

THE INFRA-RED ABSORPTION BY DIAMOND AND ITS SIGNIFICANCE

Part II. A General Survey of the Results

BY SIR C. V. RAMAN

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

Received November 28, 1961

1. INTRODUCTION

WE now proceed to indicate in broad outline the results which have emerged from the investigations envisaged in the first part of this memoir. The outstanding facts of the subject will be stated and illustrated in an appropriate manner.

A critical examination of the optical behaviour of all the one hundred polished plates of diamond in the writer's collection reveals that they fall into three groups. Two groups of diamonds which we shall designate here as group A and group B each form about ten per cent. of the entire number of specimens. The remaining eighty per cent. of the diamonds will here be designated as group C. The diamonds in group A exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. The diamonds in group B also exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. But the properties of the diamond in group A and the properties of the diamond in group B are so strikingly contrasted that the observer is obliged to infer that they represent fundamentally different forms of diamond. That this is actually the case and that the crystal structures of the diamonds in group A and group B are indeed dissimilar, is demonstrated by the characters exhibited by the infra-red absorption spectra of the two groups of diamond. Their spectral behaviours are completely identical in some respects and completely dissimilar in other respects. Considered in conjunction with the other differences alluded to, it is clear that the facts admit of no explanation other than that we are here concerned with basic differences in crystal architecture. What these differences are is indicated in an unmistakable fashion by the spectroscopic observations.

The remaining eighty per cent. of the diamonds which we have classed together as group C are shown by the studies to be *composite diamonds*, in other words, diamonds in which the structures characteristic of group A and the structures characteristic of group B are present side by side in the same specimen in juxtaposition. This is not an inference from theory but is a statement of actual facts of observation. The geometric patterns of various sorts which these composite diamonds exhibit are visual evidences that over the area of any one cleavage plate of diamond, there are some parts which exhibit the characteristic properties of the diamonds of group A while the other parts exhibit the characteristic properties of diamonds of group B. Moreover, these parts are distributed over the area in regular crystallographic patterns which by themselves conclusively demonstrate that the diamonds of group A and the diamonds of group B are distinct crystallographic entities different from each other.

2. THE PHYSICAL BEHAVIOUR OF GROUP A AND GROUP B DIAMONDS

Ten diamonds of group A in the writer's collection and eight diamonds of group B have been set side by side and examined under identical conditions. The photographs of the two groups of diamond reproduced and exhibited alongside of each other in Plate I were recorded simultaneously and with identical exposures and hence are strictly comparable with each other. The infra-red transmission curves of the largest diamond in group A and of the largest diamond in group B were also recorded in the NaCl range of the Leitz infra-red recording spectrophotometer and are reproduced respectively as Fig. 1 and Fig. 2 in the text below.

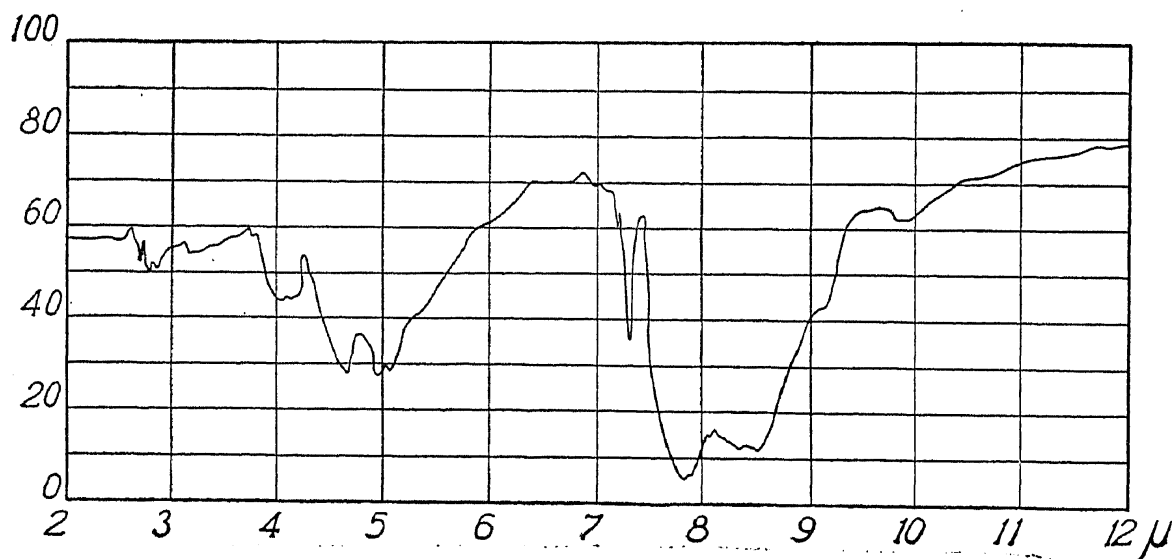


FIG. 1. Infra-Red Transmission of Group A Diamond (Thickness 1.01 millimetre).

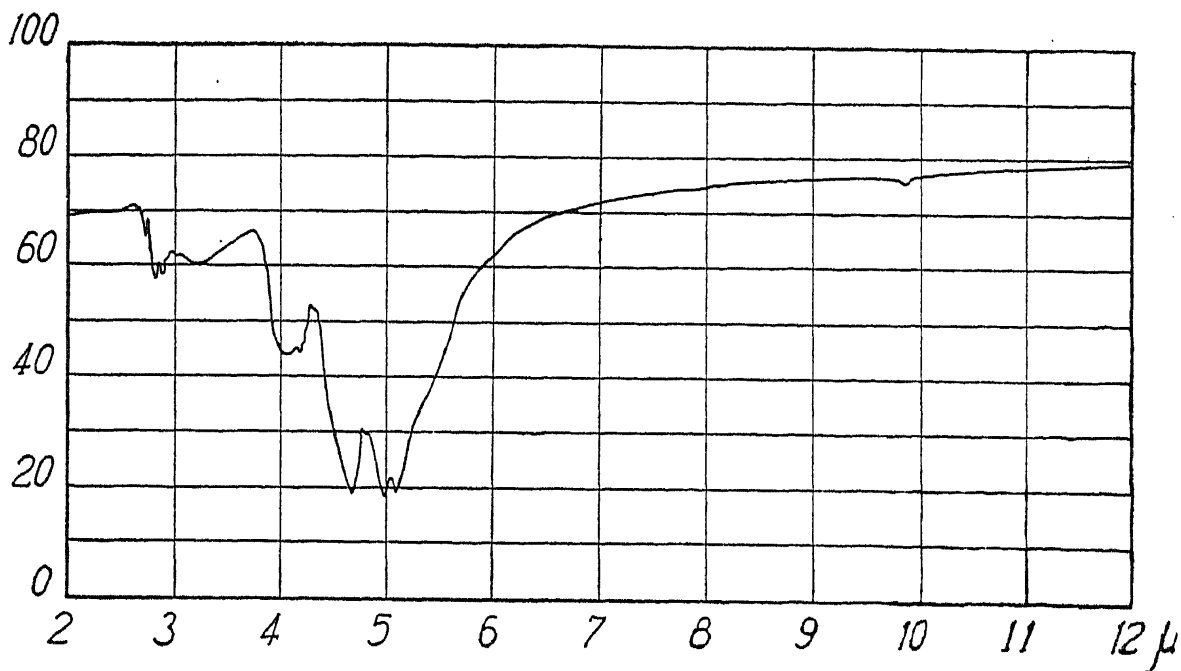


FIG. 2. Infra-Red Transmission of Group B Diamond (Thickness 1.06 millimetre).

Turning to the photographs reproduced in Plate I, we remark that the two pictures marked (a) and (a) respectively on its left and right sides exhibit the appearance of diamonds belonging respectively to the two groups as viewed between crossed polaroids against a bright white source of light. While the edges of the ten diamonds of group A are visible by reason of the light refracted at their peripheries, the plates themselves appear quite dark. In other words, the diamonds of group A are non-birefringent, and may hence be described as *truly isotropic and optically perfect diamonds*. On the other hand, all the eight diamonds of group B exhibit a marked restoration of light as seen between crossed polaroids. The patterns of birefringence which they exhibit differ from diamond to diamond both in respect of intensity and their geometric configuration, but in none of the eight specimens is the birefringence absent. Thus, we are justified in stating that the exhibition of a visible birefringence is a general characteristic of the diamonds of group B. We shall revert later to a more detailed consideration of the specific features of such birefringence.

The same ten diamonds of group A and eight diamonds of group B were examined for their transparency in the near ultra-violet region of the spectrum by the methods already described and explained in the first part of this memoir. They were placed on sheets of uranium-tinted glass and their transparency or opacity (as the case may be) in the near ultra-violet region of the spectrum stands immediately revealed by the luminosity of those sheets, as is seen from the photographs reproduced in Plate I and marked (b) and (b) respectively on the left and right of the pictures. It will be seen that all the diamonds of group A exhibit complete opacity, while those of group B are highly transparent to the part of the spectrum under consideration. As between them-

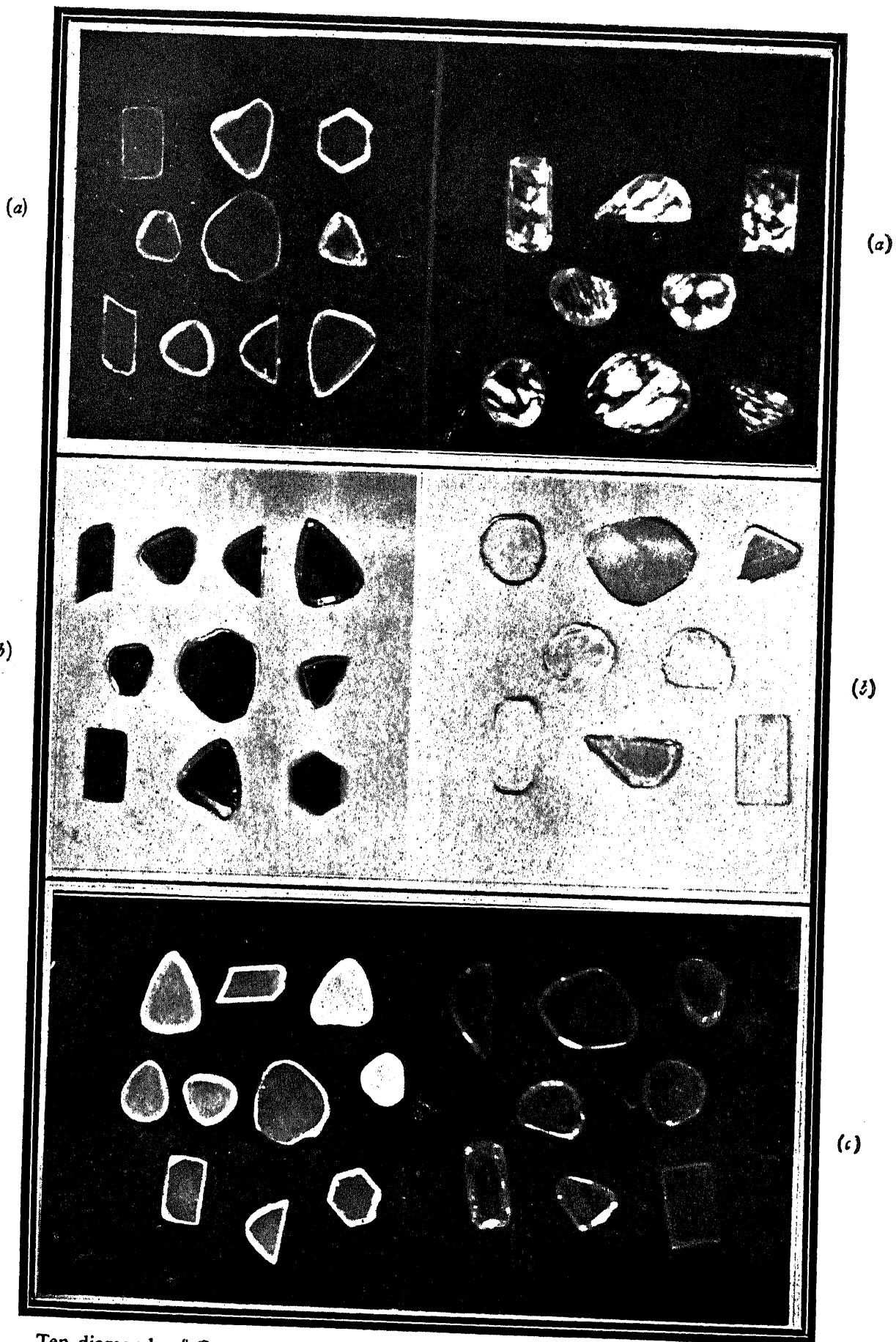
selves, the eight diamonds of group B exhibit some differences in respect of their transparency. These differences are ascribable to a slight yellowish tinge exhibited by some of the specimens, while the others are perfectly colourless.

Finally, the photographs reproduced in Plate I and marked (c) and (c) respectively on the left and the right exhibit the behaviour of the same ten diamonds of group A and the same eight diamonds of group B in respect of the luminescence excited by the incidence of ultra-violet radiation. The two groups of diamond were placed side by side on a sheet of ordinary glass and strongly illuminated by the light of three mercury lamps enclosed in Wood's glass which cut out all the visible light except some deep red. The glass sheet with the diamonds adherent to it was photographed through a cell containing an aqueous solution of sodium nitrite. This filter cuts off the scattered or reflected ultra-violet light and allows only the visible luminescence to come through. It will be seen from the Plate that all the diamonds of group A exhibit a visible luminescence but with very different intensities in the different diamonds. The colour of the luminescence as actually observed was a clear blue in all cases. On the other hand, all the diamonds of group B are seen to be definitely non-luminescent.

We may sum up the information exhibited by Plate I as follows: The diamonds of group A are isotropic and optically perfect diamonds. They are opaque to ultra-violet radiation less than 0.3μ in wavelength, and exhibit a visible blue luminescence under ultra-violet irradiation but of varying degrees of intensity. On the other hand, the diamonds of group B exhibit a readily observable birefringence, are transparent to ultra-violet radiation of wavelengths between 0.3μ and 0.25μ , and are non-luminescent. These properties of the two groups of diamond go hand in hand with the differences in the behaviour towards infra-red radiation exhibited in Figs. 1 and 2 in the text above. A detailed discussion of the features noticed in these spectrographic records will appear in later parts of this memoir. It will suffice here to draw attention to some of their outstanding features. The thickness of the group B diamond whose record is reproduced in Fig. 2 is distinctly greater than that of the group A diamond whose record is reproduced in Fig. 1. Due allowance being made for the effect of the greater thickness on the percentage transmission curves, it will be seen that in the spectral region between 2μ and 6μ , the two diamonds exhibit features which are indistinguishable from each other. On the other hand between 6μ and 12μ , the behaviour of the two diamonds is totally dissimilar. The group A diamond exhibits an absorption which goes up steeply beyond 7μ and a whole series of absorption maxima

Group A

Group B



Ten diamonds of Group A and eight of Group B examined under similar conditions.



appear thereafter, while on the other hand, the group B diamond is highly transparent throughout this range. Any attempt to explain these facts should necessarily take into account the facts revealed by the photographs reproduced in Plate I and should be based on sound physical reasoning and not on *ad hoc* suppositions of the kind which one finds frequently in the literature and which can only be described as completely irrational.

3. SUMMARY

Approximately ten per cent. of the total number of diamonds form group A and another ten per cent. group B. These two groups exhibit highly contrasting characters. Group A diamonds are isotropic and optically perfect, are opaque to ultra-violet of wavelengths less than 0.3μ and exhibit a visible blue luminescence. Group B diamonds are visibly birefringent, their transparency extends well beyond 0.3μ and they are non-luminescent. The two groups differ strikingly in their infra-red behaviour. These facts taken in conjunction indicate that the two groups of diamond differ fundamentally in their crystal structure.