LUMINESCENCE PATTERNS IN DIAMOND

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1. Introduction

The luminescence of diamond can be readily observed with sunlight and a simple fluoroscope, viz., a piece of Wood's glass and a condensing lens at one end of a tube, a holder for the diamond inside it and a transversely-mounted eyepiece. Examining the specimens in his personal collection with this simple instrument, Sir C. V. Raman made the interesting observation that polished cleavage plates of diamond not infrequently exhibit patterns of luminescence, viz., striking variations of its intensity and colour over the area of the plates. He noticed also that the luminescence pattern often bears a surprising resemblance to the birefringence pattern shown by the same specimen when viewed between a pair of crossed polaroids. Photographs exhibiting such resemblance have been secured by the author for some selected specimens and are reproduced with the paper appearing in the symposium in which Sir C. V. Raman (1944) has discussed the nature and origin of the luminescence of diamond.

To elucidate the nature of the structures which give rise to luminescence, the author undertook a systematic study of the ultra-violet absorption spectra of the diamonds in the collection. The results of the investigation are described in another paper appearing in the symposium. They show clearly that there is an intimate relationship between the ultra-violet absorption spectrum of diamond on the one hand and the colour and intensity of its luminescence on the other. Hence, it follows that a diamond which exhibits a luminescence pattern should also exhibit notable variations in its ultra-violet absorption spectrum over its area. This has also been shown to be actually the case, using the technique which has been described in the paper referred to. Typical absorption spectra illustrating such variations obtained with the diamonds D38 and D235 are reproduced as Fig. 8 in the Plates accompanying this paper.

In view of the great experimental and theoretical interest of the luminescence patterns shown by diamond, it appeared desirable to classify and describe the patterns of all the cleavage plates in the collection and also
to record them, thereby facilitating comparison with other effects exhibited by the same diamonds. Photographs in black and white convey but a faint reflection of the beauty and interest of these patterns with their varied colours. Nevertheless, they are not without value, since they can be studied at leisure, and in the case of the faintly luminescent specimens exhibit features which are not easy to observe visually.

2. Photographing the Luminescence Patterns

It has been shown by Miss Anna Mani (1944) in another paper appearing in the symposium, that the variations in the intensity and of the colour of the luminescence of diamond arise from variations in the absolute and relative intensities of two distinct sets of radiations which appear respectively in the regions of shorter and longer wave-lengths of the visible spectrum. For brevity, these will be referred to respectively as the "blue" and "yellow" luminescence spectra. The luminescence patterns may therefore also be ascribed to the local variations of the absolute and relative intensities of these spectra in the emitted light. The rendering of the patterns given by a photographic plate naturally depends on its sensitivity to the two spectral regions under consideration. The most satisfactory arrangement would evidently be to use appropriate filters and obtain two photographs in which the "blue" and the "yellow" luminescence are separately recorded. On setting these side by side, we should obtain an accurate idea of the distribution in the diamond of the structures responsible for their emission. In the present investigation, for the sake of simplicity, no such special arrangements were made, and only one photograph was obtained in each case. It should be mentioned that the patterns of "yellow" luminescence exhibit some fine detail which is not recorded except when high magnifications and plates specially sensitive to the yellow were employed, and long exposures given.

The source of light employed in securing the photographs reproduced was a carbon arc run at 220 volts with 6 to 8 amperes current. A box lined inside with black velvet served as an enclosure for the diamond during the exposure. The light of the arc, after passage through a water-cell and an aperture covered by a plate of Wood's glass, was focussed by a quartz lens on the plate of diamond. The latter was stuck on a polished sheet of copper, and its inclination to the incident beam was so adjusted as to secure a uniform irradiation. Occasionally, some trouble was encountered from the reflections at the bevelled edges of the plate which resulted in bright streaks appearing which ran across the area of the plate. By suitably varying the setting of the diamond, however, these streaks could usually be eliminated.
A rectangular glass cell containing a concentrated solution of sodium nitrate placed in front of the camera lens served as a complementary filter. A camera with a 5-inches focus lens was employed and set so that the image of the diamond appeared suitably enlarged on the plate. The Ilford selochrome plates used for the photographs gave a satisfactory rendering of the "blue" luminescence, but only weakly recorded the "yellow" luminescence even in the areas where actually it was strong. This fact has to be remembered in examining the figures reproduced in the paper. The advantage of using plates sensitive to the yellow region in some cases is illustrated by the striking photograph obtained with D198 (Fig. 5) for which a HP2 plate was employed. It should be mentioned that both the degree of enlargement employed and the photographic exposures were such as to secure the most satisfactory picture in each case. Neither the relative sizes of the diamonds nor their relative intensities of luminescence can therefore be judged from the reproductions.

3. Description of the Patterns

Photographs of 42 diamonds (mostly flat cleavage plates) are reproduced as Fig. 1 to 7 in Plates XX to XXIII. They have been grouped in these figures according to the nature of the effects exhibited by them. Fig. 1 shows the diamonds having a more or less perfectly uniform blue luminescence. (The streaks in D178 are spurious.) Fig. 2 and Fig. 3 also represent diamonds of this kind, the latter of those which exhibit striking patterns. Figs. 4, 5, 6 and 7 represent (with a few exceptions) diamonds showing a mixed blue and yellow luminescence. The exceptions are D200 and D202 in Fig. 7 which exhibit a yellow luminescence, and D182 and D236 in Fig. 7 which are blue-luminescent.

Striking examples of geometric patterns of luminescence are D38, D179 and D180 in Fig. 3, D191 and D194 in Fig. 4, D195, D198 and D235 in Fig. 5, D48 and D56 in Fig. 6, and D186 in Fig. 7. A common feature in many of the patterns is that the lines tend to run parallel to the edges of the plate; these, it may be recalled, represent its intersections with the faces of the crystal from which it was cleaved off. This feature is particularly well shown by D180 in Fig. 3, D191 in Fig. 4, D195 and D198 in Fig. 5, and indeed also by several others. It is a general feature in diamonds showing a yellow luminescence that numerous bright streaks appear running parallel to each other, sometimes in several directions simultaneously. Indications of this feature appear in some of the photographs, viz., D194 in Fig. 4, D196 and D198 in Fig. 5, D48 in Fig. 6, D200 and D202 in Fig. 7. Only traces of the numerous parallel bands seen visually in D193 can be made out in its reproduced photograph (Fig. 4). D188
shows visually numerous yellow bands traversing a blue field in several directions simultaneously, but only with difficulty can this feature be noticed in the photograph (Fig. 6).

The lack of sensitiveness of the selochrome plates has resulted in the areas showing a greenish-yellow luminescence appearing as darker in the photographs than the blue-luminescent ones. The dark areas in the photographs of D191, D192, D193 and D194 in Fig. 4 and of D210 in Fig. 5 are actually areas of greenish-yellow luminescence, while the bright areas in these figures represent a blue luminescence. In D195 (Fig. 5), a band of bright yellow luminescence running parallel to one of the sides of the triangle of blue luminescence is recorded as a dark strip. Many other examples of this kind can be quoted.

4. Origin of the Patterns

The first and most important point to be borne in mind in considering the origin of the luminescence in diamond is that the behaviour of different specimens is very varied. Some are non-luminescent, some are blue-luminescent, some are yellow-luminescent, while others again show both types of luminescence. Further, the intensity of each kind of luminescence may also show enormous variations. The natural interpretation of these facts and of the existence of the patterns is that any given specimen may be a mixture of different species of diamond intertwined with or inter-penetrating each other. As the different species are isomorphous, the geometric character of the patterns immediately becomes intelligible.

Accompanying the differences in the luminescence of diamond, we have also differences in other properties of which the ultra-violet absorption spectrum of diamond is one which is readily accessible to observation. The variation in ultra-violet absorption and its correlations with luminescence have been described in detail in another paper, and it is not necessary to set them out again here. It is sufficient to remark that using the knowledge gained by that investigation, it is possible from a study of the ultra-violet absorption over the different areas of a given specimen to infer the nature of the variations in the diamond which give rise to the luminescence pattern. *Vice versa*, the existence of such correlations between the local variations of luminescence and ultra-violet absorption spectra is evidence for the existence of a relationship between the crystal structure of diamond and its luminescence properties.

A striking example of the presence of material having very different properties in the same specimen of diamond is the dodecahedral cleavage plate D235 whose luminescence pattern appears in Fig. 5.
observed, the central area of this plate shows a fairly bright blue luminescence, while dark patches appear towards both of the extremities as seen in the figure. Visually, some faint bands of yellow luminescence can be seen traversing the plate obliquely from end to end. The ultra-violet absorption spectrum shows corresponding variations over the area of the plate. The non-luminescent areas exhibit a free transmission up to 2250 Å, while the blue-luminescent area shows a transmission extending up to about 2700 Å with moderate exposures, but with prolonged exposures right up to 2250 Å crossed by an absorption doublet at 2360 Å. The latter feature is characteristic of the diamonds which show both the blue and yellow types of luminescence.

Another example illustrating the correlation between luminescence and ultra-violet absorption is D210 (Fig. 5). The central dark region showing a yellow fluorescence gives an ultra-violet transmission spectrum which extends with sufficiently long exposures to 2250 Å traversed, however, by a set of absorption bands in the region between 2500 Å and 2250 Å. On the other hand, the blue-fluorescent marginal region of the diamond shows a transmission only up to 2500 Å even with long exposures. Another interesting case is D180. The brightly blue-luminescent part in the centre of its area shows an ultra-violet transmission up to 2600 Å only, while the marginal non-luminescent areas show a transmission extending to 2250 Å (with absorption bands between) when sufficiently long exposures are given. The blue-luminescent diamond D38 which shows a very striking pattern (Fig. 3) has a free transmission up to 2900 Å followed by a weak transmission up to 2600 Å in the luminescent areas. On the other hand, the non-luminescent strips give bands of free transmission up to about 2400 Å, showing clearly that they represent the intrusion of a more transparent variety of diamond into a less transparent one.

Considering the whole complex of facts, viz., the existence of two distinct varieties of luminescence, the enormous variations possible in their intensities, and the appearance of patterns of blue and yellow luminescence with distinctive features in each case, it appears scarcely possible to reconcile it with the idea that there are only two alternatives possible for the crystal structure of diamond. The wider range of possibilities indicated in the papers by Sir C. V. Raman in the symposium appears easier to reconcile with the observed facts.

In conclusion, the author desires to record her grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his valuable help and inspiring guidance throughout the course of this investigation.
5. *Summary*

*Geometric* patterns showing variations of intensity or colour or of both are often observed in the luminescence of cleavage plates of diamond excited by long-wave ultra-violet irradiation. The lines in the pattern not infrequently also run parallel to the natural faces of the crystal from which the plate was cleaved. Such patterns may be altogether lacking in some cases where the diamond shows a uniform blue luminescence. On the other hand, such patterns are always present when the diamond shows both blue and yellow luminescence. The appearance of numerous bright streaks running parallel to each other, sometimes in several directions simultaneously, is characteristic of yellow luminescence. A study of the local variations of the ultra-violet absorption spectrum of the diamond is usually successful in revealing that the luminescence patterns, when observed, arise from intrusion into the crystal of diamond having properties different from the rest of the material.

42 luminescence photographs are reproduced with the paper.

REFERENCES

FIG. 1

Fig. 2