

# FLUORESCENCE AND ABSORPTION PATTERNS IN DIAMOND AT LOW TEMPERATURES

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## 1. Introduction

IN an earlier investigation by the author (1944) reported in these *Proceedings*, the luminescence patterns exhibited by six cleavage plates of diamond at room temperature were studied spectroscopically. In other words, by focussing the entire image of the fluorescent diamond on the slit of the spectrograph and by moving the lens so that different regions of the diamond were successively scanned by the slit, the variations in the colour and intensity of the luminescence spectra over the area of the plate were investigated. In the present work this has been extended to an investigation of the patterns at liquid air temperature. Making use of the greater intensity and sharpness of the spectra at low temperatures, the same technique has also been employed to study the absorption spectra of a number of diamonds, although this arrangement limits the length of the available absorbing column to the thickness of the cleavage plates, which is of the order of 1 mm. or less. The spectra obtained exhibit variations in the intensity of the 4152 and 5032 systems similar to those in luminescence, giving rise to absorption patterns identical with the patterns observed in fluorescence. This is of course, to be expected from the very close correlation that exists between the spectra in fluorescence and absorption. An experimental demonstration of their existence is however, worthy of record. The low temperature investigation is also of interest in throwing light on the degree of correlation between the intensities of the principal electronic lines and those of the fainter ones which are too weak or diffuse to be observed at room temperature.

## 2. Materials and Methods

The diamonds employed were polished cleavage plates selected from Sir C. V. Raman's personal collection and had the catalogue numbers N.C. 80 (D38), N.C. 79 (D34), N.C. 100 (D180), N.C. 107 (D187), N.C. 106 (D186), N.C. 108 (D188), N.C. 110 (D190), N.C. 114 (D194), N.C. 120 (D200) and N.C. 122 (D202), the old catalogue numbers being given within brackets.

Of these, N.C. 79, N.C. 80, N.C. 100 and N.C. 107 were predominantly blue luminescent, N.C. 120 and N.C. 122 were yellow luminescent while the rest exhibited both blue and yellow luminescence with comparable intensities. Photographs of the luminescence patterns of these ten diamonds are reproduced in the plates accompanying the paper by Sir C. V. Raman (1944) on "The Nature and Origin of Luminescence in Diamond".

The arrangement for obtaining the fluorescence spectra was the same as that described in the previous paper, a demountable Dewar flask being used for the low temperature studies. The diamonds were mounted in copper holders which were screwed to the bottom of the inner brass tube of the Dewar flask holding liquid air. The vacuum between the inner brass tube and the outer pyrex tube was maintained by a Cenco Hyvac pump in good condition. A 100 W. tungsten lamp was used as the source of light in the absorption studies, the light from the lamp being so condensed on the diamond as to illuminate the plate uniformly. A number of spectra were obtained for each diamond, the absorption spectra for each region being recorded in a graded series of exposures. The fluorescence and absorption spectra were photographed on Ilford HP<sub>3</sub> and selochrome plates respectively, the instrument used being a Hilger two prism spectrograph of high light gathering power.

### 3. Results

(a) *Luminescence Patterns.*—Descriptions of the patterns exhibited by the five diamonds N.C. 80, N.C. 108, N.C. 110, N.C. 120 and N.C. 122, whose fluorescence spectra have been investigated in the present work are described in the previous paper. In Figs. 1, 2, 3 and 4, Plate VII, are reproduced representative spectra obtained for N.C. 80, N.C. 108, N.C. 110 and N.C. 120 respectively. They show the same essential features as those observed at room temperature, except for the appearance of the fainter electronic lines at 4123, 4194, 4197 and 4206 A.U., the splitting of the 4152 line and the greater intensity and sharpness of the entire spectrum.

In the spectra of every diamond studied, the prominent electronic lines are those at 4152 and 5032, the lines at 4123, 4194, 4197, 4206, 5359 and 5895 being weaker. Numerous bright and dark streaks cross the spectra, extending throughout the spectrum or in the blue and yellow regions alone and these correspond to variations in the intensity of the 4152 and 5032 lines. The variations in the intensity of the two systems are identical for N.C. 120 and N.C. 122 except for a few 'blue' streaks. For N.C. 108, N.C. 80 and N.C. 110 they are generally different, the streaks present in the two systems on the whole being independent of each other. In the intensely blue luminescent diamonds N.C. 80, N.C. 108 and N.C. 110, the

4152 line appears as a doublet. Variations in intensity of the two components are however, the same. The weaker electronic lines at 4123, 4194, 4197 and 4206 also exhibit changes in intensity, these being parallel to those of the principal electronic line at 4152 with which they are associated.

N.C. 80 shows certain new features not observed at room temperature. In the previous study the 5032 system had been reported to be absent for this diamond. The spectra taken at liquid air temperature however, show that in the regions of many of the faint and a few of the bright streaks the 5032 system is present with intensities comparable with that of the 4152 system. The failure to observe this at the room temperature is to be ascribed to its extreme diffuseness and faintness at that temperature. In many of the intense streaks in its fluorescence spectra, the 4152 system is present alone, in a few both the 4152 and 5032 systems are present while in the case of the dark streaks both the systems are absent. These three types of streaks correspond to the blue, yellow and non-luminescent types of diamond respectively.

(b) *The Absorption Patterns.*—Spectroscopic studies of the absorption patterns of all the ten diamonds have been carried out at both room temperature and at liquid air temperature. The spectra for four of these, *viz.*, N.C. 80, N.C. 108, N.C. 106 and N.C. 114 are reproduced in Figs. 5, 6, 7 and 8, Plate VII.

As may be expected, in diamonds N.C. 80, N.C. 79, N.C. 100 and N.C. 107 which are blue luminescent, the 4152 system is the prominent feature of the spectrum, the 5032 system being too weak to be recorded with the thicknesses employed. The 4152 line in every spectrum shows remarkable variations in its width and intensity and the spectrum towards shorter wave-lengths is crossed by numerous dark and bright streaks. It will be noted that the streaks in fluorescence lie towards longer wave-lengths and that while the bright and dark streaks in fluorescence correspond to luminescent and non-luminescent regions in the diamond respectively, the reverse is the case in absorption. The bright streaks in fluorescence correspond to the dark streaks in absorption and *vice-versa*. A very close parallelism is thus seen to exist between the patterns in fluorescence and absorption. In N.C. 80 the spectra in both fluorescence and absorption consist of alternately bright and dark streaks. In N.C. 100 the luminescence pattern consists of a central triangular patch of blue luminescence surrounded by regions of non-luminescence. In the absorption spectrum we find the 4152 line to be intense in the central region and weak or absent towards either edge. N.C. 79 and N.C. 107 consist of alternating regions of blue and non-luminescence and the absorption spectra show the existence of identical

patterns in absorption. It should be noted however, that the complete 4152 system appears only in N.C. 80 and N.C. 79. In N.C. 100 and N.C. 107 which are less intensely luminescent and thinner, only the 4152 line is recorded.

In the typically yellow luminescent diamonds N.C. 120 and N.C. 122, only the 5032 system is present in absorption, the 4152 system being naturally too weak to be observed. The absorption spectra in both cases show the presence of numerous parallel streaks of varying brightness, corresponding in every detail to the pattern observed in fluorescence. The spectra however, were too faint to be reproduced successfully.

N.C. 106, N.C. 108, N.C. 110 and N.C. 114 being diamonds of the mixed type, show both 4152 and 5032 systems in absorption with comparable intensities. Only in N.C. 108 however, were conditions favourable enough to exhibit the changes in intensity of both systems simultaneously. In all the other three, the 4152 and 5032 lines are alone recorded, the subsidiary bands being too weak to be obtained with any observable intensity. The distribution of intensities in the two systems are different for all the four diamonds. In the absorption spectrum of N.C. 106 reproduced in Fig. 7, it will be noticed that the 4152 line is intense in only one half of the plate. This corresponds to a region of blue luminescence as visually observed, the rest being yellow luminescent. In the absorption spectrum of N.C. 114 reproduced in Fig. 8, the 5032 line appears with uniform intensity throughout its length while the 4152 line is strong only in half the spectrum. In other spectra obtained for the same diamond the 4152 and 5032 lines exhibit variations which are complementary in nature, *i.e.*, the 4152 is strong while the 5032 is weak and *vice-versa*. The striking similarity between the fluorescence and absorption pattern for N.C. 108 is illustrated in Figs. 2 and 6. The central "blue" streak, in both spectra is specially noteworthy and corresponds to a spot of intense blue luminescence visually observed to be present at the centre of the diamond plate. N.C. 110 also exhibits similar variations in intensity in both systems, but only towards that apex of the plate where both blue and yellow luminescence are simultaneously present.

#### 4. Significance of the Results

The general results obtained may be summed up as follows:

(a) In blue luminescent diamonds the 4152 system is the predominant feature of the spectrum and variations in intensities of the weaker electronic lines at 4197 and 4206 and the subsidiary bands at longer wave-lengths are identical with those of the 4152 line.

(b) In yellow luminescent diamonds both the 4152 and 5032 systems are present the latter system being much more prominent than the former. Every variation in the intensity of the 5032 system is repeated with identical features in both the 4152 and 5359 systems and the weaker electronic lines at 4123 and 4194.

(c) In diamonds showing the mixed type of luminescence the 4152 and 5032 systems appear with comparable intensities. Their spectra are characterised by three varieties of streaks, *viz.*, those present in the 4152 system alone corresponding to blue luminescent regions in the diamond, those present in the 5032 system and weakly in the 4152 system corresponding to yellow luminescent regions and those present in both the 4152 and 5032 systems but with relative intensities varying over a wide range from one streak to another. The first two types of streaks correspond to blue and yellow luminescent structures of diamond existing in the same specimen independently of each other and in these the intensities of the subsidiary electronic lines and the lattice bands show variations similar to those of the principal electronic lines. The third type of streaks may arise from either the intermingling of the blue and yellow luminescent structures in varying proportions or from the overlapping of the spectra from different layers of the diamond due to the finite thickness of the cleavage plates used. No correlation can of course, be obtained between the intensities of the different systems for these streaks.

(d) The absorption spectra show that corresponding to the different types of patterns of luminescence, the plates exhibit variations in transparency over their area, forming absorption patterns identical with the former in the distribution of both colour and intensity. The 4152 and 5032 lines in absorption show remarkable variations in its width and intensity not only in the same spectrum but in different spectra obtained for different regions of the plate. A close parallelism exists between these and the variations in intensity of the subsidiary bands appearing at shorter wavelengths. A comparison of the absorption and fluorescence spectra show that the intimate correlation between the intensities of luminescence and absorption holds good not only for different diamonds but for individual areas of the same diamond.

In conclusion the author wishes to express her grateful thanks to Professor Sir C. V. Raman for his guidance throughout the course of this investigation.

### 5. Summary

The paper reports a spectroscopic study of the luminescence and absorption patterns shown by ten cleavage plates of diamond at liquid air

temperature. A close correlation is shown to exist in blue luminescent diamonds between the variations in intensity of the principal electronic line at 4152 and those of the fainter lines at 4197 and 4206 and the subsidiary bands at longer wavelengths, and in yellow luminescent diamonds between the intensities of the 4152, 5032 and 5359 systems and the lines at 4123 and 4194. The spectra of diamonds of the mixed type possess features characteristic of both the blue and yellow luminescent types. It is shown that in absorption the same intensity relations hold good in the different types of diamond. The variations in intensity and colour of the absorption spectra are thus identical with those in the fluorescence spectra and give rise to absorption patterns in the visible corresponding to the patterns in luminescence.

## REFERENCES

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| Mani, A.     | .. <i>Proc. Ind. Acad. Sci.</i> , 1944, 20, 155. |
| Raman, C. V. | .. <i>Ibid.</i> , 1944, 19, 199.                 |

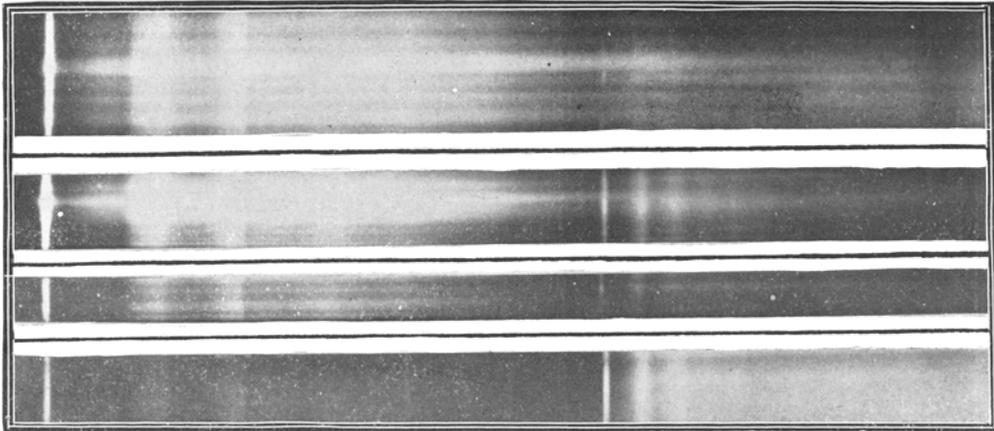


FIG. 1  
N.C. 80

FIG. 2  
N.C. 108

FIG. 3  
N.C. 110

FIG. 4  
N.C. 120

Patterns of Luminescence at Low Temperatures

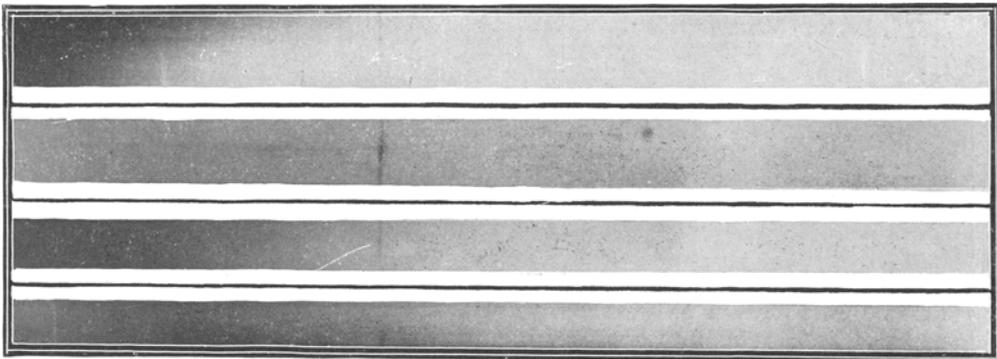


FIG. 5  
N.C. 80

FIG. 6  
N.C. 108

FIG. 7  
N.C. 106

FIG. 8  
N.C. 114

Patterns of Absorption at Low Temperatures