ON THE ORIGIN OF FLUORESCENCE IN DIAMOND *

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Plates XIXA—G

ABSTRACT. The fluorescence and absorption in the visible region exhibited by six specimens of diamond including one of type II have been investigated at different temperatures and the birefringence shown by these crystals at 30°C and 275°C has been photographed. The intensity of fluorescence excited by different monochromatic radiations in the region of 4046Å has also been studied qualitatively The results show that the integrated intensity of the band at 4156 Å increases at lower temperatures and diminishing gradually with the rise of temperature of the crystal, it vanishes abrubtly at a temperature which is different for the different crystals; but at 275°C the band is absent in all the cases. The rate of increase of intensity at lower temperatures diminishes gradualy with the lowering of temperature.

The absorption band at 4156Å and its companions also disappear at 275°C but the birefringence shown by the crystals is not altered very much at this temperature It is further observed that the intensity of fluorescence increases when the incident monochromatic radiation has the same wavelength as that of the absorption band at 4045Å but it diminishes when the wavelength lies between 4045Å end 4156Å and does not coincide with that of any of the absorption bands

It has been concluded from these results that the fluorescence behaves in the same way as impurity fluorescence and that the impurity is of chemical nature. It is pointed out that the fluorescence is not due to lattice defect produced by strain in the tetrahedral lattice, because there is no exact correlation between microscopic strain and fluorescence in diamonds of Type I.

INTRODUCTION

Fluorescence of diamond was first observed by Robert Boyle in 1663 and the subject has attracted the attention of many investigators since then. Special attention of the physicist was drawn to this phenomenon by Robertson, Fox, and Martin in 1934, who observed that there are actually two distinct classes of diamonds, one (Type II) being transparent to 2200 Å. and the other (Type I) having a continuous absorption in the ultra-violet region starting from about 3000 Å. and extending towards the shorter wavelengths. Recently, however, this subject has engaged the attention of a large number of physicists after a new theory was put forward by Sir C. V. Raman (1944) regarding the structure of diamonds. It is well known that according to the results of X-ray analysis the diamond lattice consists of two identical interpenetrating face-centred cubic lattices, one being displaced from the other along the body-diagonal. It is also known

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from study of the Raman spectra that the carbon atoms are joined to each other through covalent tetrahedral bonds and the lattice is not an ordinary molecular lattice, but the whole single crystal is a giant molecule. Further, the crystal is diamagnetic, and shows no pyroelectric properties.

It is a fact, however, that as far as the symmetry of the external facets of the crystal is concerned sometimes it is of holohedral class and sometimes only of the tetrahedral class. This latter fact, that the external symmetry of the crystal is sometimes of tetrahedral class, led Sir C. V. Raman (1944) to postulate the theory that if the electronic configuration of the carbon atoms possesses a tetra-hedral symmetry, in two different types of diamond there may not be a centre of symmetry at that point midway between two representative atoms. In fact, four different cases can arise out of this consideration giving four different kinds of structures in the diamond crystal. The four types have been called by him Td I, Td II, Oh I, and Oh II. Td I and Td II are exactly identical in all respects There is, however, no centre of symmetry at the mid point between two representative carbon atoms joined by each of the C-C bonds in these two cases In Oh I and Oh II, on the other hand, there is such a centre of symmetry. If we examine the hypothesis carefully we can see that both in Td I and in Td II the resultant angular momenta of the two electrons in each C-C bond are in the same direction, while both in Oh I and Oh II they are in the opposite directions. It is known that different types of molecules are formed by the same two atoms owing to two different orientations of the spin moments of nuclei. For instance, ortho- and para-hydrogen molecules are formed by two different orientations of the nuclear spin moments. In the same way Td I and Oh I structures are assumed to be formed in the case of diamond lattice by two different orientations of the resultant angular momenta of the bonding electrons. In that case it is difficult to understand the differentiation between Oh I and Oh II, because when two bonding electrons have got their spin moments directed in opposite directions it is very difficult to say which of them belongs to which atom and the spin moments can be represented by two arrows pointed in opposite directions only in one way. The two geometrical figures drawn to show that two different orientations are possible are in reality exactly identical. They represent the same relative dispositions of the spin moments, and as stated earlier in a bond in which two electrons take part it is not possible to say whether the spin is directed away from or towards the other atom. Similarly, when two moments are directed in the same way it is immaterial which way the resultant is formed and the two lattices Td I and Td II have exactly same physical properties. There may be, of course, slight irregularity at the surface in the crystal along which two such lattices may join each other in such a way that the resultant spin moment in one is directed in a sense opposite to that in the other. It is also well known that the directions of the C-C bonds in diamond lattice are definitely along the arrows in the figure which represents Oh I as revealed

by X-ray studies, and they cannot be along the arrows given in the other three types, Td I, Td II and Oh II. It is, therefore, difficult to understand how the structures may be different although the arrangement of the carbon atoms as well as the dispositions of the electronic bonds are exactly identical in all the four types mentioned above. It is also a fact that in both types of crystals showing respectively tetrahedral and octahedral external symmetry, the internal arrangement of carbon atoms is exactly identical, and the lack of centre of symmetry midway between two representative carbon atoms has never been detected by the results of X-ray investigation.

It has been assumed in the new theory that diamond has usually the lower symmetry and interpenetration of different types of the structures mentioned above produces different types of diamonds. It has also been assumed that inter-twinning of tetrahedral and octahedral structures may exhibit a set of planes parallel to each other in which alternate layers have got different physical properties. From study of luminescence exhibited by a large number of crystals, it has been concluded that interpenetration of Td I and Td II structures gives rise to blue luminescence without any birefringence and this diamond is opaque to ultraviolet light. The inter-penetration of octahedral and tetrahedral structures similarly gives rise to yellow luminescence and the crystal shows structural birefringence and is partially opaque to ultraviolet light The lamellar intertwinning of two structures Oh I and Oh II is assumed to produce a diamond which is both non-luminescent and transparent to ultraviolet light This crystal has been identified as those which show streaky birefringence.

Some evidences in support of the theory mentioned above have also been adduced later. These evidences have been found in the results of investigations on infra-red and Raman spectra, X-ray reflections, and luminescence. As regards the infra-red absorption spectrum of diamond, it has been pointed out that according to Placzek's (1934) theory, in the case of an octahedral symmetry the three-fold degenerate vibration should be active in the Raman effect, but inactive in the infra-red spectra. Actually in the case of certain types of diamond the 1332 cm^{-1} line appears both in the Raman spectra as well as in infra-red absorption spectrum showing a tetrahedral symmetry of the crystal, while in other types the line appears only in the Raman effect and is absent in the infra-red spectrum. The results reported by Robertson and Fox (1930) have been cited in this connection. On careful examination of the results, one can easily find that the correspondence between the infra-red band at 8μ and the line 1332 cm^{-1} is not enough to show that they are produced by the same vibration. because 1332 cm^{-1} corresponds only to about 7.5μ and not to 8μ. Further the line 1332 cm^{-1} is extremely sharp while the band at 8μ is broad. Hence it is hardly likely that the band at 8μ is produced by the same vibration as the line 1332 cm^{-1}. Although Krishnan and Ramanathan (1946) tried to show that the 1332 cm^{-1} vibration is active in the intra-red by mentioning that this frequency occurs half way

down the absorption minimum at this place in the infra-red absorption spectrum, Sutherland (1946) criticised their statement and pointed out that the frequency of absorption minimum can never be considered to be an absorption frequency. As regards Placzek's theory regarding the selection rules for the appearance of a line in the infra-red and the Raman spectra, it is the symmetry of the distribution of electric charges in the vibrating molecule which is usually taken into consideration. It is well known that if a centre of symmetry is maintained during a mode of vibration, the corresponding line is allowed only in the Raman effect and forbidden in the infra-red. The relative orientations of the angular momenta of the electrons around the oscillating atoms can hardly affect either the distribution of electric charges or the magnitude of electric moment generated during oscillation. Hence it is difficult to understand how in the case of the two structures Td I and Oh I there can be any difference as far as the selection rules mentioned above are concerned, because the distribution of electric charges is exactly the same in both Td I and Oh I structures.

As regards evidence from X-ray reflection from diamond, the intensities of Laue spots obtained from different types of diamond have been compared by Krishnan (Raman, 1943) and it has been shown that the Laue spots due to weakly blue luminescent diamond are weaker than those due to strongly blue luminescent diamond. This fact has, again, been explained on the assumption that the former diamond possesses a perfect structure of tetrahedral type and, therefore, extinction is very great ,while in the latter type there is a mixture of Td I and Td II structures which produces strains giving rise to small variations in the spacings and consequent increase in the intensity of X-ray reflections. Hariharan (1944) also measured the intensity of Bragg reflection from (111) plane of a large number of diamond crystals of different types and found a correlation between the intensity of X-ray reflection with that of fluorescence exhibited by these crystals. It has to be pointed out, however, that the presence of laminae each containing several planes of the same spacing is necessary for producing any appreciable intensity in X-ray reflection. Such mosaic structure can hardly be produced by the interpenetration of Td I and Td II structures and in fact, it has been pointed out in the original theory that no stress is produced by such inter-penetration. These crystals, on the other hand, show birefringence of widely varying magnitudes. Hence the strain present in the crystals is much too large to be accounted for on the assumption, that it is produced by interpenetration of Td I and Td II structures, and it is probably produced by some other causes during crystallisation of the molten carbon. These facts, therefore, do not seem to furnish any strong evidence in support of the new theory.

The main evidence adduced in support of this new theory of diamond structure consists in the results of investigations on the luminescence of different types of diamond carried out by different workers. The work was

systematically started first by P. G. N. Nayar (1941a, 1941b). He studied the fluorescence spectra of about a dozen diamond crystals of different types at differerent temperatures ranging from 200°C down to the temperature of liquid oxygen. He observed a sharp fluorescence band at 4156Å accompanied by a set of diffuse bands at 4278, 4387, 4514 and 4613Å with a continuous spectrum superposed on these and extending up to 6300Å These charac- teristic spectra were observed in all the crystals studied by him, but the intensities were different in different crystals and the ratio in the two ex- treme cases was of the order of 10,000 to 1. He also used monochromatic exciting radiation and found that the whole fluorescent spectrum was excited by radiation of any wavelength less than 4156Å. The intensity of the bands, however, increased when the exciting line was of wavelength 4156Å and the bands vanished when the exciting wavelength was slightly larger than 4156Å. It was concluded from the results observed by him that the fluore- scence was not due to any impurities, but was probably connected with the structural perfection of diamonds. As regards the temperature dependence of the fluorescence spectra, he observed that as the temperature rises the bands become broader unsymmetrically and shift towards longer wavelength and at temperature above 200°C, the fluorescence disappears completely

These investigations were further extended in the case of a very large collection of diamonds by (Miss) Anna Mani (1944), who studied both the absorption and fluorescence spectra of 32 diamonds of different types Some of the diamonds studied by her were of Type II. She confirmed the obser- vations of Nayar that the intensity of fluorescence varies enormously from crystal to crystal, although the fluorescence spectrum has almost the same structure in the case of all the different types of diamonds. Type II diamond was found to produce extremely feeble fluorescence spectra She also studied the absorption spectra of all these diamonds at different temperatures and found that in the case of all the different types of diamond at about −180°C, the whole absorption spectrum starting from 4152Å was a mirror image of the fluorescence spectrum. She further deduced some frequencies from those of the observed fluorescence and absorption bands and these were assumed to be those of oscillations of the diamond lattice. Recently, Chandra- sekharan (1948) studied the integrated intensity of the fluorescence band 4156Å of diamond at different temperatures and came to the conclusion that only the width of the band changes with the change of temperature and that its integrated intensity remains almost constant at different temperatures.

From a careful scrutiny of all the spectra reproduced by Nayar, Anna Mani, and Chandrasekharan it was found that the interpretation given by the authors to the results obtained by them was not quite satisfactory in all the cases, and hence a re-investigation of this problem was thought worth- while. A collection of diamonds of different varieties was, therefore, made from the local market and in this matter the firm of Messrs Benud Behari Dutt & Sons co-operated whole-heartedly. They allowed the crystals to be

examined in the laboratory of the Indian Association for the Cultivation of Science and changed for better ones if not found suitable. In this manner it was possible to collect about a dozen crystals belonging to different types varying from highly fluorescent rose diamond to the ultraviolet transparent type. Two crystals of the latter type were obtained, one having a light pinkish colour while the other was a thin small crystal absolutely colourless. The absorption and fluorescent spectra of some of these crystals have been studied at different temperatures. First of all, the integrated intensity of the fluorescence band at 4156Å has been determined at different temperatures for six of these diamonds, the intensity being compared with that of Raman line excited by 4358Å line of mercury. Next, the absorption bands at different temperatures of these diamonds have been studied in the visible region. The birefringence exhibited by these crystals at room temperature and at 275°C has also been studied. Finally, in the case of one of these diamonds the variation in the intensity of the fluorescence band at 4156 Å. with the change of wavelength of the monochromatic exciting line has been investigated. These results have been compared with those reported earlier and discussed in the light of the theory mentioned earlier and attempts have been made to offer an alternative explanation.

EXPERIMENTAL

In a series of experimental investigations special stress was laid on measurement of relative intensities of fluorescence spectra at different temperatures in the case of different crystals of diamond. Previous workers compared these intensities, taking either the intensity of 4046Å line of mercury as a standard or by keeping the time of exposure constant in all the cases and estimating the blackenings produced by fluorescence spectra in the different cases. It was, however, considered essentially necessary to find out a true standard which could be used to compare the relative intensities of fluorescence in the case of different crystals. The intensity of the Raman line excited by 4358Å line of Hg was found to be such a suitable standard. Fortunately, in the case of these specimens of diamond studied in the present investigation this Raman line was quite strong and was not masked by the fluorescence spectra in any case, although in the case of two of the crystals there was a weak fluorescence band superposed on this Raman line. This, however, did not present a very serious difficulty in estimating the intensity of the fluorescence band at 4156Å relative to that of the Raman line and this method was probably much more reliable than that adopted by previous workers. The complete mercury arc spectrum beyond 4156Å towards the ultraviolet region was used to excite fluorescence and a Fuess glass spectrograph was used to photograph the fluorescence spectra. In all the cases the direction of observation was along the normal to the (111) face and the mercury arc was placed in front of the crystal slightly on one side so that the fluorescence from the region of the crystal immediately behind

its front surface could be observed. Thus the 4156Å band was not weakened very much, although there is an absorption band exactly at this position. For studying these spectra at low temperatures, the technique used by the author for the investigations of Raman spectra at low temperatures was employed. The crystal was suspended inside a transparent Dewar vessel and liquid oxygen was introduced in this vessel through a double walled glass tube entering through the cork at the mouth of this vessel and the surface of the liquid oxygen always remained just below the crystal The crystals were mounted one by one in a copper frame part of which was kept immersed in the liquid oxygen so that in each case the crystal was in contact with copper at the temperature of liquid oxygen and was not actually immersed in the liquid oxygen itself. The temperature was measured with a pentane thermometer. A sketch of this arrangement is given in Figure 1. The dimensions of the diamonds used are as follows :
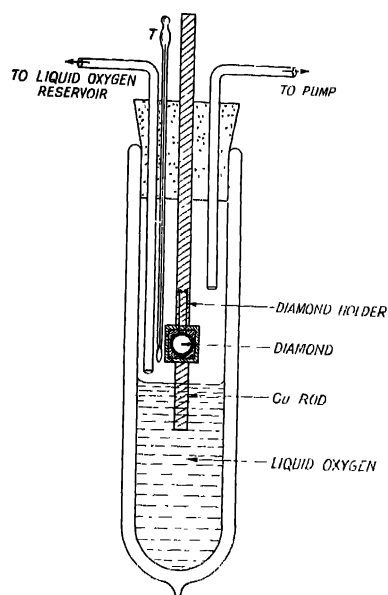

FIG. 1

D 1 (rose diamond) —9 mm. × 7 mm. × 1.5 mm., D II—8 mm. × 5 mm. × 1.2 mm., D III—5 mm. × 5 mm. × 1 mm., D IV (triangular plate) —base, 11 mm., height, 8 mm., thickness, 1.5 mm., D V—10 mm. × 8 mm. × 2 mm. and D VI—14 mm. × 12 mm. × 2 mm.

For studying the luminescence at higher temperatures, the crystal was suspended inside a cylindrical electric heater provided with a glass window,

In order to measure the integrated intensity of the 4156 Å band relative to that of the Raman line excited by 4358 Å line, microphotometric records of the band and the Raman line were taken with a Kipp and Zonen type self-recording microphotometer and the intensities were estimated after taking into account the intensity of the background with the help of blackening-log intensity curves. These latter curves were drawn with the help of intensity marks taken with a standard tungsten ribbon lamp and using different known widths of the slit of the spectrograph. The integrated intensity of the band was determined by calculating the intensities at five points in the band and finding the area of the peak obtained by plotting intensity against width

For studying the absorption spectra in the visible region, an ordinary 100-watt straight-coil filament lamp was used as the source of light and for studying these spectra at low temperatures, the technique used for studying the fluorescence spectra at low temperatures was employed. In the case of particular crystal D VI monochromatic exciting bands of different wavelengths in the neighbourhood of 4156 Å. towards the shorter wavelength side were used to find out whether the intensity of the fluorescence band at 4156 Å depended on the wavelength of the exciting line. A 100-Watt straight coil filament lamp was used as source of light and a Fuess glass spectrograph with a slit in the plane of the photographic plate was used as the monochromator.

The birefringence patterns of the six crystals mentioned above were photographed keeping the crystals first at room temperature and then at about 275° C. Only those portions of the crystals which had opposite parallel faces were used for this purpose, the other portions being covered with suitable black screens. Each of the specimens was mounted in a cylindrical electric heater with its mouths open. The birefringence pattern of one of the crystals was photographed first without passing any current through the heater. A suitable current was then passed through the heater to obtain a temperature of 275°C near the crystal and again the birefringence pattern was photographed. This was repeated for all the six crystals. A pair of large Nicol's prisms made by Messrs. Adam Hilger Ltd. was used in the crossed position and a parallel beam of light was obtained from a point source with the help of a good lens. An ordinary camera was used to photograph the patterns.

RESULTS

(a) Fluorescence spectra at different temperatures

The fluorescence spectra observed at different temperatures with the six crystals of diamond are reproduced in Plates XIX—C. In exciting these spectra unfiltered mercury arc light was used, and therefore, these spectra also contain the Raman lines excited by the Hg lines 4046Å and 4358Å. It can be seen from these spectrograms in Figures 2-7, Plates XIX A,B,C, that the nature of the fluorescence spectrum is different for different crystals, as observed by previous workers also. The band at 4156Å is present in all the spectrograms,
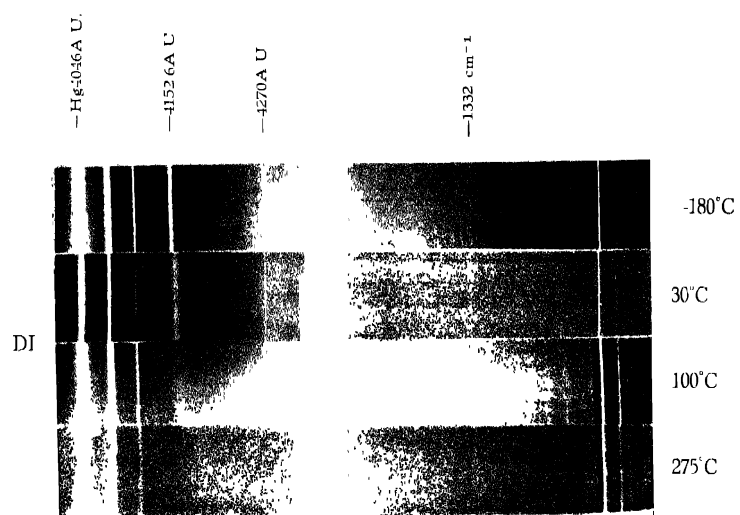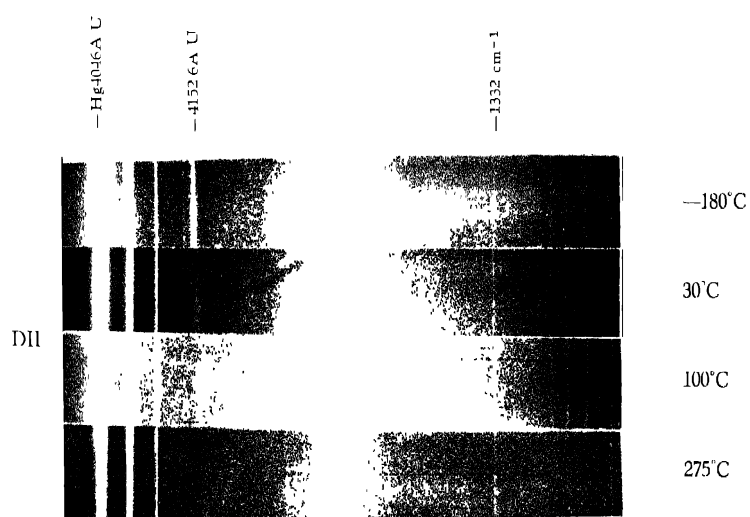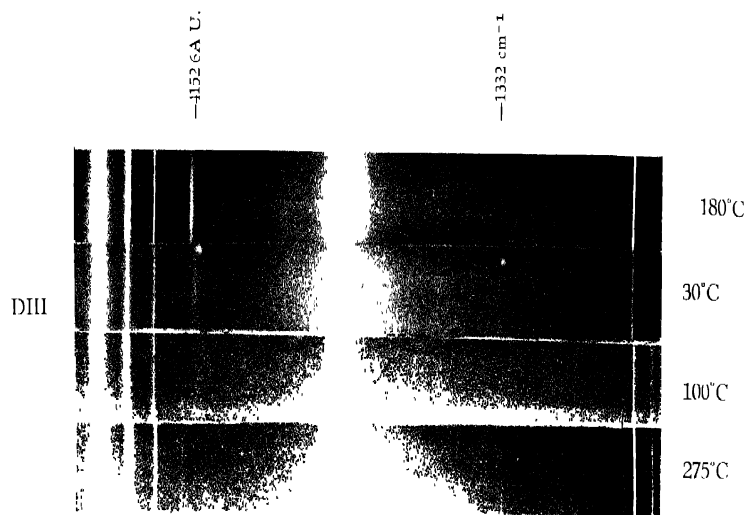
PLATE XIX A

Fig. 2

Fig. 3

PLATE XIX B

Fig. 4

Fig 5

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PLATE XIX C

Hg4045A U   4152 6A U   1270A U   1332 (m⁻¹)

DV

−180°C

30°C

100°C

275 C

Fig. 6

1152 6A U   1332 cm⁻

DVI

180°C

30°C

100 C

275°C
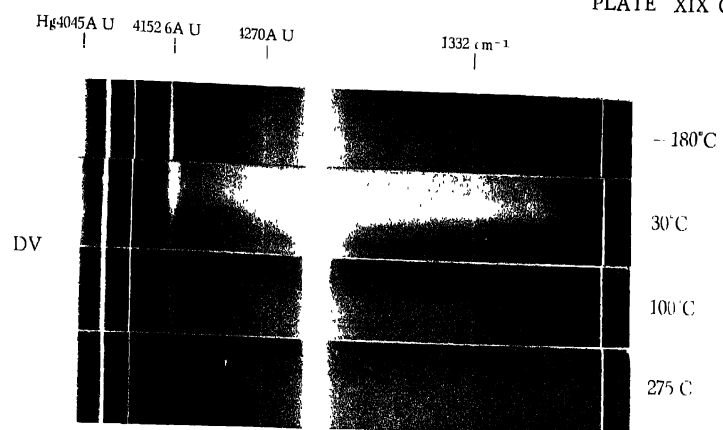
Fig. 7

5032A.U.

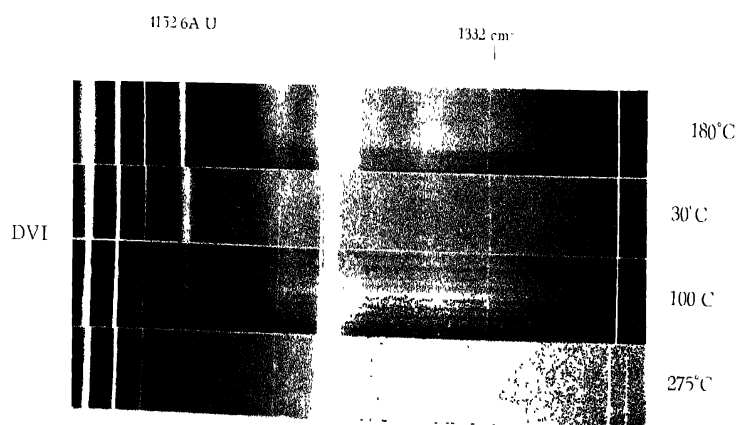DI   −180°C
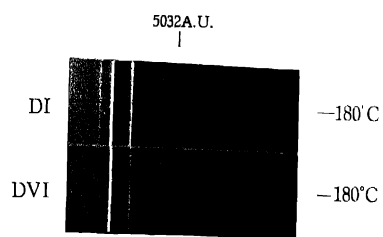
DVI   −180°C
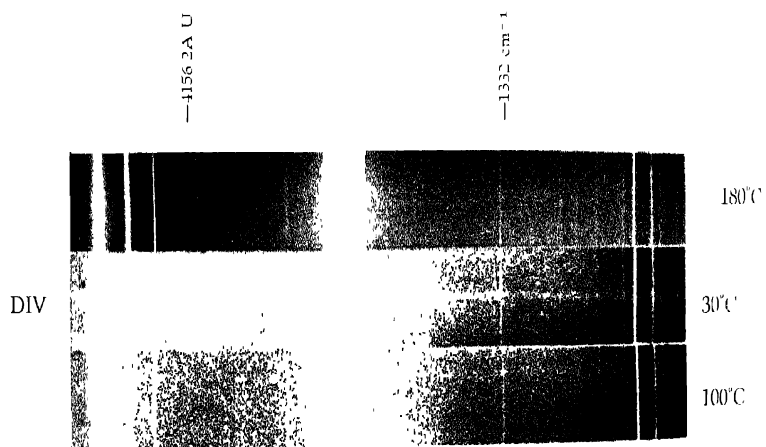
Fig. 8

but with different intensities. Even in the case of D IV, which is a diamond transparent to light of wavelength larger than 2250Å there is a feeble band at 4156 Å at room temperature. Excepting D IV, all the remaining five crystals D I, D II, D III, D V and D VI are opaque to ultraviolet light in the region of about 3000 Å and they exhibit a few fluorescence bands on the longer wavelength side of the band at 4156Å. The crystals D II and D VI are slightly pinkish in colour and the latter shows at −180°C an extra band at 5032 Å as shown in Figure 8, Plate XIXC. In the case of D V also, this band is just visible at −180°C. The broad bands accompanying the band at 4166 Å have their centres at 4278 Å, 4378Å, 4552 Å and 4648 Å respectively in the case of all the five crystals mentioned above. D V shows a peculiar phenomenon, *e.g.*, that one half of the crystal produces the fluorescence bands with great intensity, while the other half produces much feebler fluorescence, although the intensity of the Raman line 1332 cm⁻¹ is the same in case of both the halves.

The change of temperature of the crystals brings about changes in position, intensity and width of the bands. In all the cases the 4156 Å band observed at room temperature is found to shift exactly to 4152.6Å when the crystal is cooled down to −180°C. This can be seen from the Figures 2-7. The other bands on longer wavelengthside shift by different amounts towards shorter wavelengths. The band at 4278 Å shifts to 4270 Å at-180° C and this shift seems to be larger than that of the band 4156 Å. The shift of the band at 4648 Å is also the same as that of the 4278 Å band as can be seen clearly from Figure 7.

All the bands become narrower at -180°C and become gradually broader at temperatures higher than room temperature. In the case of D V, there is continuous fluorescence in the region between 4156 Å and 5200Å besides the bands mentioned above.

Quantitative data regarding the changes in the integrated intensity of the band at 4156Å with the change of temperature of the crystals are given in Table I, in which the data for the three temperatures 100° C, 30° C and −180°C are given. In each case the ratios of the integrated intensities of the Raman line 1332 cm⁻¹ excited by 4358Å at the two temperatures -180°C and 30°C and also at the two temperatures 30°C and 100°C are given. Similar data have been included also for the band at 4156Å. Hence the absolute ratio of intensities of this band at the three temperatures can be calculated. The calculated relative integrated intensities of the band at -180°C, 30°C and 100°C, assuming in each case the intensity at -180°C to be 222 are given in Table II. The curves obtained by plotting logarithms of these intensities against inverse of temperature are reproduced in Figure 9. As no point has been obtained between -180°C and 30°C, it has been assumed in drawing these curves that they are continuous between 30°C and −180°C. It will be seen from Figure 9 that the intensity increases at lower temperatures and diminishes

al higher temperatures in all the cases. The rate of increase, however, falls off at lower temperatures and in the case of D V and DVI, this rate is very
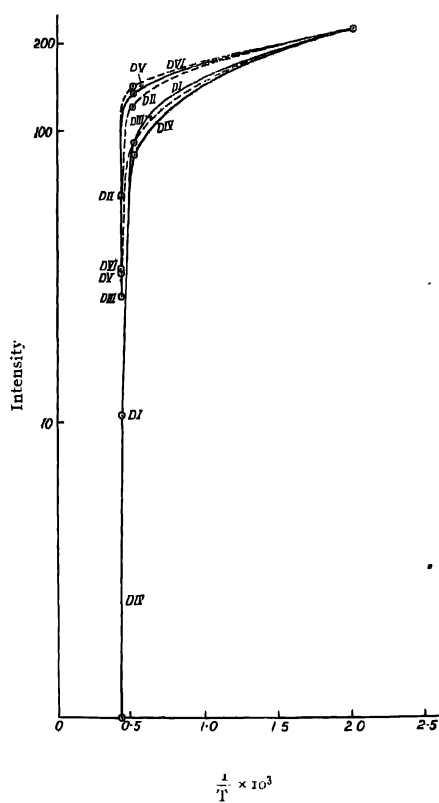

$$\frac{1}{T} \times 10^3$$

FIG. 9

small at -180°C   These results will be discussed later   Some microphoto-metric records are reproduced in Plate XIX D.   ⁻

Plates XIX A, B, C show that except in the case of D VI, all the fluorescence bands disappear completely at 275°C.   In the case of D VI, the band at 4156 Å persists with a small intensity at 275°C.   It can also be seen that the bands become only slightly broader before they just disappear, leaving no trace of any continuous background.   These results are thus contradictory to those reported by Chandrasekharan (1948) according to whom the integrated intensity remains constant at all temperatures and only the width of the bands changes with temperature.

BISHUI

PLATE XIX D
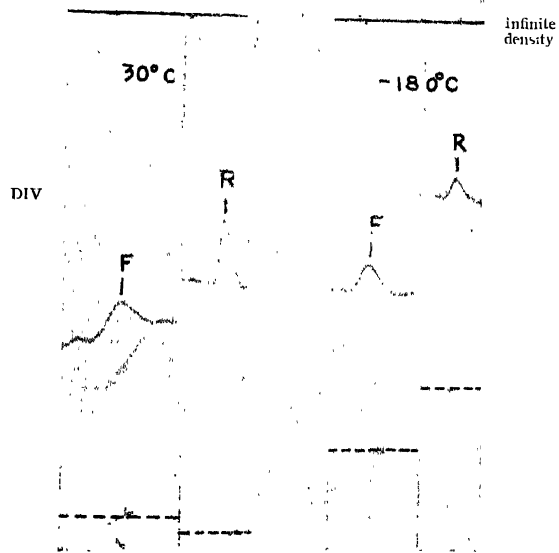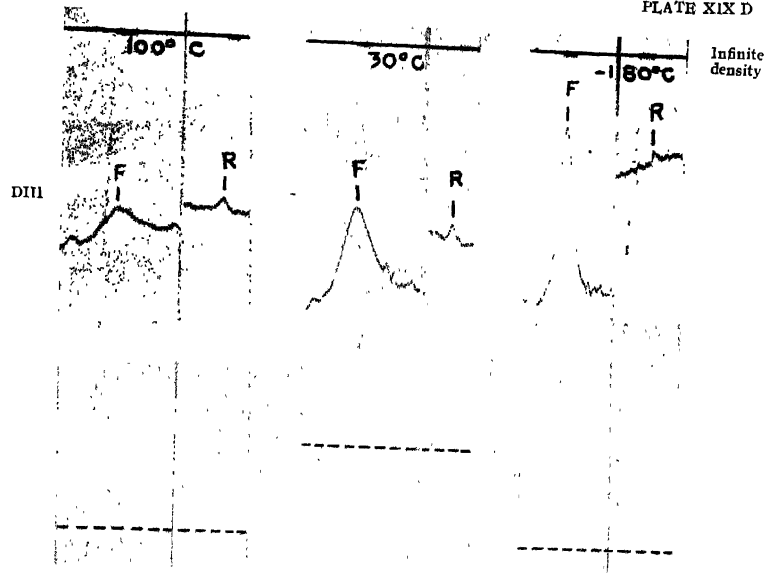
F—Fluorescence band at 4156Å   R—Raman line

FIG. 10

TABLE I

Diamond No.	Temp.	I 4156 Å (arbitrary unit)	I 1332 cm⁻¹ (arbitrary unit)	$\dfrac{I-180}{I30°}$		$\dfrac{I 30°}{I 100°}$	
				4156 Å band	1332 line	4156 Å band	1332 line
D I	100°C	23	3.5			5.4	0.63
	30°C	125	2 2	2 22	0.91		
	−180°C	277	2.0				
D II	100°C	9	2 0			3 67	1.85
	30°C	33	3 7				
	−180°C	30	1.8	91	0.49		
D III	100°C	23	2 1			3 48	1.05
	30°C	80	2 2				
	−180°C	134	1.5	1.68	0.68		
D IV	100°C	0	4				
	30°C	9	9				
	−180°C	13	5	1.44	0.55		
D V	100°C	44	4.0			12 73	3.5
	30°C	560	14 0				
	−180°C	234	3.6	0 41	0.25		
D VI	100°C	8u	6 4			3.75	87
	30°C	300	5.6				
	−180°C	500	6 0	1.66	1.07		

The advantage ot taking the intensity of the Raman line as a standard for comparing the intensities of the 4156 Å band at different temperatures can be seen at once from a glance at Figures 2 and 3, Plate XIX A and Figure 7, Plate XIX C. For instance, the Rayleigh line 4108 Å is much less intense in the spectrogram for 30°C than in the spectrogram for −180°C, but the Raman line 1332 cm⁻¹ is more intense in the former than in the latter spectrogram. Hence if any of the undisplaced Hg lines would be taken as a standard for comparing the intensities of the band at 4156 Å, results

TABLE II

Diamond No.	Relative Intensities of 4156 Å band.		
	−180°C	30°C	100°C
D I	242	91	10 6
D II	222	120	60.5
D III	222	90	27
D IV	222	84	0
D V	222	135	32 4
D VI	222	143 7	33.4

quite different from those given in Table 1 would be obtained and such results would be thoroughly unreliable. The method adopted in the present paper has another advantage, e g., the efficiency of fluorescence of the different crystals can also be estimated roughly. This is possible because, the same blackening-log intensity curve has been used to determine the intensity of the Raman line 1332 cm^{-1} in all the cases and also a single similar curve has been used to determine the intensity of the band at 4156 Å in all the cases. Hence the ratio of the intensity of the fluorescence band 4156 Å to that of the Raman line 1332 cm^{-1} calculated for any of the crystals at any temperature can be compared with such a ratio obtained in the case of any other crystal at the same temperature Such results are given in Table III. These calculated ratios are, however, not the actual ones but their relative values give the relative fluorescence efficiencies of the crystals in the band 4156 Å. Hence the values given in the last column of Table III represent these fluorescence efficiencies multiplied by a constant K.

TABLE III

Diamond No.	Temperature	K ×I$_F$/I$_R$
D I	30°C	57
D II	,,	9
D III	,,	36
D IV	,,	1
D V	,,	40
D VI	,,	54

As regards the influence of temperature on the intensities of the bands 4278 Å, 4378 Å, 4552 Å and 4648 Å, it can be seen that except in the case of D III and the D IV, in all other cases, the intensities of these bands relative to that of the Raman line increases when the crystals are cooled down from 30°C to −180°C In the case of D IV, these bands are absent at both the temperatures and in the case of D III, the intensities of the bands do not seem to increase appreciably with the lowering of temperature of the crystal.

The spectrograms also do not reveal the presence of the sharp lines in the fluorescence spectra. although such lines were observed by (Miss) Anna Mani (1944) in the case of a few crystals of diamond studied by her. Thus these lines do not seem to be produced by the diamond lattice itself and may be due to impurities.

(b) Birefringence at different temperatures.

It can be seen from the birefringence patterns reproduced in Plate XIXE that birefringence does neither diminish nor disappear at a temperature at which the fluorescence disappears almost completely. As regards the nature of birefringence shown by different types of diamonds, it is clearly seen that D III, which is a diamond showing blue luminescence, exhibits a regular birefringence pattern. In the case of D IV, which is a diamond transparent to ultra violet region up to 2250 Å, the birefringence pattern does not show any streaky character as can be seen from Plate XIXE. The restored light extends uniformly over the major portion of the crystal excepting a small region. These results do not agree with fact observed by Raman and Randall (1944) that all the crystals of Type II show streaky birefringence. Again it can be seen from Plate XIXE that percentage of the area showing birefringence in the case of D III is less than that in the case D V and it is of the same order as that in D II. Further the percentage is almost the same in the case of the two crystals D II and D VI. The relative fluorescence effeciencies of the two crystals D II and D VI at the band 4156 Å are, however, widely different from each other. The significance of these results will be dicussed later.

(c) Monochromatic excitation of fluorescence.

The spectrograms obtained by using incident light consisting of bands about 30 Å broad in the region of the 4046 Å are reproduced in Figures 12(a), 12(b) and 12(c), Plate XIXE. The wave-lengths of the centres of the bands are 3990, 4046 and 4110 Å respectively. It can be seen from Figures 12(a) and 12(b) that in both the cases the fluorescence band at 4156 Å as well as its broader companions in the visible region are present, although with small intensity. These fluorescence bands are thus excited by the bands of wavelengths 3990 and 4046 Å respectively. In Figure 12(c) the

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exciting band is at 4116 Å but the fluorescence bands are almost absent, excepting the band at 4156 Å which seems to have been excited very feebly. It thus appears that the intensity of fluorescence diminishes when the wave-length of the exciting band is increased from 4046 Å to 4110 Å, although the latter wavelength is shorter than 4156 Å. This fact was observed by Nayar (1941a) also, but he did not discuss its significance. It will be seen in the next section that there is a broad absorption band with its centre at about 4045 Å in the absorption spectrum of diamond. The facts mentioned above indicate that when any portion of the exciting band has wavelength coinciding with that of any portion of the broad band at 4045 Å, the intensity of the fluorescence bands excited by the band is increased. In fact the efficiency of a monochromatic line at 4046 Å in exciting the fluorescence band at 4156 Å is very large as can be seen from Figure 12(d) in which light from a mercury are filtered through highly concentrated solution of sodium nitrite was used as the incident light. Although all the lines of wavelength shorter than 4046 Å have been cut off and the intensity of the line 4046 Å has been diminished considerably by the filter, yet the fluorescence band at 4156 Å is distinctly visible in the spectrogram. Evidently, the line 4046 Å is responsible for exciting this band, because the lines 4077 and 4108 Å are much weaker.

Again, from a comparison of Figures 12(a) and 12(b), it can be seen that when the mean wavelength of the exciting band changes from 4046 Å to 3990 Å, the intensity of the fluorescence band diminishes considerably, this diminution being less in the case of the fluorescence band 4156 Å than in the case of the other bands on the longer wavelength side. Thus the intensity of the latter bands with respect to that of the band 4156 Å seems to depend on the wavelength of the exciting band in the region between 3990 Å to 4110 Å.

(d) Absorption Spectra in the Visible Region.

The absorption spectra of all the six diamonds mentioned earlier were investigated in the visible region both at about 30°C and at −180°C respectively and in the case of D II at 275°C also. Some of the spectrograms are reproduced in Fig. 13, Plate XIX G. No absorption band in the visible region was observed in the case of D IV inspite of repeated trials, although the fluorescence band at 4156 Å is present with small intensity in luminescence spectrum of this diamond. Evidently, the absorption at 4152.6 Å is too small to be recorded even at −180°C in this case. Both the diamonds D II and D VI show an intense absorption band at 4156 Å at room temperature accompanied by a few other bands on the shorter wavelength side. The band at 4156 Å shifts to 4152.6 Å and becomes a little sharper, when the crystals are cooled down to −180°C. These observations are in agreement with those of Nayar (1941b). In the case of the other three diamonds D I,

PLATE XIX E

Fig. 11
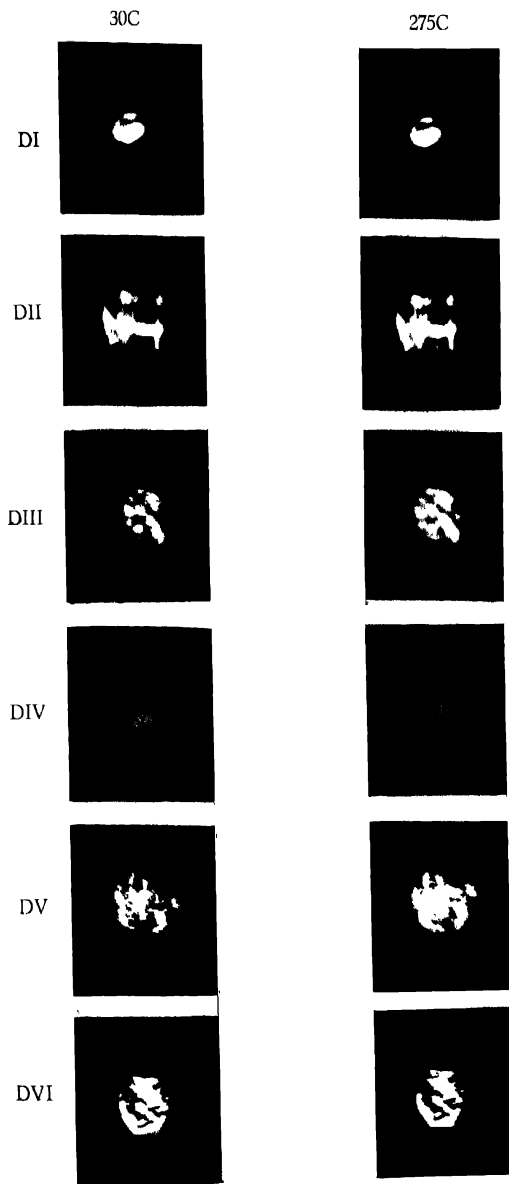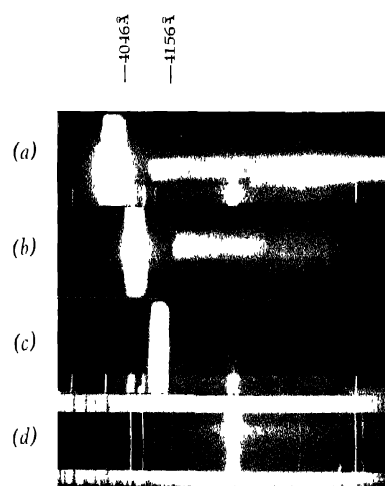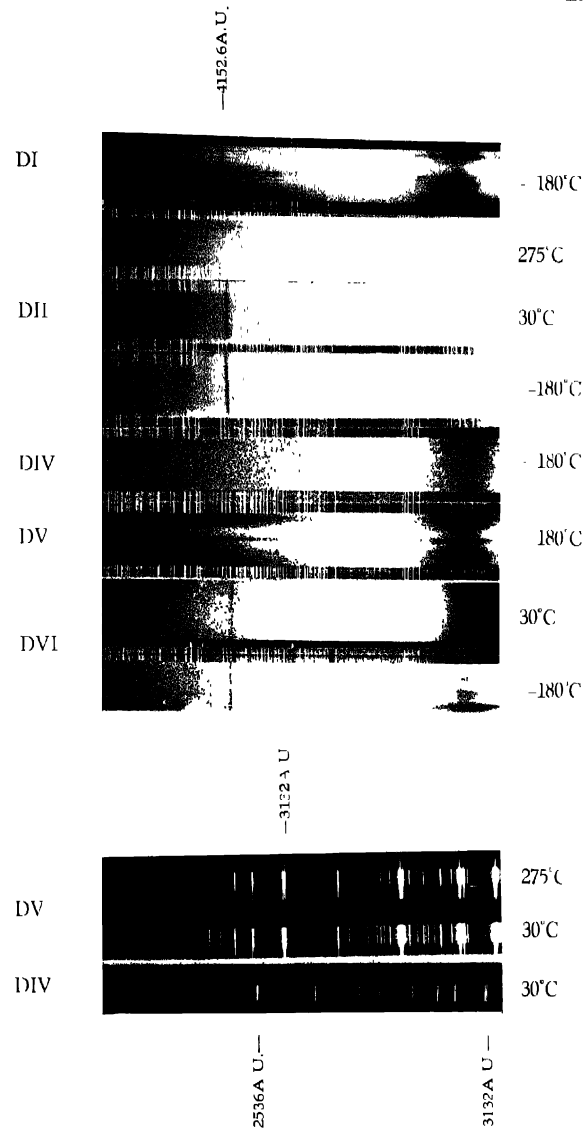
PLATE XIX I

Fig 12

PLATE XIX G

Fig. 13

Absorption spectra

D III and D V at room temperature, the absorption band at 4156 Å is found to be very feeble, but at a temperature of about −180°C the band shifts to 4152.6 Å and becomes sharper and more intense as can be seen from the spectrograms reproduced in Plate XIX G. The band with its centre at about 4045 Å observed in the case of both the diamonds D II and D VI at 30°C shifts to 4041 Å at −180°C This band is found to be more diffuse in the case of D I, D III and D V. When D II is heated to 275°C the absorption band at 4156 Å disappears. In the case of D I, D III and D V also, the intensity of this band at 30°C is very small and the band disappears at about 100°C. Thus even in the case of those diamonds which show an intense absorption band at 4156 Å at the room temperature, this band disappears at about 275°C. These results are in agreement with those observed by Nayar (1941b).

The influence of temperature on the intensity of continuous absorption beyond 3000 Å towards shorter wave-lengths has also been studied in the case of D II. The mercury lines transmitted in this region by the diamond at 30°C and 275°C are shown in Fig. 13. It can be seen that the temperature has very little influence on the position of the long wavelength edge of continuous absorption in this region. The transparency of D IV to Hg lines of wavelength shorter than 2536 Å is clearly indicated in the last spectrogram in Fig. 13. It is evident that the crystal belongs to Type II and the other five diamonds of Type I remains different from D IV even at 275°C.
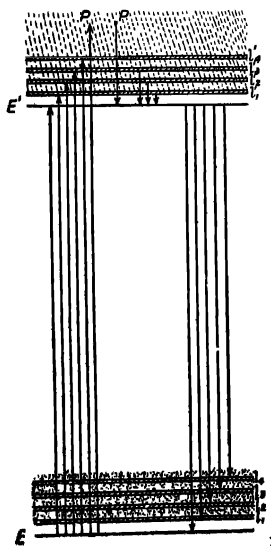

FIG. 14

It can be seen from the spectrogram for D II that there is very little absorption in the region between the band 4152 6 Å and band at 4045 Å, and in the region beyond 4045 Å towards the shorter wavelength there is continuous absorption with some broad maxima separated from each other. These observed facts are in agreement with the scheme of energy levels shown in Fig. 14 and deduced from the properties of the observed fluorescence and absorption bands. The fact that the intensity of fluorescence diminishes abruptly if the wavelength of the exciting band increases from 4046 Å to about 4110 Å is also explained satisfactorily. This happens because the absorption of light of wavelength at and in the neighbourhood of 4110 Å is very small and consequently intensity of fluorescence produced by transitions from the level E' to the sub-levels of E is very small. The absorption spectra also show that light of any wavelength shorter than about 4045 Å is absorbed in different degrees depending on the wavelength contrary to the hypothesis put forward by Nayar (1941b) that only light of energy corresponding to that of the band at 4156 Å enhanced by the energies of vibrations of the lattice is absorbed. In fact, the energy diagram shown in Fig. 14 conforms to the theory put forward by Seitz (1938) according to which the electronic energy levels in semi-conductors consist of the Bloch-Wilson bands together with narrow continuous bands lying in the forbidden region between the former bands.

It is further observed that at the lower temperature the absorption band at 4152.6 Å is much sharper than the fluorescence band of the same wavelength. Hence if a thick crystal be used, the fluorescence band may appear as a doublet because its core will be absorbed owing to self-reversal and the edges will be transmitted freely. This band has actually been observed to consist of a doublet with its centre of gravity at 4152 Å in the case of a large number of diamonds of fairly large size by (Miss) Anna Mani (1944). She has interpreted the results on the assumption that the band itself is originally a doublet. Actually, however, the appearance of the doublet is due to self reversal of the band. As thin crystals were used in the present investigation and they were irradiated from the front, the fluorescence band at 4152.6 Å was always found to be a single band and not a doublet as can be seen from Plates XIX A, B, and C.

DISCUSSIONS ON THE ORIGIN OF FLUORESCENCE IN DIAMOND

The variations in intensities of the fluorescence band at 4156 Å at different temperatures observed in the case of the six specimens of diamond indicated in Fig. 9 show that in all these cases the intensity increases as the temperature of the crystal is lowered and when the temperature is raised above room temperature the intensity gradually diminishes upto about 160°C, but the rate of diminution becomes higher at still higher temperatures, till the band disappears at about 275°C. Since the birefringence

exhibited by the crystals persists at 275°C, this disappearance is a purely temperature quenching. Such an effect is observed in the case of almost all phosphors activated by chemical impurities and is caused by the presence of a large activation energy for radiationless transition. The results reported by Williams and Eyring (1947) in the case of $Zn_2 SiO_4$ phosphor activated by manganese are similar to those observed in the present investigation. It is further observed that the absorption band at 4156 Å together with its companions of shorter wavelength disappears at about 275°C, although the continuous absorption starting from about 3000 Å persists at this higher temperature. Hence the presence of the former narrow absorption bands are necessary for the excitation of the fluorescence bands These facts suggest that the narrow absorption bands are due to some impurities and the evidences discussed below show that these impurities are of chemical nature and they are not due to lattice defect produced by strain in the pure diamond lattice.

According to the theory put forward by Sir C. V. Raman (1944) slight inhomogeneity in the lattice in diamond of Type I produces these new absorption bands while in Type II large amount of strains cannot produce such an effect. This difference in the behaviour of the two types of diamond is attributed to the difference in the relative orientations of the resultant angular momenta of the two bonding electrons in the C-C bond. Those portions of the crystal of Type I which show birefringence should, therefore, exhibit very strong fluorescence and the intensity of fluorescence would be determined by the relative volumes of the inhomogeneous and isotropic parts in the crystal. Such exact correspondence between the intensity of fluorescence and the birefringence is not observed in all the cases. For instance, in the case of D II and DVI (Plate XIXE) the difference in the volume showing birefringence is not very large, but the intensity of fluorescence in the latter case is six times that in the former case as shown in Table III. Again, D V shows birefringence throughout its volume, while only a part of the whole volume of D VI is birefringent. The fluorescence, however, is more intense in the latter case than in the former. In fact, in the arrangement for photographing the fluorescence spectrum an image of the illuminated diamond was focussed on the slit of the spectrograph, in each case, but no discontinuity in intensity along the length of the bands corresponding to the discontinuity in birefringence was observed in any case. The discontinuity observed in the case of D V also does not correspond to the birefringence pattern exhibited by this crystal, as shown in Plate XIX E. Further, it is a fact that in certain diamonds of Type I, some portions which show strong fluorescence do not show strong birefringence and on the other hand, some portions showing strong birefringence do not exhibit fluorescence at all. Such instances can also be found in the results reported by previous authors. The birefringence and luminescence patterns of D 200 studied by

Sir C. V. Raman (1944) in Plate V of his paper, indicate that some portions not showing strong birefringence fluoresce strongly, and *vice versa*. Rendall (1944) studied the ultraviolet transparency of the same diamond and it can be seen from the photograph reproduced in Plate XXVI of the paper that the portion of the crystal not showing any luminescence in Plate V mentioned above is not quite transparent to ultraviolet light, and, therefore, this portion of the crystal is not of Type II. Hence strain has failed to produce luminescence in this portion of the crystal of Type I. Thus the presence of chemical impurities is to be postulated to explain the observed fluorescence. Such impurities may be so minutely dispersed in certain volumes of the crystal that there may not be any macroscopic strain, but local lattice defects will give rise to fluorescence. Similarly, in other portions of the crystal, larger amount of the impurity may produce visible striations and strong birefringence. This would account for the correspondence of birefringence and fluorescence in certain portions of the crystal.

The difference in the positions of the edge of the continuous ultraviolet absorption by the two types of diamond strongly indicates the presence of chemical impurity in diamond of Type I. The absorption starts at about 3000Å in this type, while in Type II it starts at 2250Å. If the absorption in the former case would be the characteristic of the C-C bond, the strength of the bond would be slightly different from that in Type II. The frequency of the Raman line at 1332 cm^{-1} is, however, exactly the same in the two cases. Hence the strength of the C-C bond in the two cases is exactly the same and the difference in the absorption spectra is due to the presence of chemical impurity in diamonds of Type I and its absence in diamonds of Type II. The fluorescence band at 5032 Å is due to a different chemical impurity as this band is not present in all crystals of Type I. This band cannot be due to Oh I structure, because no amount of strain can produce any fluorescence in this crystal as can be inferred from the fact that diamond of Type II showing streaky birefringence does not exhibit fluorescence. Further, if the interpenetration of octahedral and tetrahedral structures would produce this fluorescence in diamond of Type I, there would be correspondence between fluorescent laminae and those showing alternately transparency and opacity to ultraviolet light of wavelength 2300 Å. No such general correspondence has ever been established The observations made by Blackwell and Sutherland (1949) show that even some diamonds of Type II exhibit yellow luminescence. Evidently, this is not due to interpenetration of Type I and Type II structures, because in that case these diamonds would show absorption in the region of 3000 Å. This fact indicates clearly that some type of impurity producing absorption in the region of 3000 Å is absent in this type of yellow luminescent diamond and another type of chemical impurity produces the yellow luminescence without changing the ultraviolet absorption.

There is another property of the absorption and fluorescence bands which shows that strain has nothing to do with the fluorescence exhibited by diamonds of Type I. The position of the absorption and fluorescence band in the region of 4156 Å is determined by the temperature alone and at a particular temperature, it is the same for different crystals showing different degrees of birefringence. Evidently, the position of energy level of the chemical impurity depends on interatomic distances which are determined by the temperature of the crystal.

The photo-conductivity of diamond of Type I is generally much less than that shown by diamond of Type II, as shown by Robertson, Fox and Martin (1934). This cannot be due to presence of laminae in Type I and their absence in Type II, because the latter show streaky birefringence. The difference may be due to presence of chemical impurity in Type I, which entraps the ejected electrons moving through the lattice. Further, the radiations in the region 2300 Å, which are most effective in producing photo conductivity, are absorbed by a thin layer on the surface in crystals of Type I.

Robertson, Fox and Martin (1934) have pointed out that all diamonds of Type I having origin in widely different parts of the world show the same absorption band at 4156 Å. This is not a genuine difficulty, because diamond must have crystallised from a melt contained in a particular environment and it is not unlikely that a common impurity has entered into the lattice in varying amounts in all the crystals. In exceptional cases, when this impurity was absent, diamond of Type II was formed. The streaky birefringence exhibited by diamond of this type may be due to the fact that just before crystallisation of the melt, the formation of C-C bonds was started and there was sudden contraction of the volume which produced standing ultrasonic waves in the solidifying mass. These waves were frozen in when the crystallisation was complete. In the case of the pure melt, the strata of compression and rarefaction were parallel and such a diamond shows streaky birefringence. In case any impurity was present, the waves were distorted, the distortion depending on the nature and quantity of the impurity.

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