

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part III. The Cæsium Chloride Structure

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1. INTRODUCTION

IN two previous communications the vibration spectra of diamond and rocksalt have been investigated on the basis of the new theory of crystal dynamics (1943). It is proposed here to deal with the dynamics of the cæsium chloride structure which is typical of a number of crystals. The same method as was used in the two previous publications has been applied in the present case also.

2. THE NORMAL MODES OF VIBRATION

Since the cæsium chloride structure consists of two simple cubic lattices interpenetrating in such a manner that the atoms of one lattice are located at the body centres of the cubic lattice formed by the other, the normal modes of vibration of this structure are easily derived by a consideration of the vibration modes of a simple cubic lattice. Of the five independent modes of vibration possible for a simple cubic lattice, two are the normal and tangential oscillations of the alternate cubic planes of atoms against each other with degeneracies of 3 and 6 respectively. Modes three and four with degeneracies of 3 and 6 respectively, are the oscillations of the alternate dodecahedral planes of atoms against each other, the directions of oscillation being along the cubic axis lying in the dodecahedral plane in one case and along any one of the two dodecahedral axis lying in the perpendicular plane in the other. The fifth mode is the oscillation of the alternate octahedral planes of atoms with opposite phases in any three orthogonal directions and consequently with degeneracy of 3, thus making up the 21 degrees of freedom of the 8 atoms in a supercell, besides the three translations. In the case of the cæsium chloride structure, since the two non-equivalent atoms in a unit cell can now vibrate with either the same phase or with opposite phases, the five possibilities in the simple cubic lattice will be doubled up. In addition to the 10 independent modes thus possible, there will be one

other in which the atoms belonging to the two lattices vibrate against each other in any three orthogonal directions. A symbolic description of these eleven modes of vibration is contained in columns 1 to 3 of Table II. To avoid repetition, it is not reproduced here.

The caesium and chlorine atoms in the crystal appear in separate layers parallel to the octahedral and cubic planes of the crystal and they are so spaced that the layers of atoms of one lattice are situated midway between layers belonging to the other lattice both in the octahedral and in the cubic planes. Therefore the equations of motion of the two types of atoms are independent so far as the modes concerned are the vibrations of the cubic or octahedral planes. But any dodecahedral layer contains atoms of both types and consequently for the modes in which these layers are involved, the equations for the two types of atoms are not independent.

3. THE FORCE CONSTANTS

In what follows we shall consider the forces produced on every atom due to the displacements of the 26 neighbouring atoms in addition to the forces due to its own displacements. Since there are two dissimilar atoms in the crystal, we would require $2(26 \times 9 + 3) = 474$ force-components to describe the influence of the neighbouring atoms. But, for reasons already described in the previous paper, these reduce very much in number. In the case of caesium chloride the eight nearest neighbours (of the other kind) of every atom, are situated at the eight corners of the unit cube, the atom under consideration being situated at the body centre of the cube. If we consider a cube of twice the linear dimensions of the unit cube with the atom under consideration again situated at the body centre, then the six next nearest neighbours (9 to 14 of the same kind) are those at the face centres of the big cube and the most distant of the 26 atoms (15 to 26 of the same kind) at the midpoints of the 12 cube edges of the big cube. The constants P and P' refer to the forces on any caesium or chlorine atom (atom 0) respectively proportional to their own displacements. Atoms 1 to 8 are represented by Q and R , 9 to 14 by S , T , S' and T' and 15 to 26 by U , V , W and U' , V' , W' . The description of these thirteen constants is contained in Table I.

As in the case of rocksalt, the principle that an infinitesimal translation of the entire crystal involves no work done and the fact that the work done in a small virtual displacement of the caesium ions by a small amount δx is exactly equal to the work done in a displacement of the chlorine ions by the same amount, the caesiums now remaining at rest lead to the relations

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

TABLE I
Description of Force Constants

Atoms responsible for forces	Symbol	Description of the constant
0	P, P'	Force on any atom proportional to its own displacement along any one of the cube axes
1 to 8	Q	Direction of both force and displacement along any one of the three cube axes
do	R	Direction of displacement along a cube axis and that of force along any one of the other two cube axes
9 to 14	S, S'	Both force and displacement in a direction perpendicular to the cubic plane containing the two atoms
do	T, T'	Both force and displacement along a cubic axis containing the two atoms
15 to 26	U, U'	Both force and displacement in a direction perpendicular to the cubic plane containing the two atoms
do	V, V'	Direction of both force and displacement along any one of the three cube axes
do	W, W'	Direction of displacement along a cube axis and that of force along any one of the other two cube axes

* Atom O may refer to either a Cæsium atom or a Chlorine atom. P, S, T, U and W refer to cæsium atoms, P', S', T', U' and W' to chlorine atoms and Q and R to both.

and

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

combining (1) and (2) we obtain

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

4. EXPRESSIONS FOR THE FREQUENCIES

We shall now consider the eleven normal modes one by one and derive the frequency formulæ in terms of the force-constants. m_1 and m_2 denote the masses of the cæsium and chlorine atoms respectively.

A: The oscillation of the cæsium and chlorine lattices against each other along any three orthogonal directions. If we represent the displacements of any cæsium atom by $x_1 y_1 z_1$ and that of the chlorine atoms by $x_2 y_2 z_2$ we have

$$m_1 \frac{d^2(x_1 + y_1 + z_1)}{dt^2} = (P + 4S + 2T + 4U + 8V)(x_1 + y_1 + z_1) - 8Q(x_2 + y_2 + z_2)$$

$$m_2 \frac{d^2(x_2 + y_2 + z_2)}{dt^2} = -8Q(x_1 + y_1 + z_1) + (P' + 4S' + 2T' + 4U' + 8V')(x_2 + y_2 + z_2).$$

Using the relation (3) and solving the above two equations we obtain

$$4\pi^2\nu_1^2c^2 = (P + 4S + 2T + 4U + 8V)/\mu$$

$$= (P' + 4S' + 2T' + 4U' + 8V')/\mu = -(8Q)/\mu$$

μ in the above is the reduced mass of the caesium and chlorine atoms

$$1/\mu = (1/m_1 + 1/m_2)$$

B: The caesium ions in the cubic planes vibrate against each other with alternate planes in opposite phases, normally. If we choose the YZ planes as the oscillating units

$$m_1 \frac{d^2x_1}{dt^2} = (P + 4S + 4U - 2T - 8V) x_1$$

The frequency of vibration is therefore

$$4\pi^2\nu_2^2m_1c^2 = (P + 4S + 4U - 2T - 8V).$$

C: Same as B but transversely. The direction of oscillation can be anywhere in the plane. Hence

$$m_1 \frac{d^2(y_1 + z_1)}{dt^2} = (P + 2T - 4U)(y_1 + z_1)$$

$$\text{or } 4\pi^2\nu_3^2m_1c^2 = P + 2T - 4U.$$

D: Movement of the chlorine layers in the alternate cubic planes against each other normally or transversely. The frequency expressions will be similar to those in B and C but with the dashed terms. Hence

$$4\pi^2\nu_4^2m_2c^2 = (P' + 4S' + 4U' - 2T' - 8V')$$

$$4\pi^2\nu_5^2m_2c^2 = (P' + 2T' - 4U').$$

E: Coupled oscillation of caesium and chlorine atoms in alternate dodecahedral planes with opposite phases, the directions of oscillation being along the diagonals of the cube face perpendicular to the oscillating planes: If we consider the (011) planes, then the displacements of the atoms will be such that $x = 0$ and $y = \pm z$. Therefore for the two types of atoms

$$m_1 \frac{d^2y_1}{dt^2} = (P - 2T - 4U) y_1 - 8Ry_2$$

$$m_2 \frac{d^2y_2}{dt^2} = -8Ry_1 + (P' - 2T' - 4U') y_2.$$

The two frequencies ν_6 and ν_7 are therefore given by $4\pi^2\nu_6^2c^2, 4\pi^2\nu_7^2c^2 =$

$$\frac{P - 2T - 4U}{2m_1} + \frac{P' - 2T' - 4U'}{2m_2}$$

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

F: Same as E, but the direction of oscillation being tangential to the dodecahedral plane and along a cube edge. The equations of motion for the (011) planes are

$$m_1 \frac{d^2 x_1}{dt^2} = (P - 4S + 2T + 4U - 8V) x_1$$

$$m_2 \frac{d^2 x_2}{dt^2} = (P' - 4S' + 2T' + 4U' - 8V') x_2$$

In this case the equations of motion appear separated because the forces due to the displacements of one set of atoms on any atom of the other set cancel out completely in these two modes. The two frequencies are therefore

$$4\pi^2 \nu_8^2 m_1 c^2 = (P - 4S + 2T + 4U - 8V)$$

$$4\pi^2 \nu_8^2 m_2 c^2 = (P' - 4S' + 2T' + 4U' - 8V')$$

G: Alternate caesium layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions. The x , y and z equations of any atom are identical. Therefore

$$m_1 \frac{d^2 (x_1 + y_1 + z_1)}{dt^2} = (P - 4S - 2T + 4U + 8V) (x_1 + y_1 + z_1)$$

Hence

$$4\pi^2 \nu_{10}^2 m_1 c^2 = (P - 4S - 2T + 4U + 8V).$$

H: Alternate chlorine layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions. The frequency expression for this mode will be quite similar to that of the above

$$4\pi^2 \nu_{11}^2 m_2 c^2 = (P' - 4S' - 2T' + 4U' + 8V').$$

Finally, the results are collected together and presented in Table II.

5. SOME FURTHER SIMPLIFICATIONS

It will be noticed from Table I that the displacements which give rise to the forces S , S' , U and U' involve no change in the distance between the interacting atoms. Consequently their magnitudes will be negligibly small in comparison with those of the other constants. The constants W and W' do not appear in any one of the 11 formulæ in Table II. Further, if we neglect V and V' which arise out of the displacements of the most distant neighbours considered, we will be left with the constants P , P' , Q , R , T and T' which should satisfy the relation

$$(P + 2T) = (P' + 2T') = - (8Q)$$

Also since by the nature of the forces $P \gg T$ and $P' \gg T'$, it follows that

$$P \approx P'$$

TABLE II
Expressions for the Frequencies of the Normal Modes

Degeneracy	Oscillating Units	Direction of Oscillation	Expression for the frequencies ($4\pi^2\nu^2c^2$)
3	The two lattices	Arbitrary	$(P+4S+2T+4U+8V)/\mu$ $= (P'+4S'+2T'+4U'+8V')/\mu = - (8Q)/\mu$
3	(100) Cs ions	Normal	$(P+4S+4U-2T-8V)/m_1$
6	do	Tangential	$(P+2T-4U)/m_1$
3	(100) Cl ions	Normal	$(P'+4S'+4U'-2T'-8V')/m_2$
6	do	Tangential	$(P'+2T'-4U')/m_2$
6	(011) planes	[011] or	$\left. \begin{aligned} & \frac{P-2T-4U}{2m_1} + \frac{P'-2T'-4U'}{2m_2} \pm \\ & \left\{ \left[\frac{P-2T-4U}{2m_1} - \frac{P'-2T'-4U'}{2m_2} \right]^2 + \frac{(8R)^2}{m_1m_2} \right\}^{\frac{1}{2}} \end{aligned} \right\}$
6	do	[01 $\bar{1}$]	
3	do	[100]	$(P-4S+2T+4U-8V)/m_1$
3	do	[100]	$(P'-4S'+2T'+4U'-8V')/m_2$
3	(111) Cs ions	Arbitrary	$(P-4S-2T+4U+8V)/m_1$
3	(111) Cl ions	Arbitrary	$(P'-4S'-2T'+4U'+8V')/m_2$

TABLE III

Serial No.	Degeneracy	Oscillating Units	Direction of Oscillation	Formulae
I	6	(011) planes	[011] or [01 $\bar{1}$]	$\frac{P-2T}{m_1} + \frac{P'-2T'}{m_2} + \frac{4(T+T')}{m_1+m_2}$
II	3	The two lattices	Arbitrary	$\frac{P+2T}{m_1} + \frac{P'+2T'}{m_2}$
III	3	(111) Cl ions	do	$(P'-2T')/m_2$
IV	3	(100) do	Normal	$(P'-2T')/m_2$
V	3	(011) do	[100]	$(P'+2T')/m_2$
VI	6	(100) do	Tangential	$(P'+2T')/m_2$
VII	3	(111) Cs ions	Arbitrary	$(P-2T)/m_1$
VIII	3	(100) do	Normal	$(P-2T)/m_1$
IX	3	(011) do	[100]	$(P+2T)/m_1$
X	6	(100) do	Tangential	$(P+2T)/m_1$
XI	6	(011) planes	[011 or [01 $\bar{1}$]	$-\frac{4(T+T')}{m_1+m_2}$

If the nature of the forces are such that they are along the line joining the interacting atoms, then Q and R the longitudinal and transverse forces respectively, due to the displacements of the nearest neighbours, will be equal since they are all situated along the trigonal directions with respect to the atom under consideration. Once these simplifying assumptions are made, the order of magnitudes of the eleven frequencies, at once follows. By the convention adopted, all the constants except P and P' are negative. The number of distinct frequencies is thus reduced from 11 to 7. In Table III the various modes are arranged in the order of the magnitudes of their frequencies assuming m_1 to be greater than m_2 as in caesium chloride. If $m_1 < m_2$ as for example in NH_4^+Cl^- which has the same structure, the order can be obtained by interchanging m_1 and m_2 in Table III and also P and T with P' and T' respectively.

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SUMMARY

Exact expressions have been derived for the 11 eigenfrequencies of the caesium chloride structure in terms of 12 constants which take account of the influence of the 26 nearest neighbours of every atom, the constants being connected by two additional relations. Simplified formulæ for the frequencies have also been given in terms of 4 independent constants only, which are again connected by an additional relation.