

# 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  $\text{Na}^+$  ions to be displaced a little in one direction and all the  $\text{Cl}^-$  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  $\text{Na}^+$  ion and on each  $\text{Cl}^-$  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 rocksalt 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  $\text{Na}^+$  and  $\text{Cl}^-$  ions respectively. These modes may be readily visualised with the aid of diagram of the structure of rocksalt (figure 1). As

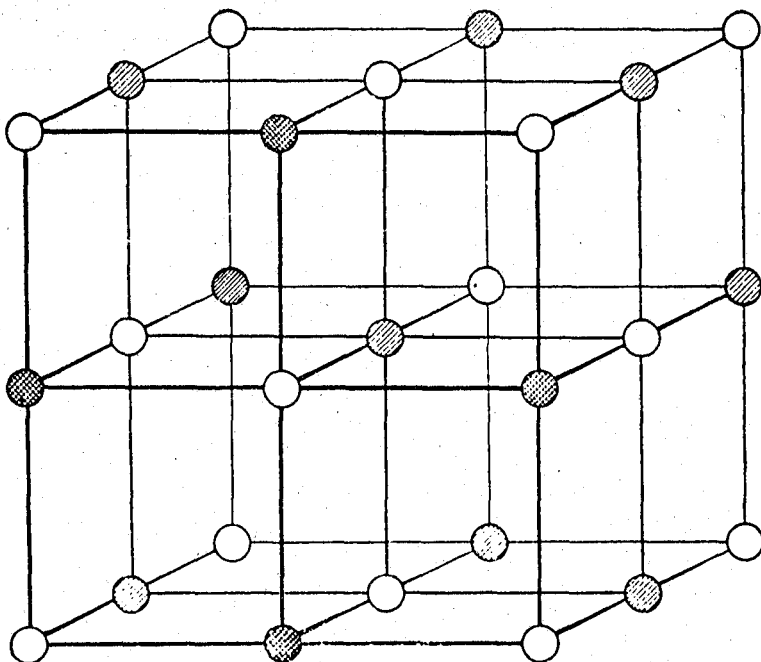


Figure 1. The structure of rocksalt.

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  $\text{Na}^+$  ion and the 6 surrounding  $\text{Cl}^-$  ions and similarly also the interaction between each  $\text{Cl}^-$  ion and the six surrounding  $\text{Na}^+$  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  $\text{Na}^+$  or  $\text{Cl}^-$ . We shall denote this force by  $P$  and assume that it arises from an approach or recession of the  $\text{Na}^+$  and  $\text{Cl}^-$  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  $\text{Na}^+$  and  $\text{Cl}^-$  ions in these planes moving *in the same phase*;  
 (II) the *tangential* oscillation of the cubic planes, with the  $\text{Na}^+$  and  $\text{Cl}^-$  ions in these planes moving *in opposite phases*; and  
 (III) the oscillation of the  $\text{Na}^+$  and  $\text{Cl}^-$  lattices against each other *in any arbitrary direction*.

It can be seen from figure 1 that the displacements of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions relatively to each other are the same in all these three cases. Accordingly, the operative force-constant is equal to  $P$  and the frequency  $\nu$  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 masses of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions respectively. The second group of eigenvibrations consists of:

- (IV) the normal oscillations of the  $\text{Na}^+$  ions in the octahedral planes, the  $\text{Cl}^-$  ions remaining at rest; and  
 (V) the tangential oscillations of the  $\text{Na}^+$  ions in the octahedral planes, the  $\text{Cl}^-$  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  $\text{Cl}^-$  ions in the octahedral planes, the  $\text{Na}^+$  ions remaining at rest; and  
 (VII) the tangential oscillations of the  $\text{Cl}^-$  ions in the octahedral planes, the  $\text{Na}^+$  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  $\text{Na}^+$  and  $\text{Cl}^-$  ions in these planes moving *in opposite phases* and  
 (IX) the tangential oscillations of the cubic planes of atoms, the  $\text{Na}^+$  and  $\text{Cl}^-$  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  $\text{Na}^+$

ions and the 12 surrounding  $\text{Na}^+$  ions, and similarly also the forces between each  $\text{Cl}^-$  ion and the 12 surrounding  $\text{Cl}^-$  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 1 summarises the foregoing results.

Table 1. 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 formulae 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 formulae may be simplified by ignoring the effect of the 8 most

**Table 2.** Frequency expressions  
(P and P' are positive; T and T' are negative.)

Descending sequence of frequency	$4n^2v^2c^2$	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

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 formulae 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  $45^\circ$  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 formulae to put  $T = U$  and similarly also  $T' = U'$ . With these simplifications, the final formulae contain only four unknown constants  $P$ ,  $P'$ ,  $T$ ,  $T'$  which are connected by the relation

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

Further,

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

from which it follows

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

The formulae for the frequency of the nine eigenvibrations as thus simplified are listed in table 2.

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<sup>-</sup> ions on each side of a Na<sup>+</sup> ion along the cube axis respectively approaching and receding from it, while the two Na<sup>+</sup> ions on each side of a Cl<sup>-</sup> 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<sup>+</sup> and Cl<sup>-</sup> 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<sup>+</sup> ions only lying in the octahedral layers, as also modes VI and VII which represent similar oscillations of the Cl<sup>-</sup> ions only. We notice that the nature of the approach of the Na<sup>+</sup> and Cl<sup>-</sup> 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<sup>-</sup> ion is very much larger than that of Na<sup>+</sup>, it follows that mode VI in which the six Cl<sup>-</sup> ions surrounding a Na<sup>+</sup> ion simultaneously approach or recede from it should display a much stronger activity in light-scattering than mode IV in which six Na<sup>+</sup> ions simultaneously approach or recede from a Cl<sup>-</sup> 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<sup>+</sup> and Cl<sup>-</sup> ions and should therefore be very weak in light scattering, while mode IX which is transverse-oscillation of the same planes should be still weaker.













