
3	Pale yellow cube with rather rough faces		1331·9	
4	Cube appearing semi-transparent	Feebly yellow luminescent	1331·6	
5	Large coarse lump	Transparent and intensely blue luminescent	1331·8	
6	Faceted tablet, blue even in ordinary light	Transparent and brilliantly blue luminescent	1331·9	
7	Small piece cut in the form of a brilliant, pale green in ordinary light	Brilliantly green luminescent	1331·7	

8	Irregular pale yellow lump	Translucent and brilliantly orange luminescent	1331·9	
9	Semi-circular plate with a polished straight edge	Transparent, feebly blue luminescent, exhibiting 8 μ infra-red absorption and ultra-violet opaque	1331·5	Used by K. G. Ramanathan for infra-red absorption studies
10	Rectangular plate with polished edges	do.	1331·6	do.
11	Rectangular thick plate with well-polished edges	Transparent, no observable luminescence under near ultra-violet light. λ 4152 band recorded after a 24 hr. exposure	1331·8	Used by R. S. Krishnan in the work on the thermal scattering of light with λ 2536·5
12	Thick semi-circular plate with a polished straight edge	Non-luminescent and ultra-violet transparent	1331·7	Used by R. S. Krishnan to record the second order. The value recorded by him is 1331·8 cm.$^{-1}$
13	Rectangular faceted piece set in a ring	Non-luminescent	1331·7	
14	Large thick plate of irregular shape with polished edges and pale yellow in colour	do.	1331·3	Recorded with a slit width of 0·1 mm.

The studies of these authors have revealed that the faintly blue luminescent diamonds which exhibit the 8μ infra-red absorption are usually very perfect and give sharp X-ray reflections. Diamonds that are strongly blue luminescent, on the other hand, give X-ray reflections characterised by an increased integrated intensity and width which goes hand in hand with increasing intensity of luminescence. The non-luminescent diamonds which exhibit lamellar birefringence between crossed polaroids exhibited a largely increased intensity of X-ray reflection. These effects have been ascribed to a mosaicity in the structure of diamonds in the cases referred to. Though the earlier investigators have not ignored the possibility that a diversity of behaviour might also manifest itself in the Raman spectrum of diamond, it appeared desirable to reinvestigate this possibility with the aid of the extensive collection of material available at this Institute.

2. EXPERIMENTAL DETAILS

The Raman spectra were recorded with a large aperture ($f4\cdot5$) Huet two-prism glass spectrograph having a dispersion of 110 cm.$^{-1}$ per mm. in the region of $\lambda 4630$. The visible radiations of a low pressure mercury arc sufficed to excite the Raman effect. In the case of the study of luminescent diamonds a concentrated solution of sodium nitrite was interposed in the path of the exciting radiation to suppress $\lambda 4046$ line and thereby reduce considerably the continuous background due to luminescence. A slit width of 0·04 mm. was used and an exposure of one hour was found to be adequate to record the line intensely in most cases. An iron arc spectrum was superposed on the Raman spectrum and the spectrograms were measured on a Hilger photomeasuring micrometer correct to 0·001 mm. The maximum error in measurement did not exceed 0·5 cm.$^{-1}$ even in the case of lines recorded only faintly.

Any expected variation in the observed Raman spectra can manifest itself as (i) a change in the frequency shift, (ii) a variation in the width of the line and (iii) a change in the observed intensity of the line. Spurious values can arise in the measured frequency shift due to variations in the temperature of the spectrograph during the exposure. This difficulty was avoided as far as possible by giving short exposures and also by obtaining more than one spectrogram in typical cases. The Raman lines from two pairs of typical diamonds (9 & 12 and 10 & 13) were photographed simultaneously by mounting them in a line and focussing their images on the slit of the spectrograph with a large aperture lens. As the instrument used in the investigation was not of very large dispersion, it was not possible to measure the width of the line quantitatively in each case. The increase

in the width of the line due to photographic broadening has to be taken into consideration even for a qualitative finding whether there is a difference in the width of the line. The intensity of the line recorded depends on the size and shape of the specimen, its general transparency and the orientation of the plane of scattering with respect to the crystal axes. In view of the several factors entering into this question, only qualitative remarks could be made about the intensity of the line.

3. DESCRIPTION OF THE DIAMONDS

In all, fourteen diamonds were examined and from the description of them in Table I given above it can be seen they are representative of the diverse optical characters known to be exhibited by diamond.

4. RESULTS AND DISCUSSION

From Table I it can be seen that the maximum difference in the measured values of the frequency shift is $0 \cdot 5$ cm.$^{-1}$ (omitting the value of No. 14, the spectrum in which case was recorded with a wide slit). The average value of the frequency shift is found to be $1331 \cdot 7$ cm.$^{-1}$, while Krishnan has reported a value of $1331 \cdot 8$ cm.$^{-1}$ using No. 12. These values fall on either side of $1331 \cdot 7$ cm.$^{-1}$ with a maximum variation of $0 \cdot 3$ cm.$^{-1}$ which is in the range of the error likely to occur in measurement.

In all the several spectra obtained, it was not possible to notice any significant variations in the width of the line after taking into account the photographic broadening in cases where the spectra were recorded intensely. It was possible to record the line in all cases with adequate intensity. Longer exposures were found to be necessary in cases where the diamonds were small, translucent or coloured. There was no observable correlation between the intensity of the Raman line and the known optical properties, *viz.*, infra-red absorption, ultra-violet transparency and the intensity and colour of the luminescence. Apparently the mosaic structure observed in diamond does not noticeably influence its Raman spectrum.

It is a pleasure to thank Prof. Sir C. V. Raman, N.L., F.R.S., for suggesting this investigation.

5. SUMMARY

The Raman spectra of fourteen different diamonds exhibiting diverse characters in their optical behaviour (*viz.*, transparency in the infra-red and ultra-violet regions of the spectrum, birefringence and the intensity and colour of the luminescence) were recorded. The principal Raman line is found to have a frequency shift of $1331 \cdot 7 \pm 0 \cdot 2$ cm.$^{-1}$ which agrees closely

with the value of $1331\cdot8$ cm.$^{-1}$ reported earlier. There were no observable variations in the frequency shift, width or intensity of the line in the several cases studied.

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