

## The infra-red absorption by diamond and its significance—Part IV. The non-luminescent diamonds

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### 1. Introduction

The special properties which distinguish group B diamonds from the group A or perfect diamonds have already been described and illustrated in the second part of this memoir. Photographs of individual diamonds of the group B class on a somewhat larger scale are however needed to exhibit these properties in an adequate fashion. Accordingly, enlarged pictures of two of these diamonds have been reproduced in plate I. Both of these diamonds are polished plates. While the semicircular diamond has rough edges, the other is a diamond cut into a rectangular shape and its edges as well as its faces given a good polish.

The two photographs marked (a) and (a) in plate I exhibit a property characteristic of the group B diamonds, viz., their transparency to the  $\lambda 2536.5$  radiations of the mercury arc. The radiations traversed the diamonds before reaching the fluorescent plate on which they were placed. The perfect transparency of the diamonds to the ultra-violet radiations is displayed by the fluorescence of the supporting plate in the areas covered by the diamond and the areas not so covered being of equal intensity. It may be remarked that the transparency of the diamonds of group B to the  $\lambda 2536.5$  radiations is of great importance from a practical point of view. For, it enables these diamonds to be used for studies of the spectrum of light-scattering with the resonance radiation from a water-cooled magnet-controlled mercury arc as the exciter. The second-order spectrum of light-scattering in diamond can then be successfully recorded.

As has already been noted in the first part of this memoir, the group B diamonds present a striking contrast with group A or perfect diamonds in exhibiting a readily observable birefringence. This effect was illustrated in plate I accompanying the second part of this memoir, but the photographs were on much too small a scale to reveal the real nature of the phenomenon. The photographs now reproduced as (b) and (b) in plate I are on a larger scale. Crossing the irregular dark and bright areas can be glimpsed numerous parallel streaks of varying brightness. A still larger magnification is, however, needed fully

to exhibit the character of the birefringence. In plate II is reproduced an enlargement of the birefringence pattern of a plate of diamond 14 mm by 9 mm in size and 1.47 mm in thickness. On the same scale below it is reproduced a photograph exhibiting the ultra-violet transparency of the diamond. It may be remarked neither in plate I (b) and (b) nor in plate II (b) does the smallest trace of the structures so clearly seen in the birefringence pattern come into evidence in the ultra-violet transparency, though the latter was observed and photographed under conditions entirely favourable for exhibiting the variations of transparency over the area of the diamond, had they been present.

Finally, we may draw attention to the photographs of the two diamonds marked (c) and (c) in plate I. These exhibit the complete absence of any luminescence of these diamonds under ultra-violet illumination.

## 2. The infra-red absorption spectra

The transparency of the group B diamonds in the ultra-violet region of the spectrum around  $0.25 \mu$  as contrasted with the opacity of the group A diamonds in the same region goes hand in hand with the absence in the group B diamonds of the characteristic absorption between  $7 \mu$  and  $10 \mu$  in the infra-red conspicuously exhibited by the group A diamonds. The relationships between the spectral behaviour of group A and of group B diamonds in the near ultra-violet and in the near infra-red are so clear and quantitatively so definite as to leave no doubt that the explanation in both cases has to be sought for on the same lines, viz., a fundamental difference in the structure of the diamonds in the two groups. We shall return to this subject later on and shall meanwhile describe and illustrate the infra-red behaviour of group B diamonds a little more fully than before.

Figure 1 below is the record of the percentage of transmission in the region between  $2 \mu$  and  $12 \mu$  of a non-luminescent diamond plate of thickness of 1.07 mm.

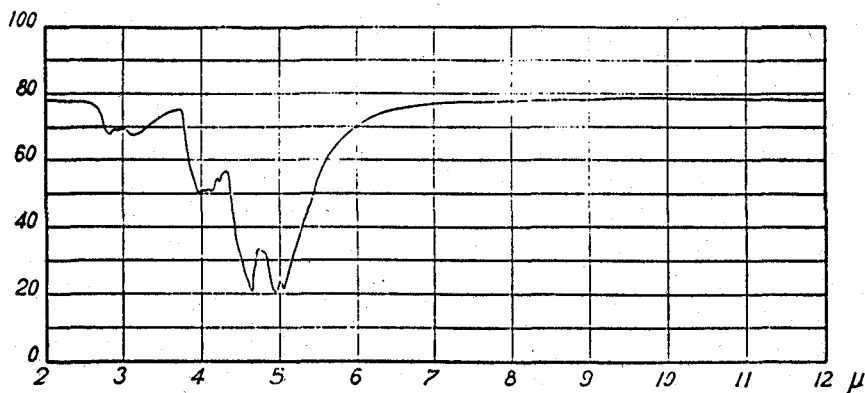


Figure 1. Transmission percentages of a non-luminescent diamond (thickness 1.07 mm).

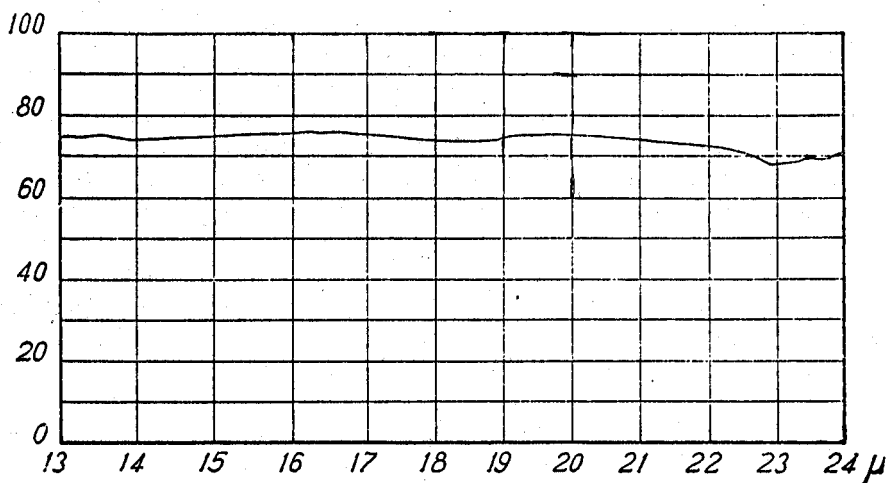


Figure 2. Transmission percentages of a non-luminescent diamond (thickness 1.07 mm).

Figure 2 is a record with the same plate for the region between  $13 \mu$  and  $24 \mu$ , and it will be noticed that this is practically featureless. From the two records taken together, it is evident that if we take into account the loss by reflection at the two faces of the plate, these diamonds exhibit a practically complete transparency over the entire wavelength range between  $7 \mu$  and  $24 \mu$ . On the other hand, between  $2 \mu$  and  $6 \mu$ , they exhibit a very marked absorption which may be identified with the second-order and third-order spectra of diamond, the first order being totally absent. We may compare these with the features noticed in the same region of wavelengths in figure 1 in the text of the third part of the memoir. That figure was the record of a perfect diamond showing all the three orders of absorption. In the region between  $2 \mu$  and  $6 \mu$ , the two figures are practically indistinguishable from each other. In particular, the sharply defined minima of transmission appear, within the limits of accuracy of the recording mechanism, at the same positions in both cases.

We may here remark that the features appearing in the second-order absorption spectra are very clearly related to the features in the first-order absorption recorded with the perfect diamonds. Some of these relationships have already been pointed out in the previous part of the memoir and we may here usefully draw attention to a few others. The steep fall in the transmission percentage which commences at  $3.75 \mu$  and terminates at  $4 \mu$  has its counterpart in the first-order absorption of the perfect diamonds which rises quickly and reaches its highest values in the wavelength range between  $7.5 \mu$  and  $8 \mu$ . The steep increase in absorption which commences at  $4.3 \mu$  and culminates at the sharp minimum at  $4.62 \mu$  in the second-order spectrum has its counterpart in the first-order in the steep increase in transmission which commences at  $8.55 \mu$  and after a

brief arrest at  $9.15 \mu$  continues again beyond that wavelength. Then again, the fall in absorption between the two sharp peaks located at  $4.62 \mu$  and  $4.95 \mu$  appearing in the second-order absorption has its counterpart in the first-order absorption in the increased transmission appearing in the region between  $9.2 \mu$  and  $9.9 \mu$ . These quantitative correspondences between the spectra of the two orders indicate that both spectra are based on the excitation of the same set of vibrational modes with discrete frequencies, though the activities of these modes in the first-order and the second-order may be altogether different. Indeed, it is clear from the facts that the fifth and sixth vibrational modes are those exhibiting the greatest infra-red activity in the second-order, whereas in the first-order absorption, when it is manifested, the first few modes are far more active than all the others.

### 3. Nature and origin of the birefringence

We may next proceed to describe and discuss the patterns of birefringence which the non-luminescent diamonds exhibit. To observe the patterns, it is a convenient procedure to place the diamond on a glass plate which can be rotated between two crossed polaroids and to view the specimen through a magnifier of suitably chosen power. As the plates of diamond are usually not very thick, it is possible to use a high-power lens and this is indeed necessary to obtain a correct idea of the characters of the birefringence.

All the diamonds of the non-luminescent class in the author's collection have been examined and their birefringence patterns have been found to exhibit certain general characteristics. The restoration of light which is observed is not uniform over the area of the diamond but is seen resolved into a series of parallel bands which are alternately dark and bright. These bands run continuously across the diamond from periphery to periphery. In nearly all the cases, one notices two sets of such bands cutting across each other, but they are not always equally prominent. As the diamond is rotated between the crossed polaroids, each set of bands disappears when it is parallel to the plane of polarisation of the polariser or of the analyser, and is seen most clearly when it bisects the angle between them. In the cases when the two sets of bands cut each other at right angles, they appear and disappear simultaneously as the diamond is rotated.

Examined under the higher magnifications, the bands in the pattern appear as bundles of fine thread-like lines of light. By reason of their criss-crossing, the pattern has a lace-like appearance. Due to the criss-crossing also, the threads exhibit a wavy outline and are not perfectly straight. Some idea of these effects can be gathered from the photographs reproduced in plates I and II accompanying this part of the memoir.

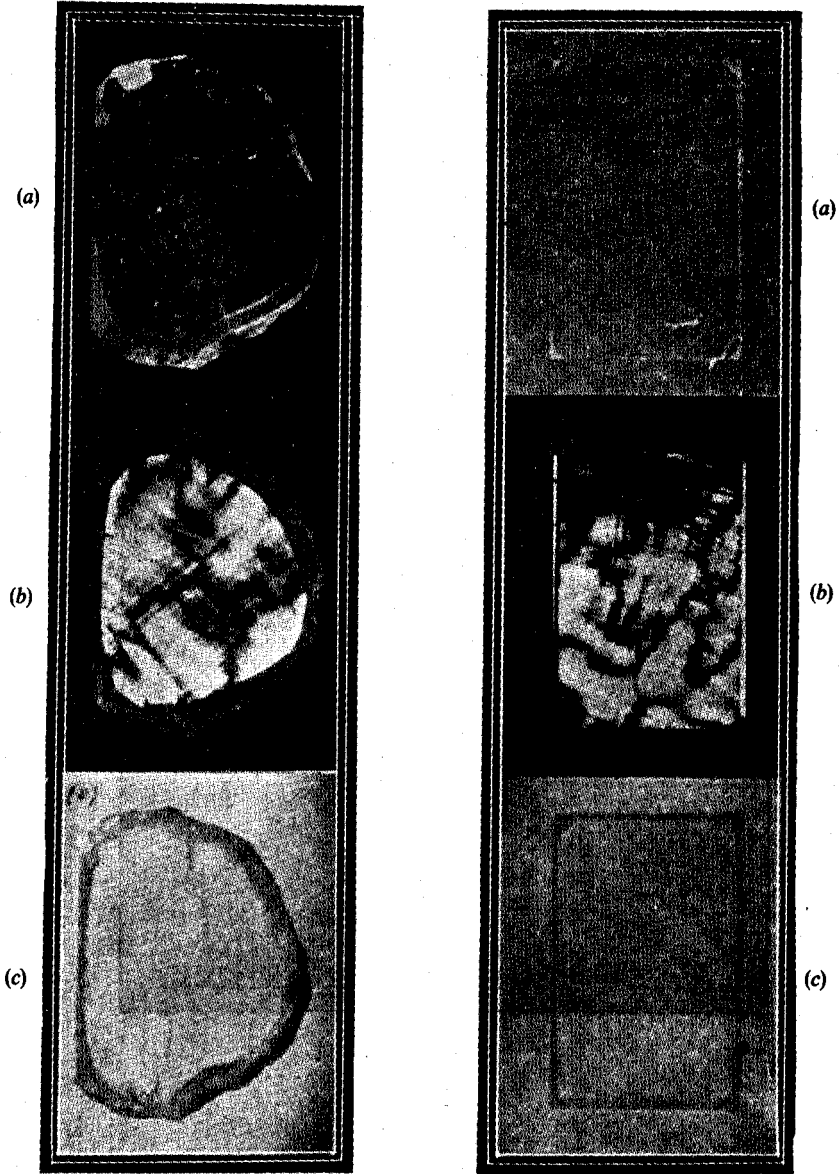
The mutual orientation of the two sets of bands and their alignment with respect to the crystal structure are obviously matters of importance. In some of the plates, they are seen to be mutually perpendicular, while in others they run at

an angle to each other which is approximately sixty degrees. To determine their crystallographic orientation, it is necessary to know the orientation of the plate of diamond in which they are seen. In this connection a reference should be made to the thorough and painstaking studies carried out by G N Ramachandran on the birefringence of diamonds (*Proc. Indian Acad. Sci.*, A24, 65, (1946)). Ramachandran's investigations covered not only the diamonds of the non-luminescent class but also the composite diamonds which will form the subject of the fifth part of this memoir. Using a petrographic microscope in conjunction with a Federov universal rotating stage, he discovered that the structural birefringence observed in diamond has its origin in the presence of laminations in the structure which are orientated parallel to the octahedral planes or to the dodecahedral planes of the crystal or to both. He also determined the magnitude of the birefringence in various cases. His observations with the non-luminescent diamonds were particularly significant. They showed clearly that the birefringence pattern exhibited by such plates when viewed normally between crossed polaroids arises from a lamellar structure of the kind referred to. Why such a lamellar structure is present in diamonds of this class associated with the various other properties described earlier is a question the answer to which is evidently to be found in the basic facts of the architecture of the diamond crystal.

#### 4. Summary

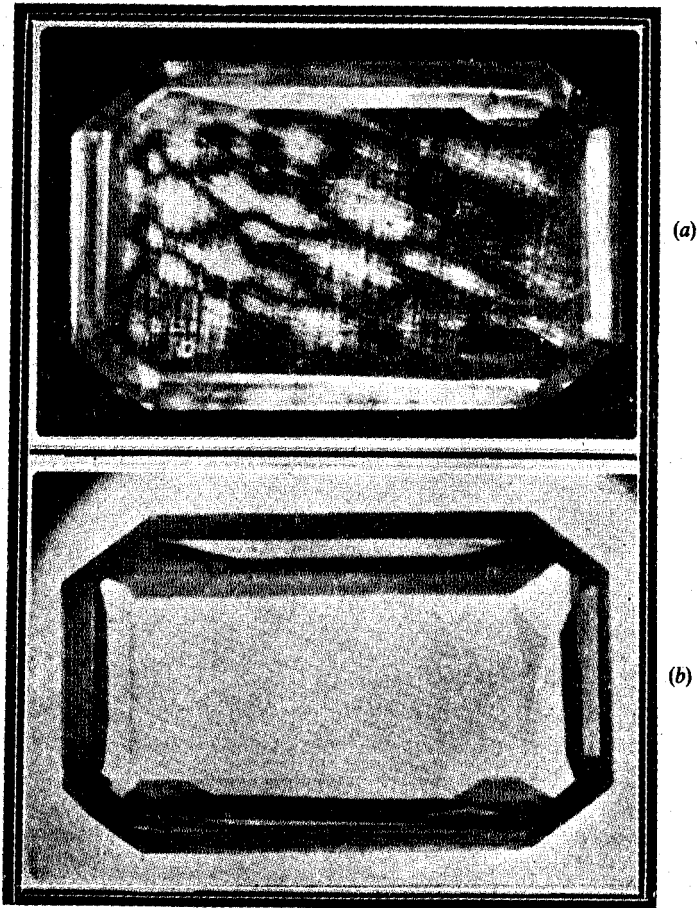
The non-luminescent diamonds exhibit the infra-red absorption spectra of the second- and third-orders, while the first-order is totally absent. A critical examination of the spectrographic records shows clearly that the second-order spectrum is based on the same vibrational modes with discrete frequencies as the first, the activities of the modes, however, being different in the two cases.

The non-luminescent diamonds exhibit a type of birefringence which arises from the presence in them of laminations orientated parallel to the octahedral planes or to the dodecahedral planes of the crystals or to both.



Two non-luminescent diamonds.

Plate I



(a) Birefringence and (b) ultra-violet transparency.

Plate II