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THE INFRA-RED SPECTRUM*

1. INTRODUCTION

THE radiations whose wave-lengths are greater than those of visible light and less than those of the shortest radio-waves constitute the so-called "infra-red spectrum". They are of great interest in relation to several subjects, as for instance, astrophysics, meteorology, thermodynamics and chemistry, to mention no others. The experimental study of the infra-red spectrum presents peculiar difficulties. For the most part, the aid of photography which makes exact studies possible with other parts of the electromagnetic spectrum is not available here. Less satisfactory devices have, therefore, to be employed, which mostly depend on the thermal or heating effect of the rays. As indicated by the Planck radiation formula, the energy of thermal radiation falls off rapidly with increasing wave-length. This makes it difficult to obtain sources of adequate strength for the larger wave-lengths and renders observation and measurement with such wave-lengths difficult and uncertain. A further problem is that of finding suitable materials for prisms which are transparent and have adequate dispersive power in the region under study. Absorption by water-vapour and by carbon dioxide in the atmosphere present other complications. The necessity of exploring the spectrum step by step also makes the work laborious and time-consuming. It is not surprising that in these circumstances our knowledge of the infra-red spectrum has progressed much less quickly than that of the visible or ultra-violet. That such difficulties have been surmounted and useful results obtained by the pioneers in the field is a tribute alike to

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their experimental skill and to their perseverance.

A quickened interest in infra-red spectroscopy is evident at the present time. This is shown by the increased output of literature and also by the several excellent treatises which have appeared of recent years dealing with the field. These developments have doubtless been stimulated by the knowledge which has become available to us since 1928 by spectroscopic investigations on the scattering of light. When monochromatic radiations traverse a transparent medium, the spectrum of the diffused light exhibits new lines, the frequency shifts of which with respect to the incident light represent the characteristic infra-red frequencies of the substance. This way of finding the infra-red frequencies enables us to enlist the powerful aid of photography, since the shifted lines appear in the visible or ultra-violet region of the spectrum; whether the frequency shifts are large or small, they are recorded and rendered accessible to study with the same facility. The insight and knowledge thus derived have proved a powerful stimulus to further study of the infra-red absorption spectra and furnished aid in the interpretation of the results. The infra-red frequencies determined by either method being those of the molecular vibrations in the substance, the two methods are complementary to each other, and also mutually helpful. Quite appropriately, therefore, the results of both methods of study are discussed together in the most recent texts dealing with this field.

It is worthwhile emphasising that studies of the molecular vibration spectra by infra-red absorption or by the scattering of light are not merely of academic interest. Indeed, they have proved to be powerful aids to industry in the chemical and other allied fields. Especially in dealing with organic chemicals are such physical methods more convenient and—with appropriate techniques—also quicker than purely chemical methods of identification or analysis. The vibration spectrum of a molecule is determined by the geometric configuration of the atoms in it, as well as by the atomic masses and the binding forces holding them together. In consequence, the characteristic features of molecular structure reveal themselves by the vibration frequencies, as also by the intensities with which they appear in the infra-red spectra. Hence, the feature of the observed vibration spectra are powerful aid to the identification of th individual substances and to the quantita tive analysis of mixtures.

2. Crystals and the Infra-Red Spectru

Crystals have played a notable part i the development of infra-red spectroscop We have only to recall the fact that th materials which are or could be utilized a dispersive prisms in infra-red work ar crystals. The optical behaviour of suc materials in relation to their chemical natur and physical structure offers much food fo thought. Taking, for instance, the case o rock-salt, the measurements of its refrac tive index which have been made in th region of wave-lengths between 1 μ and 22 indicate that the vibration frequencies whic effectively determine its dispersion lie i the remote infra-red in the region of 60 μ. We may well ask, why is it then that rock salt begins to show an appreciable absorp tion at 12 μ and exhibits a practically com pletely cut-off beyond 15·5 μ making useless as a material for prisms beyon that wave-length? Lithium fluoride agai which is another material which has latel come into use for infra-red work, has it effective "dispersion" frequency located a about 32 μ. Nevertheless the materia shows total opacity beyond 16 μ. We ar led to ask, what is the reason for suc opacity?

Standing in close relation to the question raised above, is the remarkable discover made by Rubens and Nichols that a bear of infra-red radiation is monochromatise more or less perfectly if it undergoes series of reflections at the surface of a crys tal. This method of obtaining "residua rays" by crystal reflections has been ex tremely useful in infra-red studies, as i enables a strong beam of specified wave length to be readily obtained. Variou questions arise with regard to the principl of the method. What relation does the resi dual-ray wave-length bear to the infra-re frequencies which are effective in disper sion? What thickness of the material i needed to give the desired strength of reflec tion? What is the relationship between th reflecting power and the absorption coeffi cient for wave-lengths lying in the regio of opacity?

It is evident that the answers to the ques tions raised above are closely related to th

fundamental problem of the nature of the vibration spectrum of a crystal and its activity in infra-red absorption. This, in its turn connects up with the question of the relationship between the atomic architecture of the crystal and its infra-red activity. The intimate nature of this relationship will be evident when we consider for instance, the striking difference in behaviour between, say, diamond and rock-salt. The infra-red activity of diamond is extremely weak, while that of rock-salt is extremely strong. Is this difference in behaviour due merely to the difference in the details of crystal architecture, or is it due to the difference in the nature of the binding forces in the two cases?

The power of infra-red spectroscopy to throw light on the problems of crystal structure is strikingly exemplified in the case of diamond. As mentioned above, the infra-red activity of this crystal is weak, and a thickness of the order of one millimeter is needed to exhibit a readily measurable absorption. Remarkably enough, however, it has been found that the nature of the absorption curve is not the same in all diamonds. The majority of diamonds exhibit an absorption curve of the type shown in Fig. 1 in which there is a region of strong absorption between 700 cm.$^{-1}$ and 1500 cm.$^{-1}$, while other diamonds (not so common) do *not* show the absorption in this region. All diamonds, however, show the absorption in the region of higher frequencies beyond 1500 cm.$^{-1}$, and the features of such absorption do *not* show any noticeable differences as between different diamonds. The latter fact makes it clear that the strong absorption between 1500 cm.$^{-1}$ and 2900 cm.$^{-1}$ is a characteristic property of diamond. Why then is the absorption between 700 cm.$^{-1}$ and 1500 cm.$^{-1}$ present

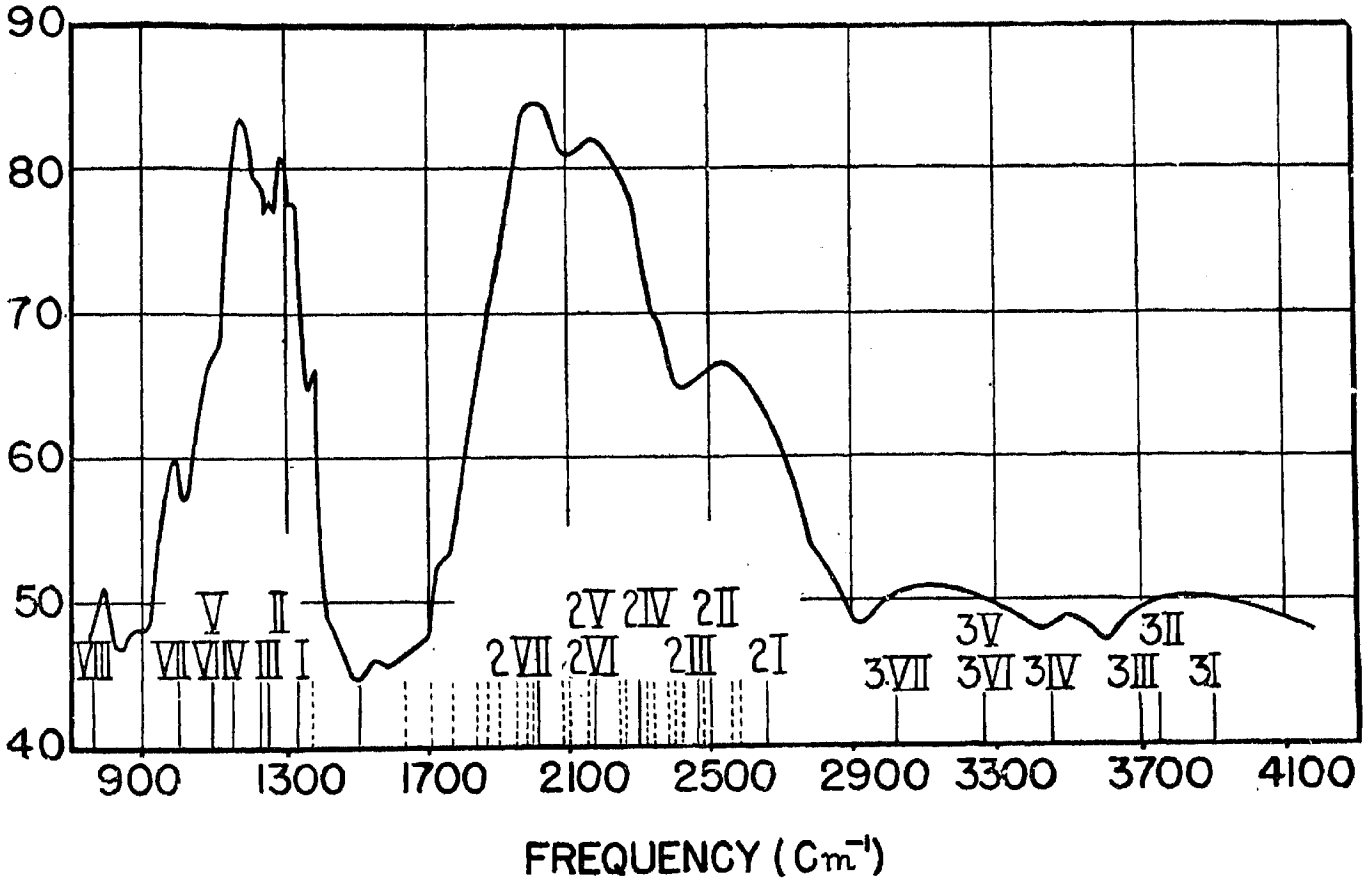

FIG. 1. Infra-Red Absorption Spectrum of Diamond
(after K. G. Ramanathan)

in some diamonds and absent in others? The answer to this question is furnished by the fact that the diamonds which show the absorption are those which exhibit the highest degree of homogeneity when examined by various optical and X-ray methods and which accordingly make the nearest approach to ideal perfection of crystal structure. *Per contra*, the diamonds which do not show the absorption show a visibly laminated structure when examined on the Federov stage under a polarizing microscope, and also various other properties indicating

a notable heterogeneity of structure. It follows that the appearance of the infra-red absorption with the diamonds exhibiting it cannot be ascribed to the presence of crystal imperfections, but must be referred to a fundamental difference in crystal symmetry between the two classes of diamonds, which results in an observable infra-red activity of the vibrations of the structure in one case and its inactivity in the other.

3. The Case of Magnesium Oxide

We shall now proceed briefly to recount the facts which have come to light as the result of experimental studies on the infra-red behaviour of magnesium oxide. Thin films of this substance are readily obtained by deposition of the fumes from burning magnesium, or alternatively by evaporation in a vacuum. Large single crystals of magnesium oxide have also been successfully prepared by solidification from the substance melted at over 2500° C. in an electric furnace. The crystals belong to the cubic class, and can be readily cleaved into flat plates in the same manner as rock-salt. Using the material in various forms, several investigators (Tolksdorf, 1928; Strong, 1931; Fock, 1934; as also Barnes and Brattain, 1935) have investigated the behaviour of the substance in respect of infra-red absorption and reflection. The results reported by these authors are exceedingly remarkable, namely, that in spite of the simplicity of its structure which is similar to that of rock-salt, the crystal has a whole series of characteristic infra-red frequencies in the vicinity of which intense absorption and reflection are observed. Tolksdorf observed a strong absorption at 14·2 μ. Strong found practically complete absorption at 20·8 μ and at 22·9 μ. He also found that at these wave-lengths, the reflection coefficient was 80% and 72% respectively and fell off rapidly with larger wave-lengths. Fock found the most intense absorption at 17·3 μ which he regarded as characteristic of MgO, though his observations also gave indications of other absorption maxima both at longer and at shorter wave-lengths. The most remarkable results of all were those of Barnes and Brattain. These authors studied the reflection coefficient of MgO over the whole range of wavelengths covered by a rock-salt spectrometer, and found a strong reflection between 13 μ and 16 μ with a double peak located at 14·8 μ and 15·3 μ respectively. Even more striking were the infra-red absorption curves in the wave-length range between 6 μ and 15·5 μ recorded by them with five plates of various thicknesses, ranging from the thinnest obtainable to very thick ones. The curves exhibit no fewer than 40 well-defined absorption *lines* in this range.

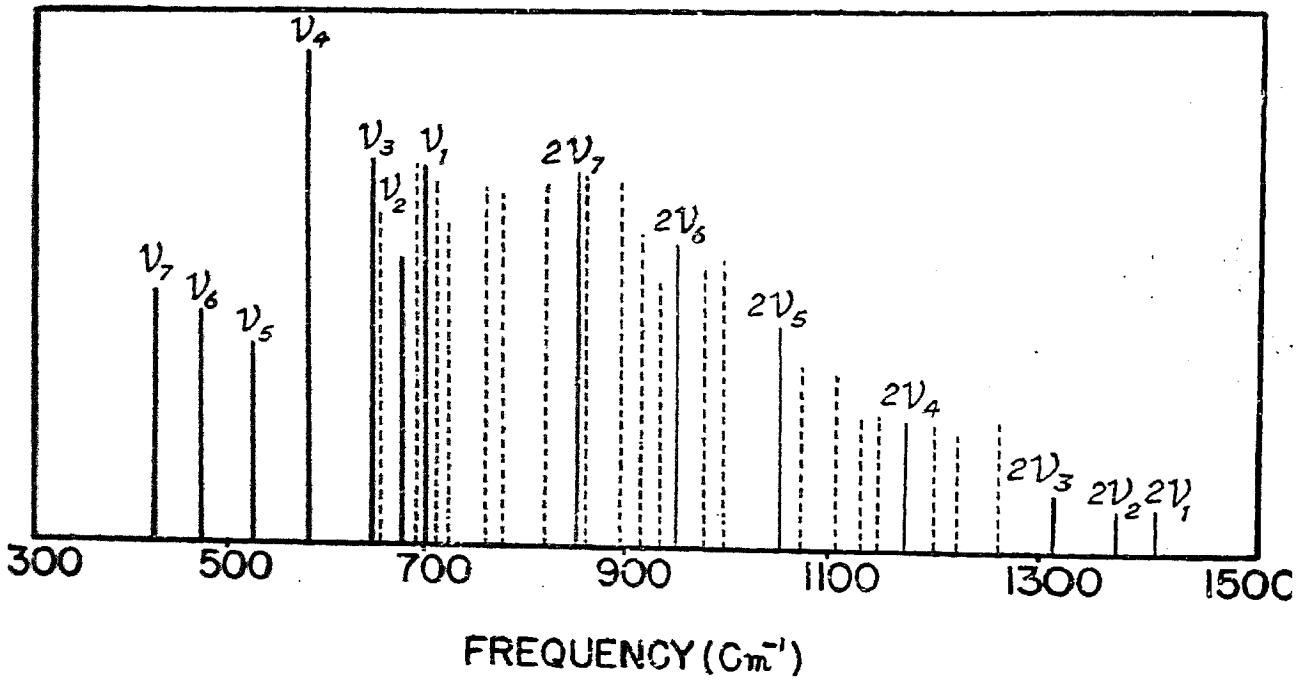

FIG. 2. Infra-Red Absorption Frequencies of Magnesium Oxide

The facts recited above are irreconcilable with the ideas regarding the spectroscopic

behaviour of crystals derived from the lattice dynamics of Max Born as applied to various actual cases by Blackman, Kellermann and others. Since the structure of magnesium oxide is similar to that of rock-salt, the only mode of vibration of the structure which according to the theory of Born would be infra-red active is the so-called "fundamental vibration" of the lattices of magnesium and oxygen atoms against each other. There would, in addition, be an immense number of other modes of vibration which taken together would constitute a continuous spectrum of frequencies. Actually, the observations indicate that the vibration spectrum of magnesium oxide in the region of infra-red frequencies is not continuous but discrete, consisting of a set of sharply defined monochromatic frequencies, all of which are infra-red active in greater or less degree.

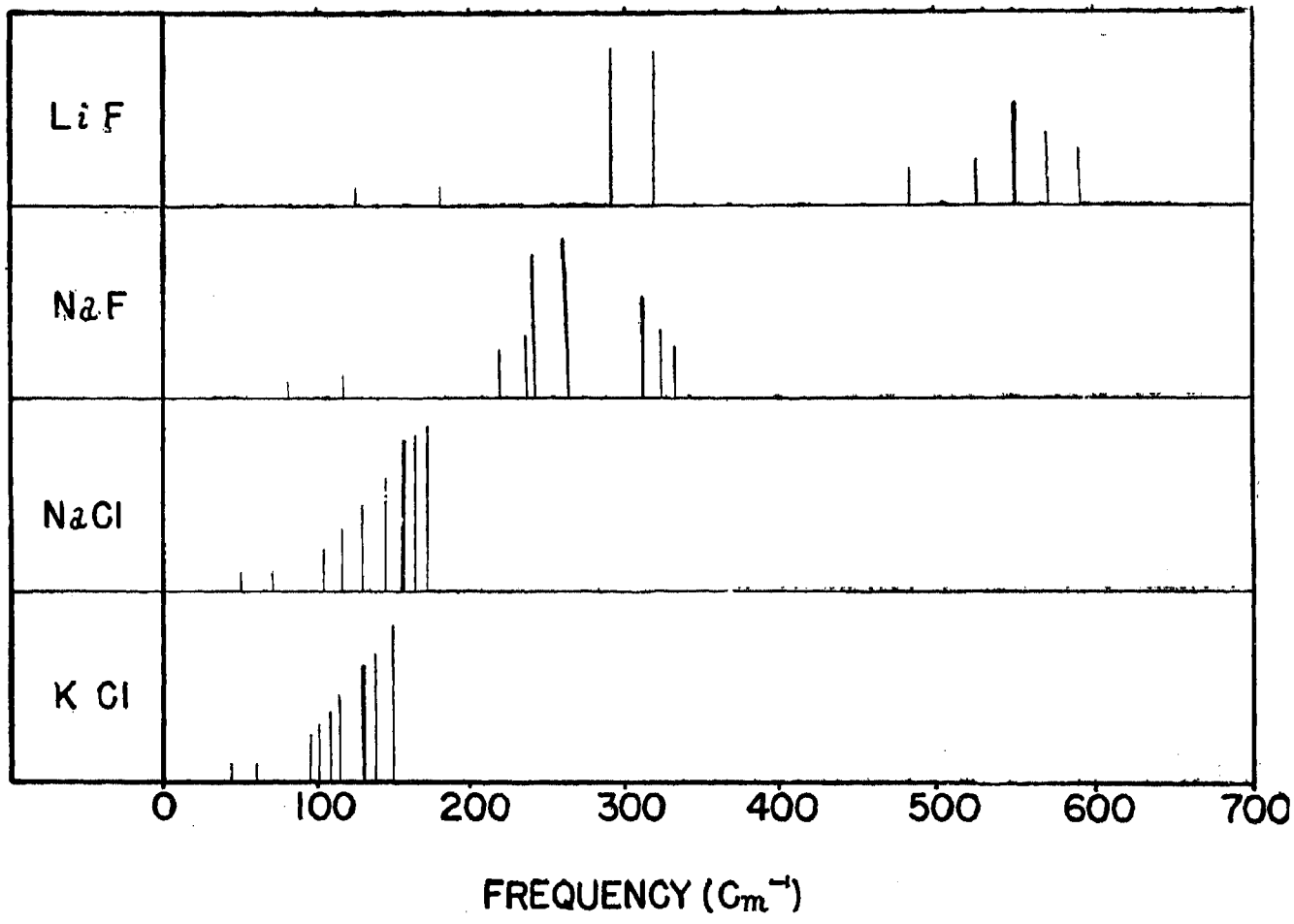

FIG. 3. Eigenfrequencies of Four Alkali Halides

4. The Eigenvibrations of Crystal Structures

To find an explanation of the remarkable facts detailed above, we have to consider the fundamental problem of the nature of the vibration spectrum of a crystal. The older theories of the subject (Debye, Max Born) approach this from the standpoint of the classical theory of elasticity. They identify the vibrations in the solid with waves traversing its interior in all directions. Such an approach is legitimate in considering the vibrations of low frequency in respect of which the discrete atomic structure of the medium may be ignored and the medium treated as continuous. But in considering the behaviour of a crystal in the infra-red range of frequency, we have necessarily to take into account its discrete structure, and the experimental facts show that the identification of the atomic vibrations with waves of all possible lengths and directions filling the volume of the crystal is not a valid procedure, and that a different approach to the problem is necessary. The fact that the crystal consists of a great many units of very small size which are exactly similar and similarly situated is the very natural starting point for such an approach. Since further, the atomic forces which determine the modes and frequencies of vibration of these units of structure are of limited range, the problem of determining these modes and

frequencies is closely analogous to the theory of the vibrations of polyatomic molecules, except that the units of structure are not isolated from each other and hence it is necessary to consider also their interactions. The problem has been handled by the present writer from this point of view (1943, 1947) and the result is reached that the structure of a crystal containing p atoms per unit cell has $(24p - 3)$ characteristic eigenvibrations. In $(3p - 3)$ of these eigenvibrations, equivalent atoms in adjacent cells of the structure oscillate with the same amplitude and the same phase, while in the remaining $21p$ eigenvibrations they oscillate with the same amplitude but with a phase which alternates in successive cells along one, two or all axes of the crystal lattice. The maximum number of distinct eigenfrequencies is $(24p - 3)$, but this number may be considerably reduced by reason of the crystal symmetry in various actual cases. For crystals of the rock-salt type, $p = 2$, and there are 45 eigenvibrations, but owing to the high crystal symmetry, many of these are similar and the number of distinct eigenfrequencies is only 9. Considered in relation to the entire crystal, these modes and frequencies are of course to be regarded as being very highly degenerate.

5. Evaluation of the Eigenfrequencies

Exact expressions for the 9 eigenfrequencies of crystals of the rock-salt type have been obtained by Mr. K. G. Ramanathan (1947). These expressions have been simplified and used by the present writer (1947) for theoretical evaluation of the frequencies for a number of crystals having this structure, including especially magnesium oxide. The eigenfrequencies of the four alkali halides with the lowest atomic weights as theoretically evaluated are shown on the wave-number scale in Fig. 3. The formulæ as simplified contain four constants, P, P', T and T'. But P and P' are nearly equal to each other and are large compared with T and T'. Hence, a further simplification may be effected by replacing P and P' by a single constant P and similarly also T and T' by a single constant T, being in each case their arithmetical mean. Even as thus highly simplified, the formulæ are sufficiently accurate to represent the facts correctly. For instance, in the case of magnesium oxide, the 9 eigenfrequencies expressed in wave-numbers come out as 704, 680, 652, 584, 527, 474, 428, 258 and 184 cm.$^{-1}$ respectively. Expressed in infra-red wave-lengths, they are 14·2 μ, 14·7 μ, 15·35 μ, 17·1 μ, 19·0 μ, 21·1 μ, 23·4 μ, 38·8 μ and 54·4 μ. The first three of the calculated egienfrequencies (ν_1, ν_2, ν_3) are recorded in the observations of Barnes and Brattain made with their thinnest plate as strong and well-defined absorption maxima. ν_4 coincides with Fock's absorption maximum, while ν_6 and ν_7 are those noted by Strong. The octaves of the first seven eigenfrequencies are also represented in the data of Barnes and Brattain as prominent absorption maxima. Some twenty other absorption lines recorded by them are also satisfactorily accounted for as summations of the eigenfrequencies taken two at a time. In Fig. 2 above, the fundamental eigenfrequencies are shown by heavy lines, their octaves by thin lines, and the summational frequencies by dotted lines. ν_8 and ν_9 are less than 300 cm.$^{-1}$ and do not therefore appear in the diagram.

It may be explained here that the constants P and P' represent the forces arising from unit displacements respectively of the two types of atoms in the structure from their positions of equilibrium, while T and T' represent the forces on a given atom due to a unit displacement of a neighbouring atom of the same kind. The magnitude of the constants is accordingly a measure of the strength of the interatomic forces which hold the crystal together. The following figures indicate how they differ in the five cases for which the frequency spectrum has been theoretically evaluated.

Table I

Substance	P	T	Units
MgO ..	$2{\cdot}82\times10^5$	$-0{\cdot}05\times10^5$	dynes per cm.
LiF ..	$1{\cdot}02\times10^5$	$-0{\cdot}015\times10^5$	,,
NaF ..	$6{\cdot}42\times10^4$	$-0{\cdot}10\times10^4$	,,
NaCl ..	$2{\cdot}422\times10^4$	$-0{\cdot}053\times10^4$	,,
KCl ..	$2{\cdot}30\times10^4$	$-0{\cdot}05\times10^4$	,,

The value of P in the case of magnesium oxide is of the same order of magnitude as the force-constants for covalent bindings known in various cases, and hence in spite of its structure being of the rock-salt type, magnesium oxide is very far indeed from being an "ionic" crystal. It may be mentioned for the sake of comparison that the force-constant P in the case of diamond is

$7{\cdot}54 \times 10^5$ dynes per centimeter. The force-constants in the two fluorides are distinctly smaller than in magnesium oxide, those for sodium fluoride being much less than for lithium fluoride. There is a further large fall in the magnitude of the force-constants in passing from the fluoride to the chloride of sodium, but only a trifling diminution as we pass from NaCl to KCl.

6. The Eigenvibrations and Their Infra-Red Activity

The *third* highest eigenfrequency (ν_3) shown by a thick line in each case for the four alkali halides is that of the mode in which the metal and the halogen atoms move together as groups in opposite phases. (In the Born theory, this is the infra-red active frequency.) The eigenfrequencies ν_4 and ν_5 are those of vibrations in which the lighter atoms alone oscillate, while the heavier atoms remain at rest. ν_6 and ν_7 are the vibrations in which the heavier atoms alone oscillate, the lighter atoms remaining at rest. In NaF and KCl, ν_4, ν_5, ν_6 and ν_7 are all close to each other, owing to the atomic weights of the metal and the halogen atoms being not very different. In NaCl, these four frequencies are more widely separated. In the case of LiF, owing to the great disparity in the atomic weights of lithium and fluorine, ν_6 and ν_7 are much smaller than ν_4 and ν_5. This has some remarkable consequences, as we shall presently notice, on the spectroscopic behaviour of lithium fluoride.

Figs. 4, 5, 6 and 7 represent respectively the reflection coefficients of NaCl, KCl, NaF and LiF in the range of infra-red frequencies in which they are completely opaque except in the thinnest layers. Under each figure, the fundamental eigenfrequencies have been indicated by heavy lines, their octaves by thin lines, and summations of the eigenfrequencies by dotted lines. [The curves have been redrawn on a frequency scale by Mr. K. G. Ramanathan from the observations of Czerny (1930) for the case of NaCl and KCl, and from the observations of Korth and of Hohls (1937) for the two fluorides]. It will be noticed that each of the four curves shows distinctive features of its own. The curve for LiF however stands out from the rest, exhibiting a strong reflection of over 70% over a wide range of frequency which appears separated into two regions by a distinct minimum. The reason for this behaviour, as will be seen from the figure, is that the fundamental eigenfrequencies fall into two widely separated groups. It is particularly remarkable that the group of lower frequency which does *not* include the so-called "active" fundamental ν_3 gives a stronger reflection than the group of higher frequency which includes ν_3. A similar feature also appears in absorption. According to Barnes (1932), the strongest absorption by thin films of lithium fluoride is at $32{\cdot}6\ \mu$ which is midway between ν_6 and ν_7 whose infra-red wave-lengths are respectively

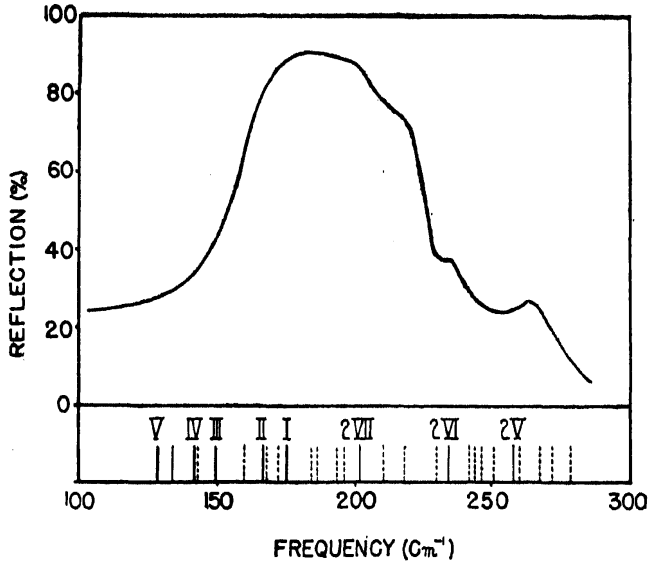

FIG. 4. Reflection Coefficients of Sodium Chloride

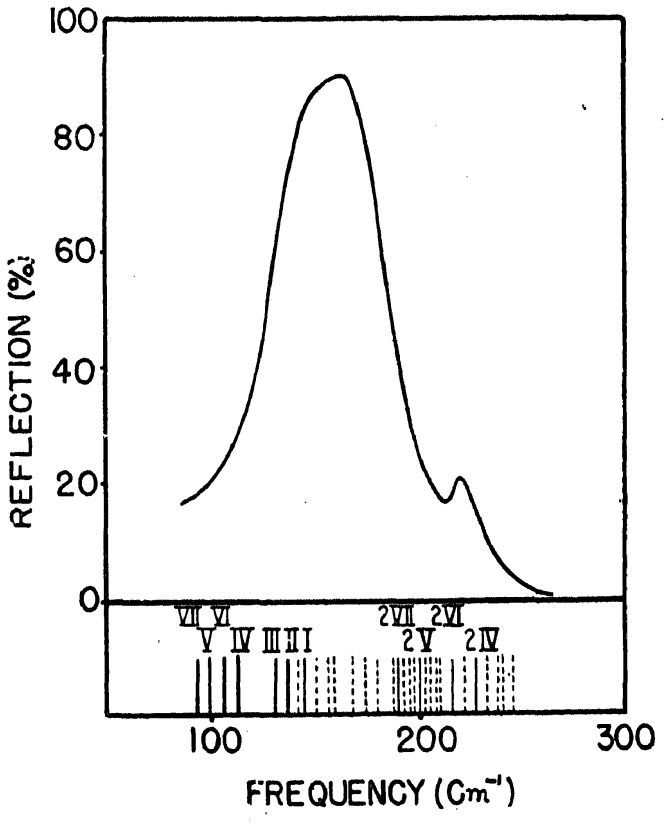

FIG. 5. Reflection Coefficients of Potassium Chloride

$31{\cdot}4\ \mu$ and $34{\cdot}2\ \mu$. In other words, the strongest infra-red activity is *not* that of the mode in which the lithium atoms and the fluoride atom move as groups in opposite

phases, but of the modes in which the fluorine atoms alone oscillate, the lithium atoms retaining at rest.

Surprising as the foregoing results may seem, they are supported by the fact that analogous results are also exhibited by the other crystals, though in a less striking fashion. In the case of sodium fluoride, Barnes (1932) found the maximum absorption by thin films to be at 40·6 μ, which is midway between 38·3 μ and 41·8 μ, the wave-lengths of ν_4 and ν_5 which are oscillations of the fluorine atoms with the sodium atoms remaining at rest. With magnesium oxide, the strongest absorption by thin films

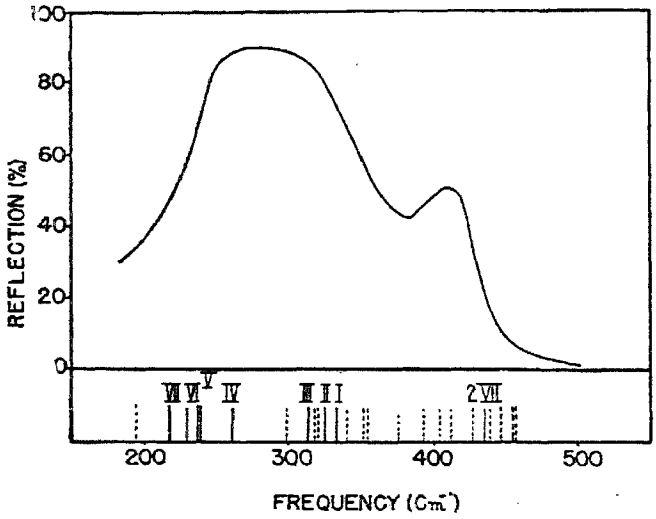

FIG. 6. Reflection Coefficients of Sodium Fluoride

as found by Fock is at 17·3 μ, nearly coinciding with ν_4 which is an oscillation of the oxygen atoms against each other, the magnesium atoms remaining at rest. In the cases of NaCl and KCl, the maximum absorption by thin films does not coincide with ν_3, but move nearly with ν_1 which is the highest of the nine eigenfrequencies, being an oscillation of the atomic layers parallel to the cubic planes, normally to themselves, with the metal and the halogen atoms which they contain moving in the same phase.

The fact which emerges clearly from the case of magnesium oxide is that all the eigenvibrations, as also their octaves and their summations, are infra-red active in greater or less measure. The measure of this activity is given by the absorption coefficient at the particular frequency. This has been evaluated by Mr. K. G. Ramanathan from the published data of Barnes and Brattain (1935) and represented on a logarithmic scale of ordinates in Fig. 2. It will be seen that the absorption coefficient falls off rapidly as we move towards higher frequencies. This suggests that the infra-red activity of the various modes in MgO and in the alkali halides is essentially an induced effect, arising from mechanical anharmonicity and consequent coupling with

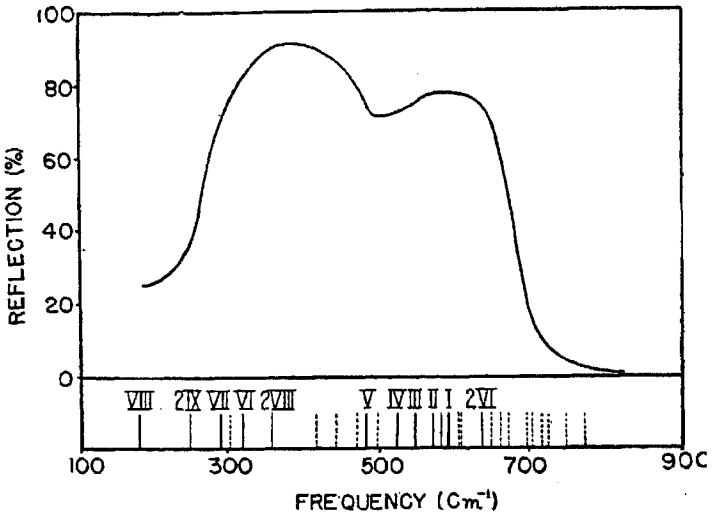

FIG. 7. Reflection Coefficients of Lithium Fluoride

each other of the various eigenvibrations, as a consequence of which all of them become active in greater or less measure, depending principally on their approximation in frequency to the "active" mode ν_3. The activity of the various possible overtones and summations necessarily falls off as we pass successively from the first-order to the second-order spectrum and from the second-order spectrum to the third-order spectrum and so on, the successive limits of frequency of these spectra being set by the highest fundamental and its overtones. The large diminution in the absorption coefficient and consequent improvement in transparency as we move towards shorter wave-lengths is readily understood on this basis.

Fuller details regarding the various topics referred to above, as well as references to the cited literature will be found in papers by the writer appearing in the *Proceedings of the Indian Academy of Sciences* for December 1947.

C. V. RAMAN.