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INFRARED ABSORPTION SPECTRA OF DIAMONDS OF DIFFERENT TYPES

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ABSTRACT. The infrared absorption spectra of ten specimens of diamond of which the fluorescence and absorption spectra had been studied earlier were investigated using a Perkin-Elmer Model 21 spectrophotometer Two of these diamonds transparent upto about 2300 Å in the ultraviolet region and producing no fluorescence band at 4156 Å exhibit only very weak infrared absorption in different regions while the other specimens show some or all the absorption bands reported by previous workers It has been concluded from these results that these infrared bands excepting the band 1360 cm^{-1} are due to impurities and are not produced by characteristic vibrations of the diamond lattice. The band 1360 cm^{-1} has been assigned to the vibration in those portions of the lattice which are under strain due to presence of impurities

INTRODUCTION

The infrared absorption spectra of a large number of diamonds were investigated by Robertson, Fox and Martin (1934) along with many other properties of the crystal and it was observed by them that all the specimens showed bands in the regions 2462–2491 cm^{-1}, 2167–2187 cm^{-1}, 2080–2106 cm^{-1} and 1992–2015 cm^{-1}, but only the specimens of common type absorbing ultraviolet radiation beyond 3000 Å showed another set of bands in the region 1196–1387 cm^{-1}. These latter bands were absent in the spectra due to the crystals transparent to ultraviolet radiation beyond 3000 Å From these results they concluded that the diamonds could be divided into two types, e.g., Type 1 showing the absorption bands at 8μ and also absorption of ultraviolet rays beyond 3000 Å and Type 2 not showing any absorption in these two regions. They, however, classified under Type 2 some diamonds which were transparent to ultraviolet radiation beyond 3000 Å but showed absorption bands in the region 2351 Å–2335 Å, as these diamonds also did not show any infrared absorption band in the region 8μ

The study of the luminescence spectra of different specimens of diamond was later undertaken by Nayar (1941*a*, 1941*b*), Anna Mani (1944), Chandrasekharan (1948) and others It was concluded by these workers that the luminescence is feeble in diamonds of Type 2 which show transparency in the ultraviolet region beyond 3000 Å and that the absorption band at 4156 Å and the fluorescence band at this position were the characteristic bands of the diamond lattice Bishui (1950) pointed out, however, that the fluorescence band at 4156 Å exhibited by diamonds of Type 1 might be due to chemical impurities, as macroscopic strain in the crystal has no influence on the intensity of the band He next studied (Bishui, 1952) quantitatively the intensity of the fluorescence band at 4156 Å relative to that of the Raman line at 1332 cm^{-1} and also the ultraviolet absorption spectra of eight selected specimens of diamond and observed that the intensity of the fluorescence band at 4156 Å does not depend on the strength of the absorption band at the same place He further observed that a specimen which is transparent to the visible region and to ultraviolet radiation upto 2270 Å and shows only two absorption bands at 2360 Å and 2363.3 Å, produces strong fluorescence band at 4156 Å, but those specimens which do not show any absorption bands in the visible or ultraviolet region upto 2240 Å do not produce the fluorescence band at 4156 Å. From these results he concluded that diamonds of these totally transparent type are pure diamonds and should be classified under Type 2, while all other specimens showing fluorescence band at 4156 Å are of Type 1 and that the fluorescence band at 4156 Å is due to the impurity which produces the ultraviolet absorption bands at 2360 Å and 2363.3 Å.

The infrared spectra of these specimens of diamond were not known and it was thought worthwhile to study the infrared spectra to find out whether the band at 8μ was a characteristic band of diamonds of Type 1 which show the fluorescence band at 4156 Å and also whether the other bands observed in the infrared spectra of diamonds of Type 2 by Robertson, Fox and Martin (1934) are exhibited by all the diamonds of both the types

EXPERIMENTAL

As mentioned above some of the specimens of diamond used previously by Bishui (1950, 1952) for investigating the fluorescence yield and ultraviolet absorption spectra were used in the present investigation The specimens selected are D 1, D 4, D 5, D 6, D 7, D 8, D 9, D 10, D 11 and D 13 Of these, D 4 and D 13 were classified by him under Type 2 and the rest under Type 1.

A Perkin-Elmer Model 21 infrared spectrophotometer was used to study the absorption spectra. As the diamonds were smaller than the full apertures in the two beams in the spectrophotometer two small apertures of the same size made in two discs of black paper were used in the paths of the two beams, so that the radiation in the sample beam could enter into the spectrophotometer only after passing through the specimen of diamond covering the aperture in this beam The size of the aperture was not less than 4.5 mm × 6 mm in any case and the smallest diamond used could wholly cover this aperture. Even when s[illegible] [illegible] [illegible] aperture was used in the reference beam and the sample beam

was shut off the pen was driven to the position 1 instead of zero, so that the heights of the absorption peaks were not affected very much by the introduction of the apertures in the two beams.

RESULTS AND DISCUSSIONS

The positions of the bands observed in the infrared absorption spectra of the specimens of diamond are given in Table I. The intensities are given as strong, medium, etc. The details about the ultraviolet absorption limit, intensities of fluorescence and absorption band at 1156 Å and the dimensions of the specimens are given in Table II. The absorption curve due to D 6 is reproduced in Fig. 1. The curves due to D 9 and D 10 are shown in Fig. 2. The curves due to D 5, D 7 and D 10 show bands similar to those given by D 6 but with

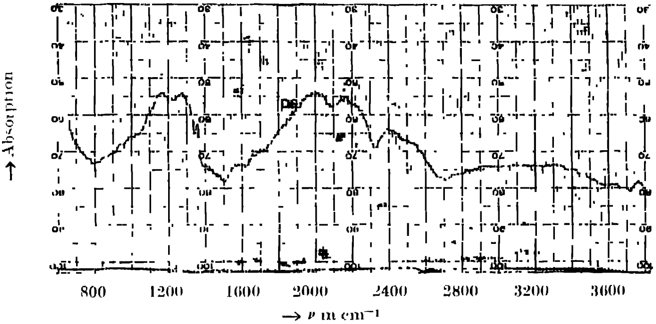

Fig. 1 Infrared absorption spectrum of D 6

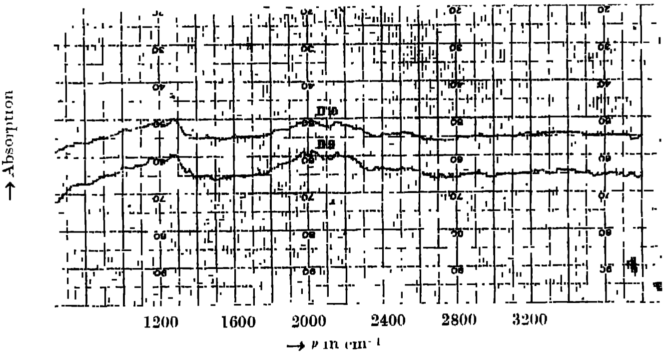

Fig. 2. Infrared absorption spectra of D 9 and D 10

smaller strengths of absorption, and therefore, these curves have not been reproduced. Fig. 3 shows the curve due to D 1, which is a rose diamond belonging to Type 1, along with the curves given by D 4 and D 13 which are of Type 2. The curve due to D 8 was found to be similar to that due to D 1 and it has not been reproduced. Fig. 4 shows the curve due to D 11 which is transparent upto 2270 Å but shows two absorption bands at 2360 Å and 2363.3 Å respectively.

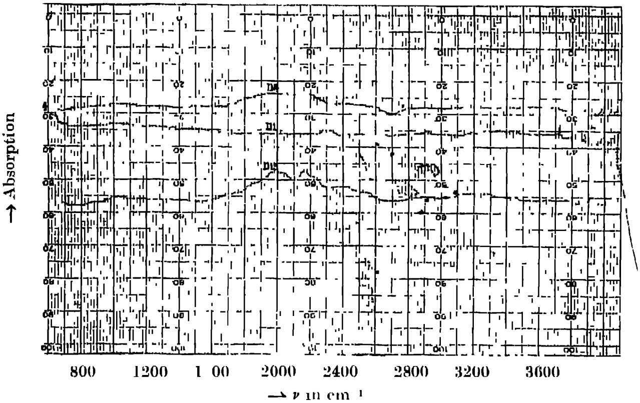

Fig 3. Infrared absorption spectra of D 1, D 4 and D 13

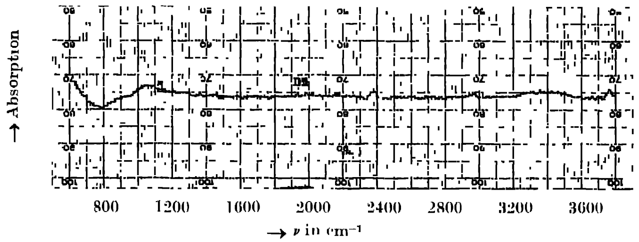

Fig. 4 Infrared absorption spectrum of D 11

It can be seen from the figures and the tables mentioned above that the diamonds D 5, D 6, D 7, D 9 znd D 10 belonging to Type 1 produce similar absorption bands in the regions from 1000 cm^{-1} to 1400 cm^{-1} and from about 1900 cm^{-1} to 2500 cm^{-1}. All these specimens show a sharp band at 1360 cm^{-1} besides the other broad bands, but the height of this sharp peak is different for the different specimens. On the other hand, the diamonds D 1 and D 8 which

TABLE I

Infrared absorption bands of diamonds

Diamond No.	Frequencies of bands in cm^{-1} and intensities								
D 1	900 – 1300 (vw). (very broad band)			—	—	—	—	—	—
D 4	—	—	—	1800 – 2200 (w). (very broad band)			—	—	—
D 5	1150 (m)	1270 (m)	1360 (vw)	2000 (mb)	2150 (mb)	2260 (w)	2400 (w)	2500 (w)	2900–3400 (wb)
D 6	1160 (s)	1280 (s)	1360 (m)	2000 (s b)	2160 (s)	2240 (m)	2400 (w)	2500 (w)	2900–3400 (w)
D 7	1180 (m)	1280 (s)	1360 (w)	2000 (s,b)	2160 (s)	2220 (m)	—	2500 (w.b)	3000–3400 (vw)
D 8	900–1400 (w,vb)		—	—	—	—	—	—	—
D 9	1000 (w)	1160 (m)	1280 (m)	1360 (vw)	1980 (m)	2020 (m)	2160 (m)	2220 (w)	—
D 10	1000 (w)	1160 (m b)	1280 (m)	1360 (vw)	1960 (m)	2020 (m)	2160 (m)	—	—
D 11	—	—	—	—	1950 (w)	2000 (w)	2150 (w)	2400 (vw)	—
D 13	—	—	—	—	2000 (w,b)	2150 (w)	2240 (vw)	2400 (vw)	—

TABLE II

Properties of the specimens of diamond used

Diamond No.	Dimensions in mm.	Intensity of absorption band at 4152 Å at −180°C	Intensity of fluorescence band at 4152 Å at −180°C	Ultraviolet absorption limit
D 1	9×7×1 5	strong	very strong	opaque beyond 3500 Å
D 4	11×8×1.5 (triangular)	zero	very weak	limit 2280 Å
D 5	10×8×2	weak	very strong	„ 3000 Å
D 6	14×12×2	medium	very strong	„ 3500 Å
D 7	9×7.5×1 35	weak	strong	„ 2560 Å
D 8	9×5.5×1.3	medium	weak	„ 3000 A
D 9	6×5×0.8	weak	very strong	„ 2550 Å
D 10	7.5×5 5×1.09	very weak	strong	„ 2810 Å
D 11	7×5×0 95 (low pyramid)	weak	very strong	„ 2270 Å bands at 2360 & 2363.3 Å
D 13	8×5×0.84 (low pyramid)	zero	zero	limit 2240 Å

also are of Type 1 and absorb all ultraviolet radiation of wavelengths shorter than 3000Å, do not produce any discrete infrared absorption bands in the region from 2000 cm^{-1} to 3500 cm^{-1}, but each of them shows only a very weak continuous absorption in the region 900–1400 cm^{-1}. The specimens D 4 and D 13 which belong to Type 2 and are transparent upto 2240 Å do not show any absorption band in the region 900–1400 cm^{-1}, but although D 13 produces a few weak and broad bands in the region 2000-2400 cm^{-1}, D 4 shows only very weak continuous absorption in the region 1800–2200 cm^{-1}. The specimen D 11 produces strong fluorescence band at 4156 Å and unlike other diamonds of Type 1 it is transparent up to about 2240 Å but shows two absorption bands at 2360 Å and 2363.3 Å It exhibits no absorption bands in the region 1000 cm^{-1}—1400 cm^{-1}.

It can be seen from the above results that all thediamonds opaque to ultraviolet radiation beyond 3000 Å and classified under Type 1 do not necessarily produce infrared absorption bands in the regions 2000–2260 cm^{-1} and 2400 cm^{-1}–2500 cm^{-1}. D 1 and D 8 are examples of such diamonds not showing any infrared bands in these regions. Again, D 11, although classified under Type 1, does not show any band in the region 1000–1400 cm^{-1}. Thus the intensity of the fluorescence band at 4156 Å cannot be correlated with infrared absorption in any of the regions mentioned above The fluorescence band was, however, ascribed to some impurities which produce the ultraviolet absorption bands at 2360 Å and 2363 3 Å by Bishui (1952). It appears from these facts that the infrared absorption in the regions shown in Table I are due to some impurities and they do not represent the characteristic frequencies of vibration of the diamond lattice.

It has to be pointed out, however, that the band at 1360 cm^{-1} is much sharper than the other bands and its frequency is also very near to the frequency of the Raman line of diamond. The vibration of frequency 1332 cm^{-1} giving the Raman line is forbidden in the infrared spectra It appears, however, that in small microscopic regions in the diamond in which impurities are present the symmetry of the lattice is destroyed and the mode of vibration is made allowed with slightly increased frequency. The intensity of the infrared band produced in this way will depend on the percentage of the total volume of the crystal which is under strain due to the presence of the impurities. This may explain the difference in the intensities of this band observed in the different cases The strength of the absorption at the 1360 cm^{-1} band is in conformity with the fact that even a 0.025 mm thick film of 1% solution of any organic liquid produces large peaks in the infrared absorption spectra

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