Proc. Indian Acad. Sci. A55 20-23 (1962)

The infra-red absorption by diamond and its significance—Part V. The composite diamonds

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received December 12, 1961

1. Introduction

The many striking differences in the physical behaviour of the perfect diamonds and of the non-luminescent diamonds are a sufficient demonstration that their crystal structures are fundamentally different. Nevertheless, their structures must be closely related to each other. For, they have infra-red absorption spectra which in the second and third orders are indistinguishable, while the first order is present only for the perfect diamonds and absent for the non-luminescent ones. Spectroscopic theory considered in the light of the mechanism of infra-red absorption gives us the clue to the origin of these differences. But the differences are evidently not of such a nature as to preclude the two structures appearing in juxtaposition in one and the same diamond. Indeed, this is so frequently the case that the composite diamonds, as we shall call them, form the large majority amongst the polished plates of diamond in the writer's collection. As has already been mentioned, about ten per cent of the specimens are perfect diamonds, another ten per cent are non-luminescent ones, while the remaining eighty per cent are composite diamonds.

2. Proofs of the composite nature

The easiest and also the most convincing demonstration that any particular specimen is a composite diamond is furnished by observations of its ultra-violet transparency. The technique of such observations has already been described. The $\lambda 2536.5$ radiation of a mercury arc lamp passes through the diamond and is then incident on a fluorescent plate in close contact with it. The luminescence of the plate then immediately reveals the variations in the transparency of the diamond over the different parts of its area.

Another very instructive demonstration of the composite nature of a diamond is furnished by observations of the luminescence excited by ultra-violet radiation.

C V RAMAN: PHYSICS OF CRYSTALS

Such luminescence may be observed either through a filter which transmits only the blue end of the spectrum or through a yellow filter which cuts out the blue and green altogether and transmits only the yellow, orange and red. The characters of the luminescence are found to be totally different as observed through the two filters and these differences are very revealing in respect of the structure of the diamond.

Still another method of observation is to view the diamond between crossed polaroids against a bright source of light. A perfect diamond would, of course, exhibit no birefringence. A non-luminescent diamond, on the other hand, would exhibit a birefringence of the kind described in the fourth part of this memoir, but no trace of the structure thus revealed would appear in its ultra-violet transparency. Composite diamonds, on the other hand, exhibit birefringence patterns of which the features can be recognised both in the ultra-violet transparency patterns and in the patterns of luminescence, and especially in the latter as seen through a yellow filter.

Seven polished plates of diamond in the writer's collection have been photographed by each of the four methods described above. These photographs are reproduced respectively in plates I–VII. In each case, the picture marked (a)exhibits the variations of the ultra-violet transparency, that marked (b) exhibits the blue luminescence, that marked (c) the yellow luminescence and that marked (d) the birefringence pattern as observed with a chosen orientation of the diamond between the crossed polaroids.

The composite nature of a diamond is also revealed by the spectrographic record of its infra-red transmission. Figures 1 and 2 below reproduce these records respectively for the two plates of diamond of which the photographed patterns appear in plate I and in plate II. From plate I (a) and (b), it is evident that the greater part of the oval area of this diamond is of the non-luminescent kind





INFRA-RED ABSORPTION BY DIAMOND-V



Figure 2. Infra-red absorption by composite diamond (thickness 0.81 mm).

transparent in the ultra-violet. Two sharply-defined areas, one large and another small, having the form of equilateral triangles are however seen in these figures which exhibit an opacity in the ultra-violet as well as a bright blue luminescence. The preponderance of non-luminescent diamond in this specimen is very clearly exhibited by the spectrographic record reproduced as figure 1. This shows the first-order absorption between 7μ and 10μ only very weakly as compared with the absorption of the second order.

On the other hand, it is evident from plate II (a) and (b) that a large part of the area of the diamond figured in it is ultra-violet opaque and blue-luminescent, while the rest is ultra-violet transparent and non-luminescent. It is, therefore, not surprising that in figure 2 which is its spectrographic chart, the first-order infrared absorption between 7μ and 10μ is more strongly manifested that in figure 1.

3. The geometric character of the patterns

Examining in detail the ultra-violet transparency and blue-luminescence patterns of the several diamonds reproduced in plates I-VII, the most striking features exhibited by them are firstly the correlations between these properties manifest in the patterns, and secondly the geometric character of the patterns which is clearly related to the orientation of the octahedral or dodecahedral planes in the crystal with respect to the surfaces of the plate.

A scrutiny of the photographs reveals other features calling for mention. One of them is the kind of luminescence not exhibited by the perfect diamonds which has been described above as yellow luminescence. The pattern of yellow luminescence is usually, though not always, different from the pattern of blue luminescence. This is evident, for example, on a comparison of figures (b) and (c) in plate I, plate

III, plate V and plate VII. The yellow luminescence often takes the form of a set of parallel bands as for example in plate I, plate III, plate V and plate VII. Finally, we may draw attention to the fact that the birefringence patterns of the composite diamonds have a configuration not dissimilar to and indeed often resembling closely the other three patterns of the respective diamonds.

We shall now briefly consider what these facts of observation signify. It is well known that diamonds are usually found in nature as complete single crystals which are ordinarily not of any great size. In these circumstances, the composition and properties of any one crystal may be expected to be uniform within its interior. The actual position is rather different, as we have seen. In about ten per cent of the cases, we find diamond to exhibit a definite set of properties and in another ten per cent of the cases a different set of properties. Moreover, in a large majority of cases the crystal exhibits regions in its interior where one kind of diamond appears and other regions where the other kind appears. Further, the regions where the two kinds appear are bounded by crystallographic planes of importance, viz., the octahedral or the dodecahedral planes. The only reasonable explanation that can be put forward for this situation is that the crystal structure of diamond may assume one or another of certain alternative forms which are different but nevertheless resemble each other sufficiently to appear in juxtaposition in the same crystal. All the phenomena with which we have been confronted in our studies have to be explained on this basis.

4. Summary

Photographs are reproduced of seven plates of composite diamond exhibiting in each case the variations over its area of the ultra-violet transparency, the blue luminescence, the yellow luminescence and the birefringence. The composite nature of the diamond is also demonstrable by the spectrographic record of its infra-red absorption. The significance of the geometric character of the patterns and of their mutual relationships is discussed.



- (d) Birefringence

Plate I



(b) Blue luminescence(d) Birefringence

Plate II



(d) Birefringence

Plate III



(a) Ultra-violet transparency(c) Yellow luminescence

Plate IV



(a) Ultra-violet transparency (c) Yellow luminescence



Plate V



(a) Ultra-violet transparency(c) Yellow luminescence

(b) Blue luminescence(d) Birefringence

Plate VI



Plate VII