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The infra-red absorption by diamond and its significance—Part III. The perfect diamonds and their spectral behaviour

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1. Introduction

A perfect diamond should be colourless and transparent and should be free from internal cracks and inclusions and should further exhibit no visible birefringence when placed between crossed polaroids and viewed against a bright source of light. This last test is a stringent one and it serves to exclude a large majority of diamonds. The specimens that do satisfy the test also exhibit the other properties characteristic of the group A diamonds described and illustrated in the second part of this memoir. We shall in the present part deal a little more fully with their optical characters and especially with their infra-red behaviour.

A fine example of a perfect diamond is the tabular crystal in its natural hexagonal form which was presented to the author by the late Dr Paul Grodzinzki. Photographs of this diamond obtained by four different techniques are reproduced in plate I. The picture marked (*a*) was obtained with the diamond placed on a fluorescent plate and illumined by the $\lambda 2536{\cdot}5$ radiations of a mercury arc which traversed the diamond before reaching the plate. The photograph exhibits the opacity of the diamond to the radiations. The photographs marked (*b*) was obtained with the diamond held between crossed polaroids and exhibits its perfect freedom from birefringence. The photographs marked (*c*) and (*d*) were obtained with the diamond illuminated by sunlight filtered through a plate of Wood's glass. Photograph (*c*) exhibits the faint blue luminescence of the diamond as seen through a filter of blue glass. The exposure was so prolonged that the luminescence was recorded with great intensity. Photograph (*d*) represents the luminescent diamond in the same circumstances as viewed through a filter of yellow glass. It will be noticed that the luminescence is then unobservable.

The photographs reproduced in plate II and marked (*a*), (*b*), (*c*) and (*d*) were obtained using similar procedures with a cleavage plate of diamond of Indian origin. It will be noticed that the effects exhibited by it are in each case similar to those seen in plate I.

2. Characteristic features of the absorption

In the first part of this memoir, reference was made to the desirability of recording the transmission curves with the Leitz instrument at a very low speed. The importance of this remark is illustrated by figure 1 in the text below which is the record in the $2\,\mu - 12\,\mu$ region obtained with a perfect diamond 0·81 mm thick, the speed of recording being at the rate of 10 minutes per μ of wavelength. A comparison with the record of another diamond of the same class but recorded at a speed of 3 minutes per μ and reproduced as figure 1 in the second part of this memoir shows that the slower speed greatly improves the sharpness and precision of the recording. This is especially evident in the region of wavelengths between 7 μ and 10 μ where the features exhibited by the perfect diamonds make their appearance and which we shall now proceed to discuss.

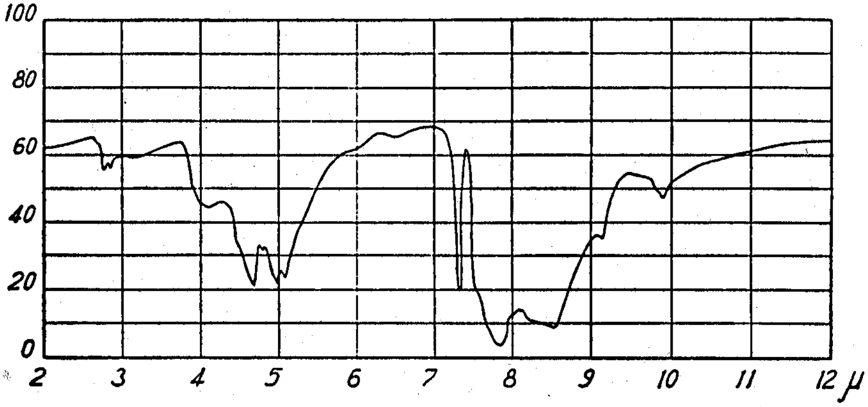


Figure 1. Percentage transmission curve of a perfect diamond (thickness 0·81 mm).

A very remarkable feature of the absorption spectra of the perfect diamonds is the sudden increase in absorption which appears between 7·4 μ and 7·5 μ. This is very clearly shown in figure 1, the transmission falling from 62 to 20% within a range of only 0·1 μ. The curve coincides with the 7·5 μ ordinate in the region where the transmission falls from 40 to 20% and then suddenly alters its course. The sharp absorption edge at 7·5 μ (or in wave-numbers 1332 cm^{-1}) is thus a highly characteristic feature exhibited by the perfect diamonds. It is well known that in the spectrum of the scattering of light by diamond, a sharply defined frequency shift of 1332 cm^{-1} is recorded. This quantitative agreement in respect of frequency makes it evident that in both cases we are concerned with effects arising out of the structure of diamond itself.

Besides the edge at 7·5 μ, the record reproduced as figure 1 shows other well-marked features at longer wavelengths, viz., an absolute minimum of transmission at 7·85 μ, a sharp turn in the course of the record at 8·2 μ, another very sharp turn at 8·5 μ, another turn followed by a very steep rise at 9·2 μ and finally a well-defined peak at 9·9 μ. Diamond thus exhibits in its absorption spectrum in this range six clearly defined features at 7·5 μ, 7·85 μ, 8·2 μ, 8·5 μ, 9·2 μ and 9·9 μ respectively. Expressed as frequencies in wave-numbers, these are at 1332, 1273, 1219, 1176, 1087 and 1010 cm^{-1} respectively. The appearance of these features in infra-red absorption would be accounted for if the crystal structure had specific vibrational modes having the frequencies listed and the radiations traversing diamonds of this class excited such vibrations. In other words, the region of wavelengths between 7·5 μ and 10 μ exhibits the infra-red absorption spectrum of the first order of the perfect diamonds.

3. The absorption spectra of higher orders

Since, as we have seen, the first-order absorption spectrum commences at 1332 cm^{-1} and extends towards lower frequencies, the second-order spectrum exhibiting the first overtones of the fundamental frequencies should commence at 2664 cm^{-1} and extend towards lower frequencies. Likewise, the third-order spectrum should commence at 3996 cm^{-1} and continue to lower frequencies. The same limits expressed as wavelengths are 7·5 μ, 3·75 μ and 2·5 μ respectively. Actually, it is seen from figure 1 above that there is a large and sudden drop in the percentage transmission at about 3·75 μ and another but less conspicuous drop in transmission at about 2·6 μ. It is thus evident that the perfect diamonds exhibit the complete absorption spectrum including the first, second and third orders at the appropriate wavelengths and frequencies.

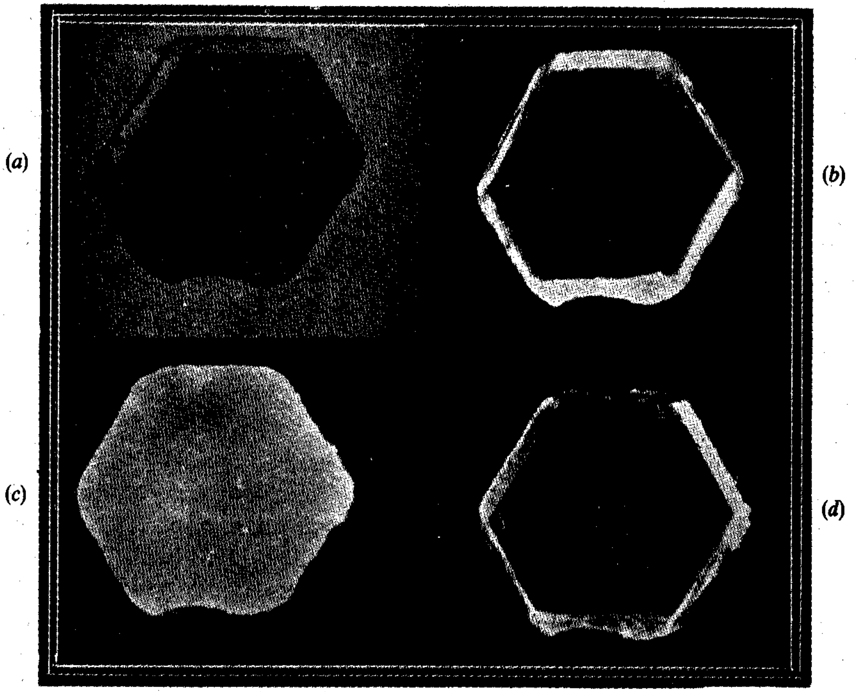
We may here draw attention to the most conspicuous features in the second-order spectrum, viz., the extremely sharp minimum of transmission at 4·60 μ or 2174 cm^{-1}, the double peak at 4·95 μ and 5·09 μ or 2020 cm^{-1} and 1965 cm^{-1}. We may also draw attention to the sudden fall in transmission from 68% at 7 μ to 21% at 7·30 μ followed by an equally sudden rise to 62% at 7·40 μ. This very remarkable feature in the second-order spectrum evidently stands in a close physical relationship to the sharp absorption edge at 7·5 μ appearing in the first-order spectrum, as is shown by the fact that it does not appear in the case of group B diamonds which show only the second and third-order spectra, and not that of the first order. As will be explained in a subsequent part of this memoir, the sharp dip at 7·30 μ or 1370 cm^{-1} is the result of the excitation of a summation of the two lowest, viz., the seventh and eighth vibrational frequencies of the diamond structure which are at 746 cm^{-1} and 624 cm^{-1} respectively (13·40 μ and 16·02 μ when expressed as wavelengths). The summational frequency is powerfully excited in absorption by reason of its close contiguity to the principal 1332 cm^{-1} frequency which is active in the perfect diamonds.

It may also be remarked that the sharp peaks at 2174 cm^{-1} and 2020 cm^{-1} are the octaves of the fifth and sixth vibrational frequencies of diamond which, as we have already noticed, manifest themselves clearly as fundamentals in its first-order absorption spectrum. The third sharply defined peak at 1965 cm^{-1} results from a summation of two fundamental frequencies of vibration, viz., 1219 cm^{-1} and 746 cm^{-1} respectively.

The various sharply defined features observed in the second-order absorption of diamond are thus a clear demonstration that the *atomic nuclei in the structure of diamond possess a set of free vibrational modes with discrete monochromatic frequencies.* On the other hand, the infra-red absorption spectrum represents the *forced vibrations* of the structure produced by the field of the incident radiation acting on the electrons which hold the nuclei in place. It is necessarily recorded as a continuous curve exhibiting peaks or sharp turns or sudden drops at positions determined by the nuclear vibration frequencies.

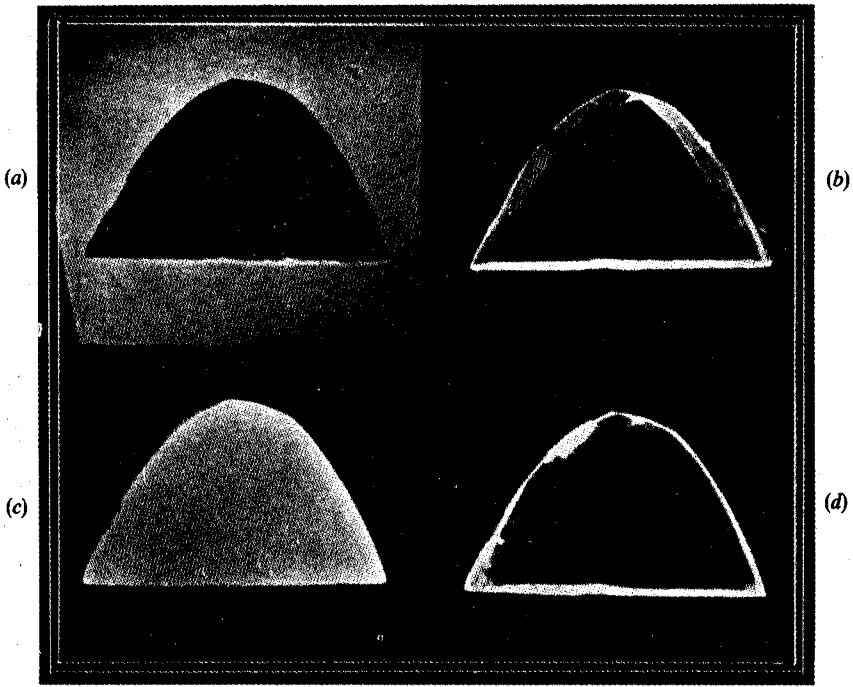
4. Summary

The perfect diamonds exhibit an absorption which is readily recognised as including the first, second and third order spectra. From the features observed in these spectra it is inferred that the diamond structure has eight discrete frequencies of free vibration, viz., 1332, 1273, 1219, 1176, 1087, 1010, 746 and 624 cm^{-1}. The fifth and the sixth frequencies appear very prominently with doubled frequency as sharp peaks in the second-order absorption spectrum, while a summation of the seventh and eighth frequencies is recorded with extraordinary strength and sharpness by reason of its contiguity to the active fundamental of highest frequency.



A perfect diamond (tabular crystal).

Plate I



A perfect diamond (cleavage plate).

Plate II