# SPECTROSCOPIC STUDY OF LUMINESCENCE PATTERNS IN DIAMOND

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Received August 21, 1944

(Communicated by Sir C. V. Raman, KT., F.R.S., N.L.)

## 1. *Introduction*

A PREVIOUS communication to these *Proceedings* by the author (1944) contains a detailed report on the fluorescence and absorption spectra of thirty-two diamonds of widely different intensities and colours of luminescence. Numerous sharp electronic lines of varying intensities have been found in the visible region in the recorded spectra. The two most prominent of these are the lines at 4152 and 5032 A.U., and in combination with these two electronic lines, the vibration spectrum of the crystal lattice also appears towards longer wavelengths. The appearance of the 4152 electronic line and the associated lattice vibrations are characteristic of blue luminescence, while the 5032 system is similarly associated with the yellow luminescence. Whenever the 5032 system is recorded with any specimen, the 4152 system is an invariable accompaniment though its strength may be greater or smaller than that of the former system. The converse is not true, in other words the 4152 system may and indeed often does appear without a trace of the 5032 system being noticed.

The colour and intensity of luminescence may differ not only from diamond to diamond, but also in different parts of the same diamond. The luminescence patterns which arise in this way are often seen very conspicuously in polished cleavage plates of diamond. They have been described in detail by Sir C. V. Raman (1944), and their relationship to similar marked variations in other properties of the diamonds over their area have also been remarked on by him. Detailed studies of the luminescence patterns (Sunanda Bai, 1944), the patterns of transparency in the ultraviolet (Rendall, 1944), of the birefringence patterns (Raman and Rendall, 1944) and of the variations of X-ray reflection intensity (Ramachandran, 1944) have been published. The existence of parallel variations in such widely different physical properties indicates a common physical origin, *viz.*, a variation in the ultimate structure of the crystal, and it thus becomes of importance to make also a spectroscopic study of the luminescence patterns. In the previous investigation

of the author, the fluorescent light from the diamond was condensed by means of a cylindrical lens on the slit of the spectrograph. This procedure prevents the spectra from different parts of the diamond being separately observed. If however, a cleavage plate is exposed and an image of it when excited to luminescence is thrown on the slit and moved over it in a series of exposures, the resulting spectra exhibit the variations in the nature and ntensity of the light emitted by the different parts of the diamond. The interest of such a study is that it enables us to understand the nature of the luminescence patterns more fully than is possible by simple visual observation and also to correlate the results with those obtained in the earlier spectroscopic investigation.

### 2. *Experimental Technique*

The diamonds employed were polished cleavage plates selected from Sir C. V. Raman's personal collection, to be representative of the various types of luminescence pattern wihch have been noticed. They have the new catalogue numbers N. C. 80 (D38), N. C. 82 (D235), N. C. 108 (D188), N. C. 110 (D190), N. C. 120 (D200) and N. C. 122 (D202), the numbering in the older catalogue being given within brackets. N. C. 80 was blue-fluorescent, N. C. 120 and N. C. 122 were yellow-luminescent, while N. C. 110, N. C. 108 and N. C. 82 exhibited both yellow and blue luminescence. Photographs of the luminescence patterns of all these specimens except N. C. 122 (202) are reproduced in the plates accompanying Sir C. V. Raman's paper quoted above.

The diamonds were mounted in metal blocks with suitable apertures for the entrance and emergence of light. Observation of the luminescence pattern was made normal to the area of the plate, the illuminating beam being obliquely incident. The source of light for exciting fluorescence was a carbon arc run at 220 volts with a current of 5 amperes. The light from the arc after passage through a water cell and a plate of Wood's glass which cuts off all visible radiation, was focussed on the diamond so as to illuminate the whole area uniformly. The image of the diamond was carefully focussed on the slit of the spectrograph by means of a high-quality Sonnar lens of 5 cm. focal length. By moving the lens, different parts of the image were made to pass over the slit. The whole area of the diamond could be scanned in this way, a series of fluorescence spectra being obtained for each specimen studied. Exposures of the order of two to four hours were sufficient to record each spectrum in the case of the strongly luminescent diamonds N. C. 80, N. C. 108, N. C. 110, N. C. 120 and N. C. 122, while twelve to fifteen hours were necessary to obtain a spectrum of N. C. 82 with satisfactory intensity. The

spectra were photographed on Ilford H. P2 plates by means of a Hilger two-prism spectrograph. All observations were made at room temperature. It is hoped to take up studies at liquid air temperature later.

### 3. *Results*

(*a*) *Observations with diamond N. C.* 80 (D38).—N. C. 80 is a striking example of a diamond which exhibits geometrical patterns in blue luminescence and as visually observed, shows no trace of yellow luminescence. The pattern consists mainly of four pairs of intensely fluorescent bands inclined to each other at about 60°, interspersed by regions of non-luminescence. A series of four spectra were obtained for the diamond, the scanning slit traversing the plate so as to cut across both pairs of bands. Numerous bright streaks of varying intensities running throughout the length of the spectrum are present in every spectrogram, the pattern of streaks changing with the portion of the diamond scanned. Every bright streak is seen to correspond to a region of luminescence and the completely dark portions between them to regions of non-luminescence. From Fig. 1, Plate IV, where one of the spectra obtained is reproduced, it will be seen that the 4152 system is the prominent feature of the spectrum and that the 5032 system is completely absent. Sunanda Bai (1944) has shown that in N. C. 80 the non-luminescent regions transmit ultra-violet light up to 2400 A. U., whereas absorption commences at 3000 A. U. for the luminescent portions.

(*b*) *Observations with diamond N. C.* 82 (D235).—This is a predominantly blue-luminescent diamond which however, exhibits non-luminescent areas towards its two ends. The region of the plate which shows blue luminescence is also traversed diagonally by a series of faint yellow bands. Eight spectrograms were obtained, one of which is reproduced in Fig. 2. Four electronic lines at 4152, 5032, 5359 and 5895 A. U. are present in the spectrum and it will be noticed that the 4152 line and its subsidiary bands are more intense than the other three. The absolute and relative intensities of these four lines are different in the different spectrograms obtained, but in the same spectrogram, although the intensity of the lines vary along their length, their relative intensities remain constant, except where they are crossed by bright streaks.

The streaks exhibit a wide variation in intensity and many of them extend throughout the spectrum, while a number of streaks will be noticed to be present only in the blue, green, yellow or red regions. The 'blue' streaks belong to the 4152 system and appear with high intensity between 4100 and 5300 A. U. and extend weakly to 6500 A. U. The 'green' streaks similarly belong to the 5032 system and as is to be expected are present very weakly in the blue also. The 'yellow' and 'red' streaks are independent

of the 4152 and 5032 systems and appear to commence from the electronic lines at 5359 and 5895 and extend up to 6500. It appears likely that the 'yellow' and 'red' streaks form two new independent systems, which may be called the 5359 and 5895 systems respectively. The line at 5895 deserves special mention. Crookes (1909) had reported a citron line in red-luminescent diamonds, having the wave-length of the sodium doublet and which he attributed to the presence of sodium in diamond. The line he observed was evidently the 5895 line which the present investigation shows to be a genuine electronic line of diamond that is probably responsible for the red luminescence.

Fig. 2 illustrates the different kinds of streaks obtained for N. C. 82 and shows that the majority of them lie in the 4152 system. The lower half of the spectrum corresponds to the region of the diamond which contains non-luminescent areas interspersed by luminescent patches. It will be noticed that a number of 'blue', 'green' and 'yellow' streaks are present in this region. The 'yellow' streaks in the upper portion of the spectrum testify to the existence of yellow luminescence bands visually observed to be present in this region.

(*c*) *Observations with diamond N. C.* 120 (D200).—As visually observed, this is purely yellow-luminescent showing no trace of blue fluorescence. The most prominent feature of its luminescence pattern is a set of four parallel bands. A series of six spectrograms were taken and one of these is shown reproduced in Fig. 3. Only the 4152 and 5032 systems appear in the spectrum, the 5032 system being more intense than the other. Numerous streaks traverse the spectra throughout the region of fluorescence, and though their intensities vary from point to point in the diamond, the relative intensities of the two systems are uniformly constant, every variation in the intensity of the 5032 system being repeated in the 4152 system.

(*d*) *Observations with diamond N. C.* 122 (D202).—Like N. C. 120 this is also yellow-luminescent; its whole area, however, is covered by a series of parallel yellow bands. Eight spectrograms were obtained with the diamond, one of which is reproduced in Fig. 4. The pattern of streaks is different in the different spectra obtained, but in the same spectrogram the 4152 and 5032 systems show identical variations in intensity. There is, however, one exception of a 'blue' streak where the 4152 system is more intense than the 5032.

(*e*) *Observations with diamond N. C.* 110 (D190).—N. C. 110 is a triangular shaped plate showing the mixed type of luminescence. The luminescence pattern consists of numerous wavy bands of blue and yellow near the apex

of the triangle, the rest of the plate being fairly uniformly fluorescent. A series of ten spectrograms were taken, the plate being scanned from the apex to the base. Both the 4152 and the 5032 systems appear with comparable intensities. The spectra obtained in the region of uniform luminescence show little change in the relative intensities of the two systems, despite the many streaks that run through them. On the other hand, for spectra obtained near the apex, one of which is reproduced in Fig. 5, the structure and intensity of the ' blue ' and ' green ' streaks are seen to be quite different.

(*f*) *Observations with diamond N. C.* 108 (D188).—N. C. 108 is a typical example of a diamond exhibiting both blue and yellow luminescence and shows a very interesting pattern consisting of an intense blue spot surrounded by fainter blue and yellow hexagonal rings forming a figure similar to that of a spider web. A series of nine spectra were obtained, showing an amazing number and variety of streaks. No two of the spectra were found to be similar, in the intensities and the pattern of the ' blue ', ' green ', ' yellow ' and ' red ' streaks obtained. The four prominent electronic lines are those at 4152, 5032, 5359 and 5895, with which are associated the four kinds of streaks mentioned above. The 4152 and 5032 systems have comparable intensities. In many cases the streaks extend throughout the spectrum with approximately constant intensity. More interesting however, are the streaks present only in one or other of the four systems and whose intensities are completely independent of each other. In Fig. 6 is reproduced one of the spectra obtained.

### 4. *Significance of the Results*

It is now well established that the subsidiary bands observed in the 4152 and 5032 systems arise from combinations of the lattice vibrations with the electronic lines at 4152 and 5032 A.U. Hence, the intensities of the subsidiary bands should vary with that of the principal electronic lines. The spectroscopic study of the luminescence pattern shows this to be clearly the case. A close parallelism exists between the intensities of the 4152 line and the bands associated with it at longer wave-lengths, the variations which appear in the former being also clearly seen in the latter. A similar relationship is observed to exist between the 5032 line and the subsidiary bands associated with it.

The variations observed in the relative intensities of the 4152 and 5032 systems are also noteworthy. It is noticed that in blue-luminescent diamonds the 4152 system is present alone, the subsidiary bands of this system itself extending to 6500 A.U. In yellow-luminescent diamonds on the other hand, both the systems are present, the 5032 system being the prominent feature in the

spectrum. The intensities of the two systems in any one diamond always bear a constant ratio to each other, every variation in the 5032 system appearing in the 4152 system also. In diamonds which, as visually observed, show both blue and yellow luminescence, the two systems appear with comparable intensities. But the relative and absolute intensities of the two systems vary not only from diamond to diamond, but in the same diamond from one region to the other. Among the numerous bright and faint streaks that cross the spectra, it is observed that some are present in both the systems and some in either the 4152 or 5032 systems while in the case of the third kind of streaks, neither their structure nor their intensities are similar in the two systems. In fact, fine streaks or dark regions in the 4152 system in many cases correspond to broad streaks in the 5032 system.

The facts observed are comprised in the statement that diamond may be either non-luminescent, blue-luminescent or yellow luminescent, and that in diamonds exhibiting luminescence patterns the different kinds of behaviour may manifest themselves simultaneously in different parts of the same specimen lying in close juxtaposition. The differences in behaviour are evidently associated with differences in the ultimate structure of the diamond. It is particularly interesting that yellow luminescence usually appears in thin layers exhibiting a stratification of intensity. Besides the 4152 and 5032 systems, we have also to consider two other and apparently independent kinds of luminescence appearing in the yellow and red regions of the spectrum respectively. They consist of the electronic lines at 5359 and 5895 and the subsidiary bands associated with them at longer wavelengths. The exact origin of these systems and their correlation with the 4152 and 5032 systems is a problem that demands further investigation.

In conclusion, the author wishes to express her respectful thanks to Professor Sir C. V Raman for his interest and constant encouragement in the work.

## 5. *Summary*

A spectroscopic study has been made of the local variations in intensity and colour of the fluorescent radiation from six cleavage plates of diamond exhibiting blue, yellow and mixed types of luminescence. It is found that a close correlation exists between the variations exhibited in the intensities of the electronic lines at 4152 and 5032 and of their subsidiary bands, and also between the two systems themselves. The 4152 system is present alone in blue-luminescent diamonds, while both systems appear in diamonds of the yellow-luminescent and mixed types. In the former, the 4152 system occurs weakly and a close correspondence is found to

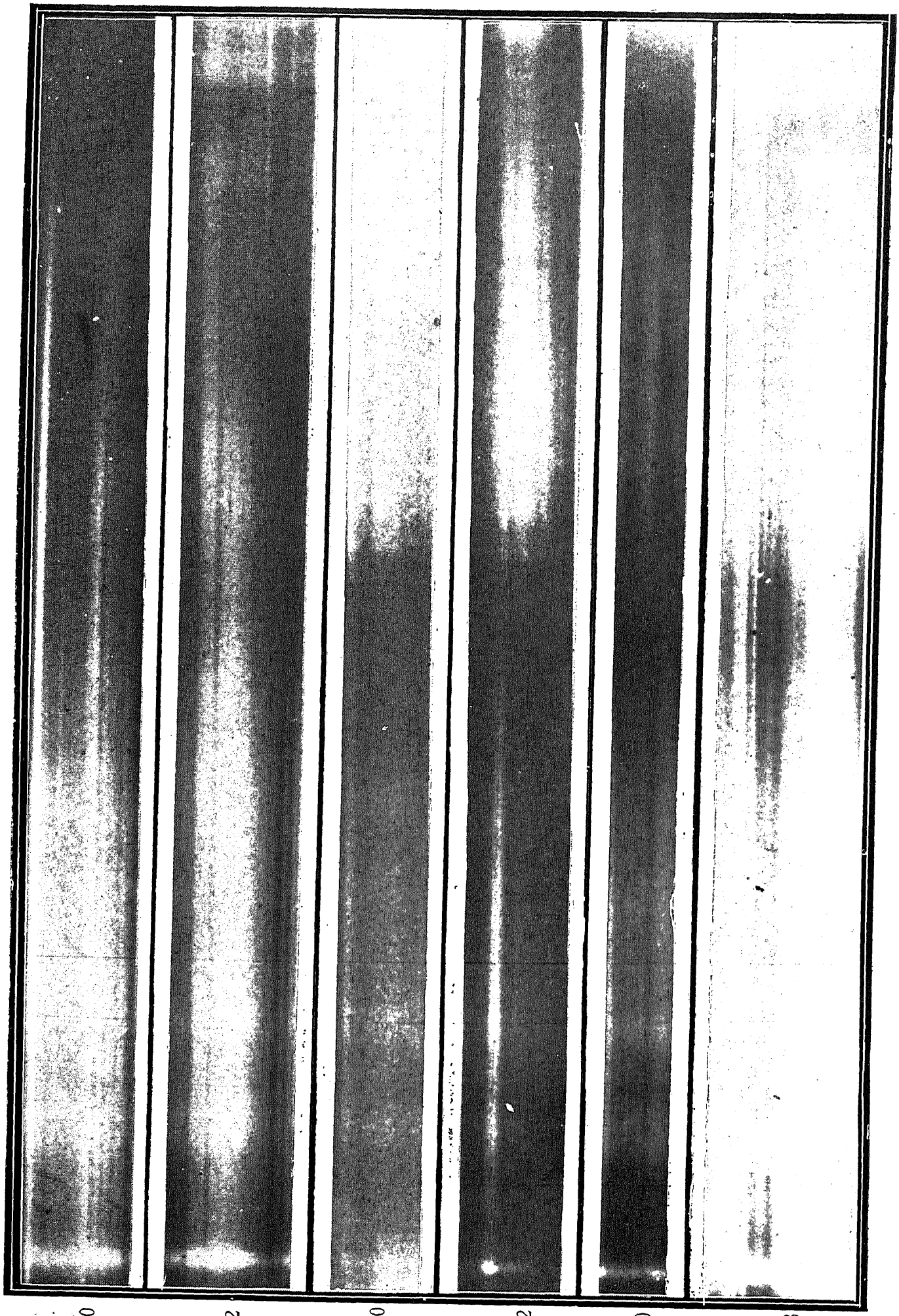

FIG. 1
N.C. 80

FIG. 2
N.C. 82

FIG. 3
N.C. 120

FIG. 4
N.C. 122

FIG. 5
N.C. 110

FIG. 6
N.C. 108

exist between the intensities of the two systems. In the latter, the 4152 and 5032 systems appear with comparable intensities no correlation between them being observed except in a few cases. There is also evidence of the existence of two other systems of luminescent bands, associated with the electronic lines at 5359 and 5895 A.U. respectively.

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