

# FLUORESCENCE AND PHOSPHORESCENCE OF DIAMOND AT DIFFERENT TEMPERATURES

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## 1. INTRODUCTION

MANY diamonds are fluorescent under ultraviolet irradiation and phosphoresce on cutting off the incident light. The fluorescence spectrum of all diamonds at room temperature consists mainly of an electronic line at  $\lambda$  4156 accompanied by subsidiary vibrational bands on the longer wavelength side and a continuous background (Nayar, 1941). Green fluorescent diamonds exhibit, in addition, an electronic line at  $\lambda$  5032 accompanied by its vibrational bands and continuum (Mani, 1944). On cooling the diamond to  $-180^{\circ}$  C., the electronic lines and bands sharpen and shift to shorter-wavelengths. Nayar studied also the effect of heating the diamond. With increase of temperature, the line at  $\lambda$  4156 and its subsidiary bands broaden and shift to longer wavelengths. Ultimately at about  $350^{\circ}$  C, no trace of the line or bands is noticeable, only a continuous spectrum being present. Naturally, as the line broadens, its apparent intensity diminishes and it becomes diffuse. It is of great interest to find out whether the integrated intensity of the line at  $\lambda$  4156 changes. The results presented in this paper reveal no appreciable change in the intensity of the line as a whole between  $-180^{\circ}$  C. and  $+150^{\circ}$  C., while the results at higher temperatures are inconclusive. In the range  $-180^{\circ}$  C. to  $400^{\circ}$  C. the intensity of fluorescence of diamond, viewed through a filter transmitting between  $\lambda$  4050 and  $\lambda$  4300, does not markedly change as far as the eye could detect. This fact supports the result mentioned above.

The present opportunity has been taken to continue the studies on the phosphorescence of diamond by the author reported in earlier papers (1946), and some remarkable effects observed have been set forth in this paper.

## 2. EXPERIMENTAL TECHNIQUE

For work at liquid-air temperature, the experimental set up for the investigation is the same as that employed by Nayar and Miss Mani (1944). The special demountable Dewar Flask employed by them is used and a

brightly fluorescent (blue) diamond NC 67 is fixed in a copper block by means of Wood's metal and this is screwed on to the bottom of a metal tube which holds the liquid air. The tube is inserted into the pyrex flask and is sealed at the top by means of Apiezon wax, while the flask is evacuated continuously from the bottom by a Cenco pump.

For higher temperature work, a small heater consisting mainly of a rectangular brass tube  $1\frac{1}{2}'' \times \frac{1}{2}'' \times \frac{1}{2}''$  is constructed. At the centre of one of the sides of the tube a small opening is made for irradiation purpose. This opening and one of the sides are closed by glass windows. The tube is wrapped up with a thin layer of mica over which is wound nichrome wire and is covered by asbestos. The diamond is stuck on a small copper plate by means of sodium silicate solution and placed at the centre of the heater. The open end is closed by a mica strip through which is inserted a calibrated nichrome-constantan thermocouple for measuring the temperature of the diamond. The diamond is assumed to be at the temperature of the surrounding air. The assumption is a good approximation as diamond is an excellent thermal conductor.

The unfiltered light from a mercury pointolite lamp is focussed on the diamond by a lens and excites fluorescence. The fluorescent light is focussed on the slit of a two-prism Hilger glass spectrograph (E 328) by means of a short focus cylindrical lens. Since the integrated intensity of the electronic line at  $\lambda 4156$  alone is required, the slit of the spectrograph is kept fairly broad at 20 divisions ( $= 0.004''$ ) so that the doublet nature of the line is not revealed at  $-180^{\circ}\text{C}$ . The fluorescence spectra of the diamond at both liquid-air and room temperatures are recorded on a Selochrome plate (D 41) side by side to minimise the errors due to non-uniformity of the plate and identical exposures are given at both temperatures. In one set the exposure is one hour, while in the other it is 2 hours. Similarly a number of spectra at  $25^{\circ}$ ,  $60^{\circ}$ ,  $100^{\circ}$ ,  $150^{\circ}$ ,  $200^{\circ}$ ,  $250^{\circ}$ ,  $300^{\circ}$ ,  $350^{\circ}$  and  $400^{\circ}\text{C}$ . are taken, the exposure being 23 minutes in each case. During any set of exposures great care is taken to see that the position of the diamond is undisturbed and that all other conditions are identical.

Enlarged microphotometer curves of the electronic line using the gear ratio of 1:50 for the recording drum is obtained for each of the four spectra of the first plate. For spectra at higher temperatures microphotometer curves of a large region around the electronic line is recorded using the normal gear ratio of 1:7.

Using the well-known method of graded intensity marks the density-intensity curve of a Selochrome plate—from the same packet as that used

for recording the fluorescence spectra—is obtained. The density of blackening of the electronic line at various distances from its centre is deduced from the microphotometer records and the corresponding intensity distribution curve in each case is plotted, using the density-intensity curve of the plate.

### 3. RESULTS

Photographs of fluorescence spectra of diamond kept at 25° and -180° C. are reproduced in Fig. 1, Plate IV. Fig. 2 shows spectra with the diamond at 25°, 60°, 100°, 150°, 200°, 250°, 300°, 350° and 400° C. These pictures reveal the shifting and broadening of the electronic line at  $\lambda$  4156 with increasing temperature. The diminution in peak intensity is also seen clearly. In addition the intensity of the continuous spectrum diminishes.

As the electronic line is symmetrical at liquid air and room temperatures, the area enclosed by the intensity distribution curve between the two ordinates at half intensity gives a measure of the integrated intensity of the electronic line. This is found to be appreciably constant at the two temperatures within limits of experimental error.

On the other hand at high temperatures, the line is apparently unsymmetrical due to decrease in peak intensity and broadening and consequent large overlapping of the continuous spectrum. The effect due to this is eliminated by extrapolating the curve of the continuous spectrum at large distance from the centre of the electronic line and subtracting this intensity from the original intensity distribution curve. The resulting curve for the electronic line is considerably more symmetrical. Even in this curve, only the integrated intensity over half width on the shorter wavelength side is calculated. This is found also to be appreciably unaltered for the temperatures between 25° C. and 150° C. At higher temperatures it is difficult to distinguish the peak of the electronic line from the background. But it seems fairly probable that the broadening accounts for the diminution in the peak intensity of the line even at higher temperatures and that the intensity of the electronic line as a whole does not change in any marked manner. As far as the continuous spectrum is concerned, the author is of the opinion that it decreases to some extent with temperature but does not vanish even at 400° C. Tables I and II give the results obtained.

The ratios in the last column are very nearly equal to one, allowing for experimental errors. The microphotometer curves of a few mercury lines scattered by the diamond showed that the intensity of the source did not vary by more than one per cent. during the course of the investigation.

TABLE I

Temperature	Exposure	Integrated Intensity of $\lambda$ 4156	Ratio of the Integrated intensities
25° C.	60 min.	138.9	1.05
-180° C.	60 min.	146.2	
25° C.	120 min.	242.0	0.99
-180° C.	120 min.	239.3	

TABLE II

Temperature	Exposure	Integrated Intensity of $\lambda$ 4156	Ratio of the Integrated intensities
25° C.	23 min.	8.48	0.96
150° C.	23 min.	8.17	

Hence, no correction for this factor is necessary. As two spectral lines to be compared have nearly the same frequency and as they are in juxtaposition on the plate, most of the errors due to non-uniformity of the plates and of development are almost entirely eliminated. Finally the accuracy of the experimental results can be verified as follows:—

The ratio of the integrated intensities for the two exposures at room temperature given in Table I is 1.74. According to the well-known Schwarzschild's relation this value is to be expected as the effect of doubling the exposure time is equivalent to increasing the intensity by  $2^{0.86}$  (= 1.81).

#### 4. PHOSPHORESCENCE OF DIAMOND

For making visual observations on the fluorescence and phosphorescence of diamond at various temperatures, sunlight passed through a Wood's glass filter is used for exciting fluorescence. The extremely bright fluorescence of the diamond NC 67, blue in colour, does not show any great change in intensity or colour between  $-180^{\circ}$  C. and  $+400^{\circ}$  C. On the contrary, the after-glow on shutting off the incident light is very feeble and greenish-yellow at low temperatures. At  $150^{\circ}$  C. the colour changes to blue and the glow is brighter and lasts a longer time. At  $400^{\circ}$  C., the glow is extremely bright and blue. On shutting off the incident light no discontinuity between the brightness of fluorescence and of phosphorescence is observed. The bright and blue glow slowly decays starting with an initial intensity nearly as bright as that of fluorescence. Even at  $400^{\circ}$  C., surprisingly enough in order to build up this great store of energy released as

after-glow, it is necessary to expose the diamond only for less than a fraction of a second to the exciting radiation.

The slow decaying bright and blue glow can be quenched by irradiating the diamond with intense red or green light for a few seconds. Also if full sunlight without any filter is used for exposing the diamond a flash of blue after-glow can be seen for a second or two and it turns to a comparatively feeble and greenish-yellow glow lasting only for a few seconds. These results are similar to the quenching effect by light or heat on the stored-up energy of diamond at room temperature.

Again, the after-glow is blue when ultra-violet or violet light is used for irradiating the diamond. On the other hand, with green light ( $\lambda$  5000 to  $\lambda$  6000) as the exciting source, the glow is distinctly greenish-yellow and very weak comparatively. With red light no perceptible glow can be detected. All these results are in agreement with the Stokes Law of fluorescence.

In conclusion the author wishes to thank Sir C. V. Raman, kt., F.R.S., N.L., for his constant interest in this problem suggested by him.

#### SUMMARY

The electronic line at  $\lambda$  4156 present in the fluorescence spectrum of all diamonds sharpens and increases in peak intensity on cooling the diamond; *per contra*, it broadens and decreases in peak intensity on increasing the temperature of the diamond and finally at 350° C. is lost in the background. The integrated intensity of the line has been investigated and found to be unaltered to any marked degree between -180° C. and +150° C.

The phosphorescence of diamond at various temperatures has also been dealt with. At low temperatures the after-glow is weak and greenish-yellow in colour, while at 400° C., the glow is extremely intense and blue. The effect of quenching by red or green light on this bright and blue glow has been reported in this paper.

#### REFERENCES

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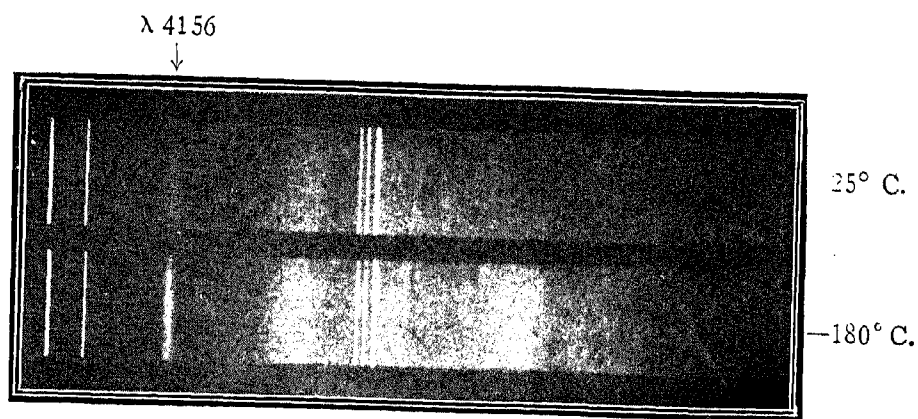


FIG. 1

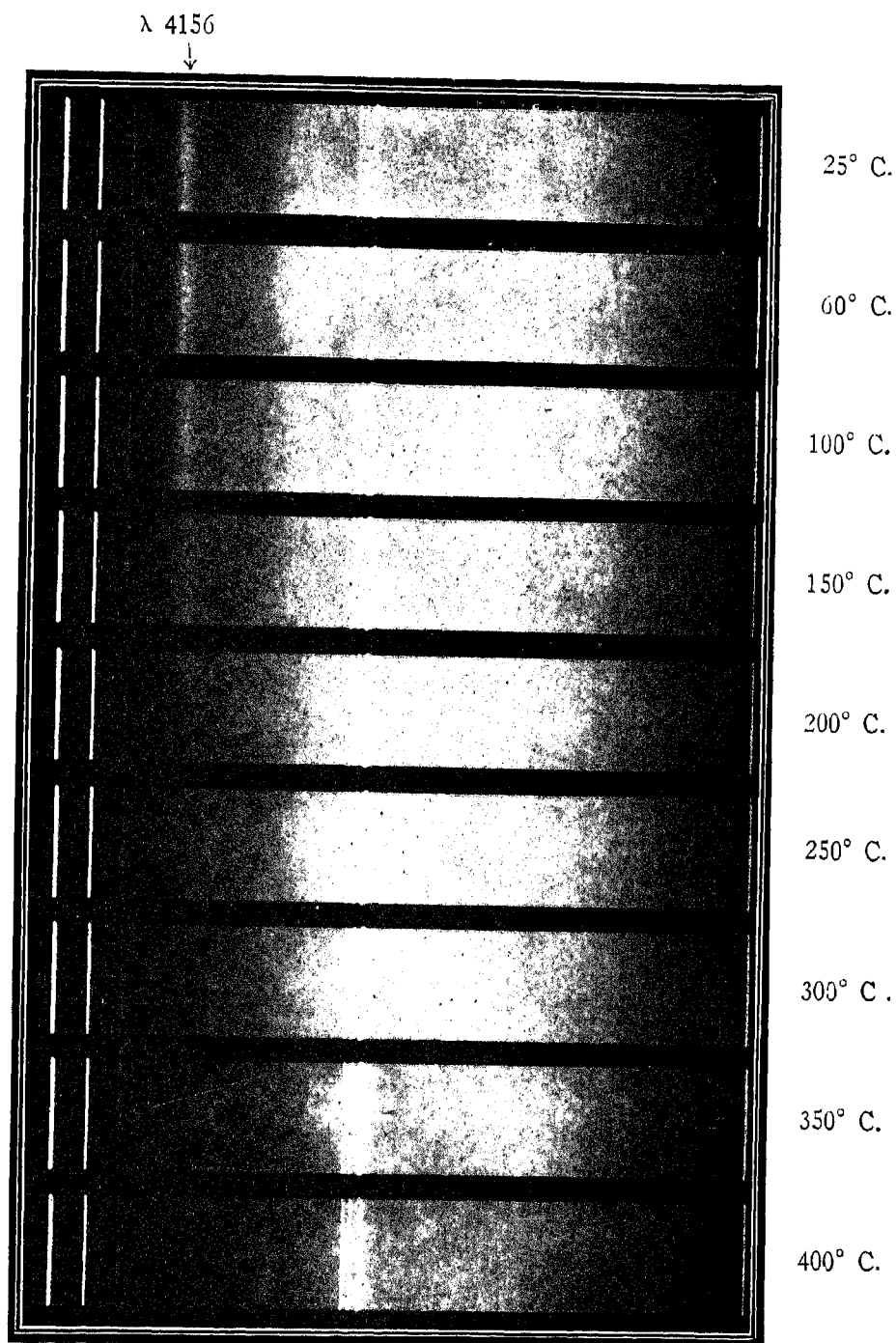


FIG. 2

Fluorescence Spectra of Diamond at Different Temperatures