DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part II. The Rocksalt Structure

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1. Introduction

Many solids crystallise with a structure similar to that of rocksalt and it is therefore of importance to investigate the vibration spectrum of this crystal. Expressions for the frequencies of its nine eigenvibrations are derived in this paper by methods similar to those adopted in the case of diamond in the preceding communication.

2. Description of the Modes

As in the case of diamond, the modes of vibration of the rocksalt structure can be derived directly from the four possible modes of vibration of the face-centred cubic lattice, *viz.*, the normal and tangential oscillations of the octahedral planes of atoms and the normal and tangential oscillations of the cubic planes of atoms with degeneracies of 4, 8, 3 and 6 respectively. Since there are two atoms per unit cell in rocksalt, the number of possibilities is doubled up just as in diamond. The atoms in any particular cell can move either with the same phase or with opposite phases in every one of the four possibilities of a simple face-centred lattice. But, the case of rocksalt differs from diamond in some important respects. Firstly, the two atoms in the unit cell have different masses. Secondly, while in diamond, the layers of atoms belonging to the two interpenetrating lattices appear separated both in the octahedral and in the cubic planes, in rocksalt the layers are separated only in the octahedral planes, the cubic planes consisting of atoms of both kinds located in the same layer. Further, the octahedral layers are spaced at equal intervals, any layer of atoms of one kind being situated exactly midway between neighbouring layers of the other kind. Because of this, the equations of motion of the two types of atoms for the four octahedral modes are independent of each other. These modes are the normal and tangential oscillations of the octahedral layers of sodium atoms and the normal and tangential oscillations of the octahedral layers of chlorine atoms

having degeneracies of 4, 8, 4 and 8 respectively. In the case of the modes in which the cubic planes are involved, the equations of motion of the two types of atoms are not independent of each other for the reason stated above. There will be two modes in which the planes move normally with respect to themselves. In one of these, the atoms belonging to the two lattices situated in any cubic plane move with the same phase and in the other with opposite phases. The degeneracies for these two modes are three each. Similarly, corresponding to the above two possibilities, there will be two tangential modes with degeneracies of 6 each. In addition to the eight modes described already, there will be one more triply degenerate mode in which the atoms belonging to the two lattices move against each other in any three orthogonal directions.

3. The Force-Constants

In the discussion below, we shall deal with the forces produced on any sodium atom proportional to its own displacement and those due to the displacements of the 26 atoms nearest to itself. Similarly we shall have to consider also the forces produced on any chlorine atom due to its own displacement and the displacements of its 26 nearest neighbours. There will therefore be $2(26 \times 9 + 3) = 474$ force-components in all. The 26 neighbours of any atom (sodium or chlorine) are situated in such a manner that if we consider any unit cube of the crystal with the atom under consideration at the centre of the cube, then the six atoms (of the other kind, 1 to 6) situated at the face-centres of the cube are the nearest neighbours. The twelve atoms (7 to 18 of the same kind) located at the midpoints of the 12 cube edges and the eight atoms (19 to 26 of the other kind) situated at the eight corners of the cube form the next nearest and the more distant neighbours respectively. The 474 force-components mentioned above, would be greatly reduced in number for various reasons. There are actually three different factors which contribute to such reduction. Firstly, the 26 neighbours divide themselves into three different groups of atoms of 6, 12 and 8 such that the forces on the atom under consideration due to the displacements of all the atoms of a particular species can be described by the same set of constants. Secondly, the forces produced on any atom of one kind (say chlorine) due to the displacements of any other atom of the second kind, are the same as the forces produced by the displacements of the particular atom of the first kind on the same atom of the second kind. Thirdly, symmetry effects a great simplification and reduction of the number of independent constants. In addition to the fact that the force constants of different atoms of a particular group transform among themselves, it may also happen that some of the constants

vanish. If by the application of a symmetry operation, the force in a particular direction on any atom (i) due to the displacements of another atom (j) in a particular direction comes out to be equal to the force on the same atom, (i) in the same direction by the displacement of (j) in the opposite direction then the force must vanish. Applying these principles, we find that the 474 force components can be reduced to 12 independent constants. A description of all the force constants is contained in Table I.

TABLE I

(See Explanatory note below)

Atoms responsible for forces	Symbol	Description of Force-Constants
0	P, P′	Force on atom proportional to its own displacement.
1 to 6	Q	Force and displacement parallel to each other and to the line joining the two atoms.
1 to 6	R	Force and displacement perpendicular to the cubic plane containing the two atoms.
7 to 18	S, S′	Force and displacement perpendicular to the cubic plane containing the two atoms.
7 to 18	T, T′	Force and displacement along the same cube axis, the plane containing the two being the cubic plane containing the two atoms.
7 to 18	U, U′	Force and displacement along different cube axes, the plane containing the two being the cubic plane containing the two atoms.
19 to 26	V	Directions of both force and displacement along a cube axis.
19 to 26	W	Direction of displacement along a cube axis and that of the force along any one of the other two axes.

Atom 0 may refer to either sodium or chlorine and the other numbers accordingly. The symbols P, S, T and U refer to sodium atoms and P′, S′, T′ and U′ to chlorine atoms. The other symbols Q, R, V and W are common to both.

In addition to the simplifications already described, we can derive two relations between the force constants, one representing the fact that the work done in any small displacement (δx) of the entire crystal is zero and the other that the work done in any small displacement (δx) of all the chlorine atoms is exactly equal to the work done in an equal displacement of all the sodium atoms, the chlorines now remaining at rest. These two relations are :

$$\{(P+2Q+4R+4S+8T+8V) + (P'+2Q+4R+4S'+8T'+8V)\}\,\delta x^2=0 \quad (1)$$

and $$(P+4S+8T)\,\delta x^2 = (P'+4S'+8T')\,\delta x^2 \quad (2)$$

combining (1) and (2), we find that

$$(P+4S+8T) = (P'+4S'+8T') = -(2Q+4R+8V) \quad (3)$$

4. The Frequency Expressions

We will now proceed to derive expressions for the frequencies of vibration of the nine modes. In what follows, the masses of the sodium and chlorine atoms will be represented by m_1 and m_2 and their displacements by $x_1 y_1 z_1$ and $x_2 y_2 z_2$ respectively. The x, y and z displacements of any sodium atom in a particular normal mode will be numerically the same as the corresponding displacements of any other sodium atom, the directions of displacement being defined by the normal mode. Similarly the numerical values of the displacements will be the same for all the chlorine atoms. The deduction of the equations of motion of the various normal modes has not been shown here in detail as they can be written out in all the cases by mere inspection of a model.

A: The two lattices oscillating against each other in any three orthogonal directions. At any instant of time the two types of ions will be moving in opposite directions. The direction of motion in this case can be anything. So let us put $y = ax$ and $z = bx$; the constants (a) and (b) depending on the direction of displacement. The equations of motion involving x will be

$$\left.\begin{aligned} m_1 \frac{d^2x_1}{dt^2} &= (\mathrm{P} + 4\mathrm{S} + 8\mathrm{T})\, x_1 - (2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})\, x_2 \\ m_2 \frac{d^2x_2}{dt^2} &= -(2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})\, x_1 + (\mathrm{P}' + 4\mathrm{S}' + 8\mathrm{T}')\, x_2 \end{aligned}\right\} \quad (4)$$

The y and z equations of motion will be quite similar to these two. The constants (a) and (b) do not enter the equations, showing that the frequency of vibration is independent of the direction of motion. Denoting the expression $\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$ by $1/\mu$, the two equations (4) lead to the solution

$$4\pi^2 c^2 \nu_1^2 \mu =$$

$$(\mathrm{P} + 4\mathrm{S} + 8\mathrm{T}) = (\mathrm{P}' + 4\mathrm{S}' + 8\mathrm{T}') = -(2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})$$

B: Oscillation of the alternate octahedral layers of sodium atoms against each other normally with respect to themselves. In this case the displacements of the chlorine atoms will be zero. If we assume the (111) planes to be the oscillating units $x = y = z$. The equation of motion for x becomes

$$m_1 \frac{d^2x_1}{dt^2} = (\mathrm{P} - 8\mathrm{U})\, x_1 \quad (5)$$

with two identical equations for y_1 and z_1. Therefore

$$4\pi^2 c^2 \nu_2^2 m_1 = (\mathrm{P} - 8\mathrm{U}).$$

C: Oscillation of the alternate octahedral layers of sodium atoms against each other tangentially with respect to themselves. The direction of motion can be anywhere in the plane, since the vibration is degenerate in the plane. Also the equation of motion comes out to be the same whatever the direction of motion, provided it is confined to the octahedral plane under consideration. If we suppose the direction of motion to be along any one of the three dodecahedral directions lying in the plane, for example $x = 0$ and $y = -z$, then

$$\left.\begin{aligned} m_1 \frac{d^2y_1}{dt^2} &= (\mathrm{P} + 4\mathrm{U})\, y_1 \\ \text{and} \qquad m_1 \frac{d^2z_1}{dt^2} &= (\mathrm{P} + 4\mathrm{U})\, z_1 \end{aligned}\right\} \tag{6}$$

Hence $$4\pi^2 c^2 \nu_3^2 m_1 = (\mathrm{P} + 4\mathrm{U})$$

D: Similarly the frequencies of vibration of the normal and tangential oscillations of the alternate octahedral layers of chlorine atoms come out as

$$4\pi^2 \nu_4^2 c^2 m_2 = (\mathrm{P}' - 8\mathrm{U}')$$

and $$4\pi^2 \nu_5^2 c^2 m_2 = (\mathrm{P}' + 4\mathrm{U}').$$

E: Coupled oscillation of the alternate cubic planes of atoms normally to each other. The direction of displacement can be along any one of the three cube axes. Let y and z be zero. Then, there are two possibilities corresponding to whether the sodium and chlorine atoms in any particular YZ plane move with the same phase or with opposite phases. When these displacements are in the same phase

$$\left.\begin{aligned} m_1 \frac{d^2x_1}{dt^2} &= (\mathrm{P} + 4\mathrm{S} - 8\mathrm{T})\, x_1 - (2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})\, x_2 \\ m_2 \frac{d^2x_2}{dt^2} &= -(2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})\, x_1 + (\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}')\, x_2 \end{aligned}\right\} \tag{7}$$

The frequencies ν_6 and ν_7 are therefore given by

$$4\pi^2 c^2 \nu_6^2 \text{ and } 4\pi^2 c^2 \nu_7^2$$

$$= \frac{\mathrm{P} + 4\mathrm{S} - 8\mathrm{T})}{2m_1} + \frac{\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}'}{2m_2}$$

$$\pm \left\{ \left[\frac{\mathrm{P} + 4\mathrm{S} - 8\mathrm{T}}{2m_1} - \frac{\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}'}{2m_2} \right]^2 + \frac{(2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})^2}{m_1 m_2} \right\}^{\frac{1}{2}}$$

The case in which the sodium and chlorine atoms of any YZ plane move with opposite phases also leads to the same two solutions. The + *ive* sign refers to the case in which the sodium and chlorine atoms of any YZ plane move

with the same phase and the $-$ *ive* sign to the case in which they move with opposite phases.

F: Coupled oscillation of the alternate cubic planes of atoms tangentially to themselves. Here again if we consider the YZ planes as the oscillating units, the direction of motion can be anywhere in the plane. But, the y and z equations of motion come out to be identical. When the motion of sodium and chlorine atoms are in phase

$$\left.\begin{aligned} m_1 \frac{d^2y_1}{dt^2} &= (\mathrm{P} - 4\mathrm{S})\, y_1 + (2\mathrm{Q} - 8\mathrm{V})\, y_2 \\ m_2 \frac{d^2y_2}{dt^2} &= (2\mathrm{Q} - 8\mathrm{V})\, y_1 + (\mathrm{P}' - 4\mathrm{S}')\, y_2 \end{aligned}\right\} \qquad (8)$$

Therefore ν_8 and ν_9 are given by

$$4\pi^2c^2\nu_8^2 \text{ and } 4\pi^2c^2\nu_9^2$$
$$= \frac{\mathrm{P} - 4\mathrm{S}}{2m_1} + \frac{\mathrm{P}' - 4\mathrm{S}'}{2m_2}$$
$$\pm \left\{\left[\frac{\mathrm{P} - 4\mathrm{S}}{2m_1} - \frac{\mathrm{P}' - 4\mathrm{S}'}{2m_2}\right]^2 + \frac{(2\mathrm{Q} - 8\mathrm{V})^2}{m_1 m_2}\right\}^{\frac{1}{2}}$$

TABLE II

The Expressions for the Frequencies of Vibration of the Normal Modes of NaCl type Structures

Degeneracy	Oscillating units	Direction of Oscillation	$4\pi^2c^2\nu^2$
3	The two lattices	Arbitrary	$(\mathrm{P}+4\mathrm{S}+8\mathrm{T})/\mu = (\mathrm{P}'+4\mathrm{S}'+8\mathrm{T}')/\mu' = -(2\mathrm{Q}+4\mathrm{R}+8\mathrm{V}/\mu$
4	(111) Na ions	Normal	$(\mathrm{P}-8\mathrm{U})/m_1$
8	,,	Tangential	$(\mathrm{P}+4\mathrm{U})/m_1$
4	(111) Cl ions	Normal	$(\mathrm{P}'-8\mathrm{U}')/m_2$.
8	,,	Tangential	$(\mathrm{P}'+4\mathrm{U}')/m_2$
3	(100) planes	Normal	$\frac{\mathrm{P}+4\mathrm{S}-8\mathrm{T}}{2m_1} + \frac{\mathrm{P}'+4\mathrm{S}'-8\mathrm{T}'}{2m_2} \pm \left\{\left[\frac{(\mathrm{P}+4\mathrm{S}-8\mathrm{T})}{2m_1} - \frac{(\mathrm{P}'+4\mathrm{S}'-8\mathrm{T}')}{2m_2}\right]^2 + \frac{(2\mathrm{Q}-4\mathrm{R}+8\mathrm{V})^2}{m_1m_2}\right\}^{\frac{1}{2}}$
3	,,	Normal	
6	,,	Tangential	$\frac{\mathrm{P}-4\mathrm{S}}{2m_1} + \frac{\mathrm{P}'-4\mathrm{S}'}{2m_2} \pm \left\{\left[\frac{\mathrm{P}-4\mathrm{S}}{2m_1} - \frac{\mathrm{P}'-4\mathrm{S}'}{2m_2}\right]^2 + \frac{(2\mathrm{Q}-8\mathrm{V})^2}{m_1m_2}\right\}^{\frac{1}{2}}$
6	,,	Tangential	

As in the case of the modes ν_6 and ν_7, here also the mode in which the sodiums and chlorines of any one plane move in opposite phases leads to the same two solutions. In this case, the mode with which the motions are in the same phase corresponds to the $-$ *ive* sign and the $+$ *ive* sign to the mode in which the phases of sodium and chlorine atoms in any oscillating plane, are opposite. Finally, we give a table containing all the expressions collected together with a description of the various modes of vibration.

In conclusion the author's sincere thanks are due to Prof. Sir C. V. Raman for the many illuminating discussions he had with him.

SUMMARY

Exact expressions for the frequencies of the nine eigenvibrations of rocksalt have been derived in terms of 11 independent constants which take account of the influence of the 26 nearest neighbours of each atom, the constants being connected by two additional relations.