VARIATIONS IN THE ABSORPTION OF INFRA-RED RADIATION BY DIAMOND

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1. Introduction

The investigation by Reinkober (1911), of the infra-red absorption spectrum of diamond established that diamonds are not all alike with regard to their infra-red absorption. He noticed the presence of the three bands at 3·0, 4·1 and 4·8 μ in the absorption spectrum of his diamond but failed to record the intense band at 8 μ previously registered by Angstrom (1892) and Julius (1893). More recently Robertson, Fox and Martin (1934), after a detailed investigation of the infra-red absorption of a large number of diamonds, were led to classify the substance into two types I and II, the type I showing the absorption band round about 8 μ which is absent in type II. Recent investigations at this Institute (Raman, *et al.*, 1944) of the various other physical properties of diamond, have however shown that they cannot be described as falling into one or the other of two types only, but show a more diversified behaviour. It appeared probable therefore that the infra-red absorption of diamond should similarly show a diversified behaviour. The present investigation was undertaken to test this idea, and also to obtain quantitative data on the strength of the 8 μ absorption band of diamond for numerous samples. It was also desired to obtain quantitative data on the strength of the absorption band between 4 and 5 μ for some specimens and to see whether any variation, if present, was confined to the 8 μ region alone or also to the region between 4 and 5 μ. The work was greatly facilitated by the use of the flat polished cleavage plates of diamond of which numerous examples were available in Sir C. V. Raman's collection. The present investigation has shown that the strength of the 8 μ infra-red absorption band varies greatly from diamond to diamond, and that such variations are correlated with the behaviour of the specimen in respect of ultra-violet absorption and luminescence. No such variation has, however, been noticed in the region 4–5 μ. Another striking result established by the present research is the existence of patterns of infra-red transparency in individual cleavage plates of diamond closely analogous to the patterns of luminescence and of ultraviolet transparency (Raman, *et al.*, 1944) exhibited by them.

2. Experimental Arrangements

As a source of continuous infra-red radiation, an electrically heated globar element has been used. For detecting the radiation, a thermocouple with a receiver 1·5 millimetre square, which was made in this laboratory, was used in combination with a Hartmann and Braun galvanometer having a coil resistance of 5 ohms and sensitivity of 0·8 millimetre deflection on a scale at one metre distance for one microvolt. In order to monochromatise the radiation for making measurements of absorption coefficients, two different arrangements (*a*) A Residual-ray apparatus and (*b*) An Infra-Red monochromator, have been used.

(*a*) *The Residual Ray Apparatus.*—In this arrangement which is useful only for investigating the 8 μ region, the residual ray band of crystalline quartz which lies in the wavelength range 7·7–9·5 μ is made use of. The radiation from the globar source was reflected two times from surfaces of crystalline quartz at nearly 20° incidence. The radiation thus partially monochromatised by reflections from quartz, was allowed to pass through a one-millimetre aperture before finally being focussed on the thermocouple. The diamond was kept close to the aperture so that the radiation passed through it before falling on the aperture. After passing through the aperture and before falling on the thermocouple the radiation was made to pass through a one-centimetre filter of clear, transparent fluorspar crystal which served to cut off the 20 μ residual rays from quartz and also to further monochromatise the radiation. The radiation finally obtained, occupies a position in the spectrum approximately the same as the 8 μ absorption band of diamond.

(*b*) *The Infra-Red Monochromator.*—This is a rocksalt-prism spectrometer which was recently constructed in this laboratory. The two concave spherical aluminized mirrors used in the instrument are of 9 centimetres clear aperture and 25 centimetres focal length. The 54° prism of rocksalt also made in this laboratory, has got refracting faces about 5 centimetre square. The instrument was used to determine quantitatively the absorption coefficients of a few representative specimens of widely different behaviour in the region 4–5 μ and also to check up by an independent method the results obtained with the Residual-ray apparatus. Using a wide slit (0·5 millimetre for 4–5 region and 1·5 millimetres for the 8 μ region), the monochromator was first adjusted at the peak of either the 4–5 μ band or the 8 μ band of diamond whichever was to be investigated. Then keeping the adjustments fixed, the absorption coefficients were determined for some representative specimens.

For focussing the radiation, wherever not stated, concave (spherical) aluminized mirrors having very high reflectivity for the infra-red were used. The deflections of the galvanometer, which, with both the apparatus, were of the order of a few millimetres could be conveniently measured with a travelling microscope to an accuracy of 0·05 millimetre. The procedure for determining the absorption coefficients consisted in noting the deflections of the galvanometer with and without the diamond in the path of the radiation. For diamonds which do not show appreciable variations of absorption within their areas, the transmission was taken to be the mean of three or more values obtained through different parts within the area of the specimens. Diamonds showing appreciable variations of transparency within their areas were investigated carefully by moving them before the one millimetre aperture of the Residual-ray apparatus between successive readings and noting the transmission and also the portion of the diamond which covered the aperture during each reading. Altogether, thirty-seven cleavage plates of diamond have been examined for their absorption in the 8 μ region.

Reinkober (1911) has shown that the reflecting power of diamond for reflection from a single surface, is 16% ($r = 0{\cdot}16$) of the incident energy, for the entire infra-red region between 1·0 to 18·0 μ. The theoretical value of the reflecting power calculated from the expression derived on the basis of the electromagnetic theory is also 17%. Hence it can be safely assumed that if infra-red radiation in the 4–5 μ or 8 μ region is incident on a plate of diamond, 16% of the energy is lost at every reflection taking place from a diamond-air surface in a direction perpendicular to it. If the diamond be considered to have a thickness t centimetres and an absorption coefficient k per centimetre, then the transmitted fraction of the incident energy σ is given by

$$\sigma = (1 - r)^2 e^{-kt},$$

considering the effect of two reflections only. The quantities σ, r and t being known for a plate of diamond, the coefficient of absorption k per centimetre can be calculated. Since the radiation used for the measurements is not strictly monochromatic, but has a varying intensity distribution in itself, k is the mean coefficient of absorption for this band.

3. Results

The results obtained with different types of diamond are entered in Table I together with the ultraviolet transmission limits of the diamonds for short photographic exposures and the nature of luminescence of the diamond. The results entered in the table can be summarised as follows:—

TABLE I

Absorption and Luminescence of Diamonds

New Catalogue Number	Thickness	Infra-Red Absorption Coefficient in the 8μ Region	Ultraviolet Transmission Limit for short Photographic Exposures	Colour and Intensity of Luminescence
	mm.	per cm.	A.U.	
N. C. 93 ..	0·56	16·5	2950	Weak Blue
N. C. 94 ..	0·59	15·1	3030	Do.
N. C. 98 ..	0·47	14·9	—	Do.
B_3 ..	1·37	12·0	—	Do.
N. C. 99 ..	0·58	10·7	2900	Do.
N. C. 78 ..	1·39	10·2	3100	Moderate Blue
N. C. 177 ..	0·82	10·0	—	Do.
N. C. 77 ..	0·97	9·2	3010	Weak Blue
N. C. 75 ..	0·94	8·6	2950	Do.
N. C. 71 ..	0·79	8·2	2910	Moderate Blue
N. C. 80 ..	0·89	7·6	—	Do.
N. C. 157 ..	0·59	7·6	—	Weak Blue
N. C. 176 ..	1·18	7·0	—	Moderate Blue
N. C. 74 ..	0·66	6·8	—	Weak Blue
N. C. 92 ..	0·61	6·7	2910	Do.
N. C. 70 ..	2·20	6·5	2950	Intense Blue
N. C. 179 ..	1·18	6·2	—	Moderate Blue
N. C. 79 ..	1·20	5·4	2800	Intense Blue
N. C. 73 ..	0·68	5·4	2830	Weak Blue
N. C. 62 ..	1·50	5·0	2700	Intense Blue
N. C. 126 ..	0·78	4·4	2270	Faint
N. C. 127 ..	0·66	4·0	2660	Do.
N. C. 117 ..	0·87	3·3	2680	Do.
N. C. 122 ..	0·74	1·9	2700	Yellow
N. C. 120 ..	0·78	1·7	2300	Do.
N. C. 124 ..	0·94	1·7	2260	Non-fluorescent
N. C. 121 ..	0·54	1·5	2260	Strong-Yellow
N. C. 89 ..	1·10	1·3	2260	Non-fluorescent
N. C. 125 ..	0·66	0·6	2300	Do.
N. C. 178 ..	0·85	0·6	2250	Do.
N. C. 174 ..	1·62	0·4	2250	Do.
N. C. 60 ..	1·27	0·2	2250	Do.
N. C. 123 ..	0·63	$\lesssim 0$	2260	Do.

— indicates not investigated.

(*a*) The diamonds which absorb most strongly in the region of the 8μ band are those which show a weak blue fluorescence. The infra-red absorption tends to be less for the strongly blue-luminescent diamonds. The absorption coefficient exhibits a wide variation ranging between 5·0 per centimetre and 16·5 per centimetre.

(*b*) Diamonds showing a yellow luminescence or a mixed type of luminescence exhibit infra-red absorption coefficients which are much less than those of blue-luminescent diamonds, the values lying between 2·0 per centimetre and 4·0 per centimetre.

(*c*) Non-luminescent diamonds are highly transparent in the 8 μ region, the loss of energy when this radiation passes through a plate being mostly due to reflection.

(*d*) Allowing for the effect of varying thickness, it is seen that the ultra-violet transmission limit of a diamond progresses further and further into the ultraviolet as the diamond becomes less and less absorbing in the 8 μ region of the infra-red.

In the following Table (II) are reproduced the results of absorption coefficient measurements in the region 4-5 μ together with those obtained for the 8 μ region.

TABLE II

Comparison of Infra-Red Absorptions in the 4–5 μ and 8 μ Regions

New Catalogue Number	4–5μ Region	8 μ Region	
	Monochromator	Monochromator	Residual-Ray Apparatus
	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
N. C. 60 ..	6·8	0·3	0·2
N. C. 174 ..	7·0	—	0·4
N. C. 73 ..	7·7	—	5·4
N. C. 74 ..	7·6	8·7	6·8
N. C. 71 ..	7·1	11·0	8·2
N. C. 77 ..	7·0	—	9·2
B_3 ..	6·8	13·0	12·0
N. C. 94 ..	7·5	—	15·1

— indicates not investigated.

In Table II the values in the second column remain constant within the limits of experimental error. In columns three and four containing the mean absorption coefficients for the 8μ region measured with the Infra-Red monochromator and the Residual-ray apparatus respectively, the values exhibit a wide range of variation. It can be seen that due to the comparative narrowness of the band used with the monochromator, the values given there are higher than those obtained with the Residual-ray apparatus.

4. Patterns of Infra-Red Transparency

Four diamonds out of the thirty-seven cleavage plates examined have been observed to show striking variations in their infra-red transparency within their area. An attempt has been made in Fig. 1 to represent the variations in infra-red transparency for the four diamonds together with their luminescence and ultraviolet transparency patterns. The drawings of

infra-red transparency-variation, made from a visual examination of certain regions of the diamond chosen to cover their full area, are reproduced just to show their similarity to the luminescence and ultraviolet transparency patterns and are not to be regarded as an exact representation of the absorption patterns. However, methods have been devised in this laboratory to obtain photographically the variations in infra-red transparency of diamonds, but as the details have not yet been fully worked out, it is hoped to investigate the question at some later date.

Out of the four diamonds investigated at present, the cleavage plate N.C. 82 (see Fig. 1) shows both blue and yellow luminescence. The central

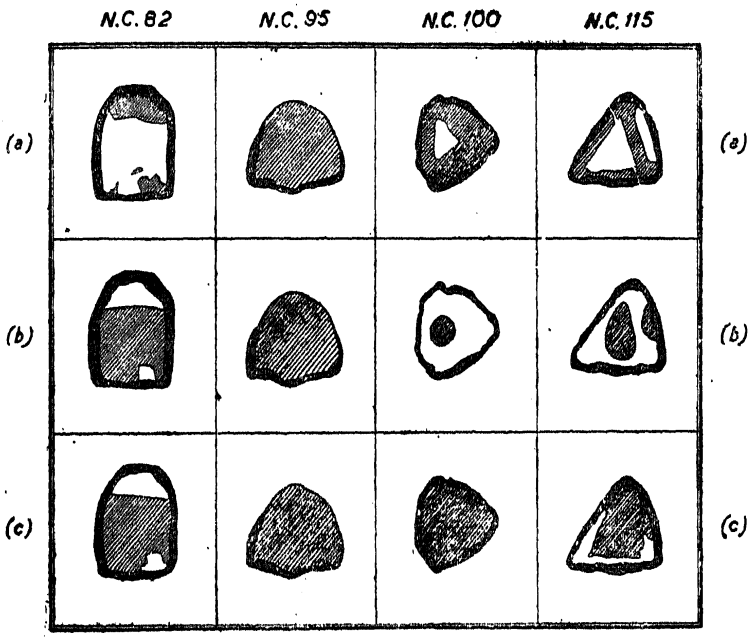

FIG. 1.

(*a*) Patterns of Luminescence. (*b*) Patterns of Infra-Red Transparency.
(*c*) Patterns of Ultraviolet Transparency.

area of the plate shows a fairly bright blue luminescence covered by bands of yellow luminescence. The two extremities of the diamond (top and bottom right-side corner) are non-luminescent and also more transparent to the ultraviolet in the 2536 Å region than the central area. The infra-red absorption coefficient is 5·3 per centimetre in the central part and 1·9 per centimetre at the top non-luminescent area and varies between these values at other regions. N.C. 95 which also shows both blue and the yellow luminescence, has got a gradual variation in the intensity of its luminescence over its area. Observations on infra-red transparency show that the brighter regions in the luminescence photograph correspond to regions more transparent to the infra-red. The diamond N.C. 100 has got a blue luminescent spot in the centre surrounded by non-luminescent area on all sides. The

infra-red transmission through the central spot is lower than in the surrounding area, the coefficients of absorption being 10·0 per centimetre and about 7·0 per centimetre for the two regions respectively. Lastly, the diamond N.C. 115 is again of the mixed type, showing blue and yellow fluorescence. The central triangular area and the narrow strip at one of the sides which are luminescent and opaque to the ultraviolet at 2536 Å are found to be more opaque to the infra-red than the other regions. It is thus quite clear that there is a close correlation with luminescence, and one of a different nature with the ultraviolet transparency. A non-luminescent area must be carefully distinguished from either a weakly blue-fluorescent area or a weakly yellow-fluorescing area. As was shown in Table I, a weakly blue fluorescent diamond is highly opaque in the 8 μ region, while a non-luminescent diamond or one showing weak yellow fluorescence is highly transparent. All these features are shown by diamonds showing infra-red transparency patterns, sometimes one and the same diamond showing all the above-mentioned behaviours.

I take this opportunity to express my heartfelt gratitude to Sir C. V. Raman under whose direction the present work was done. I am also thankful to Dr. R. S. Krishnan whose kind help was always available to me during the progress of this research.

Summary

Using a Residual-ray apparatus, the infra-red absorption coefficients have been measured for 37 cleavage plates of diamond in the 8 μ region. While the absorption coefficients measured with an infra-red monochromator in the region 4–5 μ remain constant within the error of the measurement for all diamonds, those in the 8 μ region show a wide range of variation. The results are correlated with the behaviour of diamond in respect of luminescence and ultraviolet absorption. Some cleavage plates of diamond have also been shown to exhibit patterns of infra-red transparency in the 8 μ region, closely analogous to the patterns of ultraviolet transparency and of luminescence.

References

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