

The infra-red behaviour of diamond

SIR C V RAMAN

Diamond was recognised and esteemed as a precious stone in India since ancient times. The ready cleavage parallel to the octahedral planes of the crystal which it exhibits was discovered and made use of in shaping the diamond for various purposes. Indeed, flat plates obtained by such cleavage were polished and inserted as such into jewellery with a view to exhibit the characteristic lustre of the gem. Such jewellery having gone out of fashion, it was found possible to acquire material for research in this form, which is obviously the most suitable for precise investigations on the optical properties of diamond. The four largest plates in the collection acquired by the author in the course of years are roughly circular or oval in shape and have a superficial area of about three square centimetres each. The total number of plates, a hundred in all, is sufficiently great for the collection to be considered truly representative of diamonds of the first quality.

Using polished flat plates of diamond, the following studies are readily carried out: firstly, the determination of the presence or absence of birefringence in the diamond, revealed by the restoration of light appearing when the plate is held between crossed polaroids and viewed against an extended source of light; secondly, the ultra-violet transparency or opacity of the diamond in the wavelength range between 3000 Å and 4000 Å which is readily determined by placing the diamond on a plate of fluorescent glass so as to cover it in part and observing the effect of passage of the ultra-violet rays through the diamond; thirdly, the manifestation of visible luminescence by the diamond itself under irradiation in the same range of wavelength; fourthly, the infra-red absorption spectrum of the diamond which is studied with an infra-red recording spectrophotometer in the wavelength range between 2μ and 12μ .

In a memoir¹ which has been recently published, the results of the investigation by the methods indicated above of the author's entire collection of plates of diamond have been set out, illustrated by numerous photographs and spectrophotometer records, and discussed in detail. A very clear picture emerges from the study of the close relationship which exists between all the four properties referred to and the dependence of all of them on the crystal structure of diamond. In

¹Raman, C V, "The infra-red absorption by diamond and its significance," *Memoirs of the Raman Research Institute*, No. 129. Also, *Proc. Indian Acad. Sci.*, 55, 1-61 (1962).

particular, the infra-red records made with the four largest plates in the collection and with the spectrophotometer running at its slowest speed have revealed much significant detail. In consequence, the conclusions which have emerged from the investigation have a firmly established factual basis.

Nothing in the nature of a full review of the contents of the memoir will be attempted in the present article. Its object is to present a few considerations of a general nature regarding the origin of the infra-red activity exhibited by diamond and its relation to the structure of that crystal. The perusal of the article may be useful as a preliminary to a detailed study of the memoir cited above.

The free vibrations of the structure

The structure of diamond is well known, but may be usefully recalled here. It may be described as the result of the interpenetration of two rhombohedral lattices, the points of which are occupied by atoms of carbon. The two lattices are so located with respect to each other that each carbon atom in one lattice is surrounded by four atoms in the other lattice in a tetrahedral Configuration. In the octahedral and cubic layers of the structure, the atoms belonging to the two lattices appear alternately. The octahedral layers are unequally spaced, being alternately closer together and further apart. On the other hand, the cubic layers of the structure are all equally spaced.

The absorption of infra-red radiation by a crystal is an effect arising from the interaction of the electromagnetic field in the radiation with the structural units composing the crystal. As a first step towards an understanding of this effect, it is necessary to consider the nature of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose, the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together. The relevant theory is fully set out in the memoir cited above and it is sufficient here to state the results to which it leads.

It emerges that the vibrational mode of highest frequency is one in which the two non-equivalent sets of carbon atoms oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described very simply in terms of the crystal structure. Four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers in the structure. The movements may be either normal or tangential to those layers and they alternate in phase as we pass from any one layer to the next equivalent layer in the structure. Since the movements of the non-equivalent atoms appearing in adjacent layers may be either in the same phase or in the opposite phases, we have eight modes in all, besides the principal mode of highest frequency already mentioned.

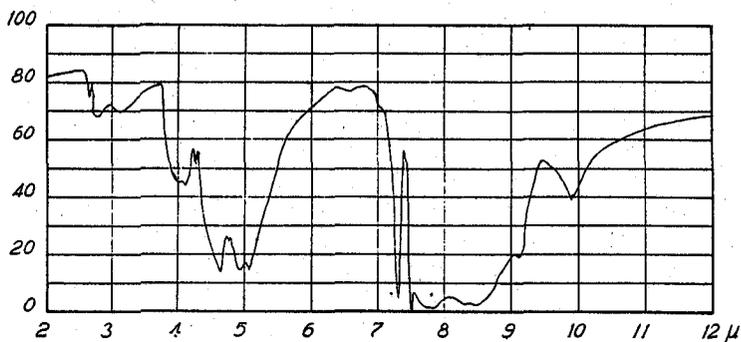


Figure 1. Infra-red absorption spectrum of diamond (plate thickness 1.44 mm).

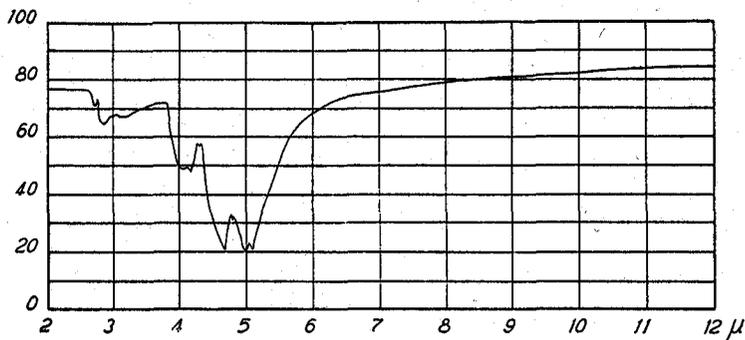


Figure 2. Infra-red absorption spectrum of diamond (plate thickness 1.06 mm).

The origin of infra-red activity

We next proceed to consider the relation between the free vibrations of the crystal and the effects arising from the passage of infra-red radiation through it. The electric field in the incident radiation acts both on the positively charged nuclei and on the negatively charged electrons. But in all the modes of vibration with which we are concerned, there are as many positively charged nuclei moving in one phase as there are others moving in the opposite phase and with an equal amplitude of vibration. It follows as a consequence that the displacements of positive charge when totalled up cancel out in all the modes under consideration. Hence, the free vibrations of the structure cannot be excited by the forces exerted

by the field on the atomic nuclei. Necessarily, therefore, the movements of the atomic nuclei can have no effect on the radiation passing through the crystal. We conclude that the infra-red activity of the crystal arises solely by reason of the forces exerted by the field on the negatively charged electrons and of the resulting movements; such activity is only possible when the displacements of negative charge produced do not cancel out when summed up over each structural unit.

Since the electrons are held in position by their interactions with each other and with the positively charged nuclei, the displacements of negative charge would necessarily disturb the nuclei from their positions of equilibrium. But the nuclear movements thus arising would not contribute to the infra-red activity. Thus, while in the free vibrations of the structure, the massive positively charged nuclei play the leading role and the electrons a subsidiary one, the situation is reversed in respect of the infra-red activity, the electrons here playing the leading role and the nuclei a subsidiary one. In other words, the spectrum of infra-red absorption are essentially different in their nature and origin. Being both properties of the same structure, we may expect to find some resemblances, but nothing in the nature of an identity or complete correspondence is to be expected.

From what has been stated, it follows that in seeking for an explanation of the infra-red activity of diamond, we have to fix our attention on the electronic charge-clouds in the crystal. It is the distribution of the negative electric charges in its undisturbed state as well as when it is modified by the nuclear movements which would determine the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

The electronic configuration

Diamond exhibits in its structure a perfect demonstration of the validity of the concept of the tetrahedral carbon atom. For, the four valence bonds joining each carbon atom with its four nearest neighbours are parallel to the four tetrahedral axes of the crystal. There is no reason to believe or assume that the two sets of carbon atoms thus linked together are in any way different from each other. Indeed, we may take it for granted that both sets of atomic nuclei have associated with them equal distributions of negative charge. But it would not necessarily follow from this that the electronic configuration in the crystal would exhibit centres of symmetry located at the midpoints between every pair of adjacent atoms in the structure. For, we have to consider not only the static distribution of negative charge but also the movements of the electrons linking the carbon atoms and circling around the four tetrahedral axes of the structure. These movements would be such that the structure as a whole is diamagnetic. The tetrahedral setting of the axes of the structure ensures that whatever be the sense of the electronic movements about these axes, the magnetic moments arising therefrom

would cancel out completely, provided the sense of the movements is the same for all four axes. This leaves the sense of the movements of the individual electrons in each pair forming a valence bond, an open question. If the senses of the movements of the two electrons are opposed to each other, then both in the static and dynamic pictures, there would be a centre of symmetry located at the midpoint between the nuclei under consideration. But, if on the other hand, the senses of the movements of the two electrons around the tetrahedral axes are the same, then there could be no centre of symmetry located at that point.

Thus, considerations of a very general nature indicate the possibility of the structure of diamond either possessing or not possessing the maximum symmetry of the cubic system. In other words, diamonds may belong either to the octahedral or to the tetrahedral class of that system. This is indeed the case as is evident from studies on the naturally occurring crystal forms of diamond, as also from studies of the various physical properties of diamond which are influenced by the symmetry of the electronic configuration within the crystal. In particular, spectroscopic theory indicates that studies of the infra-red behaviour of diamond should yield clear and unquestionable evidence bearing on this issue.

The effects of crystal symmetry

If the midpoint between every pair of adjoining carbon atoms in the crystal is a centre of symmetry, it follows that the principal mode of oscillation of the structure in which the two sets of atoms move with equal amplitudes but in opposite phases would not give rise to any displacement of electric charge. Hence, the frequency of this mode would fail to manifest itself in the absorption of infra-red radiation. The frequencies of the remaining eight modes of vibration would also fail to appear, but for a wholly different reason. In each of these eight modes, the phase of the movement is reversed as between any one layer of atoms and the next equivalent layer. The displacement of charge resulting from the relative displacement of two adjacent layers of atoms in the crystal would be cancelled out by the displacement in the opposite direction due to the next pair of equivalent layers. It should be remarked however that such cancellation would be complete only in the first approximation. If the finiteness of the amplitudes of oscillation in the structural units is taken into account, there would be a difference left over, as a consequence of which each of the eight modes would be active in the second approximation. Hence, they would manifest themselves in absorption with doubled frequencies.

The strength of the second-order effect referred to above would necessarily be different for each of the eight different modes of vibration, since it would depend on the movement of charge resulting from the approach or recession of the adjacent layers of atoms in the crystal. As has already been remarked, the spacing

of these layers is different in the cubic and octahedral planes and in the latter case alternates between two very different values. Since the movements of the layers may be either normal or tangential to the layers, very large differences may be expected between the magnitudes of the second-order infra-red activities of the eight modes. Thus, the situation may be summed up by the statement that the centro-symmetric diamonds would fail to exhibit any infra-red absorption of the first order, but that a second-order absorption would be manifested by them.

If, on the other hand, the electronic configuration in the crystal is such that the midpoints between every pair of adjacent carbon atoms are *not* centres of symmetry, an oscillation of the two sets of atoms in opposite phases with respect to each other would give rise to a periodic displacement of the negative electric charges with the same frequency. The principal mode of free vibration of the structure having the highest frequency would accordingly manifest itself as a first-order absorption frequency. Thus, the presence of a first-order absorption would reveal that the crystal lacks centres of symmetry in its inner structure and hence should be assigned to the tetrahedral class of the cubic system instead of the octahedral or highest class of symmetry of that system. Since such lack of centro-symmetry is a consequence of the dynamic characters of the electronic configuration and not of any lack of symmetry in the static distribution of electric charge, the resulting first-order absorption cannot be expected to manifest the extraordinary strength with which it appears in such cases as, for example, the alkali halides. Indeed, it should not surprise us to find that the first and second-order absorption spectra of the diamonds exhibiting both of them are of comparable strength, instead of the first-order absorption being enormously more intense than the second-order as in the case of the alkali halides.

A few further remarks are here necessary. For the same reason that the first-order and second-order infra-red absorptions are of comparable strengths with the diamonds exhibiting both of them, we should expect to find that the characters of their second-order absorption spectra do not sensibly differ from those observed with the diamonds which exhibit only the second-order absorption. For, the origin of the second-order absorption would in both cases be the same, viz., the finiteness of the amplitudes of oscillation and the resulting incomplete cancellation of the displacements of electric charge of opposite sign in the alternate layers of the structure. Such cancellation would however continue to be operative in the first approximation even in the case of diamonds lacking centres of symmetry. The excitation of the principal mode of vibration having the highest frequency may, however, be expected to result also in the excitation of the modes of lower frequency as an accompaniment, the strength of such excitation being determined by the difference between their frequencies and that of the mode of highest frequency. In other words, in the first-order absorption spectrum of the diamonds exhibiting it, not alone the mode of highest frequency but also the modes of lower frequencies may be expected to appear, their strength falling off rapidly as the frequency deviates more and more from the highest.

Concluding remarks

Figures 1 and 2 above are reproductions of a selection from amongst the numerous spectro-photometer records illustrating the memoir cited above. They represent two typical cases and serve to show that the resemblances and differences between the absorption spectra of diamonds having the lower and the higher symmetries as observed are fully in accord with those indicated by the considerations set forth above. Attention may also be drawn to the extreme sharpness of the peaks of absorption as recorded by the spectrophotometer in both figures. Such sharpness is a natural consequence of the free vibrations of the structure of diamond exhibiting a set of nine precisely defined monochromatic frequencies. It should also be remarked that the frequencies determined spectroscopically as well as their observed activities are in satisfactory accord with those deduced theoretically. Further on the basis of the spectroscopically determined frequencies alone and without using any other data, the heat capacity of diamond can be evaluated theoretically over the entire range from the lowest to the highest temperatures: the results obtained are in highly satisfactory agreement with the thermally determined values. The reader will find these and many other matters set out and discussed in the memoir cited.