

THE INFRA-RED ABSORPTION SPECTRUM OF DIAMOND AND ITS VARIATIONS

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1. INTRODUCTION

IN a previous work (Ramanathan, 1946) the infra-red absorption spectra of four typical diamonds were investigated in the region between 750 and 2200 wavenumbers. Due to the inadequate resolution of the spectrometer used, the curves reproduced there do not show much detail in the region between 1500 and 2200 cm^{-1} . The present work was therefore undertaken with a view to improve upon the technique and to examine as many cleavage plates of diamond as possible in the region of the spectrum 750–4000 cm^{-1} . It was also the aim of the present research to investigate the local variations in infra-red absorption spectrum within its area of a typical specimen exhibiting patterns of luminescence and ultra-violet transparency.

2. IMPROVEMENTS IN TECHNIQUE

Since the author's previous studies mentioned above, several improvements in technique have been made with a view to increase the resolving power of the instrument. To prevent undue heating of the surroundings, the original globar source was dispensed with and an ordinary incandescent filament source, enclosed in an aluminium box with an aperture for the exit of radiation, substituted. The dispersing device now being used is a 60° prism of rocksalt with refracting faces 2" by $1\frac{1}{2}$ " in place of the 54° prism with 2" square faces previously used. Nearly a tenfold increase in the sensitivity of the Boy's radiomicrometer has been achieved by the use of Hutchin's alloys for the thermocouple and a fine quartz fibre for the suspension. The instrument mounted on rubber shock absorbers on a heavy concrete platform inside an airtight chamber is very steady in quiet weather during which readings can be taken correct to a millimetre or two. The infra-red spectrometer was calibrated by employing the method described by Rawlins and Taylor (1929). The 5461 Å radiation of the mercury arc and the CO_2 emission maximum at $4.38\ \mu$ from a Bunsen flame have been used as calibration wave-lengths. The procedure adopted for obtaining the absorption curves has already been described in the previous work.

3. RESULTS

With the above arrangement, the infra-red absorption spectra of nine cleavage plates of diamond have been investigated and the results obtained are described below.

(a) *The 1500–2700 Band.*—This region comes first for consideration because all diamonds irrespective of their other physical properties exhibit a band in this region with a number of absorption maxima. In comparing the relative strengths of any absorption band in different diamonds, one has of course got to consider the thicknesses of the specimens. It is also necessary to take into account the small variations in transmission which may result from the slight curvature of its surfaces. Allowing for the discrepancies resulting from these two facts, it is seen that the absorption band in this region shows no observable variations in strength or structure from diamond to diamond (see Figs. 1 to 9).

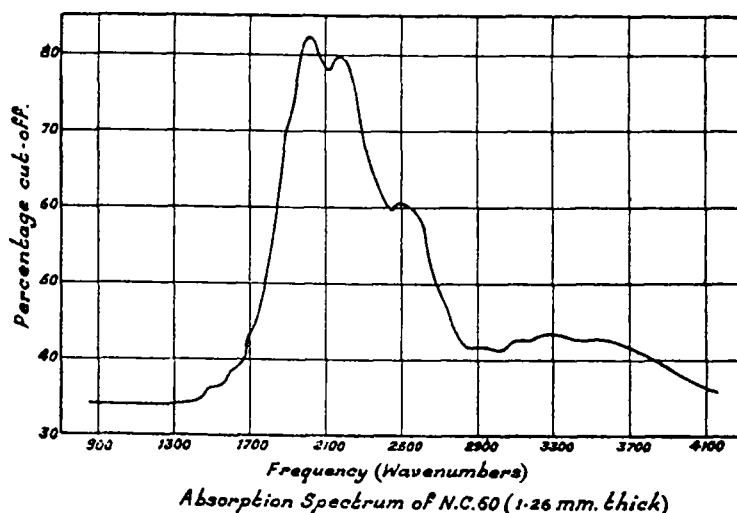


FIG. 1

All the diamonds without exception exhibit in this band two very strong absorption maxima centred at 2010 and 2170 wavenumbers and a third one at 2470 cm^{-1} which is much weaker than the former two. In addition a number of step-like falls in absorption have been observed in many diamonds in this region. This feature appears in the curves reproduced for most of the diamonds and the effect therefore appears to be a genuine one. The step-like falls or inflexions are not so prominent in the curves of the thicker diamonds, while in the thinnest of them investigated, they are in a few cases even resolved into peaks of absorption. The approximate frequencies

corresponding to these points of inflexion are 2300 cm.^{-1} , 1900 cm.^{-1} , 1800 cm.^{-1} , 1660 cm.^{-1} and 1560 cm.^{-1}

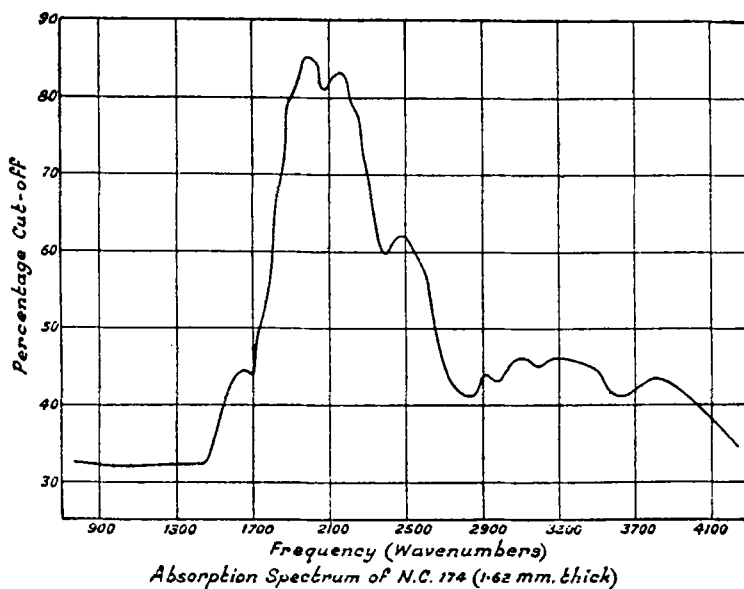


FIG. 2

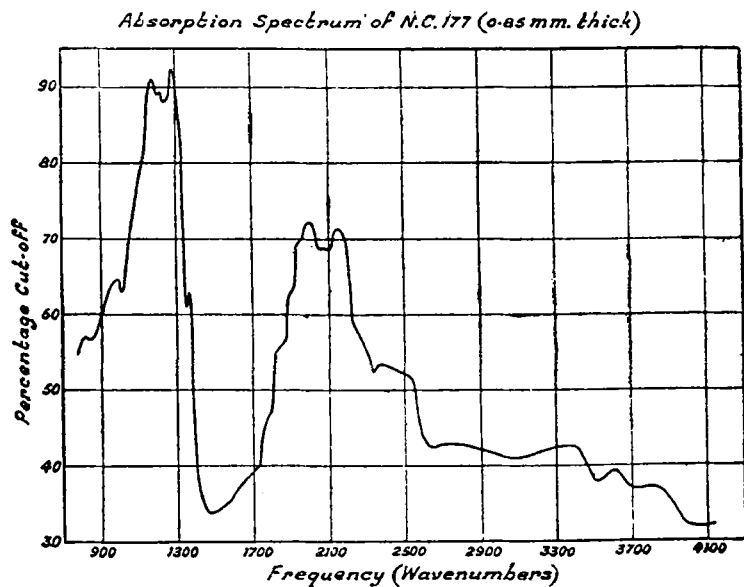


FIG. 3

(b) *The 750–1400 cm.^{-1} Band.*—The variations in the intensity of this band are shown most strikingly by the series of curves reproduced for eight of the diamonds investigated (Figs. 1 to 8). The band is completely absent

in the diamonds N.C. 60 and N.C. 174 (Figs. 1 and 2 respectively) which after allowing for reflection of radiation from the two surfaces of a cleavage

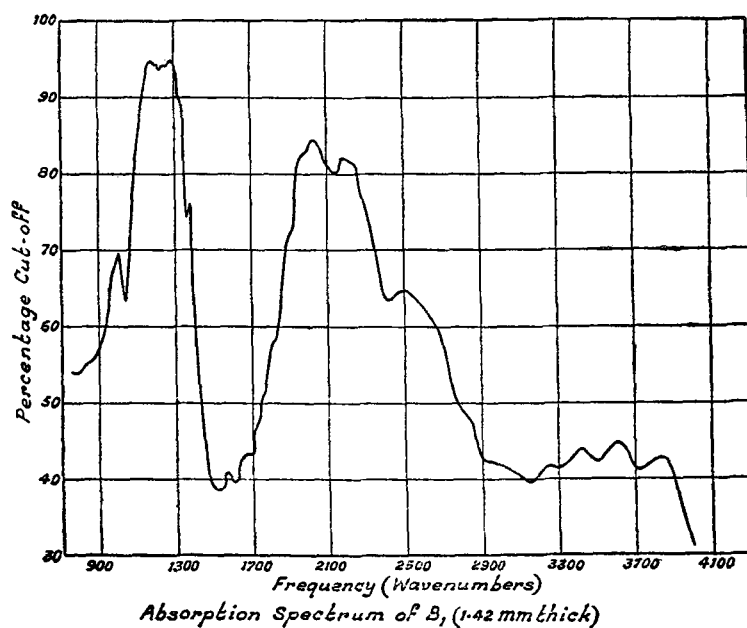


FIG. 4

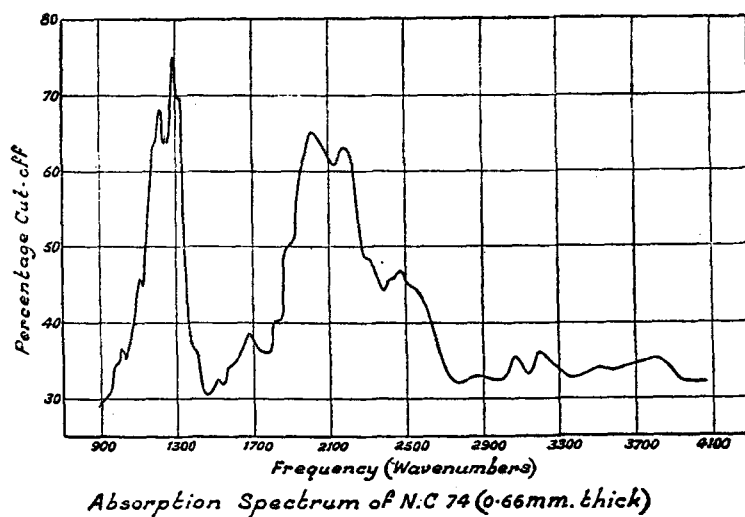


FIG. 5

plate, are found to be completely transparent in the region between 750 and 1400 cm^{-1} . It is strongest in the weakly blue-fluorescent diamonds N.C. 175

B₁, N.C. 74 and N.C. 73 (Figs. 3, 4, 5 and 6 respectively), somewhat weaker in the strongly blue-fluorescent diamond N.C. 79 and weakest in the diamond N.C. 110 exhibiting a yellow luminescence. The extent of variation in the

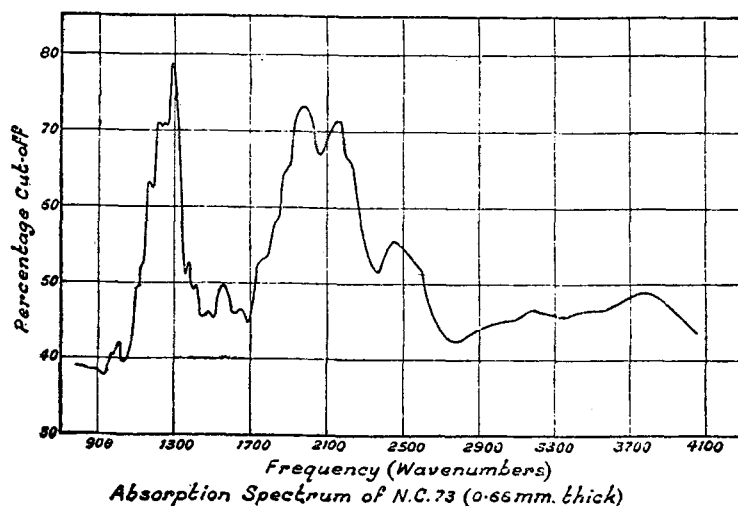


FIG. 6

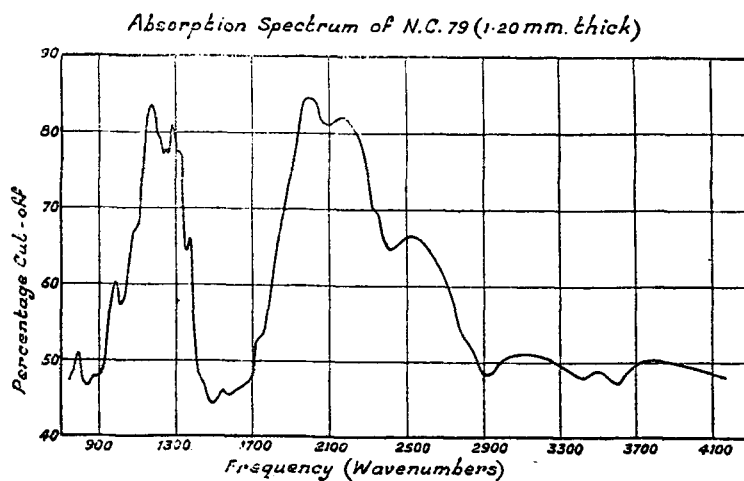


FIG. 7

strength of the band can be appreciated from Table I which shows the coefficient of absorption at three of the peaks in this band (1000 cm⁻¹, 1170 cm⁻¹ and 1290 cm⁻¹) together with those at the three peaks 2010 cm⁻¹, 2170 cm⁻¹ and 2470 cm⁻¹ shown for comparison.

TABLE I
Intensities of Absorption Peaks in Various Diamonds

Catalogue Number of Diamond	Coefficient of Absorption at the various peaks (per cm.)					
	1000 cm. ⁻¹	1170 cm. ⁻¹	1290 cm. ⁻¹	2010 cm. ⁻¹	2170 cm. ⁻¹	2470 cm. ⁻¹
N. C. 177 ..	8.1	24.0	30.0	10.9	10.4	4.8
B ₁ ..	5.8	17.6	18.0	10.4	9.5	4.8
N. C. 74 ..	1.6	10.2	15.7	10.6	9.7	4.2
N. C. 73 ..	3.0	9.8	18.0	14.5	13.5	7.0
N. C. 79 ..	4.7	12.0	10.9	12.6	11.4	6.2
N. C. 110 ..	2.1	6.6	5.3	12.8	11.9	5.1
N. C. 175 (a)	1.6	12.2	10.9	5.1
N. C. 175 (b)	0.7	11.8	10.4	4.9
N. C. 60 ..	0.4	0.4	0.4	10.8	9.8	4.6
N. C. 174 ..	0.2	0.2	0.2	9.6	8.8	3.8

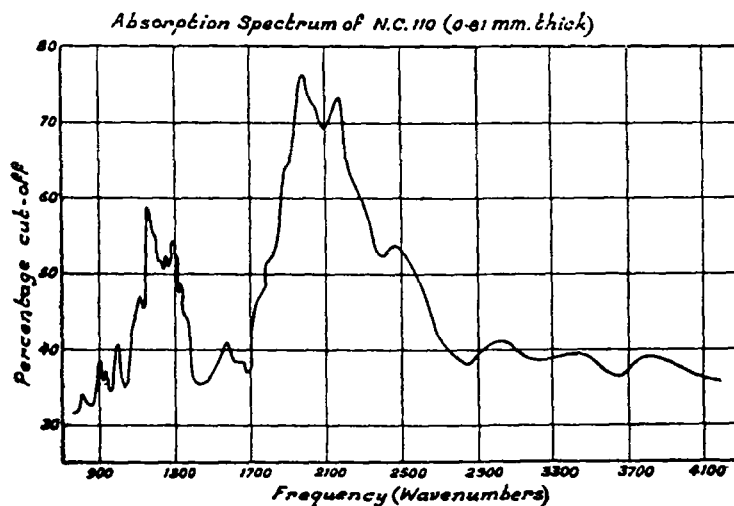


FIG. 8

In comparing the intensities of any absorption band in various diamonds, one must take into account the optical imperfections of the specimens which increase the apparent coefficient of absorption in some cases. That such an increase is caused by the irregularities is obvious from the fact that in some diamonds the coefficient of absorption comes out higher for all the three peaks in the 5μ band ($1500-2700\text{ cm.}^{-1}$) and if proportionately

decreased, they become equal to the values obtained for the other diamonds which are free from such imperfections.

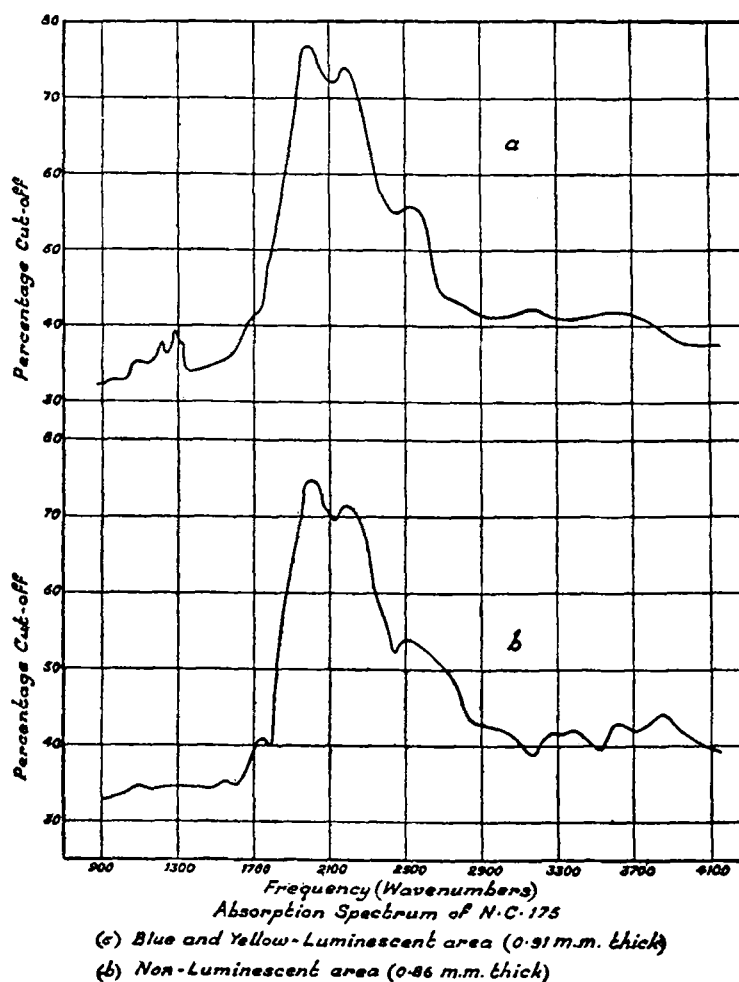


FIG. 9

The various absorption maxima observed in the previous work, are recorded here under better resolution. The inflexion at 1330 wavenumbers has also been observed in most of the diamonds exhibiting this band.

The diamond N.C. 175 shows a pattern of luminescence and so has been used for investigating the spectral character of the local variations. (a) and (b) denote respectively the luminescent and non-luminescent areas in the diamond. The remarkable changes observed in the absorption spectrum can be seen from Figs. 9 (a) and (b). The non-luminescent area shows no

absorption band in the region $750\text{--}1400\text{ cm.}^{-1}$. A very weak band is however exhibited by the luminescent area, the structure of the band being essentially the same as in most other diamonds.

(c) $2700\text{--}4000\text{ cm.}^{-1}$ region.—The absorption in this region is very weak. All the diamonds investigated exhibit some absorption bands, but due to the inadequate resolution of the rocksalt prism, the positions of the maxima could not be measured accurately.

4. INTERPRETATION OF THE RESULTS

In another paper appearing in these *Proceedings* (Ramanathan, 1947), expressions for the frequencies of the nine modes of atomic vibration in diamond have been derived in terms of 8 independent force constants. The frequencies used there in evaluating the constants, obtained from the most reliable spectroscopic data are contained in Table II below together with a description of the nine modes of vibration.

TABLE II

The Nine Fundamental Frequencies of Diamond

Frequency Sequence	Degeneracy	Oscillating Units	Direction of oscillation	Observed and calculated Frequencies
I ..	3	The two lattices (111) planes	Arbitrary	cm. ⁻¹ 1332
II ..	8		[011] direction	1250
III ..	6		[011] ..	1232
IV ..	4		[111] ..	1149
V ..	3		[100] ..	1088
VI ..	3		[100] ..	1088
VII ..	4		[111] ..	1008
VIII ..	6		[100] ..	752
IX ..	8		[111] ..	620

From the table it can be seen that the absorption band appearing in the region $750\text{--}1400\text{ cm.}^{-1}$ is due to the fundamental frequencies, the one at $1500\text{--}2700\text{ cm.}^{-1}$ as due to second-order effects and the band at $2700\text{--}4000\text{ cm.}^{-1}$ as due to third-order effects. We shall not deal with the third order band in this paper as the data available regarding it are very meagre.

The two strongest absorption maxima appearing at 2010 and 2170 cm.^{-1} in the second-order band are obviously due to the octaves of the modes VII and V and VI with frequencies of 1008 and 1088 cm.^{-1} respectively. The broad maximum around 2470 cm.^{-1} whose doublet character is revealed in many of the curves, is evidently due to the octaves of modes II and III with frequencies of 1232 and 1250 cm.^{-1} respectively, as also their summation.

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In addition, an inflexion appearing at about 2300 cm.^{-1} has to be interpreted as the octave of mode IV (1149 cm.^{-1}) which is not well resolved owing to its falling on the steep portion of a much stronger band at 2170 cm.^{-1} . The inflexions appearing on the lower frequency side of 2010 cm.^{-1} can be interpreted as the combinations of the two low frequency modes with those having higher frequencies.

If the various modes of vibration are dynamically independent of each other, then as pointed out in the paper referred to, mode I of Table II representing the fundamental lattice frequency should be inactive in the non-luminescent diamonds and active in others. The other modes II to IX should be inactive in all diamonds as fundamentals, due to the reversal of phase of the vibrations in the successive layers of atoms. Owing to anharmonicity, however, there will be some coupling between the various modes as a result of which, the activity of the fundamental lattice frequency will be necessarily followed by the activity of all the other modes situated in the neighbourhood. The coupling between the various modes might also result in slight shifts of the absorption maxima as well as in the appearance of absorption in regions midway between two fundamental frequencies. The strong peak at 1290 cm.^{-1} situated midway between 1330 and 1250 cm.^{-1} has probably such an origin. The rapid fall of intensity of the various peaks with increasing distance from mode I adds support to the above explanation of their appearance. The peak at 1375 cm.^{-1} is the combination of modes VIII and IX of Table II, rendered active owing to its contiguity with the mode I.

From the curves reproduced for the six diamonds exhibiting the first-order band, it will be seen that it is most striking in diamond N.C. 177 which has got the feeblest blue luminescence and is characterised by the maximum homogeneity of structure. The diamonds in which the band is absent (N.C. 60 and N.C. 174, Figs. 1 and 2) are, on the contrary, characterised by inhomogeneities in structure and optical birefringence. The presence of the band in some diamonds and its absence in others is therefore to be attributed neither to the presence of impurities, nor to crystal imperfections, but to a deeper reason, *viz.*, a fundamental difference in crystal symmetry, which is tetrahedral in one case and octahedral in the other.

It is observed, however, that mosaicity of structure can influence an absorption band by giving rise to changes in its intensity distribution. In the absorption spectra of the strongly luminescent diamonds N.C. 79 and N.C. 110, the intensity distribution in the entire band is different from that for the other diamonds. The strongest peak in these two curves is the one

at 1170 cm.^{-1} . It will be seen from Table II that this frequency corresponds to the normal oscillation of the octahedral planes of atoms with the closely spaced layers moving with the same phase. If interpenetration of structures having different crystal symmetry takes place in such manner that they appear as alternate finely spaced laminæ parallel to the octahedral planes of the diamond, then the electric moment developed in neighbouring layers would no longer cancel out for mode IV (1149 cm.^{-1}) and mode VII (1008 cm.^{-1}). It has been shown by Ramachandran (1946) that in most luminescent diamonds, interpenetration of the different structures takes place with the laminations parallel to the octahedral planes of the diamond.

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SUMMARY

The infra-red absorption spectra of nine cleavage plates of diamond have been investigated in the region of frequencies between 750 and 4000 cm.^{-1} and their observed spectral behaviours have been elucidated. While the second-order spectrum is similar for all diamonds, the first-order spectrum shows large variations. From the nature of these variations it is concluded that the first-order activity is due neither to chemical impurities nor to mosaicity of structure, but must be attributed to the tetrahedral symmetry of structure possessed by such diamonds.

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