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The luminescence of diamond—II

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1. Luminescence and crystal structure

The spectral character of the visible luminescence excited in diamond by irradiation with long-wave ultra-violet light was described and illustrated in an earlier article of this series, and the remarkable diversity of behaviour displayed by different specimens of diamond in these circumstances was duly stressed. Why this should be so is a problem which might well have remained unsolved, had it been an isolated issue. At our early stage of the Bangalore investigations, however, it became apparent that luminescence was only one of a whole group of physical properties of diamond which exhibit large variations, and that these are interrelated with each other. A detailed study of the situation was made possible by the circumstance that the collection of material included a large number of polished cleavage plates of diamond—a form which is exceptionally well-suited for such investigations. It will suffice here to mention four series of studies made with these plates which covered the following topics: (*a*) the absorption in diamond of ultra-violet radiation of wavelengths between $\lambda 2000$ and $\lambda 3000$; (*b*) the absorption of infra-red radiation of wavelengths between $6\,\mu$ and $12\,\mu$; (*c*) its structural birefringence; and (*d*) the intensity of X-ray reflections by the lattice planes of the crystal.

That physical properties so different in their nature as those stated above exhibit variations correlated with each other and with luminescence is by itself an indication that a common cause underlies all the variations. Of particular importance in this connection was the discovery that a good many of the plates exhibited luminescence of varying colour and intensity over their area, showing geometric patterns with a configuration related to the structure of the crystal. This suggested investigations by appropriate methods of the other properties listed above, and the result emerged that the cleavage plates which showed geometric patterns of luminescence also exhibited patterns of ultra-violet transparency, patterns of infra-red transmission, patterns of structural birefringence and patterns of X-ray reflection intensity; the geometric features of all these patterns bore a recognizable relationship with each other. The evidence for the structural origin of the whole group of effects was thereby greatly strengthened.

It is proposed in this article to present the experimental facts briefly summarised above, in somewhat greater detail. Of particular significance and importance is the relationship between luminescence and birefringence in diamond. The technique of photographing their patterns so as to exhibit the relationship between them has recently been greatly improved, and a whole series of new photographs by Mr A Jayaraman were reproduced with a paper which appeared in the *Proceedings* of the Indian Academy of Sciences for August 1950. Other photographs taken with the same apparatus illustrate the present article (figures 1 and 6 below).

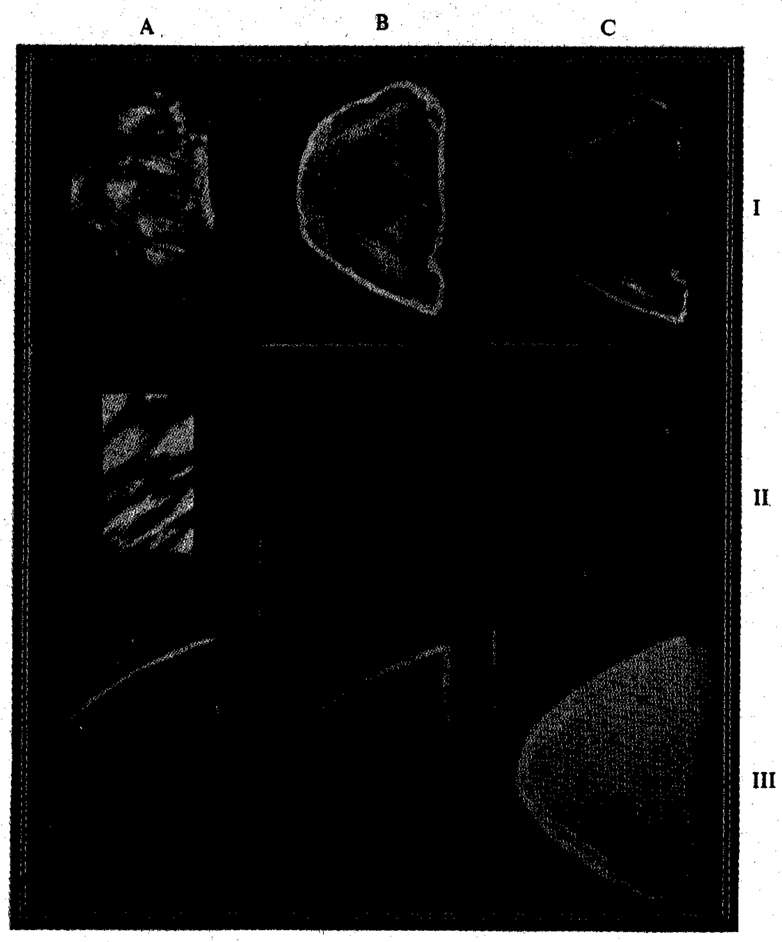

Figure 1. Luminescence and birefringence patterns of three representative diamonds. (A) Birefringence, (B) Green luminescence and (C) Blue luminescence.

2. The luminescence patterns

In order to observe or photograph its luminescence, the diamond is placed on a piece of black glass and irradiated by a beam of sunlight filtered through a plate of Wood's glass and focussed on the specimen. Viewing the diamond through a blue filter, one isolates the part of the luminescence which arises from the electronic transition at λ 4152 and its associated vibrational transitions. Similarly, viewing the diamond through a filter which has a cut-off for wavelengths shorter than λ 5400, the blue part of the luminescence is extinguished, while the luminescence

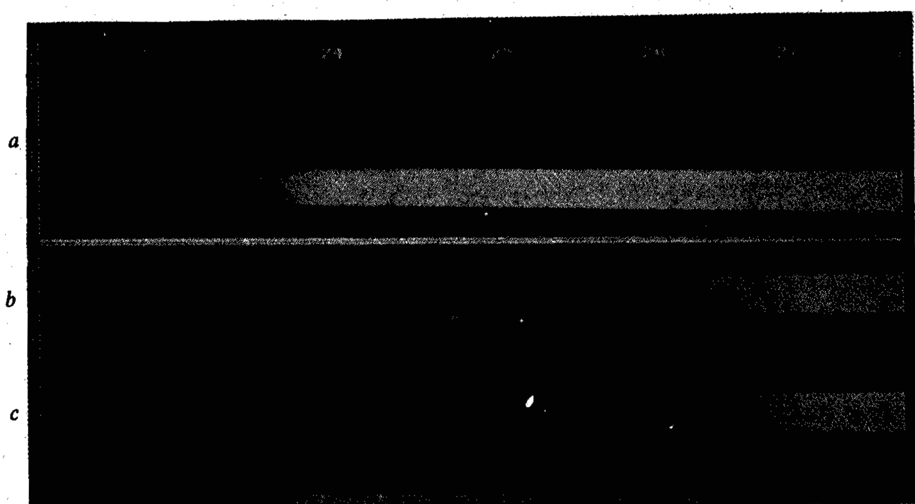

Figure 2. Ultra-violet absorption in blue-fluorescent diamond of different thicknesses. (*a*) 0·15 mm, (*b*) 0·30 mm and (*c*) 0·37 mm (after K G Ramanathan).

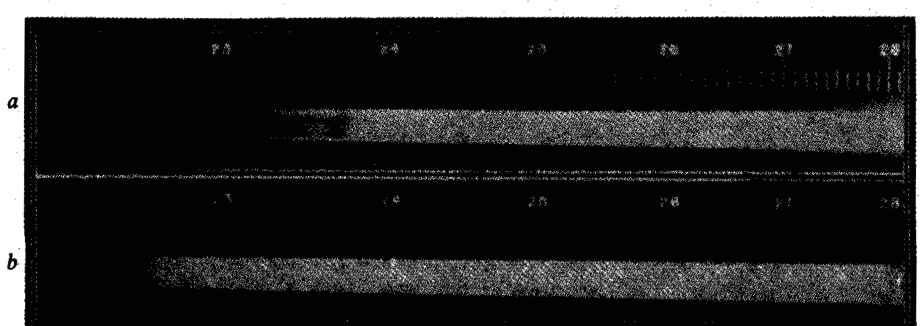

Figure 3. Ultra-violet absorption in (*a*) green-fluorescent diamond and (*b*) non-fluorescent diamond (after K G Ramanathan).

arising from the electronic line at λ 5036 and its associated vibrational transitions can be seen, though with considerably reduced intensity.

Over a hundred cleavage plates of diamond included in the Bangalore collection have been studied in the manner described. They are found to fall into three groups. *Firstly*, we have a group which exhibits "*blue*" *luminescence*. This is more or less perfectly uniform in intensity over the area of the plate, while observations through the appropriate filter show the "green" luminescence to be either weak or wholly absent. *Secondly*, we have a group which exhibits neither the blue nor the green luminescence with observable intensity. Such diamonds may, therefore, be classed as *non-fluorescent*. *Thirdly*, we have a group comprising the majority of our specimens. These exhibit geometric luminescence patterns, the nature of which varies greatly from specimen to specimen. In some diamonds, part of the area is non-fluorescent while the rest exhibits the "blue" luminescence usually accompanied by a weak green luminescence, as shown by observation through the filter. There are, however, many specimens in which the presence of both types of luminescence is evident even without the aid of the filter. Viewed through the filter which cuts out the blue luminescence, the "green" luminescence becomes apparent as parallel bands of a greenish-yellow colour traversing the plate in different directions. The assistance of the filter enables such bands to be detected in areas which show only blue luminescence without such aid.

We may summarise the position by the statement that some diamonds are non-luminescent, others exhibit only blue luminescence, while a third class exhibits a more complex behaviour in which the appearance of both the blue and green types of luminescence with varying relative intensities is a characteristic feature. The facts observed suggest that this third category of specimens may be described as being a "mixture" of the first two kinds of diamond, namely, the non-fluorescent and blue-fluorescent ones. Their juxtaposition is evident in some specimens on a simple inspection of their luminescence patterns. In other specimens, especially those showing the green luminescence prominently, the mixture appears to be on a finer scale.

3. Patterns of ultra-violet transparency

A simple technique was developed for the study of the transparency of cleavage plates of diamond to the ultra-violet radiations of the mercury arc in quartz. The most intense part, viz., the resonance radiation of wavelength λ 2537 is separated from the rest by the use of a dispersing assembly composed of a quartz prism and a pair of quartz lenses. The radiation thus isolated falls on the cleavage plate of diamond which is held attached to a thin sheet of canary-yellow or uranium glass. The fluorescence excited in the latter in the parts screened by the diamond reveals whether any of the incident radiation is transmitted by the latter. The parts that are opaque to the radiation appear dark in the fluorescent glass. Those that are

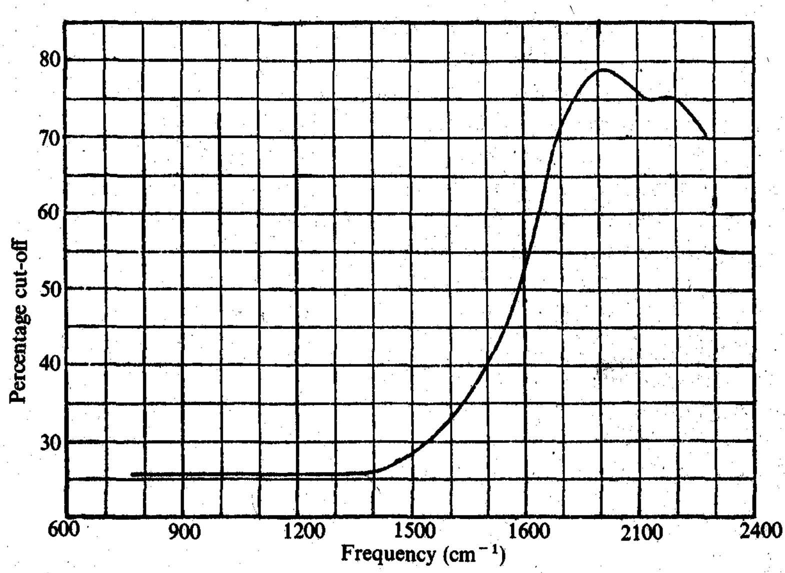

Figure 4. Infra-red transmission by non-fluorescent diamond.

transparent show the full intensity, while partial transparency is indicated by a diminished brightness of fluorescence.

Observations made by this technique reveal the correlation which exists between the ultra-violet transparency of a diamond to the λ 2537 radiation and the luminescence excited in it by ultra-violet radiation of much greater wavelengths. Non-fluorescent diamonds are completely transparent to the λ 2537 radiation. Diamonds which fluoresce blue with weak or moderate intensity are opaque to the same radiation. "Mixed" diamonds which are in part non-luminescent and in part blue-luminescent show these parts as respectively transparent and opaque to the λ 2537 radiation. The diamonds which are green-fluorescent exhibit a marked transmission, which is however distinctly inferior to that of non-fluorescent diamond. Strongly blue-luminescent diamonds show a weak but nevertheless observable transmission of the λ 2537 radiation.

It is obvious that the terms transparency and opacity used above can have a precise meaning only if the thickness of the plate and its percentage of transmission are specified. The investigations made reveal that while all diamonds show a complete cut-off for wavelengths less than λ 2250, it is possible by reducing the thickness sufficiently to observe a transmission down to that limit even in the case of diamonds which in thick layers are opaque beyond λ 3000. This effect is illustrated in figure 2 for a diamond of the blue luminescent type.

4. Patterns of infra-red transmission

Investigations reveal a precise correlation between the transparency of diamond to infra-red radiation in the 8 μ region of wavelength and its behaviour in respect of luminescence. When appropriate corrections are made for reflection at their surfaces, non-luminescent diamonds are found to be completely transparent to infra-red radiation of wavelength 8 μ, while diamonds which are blue-fluorescent with weak or moderate intensity show a strong absorption in that region. The absorption is, however, distinctly less for diamonds which exhibit an intense blue luminescence. Diamonds which exhibit a green luminescence have only a weak absorption in the 8 μ region and indeed approach the non-fluorescent diamonds in their behaviour. It should be remarked that all diamonds irrespective of their behaviour in luminescence show an absorption in the infra-red region between 7 μ and 4 μ. This is a second-order absorption due to the octaves and combinations of the characteristic frequencies of the crystal lattice.

5. Patterns of structural birefringence

We are not here concerned with the accidental birefringence due to visible flaws or inclusions in diamond, but will consider only the birefringence having a structural origin observed in plates which appear otherwise faultless. The effect, if present, is readily observed when the plate is held between crossed polaroids and viewed against a bright source of light. Since the optical effects arising from a local stress extend far beyond the point of its application, while, on the other hand, luminescence is an essentially localised phenomenon, we cannot expect a perfect

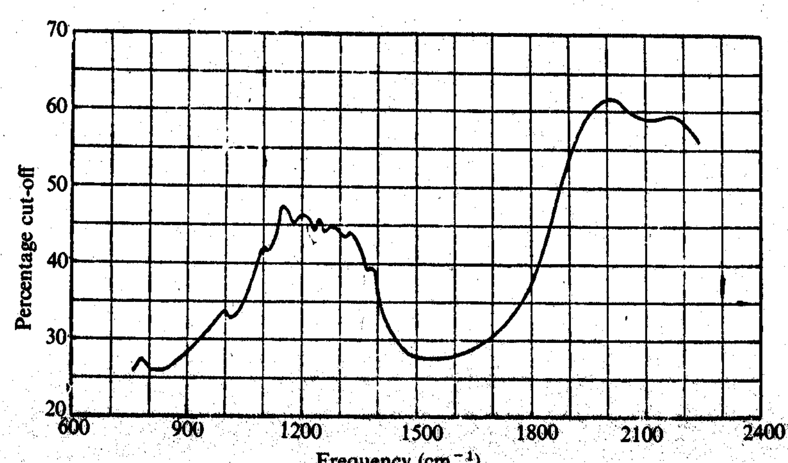

Figure 5. Infra-red transmission by green fluorescent diamond.

correspondence between the luminescence and birefringence patterns. Nevertheless, the effects observed, especially in plates of small thickness, are sufficiently striking to carry conviction. The numerous specimens available for the study enable a complete correlation to be established.

The diamond plates in the collection may be divided into three categories. *Firstly*, we have a group, which exhibits little or no birefringence and makes a near approach to the perfect optical isotropy to be expected in a cubic crystal. Such diamonds invariably exhibit "blue" luminescence, its intensity being more or less perfectly uniform over the area of the specimen. *Secondly*, we have a group of diamonds which exhibit a characteristic type of lamellar birefringence: fine

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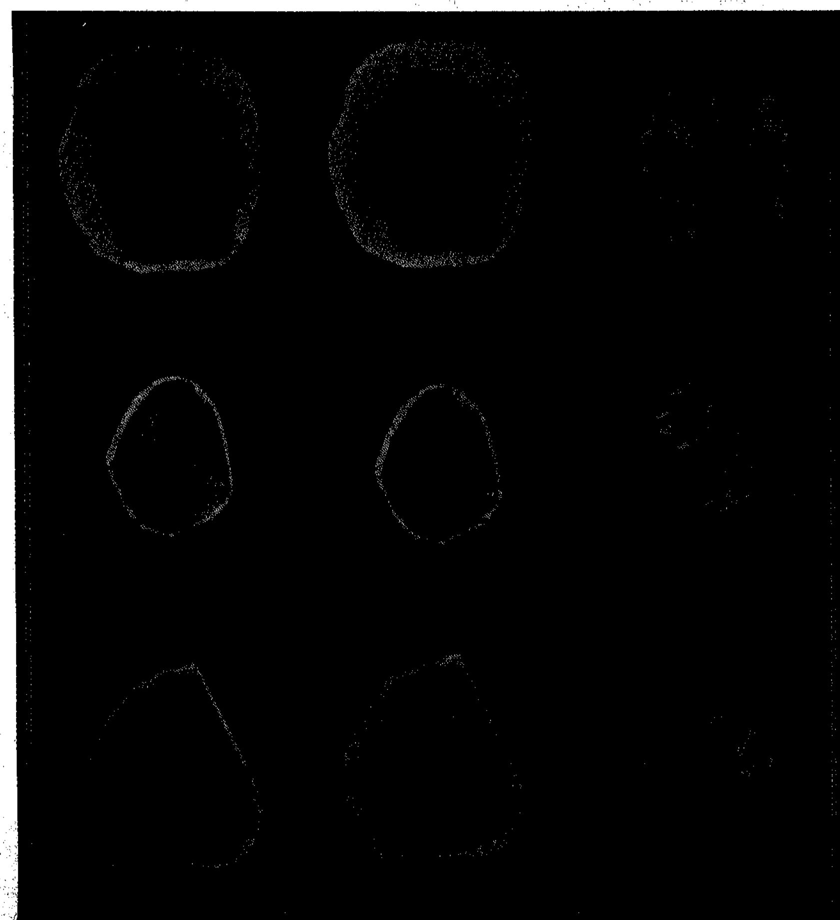

I

II

III

Figure 6. Luminescence and birefringence patterns. (A) Birefringence, (B) green luminescence and (C) blue luminescence.

streaks are seen running parallel to the octahedral of the dodecahedral planes of the crystal, the alternate layers exhibiting positive and negative birefringence as determined with the aid of a Babinet compensator. Diamonds which exhibit this type of birefringence over their entire area are invariably *non-luminescent.* *Thirdly,* we have a group of diamonds in which the birefringence is a more complex character, varying from specimen to specimen. In some specimens, extensive areas are observed where the birefringence is of the type characteristic of non-fluorescent diamonds, while in other areas the birefringence is weak or absent as in the case of "blue" luminescent diamonds. More common are the specimens in which broad bands of birefringence run parallel to each other over the area of the plate. The presence of such bands in birefringence goes hand in hand with the appearance of green or greenish-yellow bands of luminescence as already described.

Figures 1 and 6 above have been reproduced from photographs taken recently by Mr A Jayaraman and illustrate the foregoing remarks. The three photographs marked III in figure 1 illustrate a typical case of a blue-fluorescent diamond exhibiting no birefringence and no green luminescence. The three pictures marked II in the same figure represents a typical non-fluorescent diamond giving neither blue nor green luminescence but exhibiting a streaky birefringence. The three pictures marked I in the figure are photographs of a diamond which exhibits both green and blue bands of luminescence over a greater part of the area, but has a central area which is non-fluorescent. The birefringence of the plate exhibits a banded structure having a recognisable relationship to the features observed in luminescence. This is better seen in figure 6 which reproduces the patterns of blue and green luminescence and birefringence of three typical diamonds of the third or mixed category. In figure 6(I), the striking feature is the appearance of broad bands of yellow luminescence traversing the crystal. These run parallel to the broad bands of birefringence seen cutting across numerous fine streaks of the kind seen in non-luminescent diamond which appear in a different direction. A careful study of figures 6(II) and 6(III) will repay the reader for his trouble. They form excellent illustrations of the relations between luminescence and birefringence described in the foregoing pages.

6. Patterns of X-ray reflection intensity

The method of recording these patterns—also called X-ray topographs—is in principle simple and has been described in detail in the papers by Dr G N Ramachandran on the subject. It makes use of white X-rays diverging from a pin hole to obtain the Laue reflections from the full area of the cleavage plate. The reflections recorded may be either from the internal or the surface crystallographic planes, the technique necessary to obtain a undistorted picture of the crystal being different in two cases. Clear photographs can only be obtained with relatively thin plates.

The features observed in the X-ray topographs are very revealing. It is found that the weakly-blue luminescent areas make a near approach to the ideally perfect crystal structure and give the weakest Laue reflections. A greater intensity of blue luminescence results in a corresponding increase in the intensity of X-ray reflection. On the other hand, areas which are non-luminescent give extremely intense X-ray reflections. The reason for this is presumably the lamellar structure of the diamond which is evident also in the birefringence. It is found that the bands of greenish-yellow luminescence crossing the areas of blue luminescence are represented in the X-ray topographs by very bright streaks. This observation supports the inference that the "green" luminescence is a consequence of the admixture on a fine scale of the blue-luminescent and the non-luminescent types of diamond.