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The infra-red behaviour of the alkali halides

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1. Introduction

X-ray diffraction techniques enable us to ascertain the distribution within the volume of a crystal of the atoms composing it. But the geometry of the structure cannot by itself form the basis for any valid deductions regarding the physical properties of the crystal. To enable any such deductions to be made, a knowledge of spectroscopic behaviour of the crystal is essential. By a careful investigation of a few particularly simple cases, the basic principles connecting structure and spectroscopic behaviour may be elucidated and established. Such an investigation has been carried out in the case of diamond which is accessible to spectroscopic study by a variety of methods. It will suffice here to refer to a recent memoir* by the author in which the infra-red absorption spectra of diamond have been described and explained in terms of its crystal structure. In an article which appeared in *Current Science* for October 1962, this work has been briefly summarised.

2. The alkali halides

Whereas diamond stands apart by itself as a crystal composed of atoms all of one kind which is favourable for spectroscopic investigation, we have in the alkali halides a whole family of crystalline solids which are accessible to study by well known spectroscopic methods. The fluorides, chlorides, bromides and iodides of the alkali metals lithium, sodium, potassium and rubidium (sixteen in all) have a similar structure. They exhibit a wide range of variation in their physical behaviour and for that very reason, are highly important as materials for study. In a recent memoir by the author**, an attempt has been made to deal with all these sixteen crystals from a unified standpoint and to establish connections between their spectroscopic behaviour and their physical properties. We may here briefly indicate the contents of that memoir.

Part I is a general introduction in which the physical constants of the sixteen

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*The infra-red absorption by diamond and its significance. Memoir No. 129 of the Raman Research Institute; also *Proc. Indian Acad. Sci.*, **A55**, 1 (1962).

The specific heats of the alkali halides and their spectroscopic behaviour. Memoir No. 131 of the Raman Research Institute; also *Proc. Indian Acad. Sci.*, **A56, 1 (1962).

halides and especially their elastic moduli are tabulated. In part II, the nine modes of free vibration of the atoms in a crystal having the rock-salt structure are deduced and described. Parts III and IV contain further developments of the dynamical theory and contain expressions for the frequencies of the nine normal modes in terms of the interatomic force-constants. In part V it is shown how these frequencies may be numerically evaluated, if only as a first approximation. The results of the evaluation are tabulated in part VI. Parts VII, VIII and IX deal respectively with the specific heat problem, the infra-red behaviour of the crystal and the spectral shifts observed in light-scattering from first principles. Parts X, XI and XII give the results of the specific heat computations for all the sixteen halides and compare them with the experimental data in the cases for which they are available.

3. The spectrum of free vibrations

The dispersion, absorption, and reflection of infra-red radiation by a crystal are effects arising from the interaction of the electro-magnetic field in the radiation with the structural units composing the crystal. As a first step toward an understanding of these effects, it is necessary to consider the nature of the spectrum 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 of the structure is one in which the metal and halogen atoms oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described 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, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the metal and halogen atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers, and hence eight in all. The oscillations of the metal and halogen atoms located in the same cubic layers would be coupled with each other. But the oscillations of the metal and halogen atoms appearing as distinct layers in the octahedral planes would be independent.

4. The mechanism of infra-red absorption

The absorption of infra-red radiation by a crystal implies the possibility of a transfer of energy from the field to the solid, a quantum of the energy of the incident radiation being taken over and transformed into one, two or more quanta of vibrational energy in the crystal. The possibility of such a transfer arises from the interaction between the electromagnetic field of the radiation and the electric charges present in the structure of the crystal. These charges are of two kinds, viz., the positive charges of the massive atomic nuclei and the negative charges of the mobile electrons. These charges hold each other in place in the crystal structure as an ordered assembly. The roles which the positive and negative charges respectively play in the absorption of infra-red radiation have, therefore, to be discussed.

In all the modes of oscillation with which we are concerned, there are as many atomic nuclei moving in one phase as in the opposite phase, the respective amplitudes of oscillation being such that the centres of inertia of the structural units in the crystal remain at rest. Now, the ratio of the nuclear charges of sodium and chlorine is sensibly the same as the ratio of their atomic weights. As a result of this situation, the movements of the positive charges of the atomic nuclei when multiplied by their displacements and summed up would also cancel out. Hence, the forces exerted by the field on the positive charges in the structure cannot possibly set it in vibration. Thus, we are led to conclude that though the masses of the atomic nuclei appear in the expressions for the frequencies of vibration, the movements of the charges carried by them would not play any role in the infra-red activity of the crystal. Likewise, the movements of the negative charges carried by the electrons would not give rise to infra-red activity if it be assumed that each nucleus has associated with it the quota of electrons needed to neutralise its charge and that these electrons are carried along with it in its movements.

Thus we arrive at the following two conclusions. Firstly, the infra-red activity of the crystal owes its origin exclusively to the movements of the electrons and of the negative charges carried by them. Secondly, the electrons thus contributing to the activity are not those which are associated with any particular nucleus and participate in its movements, but are those electrons which enter into the structure of the crystal and whose movements are therefore determined jointly by movements of more than one nucleus. Infra-red activity can only arise if the displacements of electric charge thus resulting do not vanish when summed up each element of volume in the crystal. Though these results were derived with reference to the specific case of rock-salt, it could scarcely be doubted that they are of general validity.

5. The activity of the normal modes

Basing ourselves on the foregoing considerations, we can proceed to discuss the possibility of each of the nine normal modes described earlier being excited by incident radiation having the same frequency as the vibration. It is immediately obvious that the mode of highest frequency in which the metal and halogen atoms oscillate against each other in opposite phases could be so excited. For, the movements of the negative charges set up by the movemets of the two sets of nuclei, though opposite in phase, would be of unequal magnitude, and hence their resultant would not vanish. The surviving movement of charge could therefore enable the oscillation to be excited by the field. It is also evident that no such excitation would be possible in the case of the eight other normal modes. For, in these modes, the atomic nuclei of either species oscillate in opposite phases in the alternate layers of the structure, and hence the movements of negative electric charge resulting therefrom would cancel out when summed up over any individual volume element in the crystal.

We have next to consider the cases in which the frequency of the incident radiation is a multiple of the frequency of the normal mode under consideration and a quantum of energy of the field if taken up would be transformed to two, three or more quanta of vibrational energy in the crystal. For such excitation to be possible, the movements of electric charge resulting from the vibration should include a periodic component having the frequency of the field which does not vanish when summed up over an individual volume element in the crystal. Electrical anharmonicity associated with a finite amplitude of vibration is requisite for such an effect. It can evidently arise in the case of the vibrational mode which has the highest frequency and the maximum activity of all the modes. It is readily shown also that the coupled modes of vibration of the atomic nuclei in the cubic layers of atoms could be excited by a radiation which has *double the frequency* of the vibrational mode under consideration. *Per contra*, the symmetry characters of the modes of vibration of the atomic nuclei in the octahedral layers of the structure preclude any such excitation.

6. The infra-red absorption spectrum

The considerations set forth enable us in a general way to envisage the behaviour of the alkali halides in respect of the absorption of infra-red radiation. Some supplementary remarks are, however, necessary. By reason of the excitation of the normal modes by radiations having multiple frequencies, the absorption spectrum would extend to much smaller wavelengths than the spectrum of free vibrations of the structure. The strength of the absorptions of higher orders may however be expected to fall off rapidly with the increasing order. Further, the finite amplitudes of vibration excited by the radiation would necessarily involve besides electrical anharmonicity, also a mechanical anharmonicity of the vibrations, and this in its turn involves other consequences. The several normal modes of vibration can no longer be considered as being completely independent of each other or as being strictly monochromatic in their frequencies. Modes which are inactive when considered independently would be rendered active by

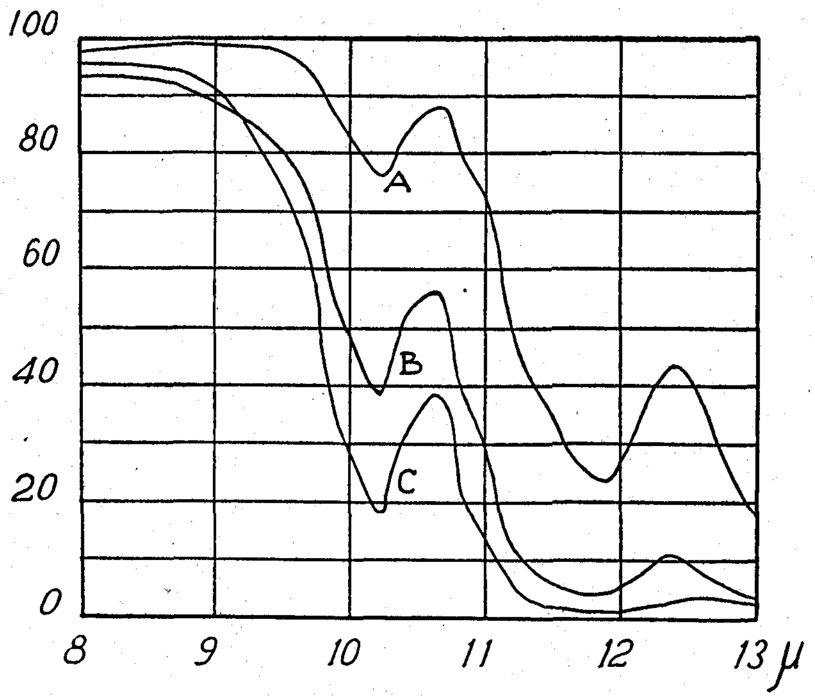

Figure 1. Magnesium oxide, infra-red transmission percentages. Plate thickness: A. 0·06 mm, B. 0·11 mm, C. 0·28 mm.

reason of their contiguity in frequency to other active modes of vibration. In particular, the principal and most strongly active mode having the highest frequency would influence all the other eight modes of lower frequency and render them active to varying extents depending on the differences of their frequencies from that of the mode of highest frequency.

It will be evident from all that has been said above that the characters of the spectrum of free vibrations could by no means be expected to manifest themselves very conspicuously in the spectrum of infra-red absorption. We have indeed to investigate the behaviour in the transmission of infra-red rays pretty thoroughly using plates of various thicknesses ranging from the largest to the smallest practicable values to enable us to disentangle the various normal modes and their overtones from each other and demonstrate the relationships between the possible free vibrations of the structure and their manifestation in the spectrum of infra-red absorption. Such investigations have been carried out by the author and the results have been presented in a series of memoirs dealing with several individual cases.

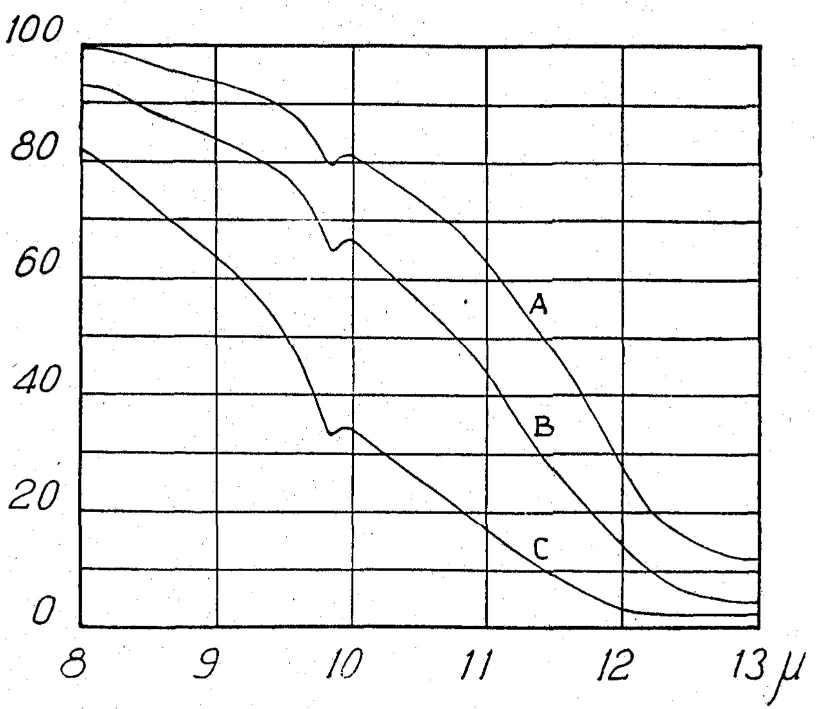

Figure 2. Lithium fluoride, infra-red transmission percentages. Plate thickness: A. 0·10 mm, B. 0·15 mm, C. 0·28 mm.

A Leitz infra-red recording spectrophotometer was available which was provided with both NaCl and KBr optics, the former covering the wavelength range between 1 μ and 15 μ and the latter the range between 13 μ and 24 μ. The materials investigated can be classed into three groups. The first included the alkali halides NaCl, KCl, KBr and KI commonly used as dispersing prisms for infra-red spectroscopy. Their characteristic wavelengths appear in the remote infra-red. The second group consisted of MgO and LiF whose characteristic wavelengths lay within the range of the KBr optics. Though MgO is not an alkali halide, its structure is similar to that of rock-salt and very significant results were obtained with it. The third group comprised the crystals NaF and CaF_2. Their characteristic wavelengths lay beyond the range of the KBr optics, but the records obtained in that range exhibited very significant features. Though the structure of CaF_2 differs from that of the alkali halides, the results obtained with it present some interesting points of comparison with LiF and NaF.

7. The spectrophotometric results

The observational data for the cases of MgO, LiF, NaF, CaF_2 and for NaCl have been set out fully in the individual memoirs dealing with these materials*. As is naturally to be expected in view of the diversity in the sizes and masses of the combining atoms and of the strength of their binding in these crystals, special features characteristic for each individual material are noticeable in the spectrophotometric records which have been reproduced in the memoirs, and these features are indeed highly significant. Nevertheless, it is possible to trace certain other features common to all the cases studied and which are to be expected in the light of the theoretical considerations set out above. To illustrate these differences and similarities, some of the records for the different thicknesses of the same materials have been grouped together and are reproduced here as figures 1, 2, 3 and 4 in the text. These refer respectively to the cases of MgO, LiF, NaF and CaF_2, and are the records obtained with the thinnest plates made use of in their cases.

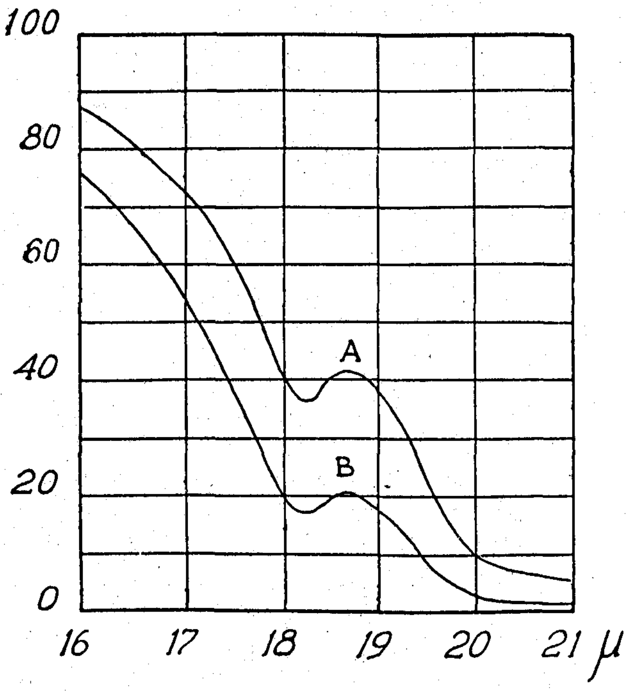

Figure 3. Sodium fluoride, infra-red transmission percentages. Plate thickness: A. 0·18 mm, B. 0·36 mm.

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* Memoirs of the Raman Research Institute, Nos. 127, 130, 132, 134 and 128—*Proc. Indian Acad. Sci.*, **A54**, 205 (1961); **A55**, 131 (1962); **A56**, 223 (1962); **A56**, 291 (1962); **A54**, 253 (1961).

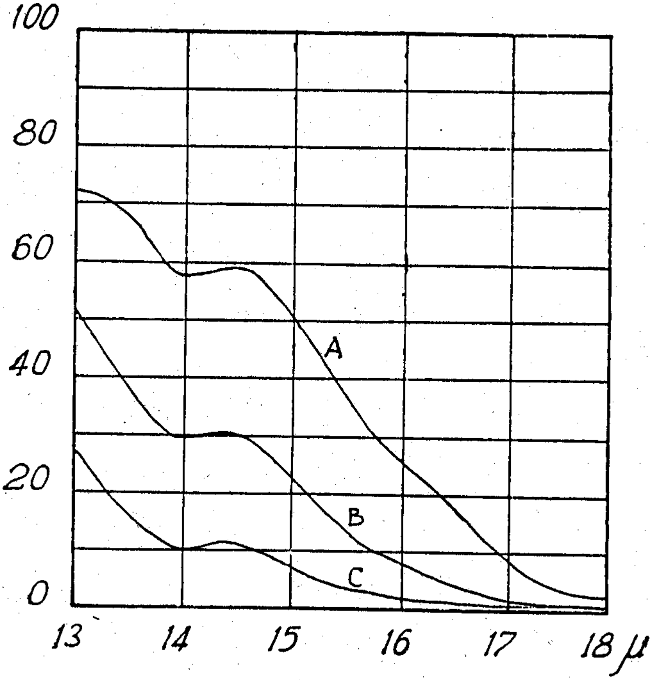

Figure 4. Calcium fluoride, infra-red transmission percentages. Plate thickness: A. 0·11 mm, B. 0·25 mm, C. 0·43 mm.

Attention may be drawn to the very steep drop in transmission noticed between 9 μ and 10 μ in each of the three curves reproduced in figure 1 for MgO. This drop is immediately followed by a sharply defined minimum of transmission at 10·20 μ. A similar but less steep fall between 8 μ and 9·8 μ is noticed in figure 2 for the case of LiF and this is followed by a shallow but sharply defined dip at 9.84 μ. Likewise in figure 3, referring to the case of NaF, we notice a steep fall of transmission between 16 μ and 18 μ and this is followed by a well-defined minimum at 18·2 μ. In all the three cases, the steep drop represents the change in the infra-red absorption due to the mode of highest frequency from the third-order to the second-order, and the observed minimum of transmission represents the wavelength corresponding to the octave of the fundamental frequency. We are thus enabled to determine the latter accurately from the spectrophotometric records. The dip at 14 μ noticed in all the three curves reproduced in figure 4 for CaF_2 is likewise identifiable as due to the octave of the mode of vibration in which the calcium atoms oscillate in one phase and the fluorines oscillate together in the opposite phase, resulting in a strong infra-red absorption.