

THE VIBRATION SPECTRA OF CRYSTALS

Part III. Rocksalt

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1. INTRODUCTION

ROCKSALT is typical of the so-called ionic crystals and is a much-discussed substance. The evaluation of its characteristic vibration frequencies on the basis of the theory set out in Part I, and the consideration of its spectroscopic behaviour in the light of that theory will form the subject of the present paper. From an experimental point of view, the case of rocksalt is a less favourable one than that of diamond, the frequencies being very low and hence crowded together into a region of the spectrum where observation is difficult and the available resolving powers are small. Nevertheless, as we shall see, the main facts have been quite clearly established and are in striking accord with the theoretical deductions.

2. NATURE OF THE INTERATOMIC FORCES

Discussions of the energy of formation of the alkali halides and of their physical properties usually proceed on the basis that the main interaction between the constituent particles in these crystals is the ordinary electrostatic or the Coulomb force between the ions, and that these forces which tend to contract the dimensions of the crystal are balanced by repulsive forces which vary much more rapidly with interatomic distance than do Coulomb forces between charges. Various additional interactions, *e.g.*, Van der Waals forces, have also been considered by way of refinement of the theory. That the electrostatic or the Madelung term is the largest in the expression for the cohesive energy of the alkali halides thus derived might lead one to believe that the electrostatic forces would also principally determine the frequencies of vibration of the ions about their positions of equilibrium. Actually, however, this is not the case, as may readily be shown by considering the consequences of the cubic symmetry of the ordering of the ions in the crystal.

Since the electrostatic forces acting on the ions vanish when they are located at the points of the lattice, it follows that at these points $(\partial V/\partial x) = (\partial V/\partial y) = (\partial V/\partial z) = 0$, where V represents the electrostatic potential in the vicinity of a lattice point due to all the ions except the one which is situated at that point. The cubic symmetry of the ordering also demands that $(\partial^2 V/\partial x^2) = (\partial^2 V/\partial y^2) = (\partial^2 V/\partial z^2)$. Combining these relations with Laplace's theorem which states that the sum of these three quantities is zero, it follows that each of them would be individually zero. In other words, not only does the electrostatic field at a lattice point due to the surrounding ions vanish, but it also vanishes in its immediate vicinity. If, therefore, one of the ions is displaced a little from its position of equilibrium, the surrounding ions being undisturbed, there would be no force tending to restore the displaced ion to its position of equilibrium. The same situation would arise if we imagine all the Na^+ ions to be displaced a little in one direction and all the Cl^- ions to be displaced a little in the opposite direction, so that each set of ions retains its cubic symmetry of arrangement. The resultant electrostatic force on each Na^+ ion and on each Cl^- ion in their displaced positions would vanish, and the frequency of the resulting oscillation would be zero, if forces of other descriptions were non-existent. We are accordingly compelled to recognize that the frequency of the vibration would be determined entirely by interatomic forces which are not primarily of electrostatic origin. It follows that these are essentially short-range forces which have a considerable magnitude as between neighbouring atoms but diminish very quickly as between more distant ones.

3. THE EIGENVIBRATIONS

As in the case of diamond discussed in the preceding paper, the rock-salt structure has nine eigenvibrations, eight of which may be described as normal or tangential oscillations of the octahedral or cubic layers of ions *alternately in opposite phases*, and the ninth as an oscillation with respect to each other of the two interpenetrating lattices of Na^+ and Cl^- ions respectively. These modes may be readily visualised with the aid of diagram of the structure of rock-salt (Fig. 1). As in the case of diamond again, the first step we shall take is to arrange these nine eigenvibrations in a descending sequence of frequency, thereby facilitating a comparison of the theoretically derived spectrum with the experimental data. Such arrangement is readily possible in view of the conclusion stated earlier, *viz.*, that the atomic interactions which determine the vibration frequencies are short-range forces.

We may, in the first instance, consider the interactions between each Na^+ ion and the 6 surrounding Cl^- ions and similarly also the interaction

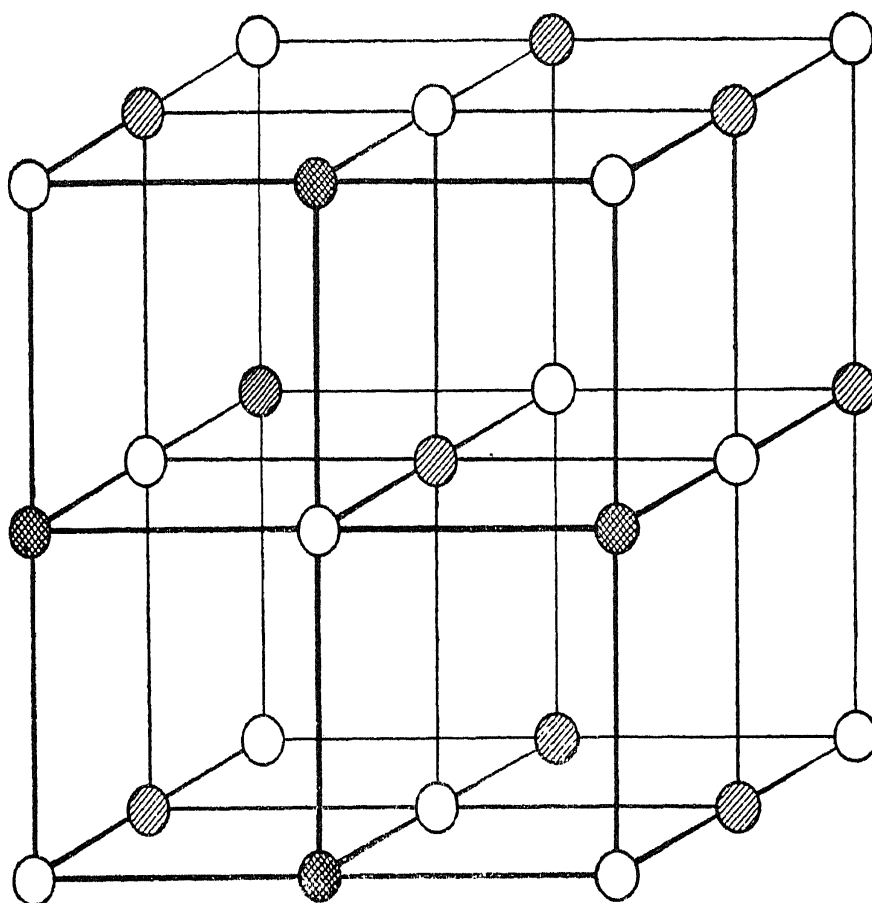


FIG. 1. The Structure of Rocksalt

between each Cl^- ion and the six surrounding Na^+ ions, *neglecting the forces due to the more distant ions in each case*. So long as the octahedral grouping of the surrounding ions is undisturbed, the restoring force per unit displacement acting on the central ion when it is displaced would be independent of direction, and it is also evident that it would be the same whether it is Na^+ or Cl^- . We shall denote this force by P and assume that it arises from an approach or recession of the Na^+ and Cl^- ions relatively to each other. The frequency of an oscillation would accordingly be determined by the magnitude of such displacements and by the masses of the moving particles. On this basis, the nine eigenvibrations fall into four groups, consisting of 3, 2, 2 and 2 respectively, each group having the same frequency. The first group of 3 eigenvibrations consists of:

(I) The *normal* oscillation of the cubic planes with Na^+ and Cl^- ions in these planes moving *in the same phase*;

(II) the *tangential* oscillation of the cubic planes, with the Na^+ and Cl^- ions in these planes moving in *opposite phases*; and

(III) the oscillation of the Na^+ and Cl^- lattices against each other *in any arbitrary direction*.

It can be seen from Fig. 1 that the displacements of the Na^+ and Cl^- ions relatively to each other are the same in all these three cases. Accord-

ingly, the operative force-constant is equal to P and the frequency ν of vibration in wave-numbers is given by the formula

$$4\pi^2\nu^2c^2 = P \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \quad (1)$$

m_1 and m_2 being the masses of the Na^+ and Cl^- ions respectively. The second group of eigenvibrations consists of

(IV) the normal oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest; and

(V) the tangential oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_1} \quad (2)$$

The third group of eigenvibrations consists of

(VI) the normal oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest: and

(VII) the tangential oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_2} \quad (3)$$

The fourth group of eigenvibrations consists of

(VIII) the normal oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in opposite phases* and

(IX) the tangential oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in the same phases*. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = 0. \quad (4)$$

For a final ordering of the nine eigenvibrations in a descending sequence of frequency, we have to consider also the forces of interaction between each Na^+ ions and the 12 surrounding Na^+ ions, and similarly also the forces between each Cl^- ion and the 12 surrounding Cl^- ions. It is readily seen that mode I would then have the highest frequency in the first group, since 8 out of the 12 like ions move in the opposite direction to the ion under consideration and thereby increase the restoring force. In mode II, 4 of the like ions move in the same direction and 4 in the opposite direction, cancelling out each other's effects. In mode III, all the 8 like ions which exert appreciable forces move in the same direction, thus diminishing the restoring force and therefore also the vibration frequency. The 3 modes thus arrange themselves in the order indicated. In the second and third groups it is readily seen from considerations similar to those stated

above, that the normal modes would have higher frequencies than the tangential ones. This is also the case in the fourth group, the frequencies of which no longer vanish when the forces between like ions are taken into consideration. These have naturally the lowest frequencies of all the nine eigenvibrations. Table I summarises the foregoing results.

TABLE I
Eigenvibrations of the Rocksalt Structure

Descending sequence of frequency	Degeneracy	Oscillating units	Direction of motion	Detailed description
I ..	3	Cubic Planes	Normal	Na and Cl ions moving in the same phase
II ..	6	Cubic Planes	Tangential	Na and Cl ions moving in opposite phases
III ..	3	Two lattices	Arbitrary	Na and Cl ions moving in opposite phases
IV ..	4	Octahedral Planes	Normal	Na ions moving and Cl ions at rest
V ..	8	Octahedral Planes	Tangential	Na ions moving and Cl ions at rest
VI ..	4	Octahedral Planes	Normal	Cl ions moving and Na ions at rest
VII ..	8	Octahedral Planes	Tangential	Cl ions moving and Na ions at rest
VIII ..	3	Cubic Planes	Normal	Na and Cl ions in opposite phases
IX ..	6	Cubic Planes	Tangential	Na and Cl ions in same phases

4. EVALUATION OF THE EIGENFREQUENCIES

To carry the matter a step further and evaluate the frequencies of each of the nine eigenvibrations, we shall make use of the exact theoretical formulæ derived by K. G. Ramanathan (1947) in a paper appearing in these *Proceedings* which take into account the interaction between the ions of each kind and their 26 nearest neighbours. They contain 11 independent constants which express the forces arising from such interactions and are connected by two additional relations. Ramanathan's formulæ may be simplified by ignoring the effect of the 8 most remote ions expressed by his constant V appearing in them, and also by putting his constants R , S and S' all equal to zero. The former step is justified on the view that we are here concerned with short-range forces, and the latter by the consideration that the constants R , S and S' refer to forces which arise from displacements which do not alter the distance between the interacting ions. On any reasonable view of the origin of the interactions in an ionic crystal with cubic symmetry, such forces should be vanishingly small in comparison with the forces arising from displacements which alter the distances between the

interacting ions. It may be remarked also that T and U in Ramanathan's formulæ represent forces between two ions of the same kind arising from a unit displacement of one of them, the force T being parallel to the displacement and the force U transverse to it, both being inclined at the same angle of 45° to the line joining the two interacting ions. In these circumstances and considering the ionic nature of the structure, it is a justifiable simplification of the formulæ to put $T = U$ and similarly also $T' = U'$. With these simplifications, the final formulæ contain only four unknown constants P, P', T, T' which are connected by the relation

$$(P + 8T) = (P' + 8T') \quad (5)$$

Further,

$$P \gg T \text{ and } P' \gg T' \quad (6)$$

from which it follows

$$P \approx P' \quad (7)$$

The formulæ for the frequency of the nine eigenvibrations as thus simplified are listed in Table II.

TABLE II

Frequency Expressions

P and P' are positive ; T and T' are negative.

Descending sequence of frequency	$4\pi^2\nu^2c^2$	Description of mode
I ..	$\frac{P-8T}{m_1} + \frac{P'-8T'}{m_2} + \frac{16(T+T')}{m_1+m_2}$	Normal oscillation of cubic planes with Na and Cl in same phase
II ..	$\frac{P}{m_1} + \frac{P'}{m_2} + \frac{8(T+T')}{m_1+m_2}$	Tangential oscillation of cubic planes with Na and Cl in opposite phases
III ..	$\frac{P+8T}{m_1} + \frac{P'+8T'}{m_2}$	Oscillation of the two lattices in opposite phases
IV ..	$\frac{P-8T}{m_1}$	Normal oscillation of Na ions in octahedral planes
V ..	$\frac{P+4T}{m_1}$	Tangential oscillation of Na ions in octahedral planes
VI ..	$\frac{P'-8T'}{m_2}$	Normal oscillation of Cl ions in octahedral planes
VII ..	$\frac{P'+4T'}{m_2}$	Tangential oscillation of Cl ions in octahedral planes
VIII ..	$-\frac{16(T+T')}{m_1+m_2}$	Normal oscillation of cubic planes with Na and Cl in opposite phases
IX ..	$-\frac{8(T+T')}{m_1+m_2}$	Tangential oscillation of cubic planes with Na and Cl in same phase

One of the noteworthy features which emerge from the table is that the vibration in which the two lattices move in opposite phases is not that of the highest frequency but is only the third in the list, though the frequency differences between it and the two others above are not large. The four modes appearing in the middle of the table fall into pairs whose frequencies are approximately as the square roots of the masses of the chlorine and the sodium ions. The two modes at the foot of the table stand out from the rest by reason of the fact that their frequencies depend only on the weak interactions between similar ions instead of on the stronger interactions between the dissimilar ones, as in the case of the other modes. It will be noticed that the ratio of their frequencies is $\sqrt{2}$.

5. ACTIVITY IN LIGHT-SCATTERING

The eight eigenvibrations which are movements of the cubic and octahedral layers of atoms in the crystal are necessarily inactive in light-scattering *in the first approximation*, since the motion is in opposite phases in alternate layers. The oscillation of the lattices of Na and Cl ions with respect to each other is also inactive but for a different reason, namely the location of the Na and Cl ions alternately along the cube axes, in consequence of which the variations of their optical polarisability resulting from their movements cancel out *in the first approximation*.

In the second approximation, all the nine modes may be active, giving rise to octaves and combinations of the fundamental frequencies as shifts in light-scattering. The intensity of the observable effects would however depend notably on various factors, including especially the nature of the movements of the neighbouring Na and Cl ions with respect to each other. These movements are very similar in modes I, II and III, the two Cl⁻ ions on each side of a Na⁺ ion along the cube axis respectively approaching and receding from it, while the two Na⁺ ions on each side of a Cl⁻ ion behave similarly with respect to the latter. *Provided the amplitude of atomic movements is sufficiently large*, which would be the case in the present theory which regards the movements as restricted to extremely small volume elements in the crystal, each pair of neighbouring Na⁺ and Cl⁻ ions at the phase of their nearest approach would have a polarisability greater than the value averaged over the whole period, thus giving rise to a variation of double frequency. Modes I, II and III would therefore all be active to much the same extent, but since mode II has a degeneracy 6, it should appear as the octave more strongly than either mode I or III which has a degeneracy of 3 only.

We may now consider modes IV and V which represent oscillations of the Na⁺ ions only lying in the octahedral layers, as also modes VI and VII

which represent similar oscillations of the Cl^- ions only. We notice that the nature of the approach of the Na^+ and Cl^- ions to each other is very different in the normal and tangential modes in each case. In the normal modes, *viz.*, IV and VI, six ions of one kind simultaneously approach or recede from an ion of the other kind, while in the tangential modes, *viz.*, V and VII, two ions of one kind approach, two recede, and two others remain at the same distance. Hence the changes of polarisability should be much larger in the normal modes IV and VI than in the tangential modes V and VII. Further, since the refractivity of the Cl^- ion is very much larger than that of Na^+ , it follows that mode VI in which the six Cl^- ions surrounding a Na^+ ion simultaneously approach or recede from it should display a much stronger activity in light-scattering than mode IV in which six Na^+ ions simultaneously approach or recede from a Cl^- ion. Indeed, one may justifiably infer that in respect of intensity in second-order scattering, mode VI would transcend in intensity all the other eight modes. Mode VIII which is a normal oscillation of the cubic planes involves only small changes in the relative distance of the Na^+ and Cl^- ions and should therefore be very weak in light scattering, while mode IX which is a transverse oscillation of the same planes should be still weaker.

6. ACTIVITY IN INFRA-RED ABSORPTION

Since the two interpenetrating lattices in the structure of rocksalt consist of dissimilar particles, their oscillation against each other (mode III in our table) is necessarily active in infra-red absorption. In all the other eight eigenvibrations, the phase of the motion is reversed at each successive layer, and hence *if regarded as independent normal vibrations of the structure*, they should be inactive in respect of infra-red absorption. The assumed independence of the modes in respect of their excitation by infalling radiation is, however, very far from corresponding with reality. Owing to the anharmonicity and the finite amplitudes of oscillation, the different eigenvibrations are in effect coupled with each other, and hence any one mode which is active would induce an activity in the other so-called inactive modes. Modes I and II are very similar to mode III in their general character, since the latter may be regarded as being either a normal or a tangential oscillation of the layers of the Na^+ and Cl^- ions in the crystal parallel to the cubic planes. They also differ from it comparatively little in frequency. Hence the intense activity of mode III, consequential on the Na^+ and Cl^- ions carrying opposite charges of electricity, must necessarily also result in inducing a strong activity of modes I and II. Mode III may likewise be regarded as a normal or tangential oscillation of the octahedral layers of the Na^+ and Cl^- ions in the crystal against each other. Hence the intense activity of mode

III would similarly induce an activity of modes IV, V, VI and VII, but in a much less measure than in the case of modes I and II, since the former involve only the Na^+ or the Cl^- layers moving but not both, and also since the approximation in frequency is much less close. We may therefore conclude that the first-order infra-red activity of rocksalt would be very strong for modes I, II and III, and would fall off rapidly as we pass successively to modes IV, V, VI and VII. Modes VIII and IX could scarcely be expected to show any such induced activity of the first order in view of their very low frequencies.

Second-order infra-red activity may arise either from mechanical or electrical anharmonicity. In the present case, since the Na^+ and Cl^- ions carry electric charges, it is the mechanical anharmonicity with which we are principally concerned. Since mode III has an intense first-order activity, it should also be active in the second order. The other eight modes being inactive in the first order if regarded as independent normal vibrations, they can be active in the second order only by reason of electrical anharmonicity. Such activity would however be much less important in the circumstances of the case than the activity induced by their proximity in frequency to the intensely active fundamental vibration, *viz.*, mode III. In other words, such of the octaves and combinations of the various primary frequencies as are not too remote from the fundamental frequency of mode III may be expected to become active to an extent determined principally by such contiguity.

7. THE SPECTROSCOPIC FACTS

The results set out in the four preceding sections taken as a whole give us a theoretical picture of the spectroscopic behaviour of rocksalt capable of being compared with the picture of the actual facts as observed by various investigators. Such a comparison shows a striking agreement, both generally and in details, and thus confirms the correctness of the theoretical approach made to the problem. For the sake of convenience, we shall make the comparison in three successive steps.

The Frequency Spectrum.—Table II gives the theoretical formulæ for the frequencies in terms of four force-constants, *viz.*, P , P' , T and T' . These constants are not all independent but are connected with each other by the relation $(P + 8T) = (P' + 8T')$, with the further indication that P and P' are nearly equal to each other, and that both are very much larger than T and T' . We can make use of these relationships to simplify the formulæ still further by replacing both P and P' in the expressions by a single constant P which is the mean of the two, and similarly replacing T and T' by a single constant T which is their mean. From the structure of the formulæ, it is evident that such replacement would not materially alter the numerical

TABLE III
Calculated and Observed Values of the Eigenfrequencies

$P=2.422 \times 10^4$ dynes per cm. $T= -0.053 \times 10^4$ dynes per cm.

Serial Order	$4\pi^2\nu^2c^2$	Calculated Frequency	Observed Frequency	Activity in Light-scattering
I ..	$\frac{P-8T}{\mu} + \frac{32T}{m_1+m_2}$	cm. ⁻¹ 172	cm. ⁻¹ 175	Strong
II ..	$\frac{P}{\mu} + \frac{16T}{m_1+m_2}$	164	167	Very Strong
III ..	$\frac{P+8T}{\mu}$	157	150	Strong
IV ..	$\frac{P-8T}{m_1}$	145	143	Strong
V ..	$\frac{P+4T}{m_1}$	128	129	Weak
VI ..	$\frac{P-8T}{m_2}$	117	117	Very Strong
VII ..	$\frac{P+4T}{m_2}$	103	101	Weak
VIII ..	$-\frac{32T}{m_1+m_2}$	70	67	Very Weak
IX ..	$-\frac{16T}{m_1+m_2}$	50	43	Very Weak

value of any of the frequencies, while on the other hand, it affords the advantage of enabling us to express all the nine frequencies in terms of two independent constants only, one of which is very much larger than the other. Table III shows the formulæ as thus simplified in the second column, μ being the usual symbol for the reduced mass of the Na^+ and Cl^- ions. With the assumed values of P and T shown at the head of the table, the numerical values have been calculated and shown in the third column in wavenumbers. The fourth column shows the observed frequencies, derived from the investigation by Dr. R. S. Krishnan on the second-order spectrum of light-scattering reported in these *Proceedings* (1947). It will be noticed that there is excellent agreement throughout.

Activity on Light-Scattering.—In his paper on the case of rocksalt appearing in these *Proceedings*, Dr. R. S. Krishnan (1947) has set out and discussed the facts ascertained by him in full detail, and it is scarcely necessary therefore to traverse the same ground here. It is sufficient to remark

that in all respects, *viz.*, the discrete structure of the spectrum, the magnitude of the frequency shifts and the relative intensities with which they appear, the experimental facts are in agreement with the indications of theory set out in Section 5 above. Of particular significance is the observation made by Krishnan that the sharp and intense line with a frequency shift of 235 cm.^{-1} , which is a conspicuous feature in the spectrum as recorded even with small instruments, remains sharp and gains in intensity relatively to the rest of the spectrum when recorded with instruments of higher dispersion and greater resolving power, thereby clearly demonstrating its monochromatic character. As will be seen from Table III, this line represents the octave of mode VI. It appears with an intensity transcending that of all other features in the spectrum, a fact which is readily understood since in this mode, the Cl^- ions which have a far higher refractivity than the Na^+ ions simultaneously approach towards or recede away from the latter in groups of six at a time.

Activity in Infra-Red Absorption.—The fundamental mode of highest frequency and its overtones sharply define the upper limits of frequency of the successive orders of spectra. Expressed in wave-lengths, these limits are respectively 57μ , 29μ , 19μ and 14μ . On our present theory, we should expect large changes in the behaviour of rocksalt on passing over these limits. In agreement with this expectation, the observational data show a transition from nearly perfect transparency to practically complete opacity for a thickness of 5 cm. in the wave-length range from 14μ to 19μ . A similar transition occurs for a thickness of 0.05 cm. in the wave-length range of 19μ to 29μ , and for a thickness of 0.0005 cm. in the wave-length range from 29μ to 57μ . For the last mentioned thickness the most intense absorption is found in the region from 57μ to 66μ which includes the frequencies of the three most strongly active modes I, II and III. The overall picture of the observed behaviour of rocksalt is thus in accord with the indications of the theory.

In view of the numerous overtones and combinations present and also considering the prominent role played by mechanical anharmonicity in the absorption of infra-red radiations by rocksalt, we would not be justified in expecting the absorption data to show up the discrete character of the vibration spectrum very obviously. Even if theoretical considerations had permitted any such result, the low resolving powers used and the difficulties of observation in the remote infra-red would prevent its realisation. Some indications of the discrete structure of the spectra are however forthcoming from the work of Czerny (1930) and Barnes and Czerny (1931). These authors have studied the variation with wave-length in the reflecting power of a rocksalt plate at nearly normal incidence, and also the variations of the transmission coefficient with wave-length for plates of different thicknesses.

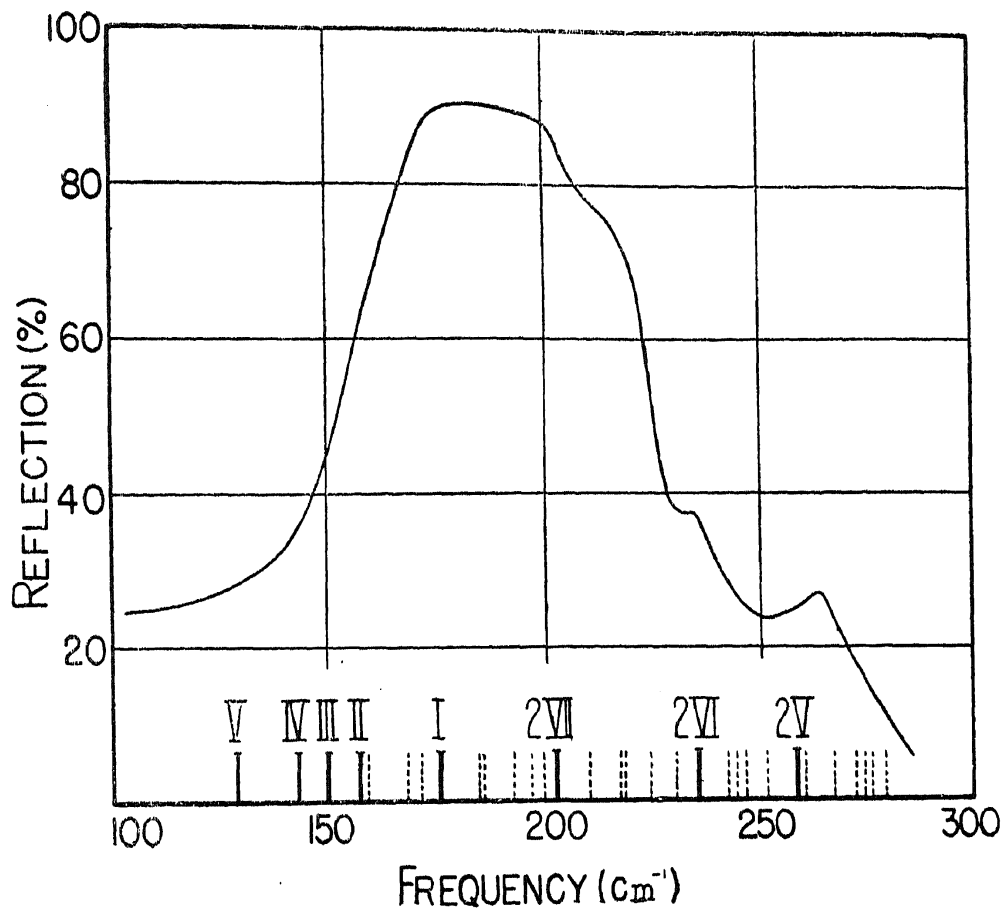


FIG. 2. Reflecting Power of a Rocksalt Plate

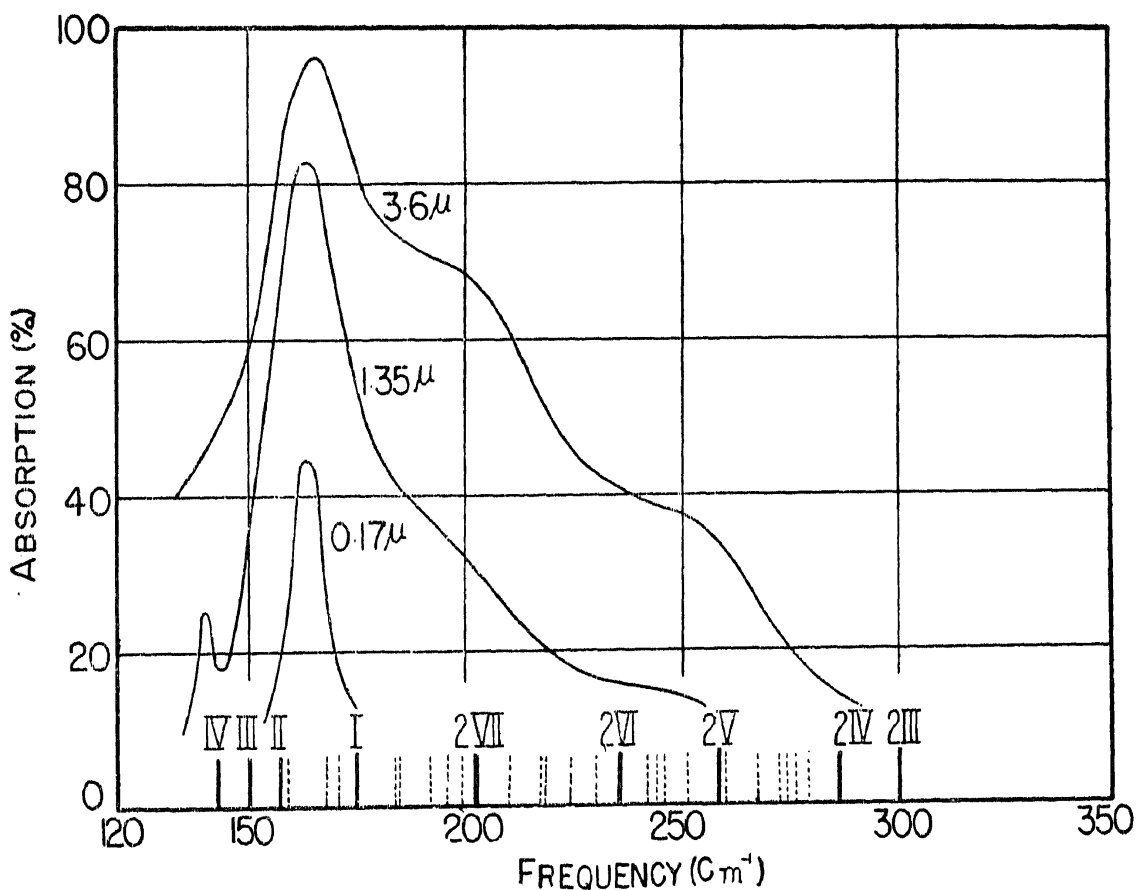


FIG. 3. Absorption Spectra of Rocksalt Films

Their results are shown in Figs. 2 and 3, carefully redrawn with wavenumbers instead of wave-lengths as abscissæ; for purposes of comparison, the fundamental vibration frequencies and their overtones have been indicated on the abscissæ by heavy lines and the various possible combinations by dotted lines. It will be seen from Fig. 2 that the reflecting power rises steeply and reaches its maximum value at the point where the first-order vibration spectrum ends. The fall of the reflecting power in the region of the second-order spectrum is less abrupt and shows undulations, the positions of which roughly agree with the overtone frequencies of our modes VII, VI and V.

It is a noteworthy feature in Fig. 3 that the "peak" of absorption even with the thinnest films does not coincide with the frequency of the oscillation of the Na^+ and Cl^- lattices with respect to each other which is our mode III, but is shifted definitely to a higher frequency. The explanation of this effect is evidently that besides mode III, there are other modes, *viz.*, I and II, and also various combinations in the vicinity which are active, and the course of the absorption curve is determined by the superposition of all their activities. The subsidiary maximum at 143 cm.^{-1} noticed in the absorption curve for the second thinnest film may be identified with the fundamental frequency of mode IV. With the thickest of the three films, undulations are noticed in the absorption curve at approximately the same frequencies as the octaves of modes VII and V. Mentzel (1934) has recorded an inflexion in the absorption curve of rocksalt at about 290 cm.^{-1} which may be interpreted as due to the activity of the overtones of modes III and IV.

7. SUMMARY

It is pointed out that the vibration frequencies of the rocksalt structure are determined entirely by short-range atomic interactions, since the effects of the Coulomb forces cancel out. The numerical evaluation of the nine eigenfrequencies on this basis leads to results in excellent accord with the observational data. Their activities in light-scattering and infra-red absorption are also discussed. The vibration most strongly active in light-scattering is that of the Cl^- ions normal to the octahedral planes, the Na^+ ions remaining at rest. It is also pointed out that the peak of the infra-red absorption at 61μ for thin films observed by Barnes and Czerny does *not* represent the frequency of oscillation of the Na and Cl lattices with respect to each other, but is shifted with respect to it owing to the activity of other modes in the vicinity.

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