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12 January 1951

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Assistant Secretary

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The paper communicated by you to the Royal Society, entitled *The frequencies and the anharmonicity of the normal modes of oscillation of alkali halide crystals* I

has been safely received.

Yours faithfully,

D. C. Martin

*Assistant Secretary*

Published in Vol. 207,

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THE FREQUENCIES AND THE ANHARMONICITIES OF THE  
NORMAL MODES OF OSCILLATION OF ALKALI HALIDE CRYSTALS.

35

I. LATTICE OSCILLATIONS

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(Received 12 January 1954)-----

ABSTRACT

Opt inset

← The frequencies and the anharmonicities of the lattice oscillations of alkali halide crystals, i.e. the oscillations of the interpenetrating lattices of the alkali and the halide ions respectively, with respect to each other, are calculated on the basis of the Born model. If  $r$  be the small relative displacement of the two lattices, and  $l, m, n$  the direction cosines of  $r$  with reference to the cubic axes of the crystal, it is found that the potential energy can be expressed in the form

$$U = U_0 + ar^2 + br^4 + cr^4(l^4 + m^4 + n^4) + \dots,$$

in which the constants  $U_0$ ,  $a$ ,  $b$  and  $c$  are readily evaluated. The coefficient of  $r^2$  determines the frequency, and of  $r^4$  the anharmonicity, of the lattice oscillation.

This oscillation is characterized by the development of a <sup>homogeneous</sup> electric polarization in the medium. It is found that the polarization field acting on an ion tending to displace the ion has just the Lorentz value, whereas the field tending to polarize <sup>(the ion)</sup> ~~it~~ is almost nothing.

The anharmonicity of the lattice oscillation, unlike its frequency, is found to vary with the direction of the oscillation, from a large positive value along  $[111]$  to a small negative value along  $[100]$ . Its effects on the frequency of the octave, and on the specific heat at constant volume, are discussed.

1. INTRODUCTION *ew*

← The frequencies of the various normal modes of oscillation of sodium chloride crystal have been calculated by Kellermann (1940) on the basis of the Born model, and the frequencies of the other alkali halide crystals, of both the NaCl and the CsCl types, can be calculated in the same manner. The frequencies of some of the simple modes have also been calculated *by Raman (1947) and* by Ramanathan (1947) in terms of certain force constants that define the restoring forces acting on the ions when they are given certain specific small displacements from their equilibrium positions. These oscillations in general are presumed to be anharmonic, and their anharmonicities have been invoked frequently to explain the occurrence of some of the octaves and combination frequencies in the infra-red and the Raman spectra of these crystals, and also to explain the possibility of a temperature variation of the specific heats of these crystals at constant volume at high temperatures (Born <sup>&</sup> Brody 1921). No attempt, however, seems to have been made to estimate the magnitudes of the anharmonicities of these oscillations, though they can be calculated on the basis of the Born model just as readily as the frequencies (Krishnan 1950).

It is the main purpose of this paper to calculate the anharmonicities of the various normal modes of oscillation of the alkali halide crystals. Part I concerns itself with the oscillations of the two interpenetrating lattices of the alkali and the halide ions respectively with respect to each other. These oscillations, unlike those in other normal modes, are characterized by the development of <sup>a homogeneous</sup> electric polarization in the crystals. Hence the calculation of the frequencies of these oscillations on the Born model is also of interest, as it throws light incidentally on the magnitude of the polarization fields in these crystals, and in particular brings out the essential difference in behaviour between the polarization due to the relative displacements of the positive and the negative ions and that due

to the dipoles induced in these ions, and the almost complete lack of interaction between the two polarizations. These and other aspects of the polarization fields are also discussed in this Part.

## 2. THE BORN MODEL

In crystals of the alkali halides, as is well known, the alkali and the halide ions form interpenetrating lattices, both the lattices being face-centred cubic in the NaCl type of crystals, and body-centred cubic in the CsCl type. The ions in the crystal may be regarded, according to Born\*, as held in their respective positions by the electrostatic forces between the charges carried by them, and by short-range forces of repulsion between them. Indeed, the fall of the repulsive forces with increase of distance is so rapid that all repulsion interactions except between the nearest neighbours may be neglected. Other types of interaction, as, for example, the interaction between the dipoles that may be induced in the ions, will be much smaller, and may be neglected to a first approximation. Further, in view of the spherical symmetry of the ions, we may regard both the electrostatic and the repulsion interactions to be central. These assumptions, which are good approximations, render the model simple.

Taking the energy of repulsion interaction between any two neighbouring ions separated by a distance  $R$  to be given by  $\phi(R)$ , the potential energy  $U$  of the crystal per pair of ions will be given by

$$U = -\frac{\alpha e^2}{R} + n_0 \phi(R), \quad (1)$$

in which  $n_0$  is the number of nearest neighbours, equal to 6 in the NaCl type and 8 in the CsCl type, and  $\alpha$  is the Madelung constant, equal to 1.748 in the NaCl type and to 1.763 in the CsCl type (Sherman 1932).

\*For a good account see Max Born and M. Göppert-Heyn (Mayer (1933) Handbuch der Physik (Springer 1933) Bd. 24/2, p. 676, or J. Sherman Chem. Rev. 11, 116 (1932). (1932, p. 116)

phi  
alpha  
Max Born

The condition for equilibrium of the crystal, namely,

$$\left(\frac{\partial U}{\partial R}\right)_{R=d} = 0, \quad \text{we} \quad (2)$$

where  $d$  is the value of  $R$  when the crystal is in equilibrium, gives

$$\varphi'(d) = -\alpha e^2 / (n_0 d^2), \quad \text{we} \quad (3)$$

Using the further relation

$$\left(\frac{\partial^2 U}{\partial R^2}\right)_{R=d} = q / (N \beta d^2), \quad \text{we} \quad (4) \quad \text{beta}$$

where  $\beta$  is the isothermal compressibility of the crystal, and  $N$  is the number of ion pairs per unit volume, we obtain

$$\varphi''(d) = 2\alpha e^2 / (n_0 d^3) + q / (n_0 N \beta d^2), \quad \text{we} \quad (5)$$

where  $N$  is equal to  $1/(2d^3)$  in the NaCl type and to  $3\sqrt{3}/(8d^3)$  in the CsCl type.

Both  $d$  and  $\beta$  appearing in these expressions refer to the Absolute Zero of temperature. Though  $d$  may be obtained by extrapolation accurately enough, a reliable estimate of  $\beta$  at absolute zero (and at zero pressure) is difficult to make.

The higher derivatives of  $\varphi$ , namely,  $\varphi'''(d)$ ,  $\varphi''''(d)$ , etc., may similarly be obtained from the known variation of the compressibility of the crystal with pressure at different pressures. Since the experimental data on pressure variation of compressibility are not sufficiently precise for this purpose, we may obtain the values of the higher derivatives of  $\varphi(R)$  more satisfactorily, by assuming for it, as usual, a suitable simple form like

$$\varphi(R) = A e^{-R/\rho}, \quad \text{we} \quad (6)$$

in which the two constants  $A$  and  $\rho$  can be evaluated with the help of relations (2) and (4). For such functions, involving only two constants, not only  $\varphi'(d)$  and  $\varphi''(d)$ , but/

but all the higher derivatives also become known from (2) and (4).

The exponential law of variation of repulsion interaction with distance postulated in (6), besides being convenient, is justifiable, as is well-known, on other considerations. Adopting (6), and denoting  $d/\rho$  by  $\delta$ , we obtain from (3) and (5),

$$\delta^{-2} = 9d / (N\alpha e^2 \beta). \quad \text{we} \quad (7) \quad \text{rho}$$

delta  
alpha

Other simple functions, like  $\varphi(R) = B R^{-m}$ , have also been proposed for the repulsion interaction between neighbours, in which the constant  $B$  can be eliminated as before with the help of (3), and  $m$  <sup>the number</sup> evaluated with the help of (5). It will be readily seen that

$$m - 1 = 9d / (N\alpha e^2 \beta), \quad \text{we} \quad (8)$$

and hence  $m$  is equal to  $\delta - 1$ .

3. POTENTIAL ENERGY CORRESPONDING TO SMALL RELATIVE DISPLACEMENT OF THE TWO INTERPENETRATING LATTICES,

crB

We shall now consider the oscillations of the interpenetrating lattices formed by the alkali and the halide ions respectively, with respect to each other. Starting with the crystal in equilibrium, and taking the coordinate axes along the cubic axes of the crystal, and the origin at the lattice point occupied by an alkali ion, let the lattice formed by the alkali ions be displaced with reference to the lattice of the halide ions by a small distance  $r$  ( $r \ll d$ ) in the direction  $\underline{l}, \underline{m}, \underline{n}$ . The alkali ion which was originally at the origin will now be at  $\underline{x} \underline{y} \underline{z}$ , where  $\underline{x} = r\underline{l}$ ,  $\underline{y} = r\underline{m}$ ,  $\underline{z} = r\underline{n}$ . Let us now calculate the potential energy of the pair of ions formed by the alkali ion at  $\underline{x} \underline{y} \underline{z}$  and each of the surrounding ions taken in succession. The sum of these potential energies will obviously be the potential energy of the deformed crystal per pair

of/

of ions. Denoting it by  $\underline{U}$ , <sup>one</sup> ~~it~~ may ~~be~~ expressed <sup>it</sup> as a power series in  $\underline{r}$ , in which, owing to the centre of symmetry of the lattice points in these crystals, terms involving odd powers of  $\underline{r}$  will obviously be absent.  $\underline{U}$  may therefore be expressed in the form

$$\underline{U} = \underline{U}_0 + a \underline{r}^2 + f \underline{r}^4 + \dots \quad \text{---} \quad (9)$$

The term  $\underline{U}_0$ , which is independent of  $\underline{r}$ , will evidently be the same as for the undeformed crystal, and will be given by

$$\underline{U}_0 = -\alpha e^2/d + n_0 \varphi(d). \quad \text{---} \quad (10)$$

The coefficient of  $\underline{r}^2$  will determine the frequency of the oscillation that we are considering, i.e. the reststrahlen frequency of the crystal, and the coefficient of  $\underline{r}^4$  the anharmonicity of this oscillation.

We now proceed to calculate these coefficients. Since the positions of the other alkali ions relative to the one at xyz remain the same as before, the potential due to them will obviously be independent of xyz. Hence, in calculating the  $\underline{r}^2$  and  $\underline{r}^4$  terms in the expression for the potential energy of the alkali ion at xyz due to the surrounding ions, it is sufficient to consider the effect of the halide ions alone.

#### 4. EXPRESSION FOR POTENTIAL ENERGY one

Let us confine attention to one of these halide ions located at say  $\xi \eta \zeta$ , and the alkali ion at xyz, and denote the interaction energy between them by  $\psi(\underline{R})$ , psi

where

$$\psi(\underline{R}) = -\frac{e^2}{\underline{R}} + \varphi(\underline{R}), \quad \text{---} \quad (11)$$

$\underline{R}$  is their distance of separation, given by

$$\underline{R}^2 = (\xi - x)^2 + (\eta - y)^2 + (\zeta - z)^2 \quad \text{---} \quad (12)$$

$$= \underline{R}_0^2 + \underline{r}^2 - 2 \underline{Q} \underline{R}_0 \underline{r}, \quad \text{---} \quad (13)$$

$\underline{R}_0$  is the distance of the halide ion from the  $\hat{x}$  origin, and

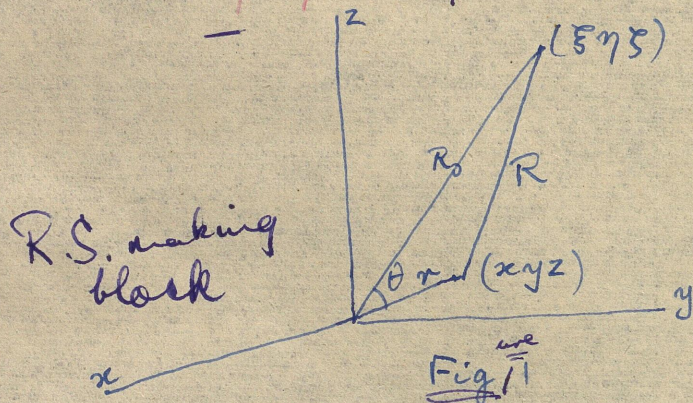
$\xi$   
 $\eta$   
 $\zeta$

phi

xi eta zeta

$$Q = (\xi + \eta + \zeta) / R_0 \quad \dots (14)$$

denotes the cosine of the angle  $\theta$  between the radius vectors  $\vec{r}$  and  $\vec{R}$ . (See Fig. 1)



theta

Keeping  $\xi$ ,  $\eta$ ,  $\zeta$  constant, and varying the magnitude of  $\underline{r}$ , we may express  $\psi(R)$  in the form

$$\psi(R) = \psi(R_0) + r \left( \frac{\partial \psi}{\partial r} \right)_{r=0} + \frac{r^2}{2!} \left( \frac{\partial^2 \psi}{\partial r^2} \right)_{r=0} + \dots \quad \dots (15)$$

in which  $R \rightarrow R_0$  as  $r \rightarrow 0$ .

With the help of (13) we may replace the differential coefficients in (15) with respect to  $\underline{r}$ , at  $\underline{r}=0$ , by the corresponding coefficients with respect to  $\underline{R}$ , at  $\underline{R}=R_0$ . The  $r^2$  and  $r^4$  terms in (15) will then reduce to

$$A r^2 = \frac{r^2}{2!} \left[ (1 - Q^2) \psi' / R_0 + Q^2 \psi'' \right] \quad \dots (16)$$

and

$$F r^4 = \frac{r^4}{4!} \left[ 3(1 - Q^2)(5Q^2 - 1) \left( \psi' / R_0^3 - \psi'' / R_0^2 \right) + 6Q^2(1 - Q^2) \psi''' / R_0 + Q^4 \psi'''' \right] \quad \dots (17)$$

respectively. The differential coefficients of  $\psi$  appearing in (16) and (17), and in the equations to follow, are with respect to  $\underline{R}$ , at  $\underline{R} = R_0$ .

Owing to the symmetry of the crystal, corresponding to every lattice point  $(\xi \eta \zeta)$  occupied by a halide ion, there are others at points obtained by the various combinations of  $(\pm \xi, \pm \eta, \pm \zeta)$ , in which the coordinates are interchangeable. Their number  $n$ , i.e. the number of negative ions at a distance  $R_0 = (\xi^2 + \eta^2 + \zeta^2)^{1/2}$  (from the origin) will be 48 when  $\xi, \eta, \zeta$  are all different and different from zero,

? R\_0

psi

xi eta zeta

but will ordinarily be less. Knowing the values of  $\underline{n}$  and  $\underline{R}_0$  for these groups of halide ions, the coefficients  $\underline{a}$  and  $\underline{f}$  of the  $\underline{r}^2$  and  $\underline{r}^4$  terms respectively, appearing in (9), can be calculated, since

$$\underline{a} = \sum (\underline{n} \bar{A}), \quad \dots \quad (18)$$

$$\underline{f} = \sum (\underline{n} \bar{F}), \quad \dots \quad (19)$$

where the bar indicates the average value taken over the  $\underline{n}$  ions forming one such group, and the summation extends over all such groups.

In calculating  $\bar{A}$  and  $\bar{F}$ , we need to know the corresponding mean values of  $\underline{Q}^2$  and  $\underline{Q}^4$  appearing in equations (16) and (17). Obviously

*bar over all letters only*

$$\bar{Q}^2 = \bar{\xi}^2 / \underline{R}_0^2 = \bar{\eta}^2 / \underline{R}_0^2 = \bar{\zeta}^2 / \underline{R}_0^2 \quad \dots \quad (20)$$

$$= 1/3; \quad \dots \quad (21)$$

$$\bar{Q}^4 = \frac{1}{2} (1 - 3\sigma) - \frac{1}{2} (1 - 5\sigma) (\underline{l}^4 + \underline{m}^4 + \underline{n}^4), \quad (22)$$

in which

$$\sigma = \bar{\xi}^4 / \underline{R}_0^4, \quad \dots \quad (23)$$

*Sigma*

and  $\bar{\xi}^4 = \bar{\eta}^4 = \bar{\zeta}^4, \quad \dots \quad (24)$

$\underline{n}$ ,  $\underline{R}_0$  and  $\sigma$  will naturally vary from group to group.

5. COEFFICIENT OF THE  $\underline{r}^2$  TERM IN THE EXPRESSION FOR POTENTIAL ENERGY *psi*

We shall now take up the calculation of  $\underline{a}$ , the coefficient of the  $\underline{r}^2$  term in expression (9) for the potential energy of the deformed crystal per pair of ions.

Substituting for  $\underline{Q}^2$  in (16) its average value, namely,

$$\bar{Q}^2 = 1/3 \quad (\text{see (21)}), \quad \text{we obtain} \quad \text{psi}$$

$$\underline{a} = \sum \left\{ \underline{n} (2 \psi' / \underline{R}_0 + \psi'') / 6 \right\}, \quad \dots \quad (25)$$

in which  $\underline{R}_0$  and  $\underline{n}$  will vary, as we have seen, from group to group, and the summation extends over all the groups of negative ions surrounding the positive ion at  $\underline{x} \underline{y} \underline{z}$ .

Considering/

psi  
 Considering first the electrostatic interaction, i.e. putting  $\psi(R) = -\frac{e^2}{R}$  in (25), one can readily see that (25) reduces to zero. In other words, the electrostatic interactions between the various ions contribute nothing to <sup>the</sup>  $\frac{1}{r^2}$  term in expression (9) for the potential energy of the crystal.\*

psi  
 Considering next the repulsion interactions, i.e. putting  $\psi(R) = \varphi(R)$ , and confining ourselves to the interactions between the nearest neighbours, one can readily see from (25), in view of relations (3) and (5), that their contribution to the coefficient a in expression (9) is given by

$$a_1 = 3 / (2 N \beta d^2) \quad \dots \quad (26) \quad \text{beta}$$

Taking the law of repulsion interaction to be exponential,  $a_1$  can also be expressed, in view of (7), in the form

alpha

$$a_1 = \alpha e^2 (\delta - 2) / (6 d^3) \quad \dots \quad (27)$$

psi  
 The magnitude of  $a_1$ , as calculated here, will obviously be independent of the explicit formulation of  $\varphi(R)$  as a function of  $R$ .

6. THE EFFECT OF THE POLARIZATION OF THE MEDIUM over

Among the various normal modes of vibration of the crystal, the particular one that we are considering, namely, the oscillations of the lattice of alkali ions with respect to that of the halide ions, is unique in that it corresponds to the development of <sup>a homogeneous</sup> electric polarization in the crystal.

As a result of this polarization, which will be proportional (and, as mentioned just now, will be the same throughout the crystal) to the displacement  $r$ , the force acting on any given ion in the crystal, tending to restore it to its equilibrium position, instead of being  $2 a_1 r$ , where  $a_1$  has the value (26), will be less by an amount equal to the force

\* There is, however, an indirect contribution to the  $r^2$  term arising from the electric polarization developed in the crystal as a result of the relative displacement of the positive and the negative ions; this will be considered in the next section.

due to the polarization field.\*

Now the polarization of the medium, equal to say  $P_r$  per unit volume, will arise primarily from the relative displacement of the two lattices; but accompanying this displacement there may be a polarization of the individual ions also, since the ions are polarizable.

There is, however, this essential difference between the polarization produced by a small relative displacement  $r \ll d$  of the positive and the negative lattices, and that induced in the ions. *(by the displacement of the electrons relative to the nucleus.)* The polarization arising from the lattice displacement may be regarded as due to small dipoles, located at the lattice points, the separation of charges in these dipoles being much smaller than  $d$ . On the other hand, in the dipoles induced in the ions, the separation of charges is comparable to  $d$ . This difference in size of the two types of dipoles renders the character of the field due to them in their close neighbourhood quite different *(Heckmann 1925; see also Mott & Gurney 1939<sup>40</sup>)*. We shall denote by  $P_1 r$  and  $P_2 r$

( $P_1 + P_2 = P$ ) the contributions to the polarization of the crystal per unit volume, from the lattice displacement and from the dipoles induced in the ions respectively, and

consider the polarization fields, due to  $P_1$  and  $P_2$  acting on an ion, that are effective (i) in displacing the ion, and (ii) in polarizing the ion. Let us designate the

New line para

polarization fields effective in (i) by  $\left[ \frac{p_1 P_1 e r}{r^3} \right]$  and  $\left[ \frac{p_2 P_2 e r}{r^3} \right]$  respectively, (28)

and those effective in (ii) by

$$\left[ \frac{p_3 P_1 e r}{r^3} \right] \text{ and } \left[ \frac{p_4 P_2 e r}{r^3} \right] \text{ respectively.} \quad (29)$$

The elementary dipoles arising from the displacements of the ions being practically point dipoles, we should expect  $p_1$  to be equal to  $\frac{4\pi}{3}$ , i.e. the polarization field

$\frac{4}{3}\pi$

pi

\* The direction of the latter force is such as to increase the separation  $r$  of the two lattices.

concerned to have the proper Lorentz value. The other  $p$ 's however, will be much smaller than  $4\pi/3$  ( $p_4 < p_3 \approx p_2 \ll 4\pi/3$ ) their actual magnitudes depending on the degree of overlap of the electric charges of neighbouring ions. Anticipating the results to be obtained in the next section, we may mention here that the experimental data point to  $p_1$  being  $4\pi/3$ , and all the other  $p$ 's being practically zero. In other words, the experimental data show that  $P_2$  is practically zero, and the only polarization in the medium is that due to the displacement of the ions alone. The polarization per unit volume is then given by  $P = P_1 = N e r$ , and the force acting on an ion tending to increase the displacement has the full Lorentz value  $(4\pi/3) N e^2 r$ .

Remembering that the displacement  $r$  of the positive ions is relative to the negative ions which may be regarded as kept fixed, the corresponding potential energy of the crystal per pair of ions will be given by

$$a_2 r^2 = -2\pi N e^2 r^2 / 3, \quad (30)$$

which will be the contribution to the coefficient  $a$  in (9) from the polarization of the crystal.

Adding this to (27), we obtain for the coefficient of  $r^2$  in expression (9)

$$a = a_1 + a_2 = \alpha e^2 (\delta - 2) / (6d^3) - 2\pi N e^2 / 3. \quad (31)$$

Knowing  $a$ , the reststrahlen frequency  $\nu$  of the alkali halide crystal is readily calculated from the relation

$$2\pi^2 \mu \nu^2 = a, \quad (32)$$

where

$$1/\mu = 1/m_1 + 1/m_2, \quad (33)$$

and  $m_1$  and  $m_2$  are the masses of the two ions. Equations (32) and (31) determining the frequency  $\nu$  of the lattice oscillation are the same as those obtained by Kellermann.

THE RESTSTRAHLEN FREQUENCIES OF THE ALKALI HALIDES

The constants needed in the calculation of the frequencies are obviously  $d$ ,  $\delta$  and  $\mu$ . For all the alkali

delta

alkali halides, both of the NaCl and CsCl types, the values of  $m$ , equal to  $\delta - 1$  (see (8)), have already been calculated from the compressibility data extrapolated to the absolute zero of temperature, by Slater (1924), and from certain independent general considerations by Pauling (1928). We have adopted Pauling's values of  $m$  to give us  $\delta$ . The values of  $a_1$ , calculated therefrom, and of  $a_2$ , are given in columns 5 and 6 Table I.

*Tables*

Table I

Crystal	$d$ in (Å)	$\delta = m + 1$ (Pauling)	$1/\mu \times 10^{-23}$	$a_1 \times 10^{-4}$	$a_2 \times 10^{-4}$	$\nu \times 10^{-12}$	Calculated	Observed (Barnes & 1932)
<u>NaCl type</u>								
LiF	2.01	7.0	1.186	4.13	-2.97	8.4		9.1
NaF	2.31	8.0	0.579	3.27	-1.96	6.2		7.4
KF	2.67	9.0	0.472	2.47	-1.27	5.4		
RbF	2.82	9.5	0.389	2.25	-1.08	4.8		
CsF	3.00	10.5	0.363	2.11	-0.89	4.7		
LiCl	2.57	8.0	1.039	2.37	-1.42	7.1		
NaCl	2.81	9.0	0.432	2.11	-1.09	4.7		4.9
KCl	3.14	10.0	0.324	1.74	-0.78	4.0		4.2
RbCl	3.27	10.5	0.241	1.63	-0.69	3.4		3.5
LiBr	2.75	8.5	0.944	2.10	-1.16	6.7		
NaBr	2.98	9.5	0.338	1.90	-0.91	4.1		4.2
KBr	3.29	10.5	0.230	1.60	-0.68	3.3		3.4
RbBr	3.43	11.0	0.146	1.50	-0.60	2.6		2.6
LiI	3.00	9.5	0.916	1.86	-0.89	6.7		
NaI	3.23	10.5	0.310	1.69	-0.72	3.9		3.5
KI	3.53	11.5	0.202	1.45	-0.55	3.0		2.9
RbI	3.66	12.0	0.118	1.37	-0.49	2.3		2.3
<u>CsCl type</u>								
CsCl	3.56	11.5	0.215	1.43	-0.69	2.8		2.9
CsBr	3.71	12.0	0.121	1.33	-0.61	2.1		2.2
CsI	3.95	13.0	0.093	1.21	-0.51	1.8		

It will be seen from the table that except in some of the fluorides the calculated values of  $\nu$  agree fairly well with the observed values.

It will also be seen that  $|a_2|$  is a large fraction of  $a_1$ . If in (28) and (29) the factors  $p_3$  and  $p_4$  determining the magnitude of the polarization fields that are effective in inducing dipole moments in the ions, and the factor  $p_2$  determining the polarization field due to these induced dipoles, tending to displace the ions, had all of them the Lorentz value of  $4\pi/3$ , like  $p_1$ , the contribution to  $a$  from the polarization of the medium, instead of being equal to  $-2\pi Ne^2/3$ , would be given by

$$a_2 = - (2\pi Ne^2/3)(n_\infty^2 + 2)/3, \quad (34)$$

where  $n_\infty$  is the refractive index of the crystal extrapolated for long wave-lengths. In NaCl, for example,  $(n_\infty^2 + 2)/3 = 1.4$ , and in some of the other crystals much higher, and if introduced in the expression for  $a_2$  would considerably decrease the calculated value of  $\nu$ . Even if  $p_2$  and  $p_3$ , which should be of comparable magnitudes, were equal to  $4\pi/3$ , and  $p_4$ , which might be much smaller, were equal to zero, the effect would be considerable. Hence the observed agreement between the experimental values of  $\nu$  and those calculated from (32) and (31), may be regarded as demonstrating empirically

- (1) that the polarization of the medium is due wholly to the displacements of the ions, and that these displacements do not induce any polarization in the ions;
- (2) that the effective polarization field acting on an ion and tending to displace it has just the Lorentz value, namely  $4\pi/3$  times the polarization per unit volume of the crystal.

Similar

Similar conclusions have been drawn by Mott <sup>&</sup> Littleton (1938) ~~and~~ Gurney (~~1939~~<sup>1938</sup>) for the NaCl type of crystals from the observed difference between the dielectric constant for static fields and the square of the refractive index extrapolated for long wave-lengths. This difference obviously represents the contribution from the relative displacement of the positive and the negative ion lattices.

8. THE LORENTZ POLARIZATION FIELD <sup>and</sup>

These results are indeed gratifying. The experimental finding that the observed variation of the refractivity of these crystals with density does not conform to the Lorentz formula has sometimes been regarded as throwing doubt on the validity of the Lorentz derivation of the polarization factor  $4\pi/3$  even in cubic crystals. The fundamental assumption implicit in this derivation is that the elementary dipoles present in the crystal to which the polarization of the medium is due, are point dipoles, i.e. that the distance of separation of the charges in the dipoles is small in comparison with  $d$ . The dipoles induced in the ions in these crystals, as for example in refraction, do not generally satisfy this condition, since the separation of charges in the ions is of the magnitude of the diameter of the ions, and hence in the larger ions comparable with the interionic distance. The polarization factor under these conditions, instead of being equal to  $4\pi/3$  as deduced by Lorentz, will be much smaller, and judging from the experimental data, almost nothing in the alkali halides. In other words, the Lorentz factor  $4\pi/3$  fails just in the case to which it was intended to apply, namely, in determining the polarization field in refracting media.

This should not, however, be interpreted as casting  
doubt/

doubt on the validity of the Lorentz derivation of the factor  $4\pi/3$ . Where the polarization of the crystal arises from a small relative displacement of the positive and the negative ion lattices, it may be regarded, as we have seen, as due to point dipoles located at the lattice points. In this case, the experimental data for the reststrahlen frequency do point to the factor  $p_1$  determining the polarization field, having just the Lorentz value  $4\pi/3$ .

Before concluding this section we wish to make two observations. We have here regarded the effect of the overlap of the electric charge on an ion with the charges on its immediate neighbours as affecting the magnitude of the polarization field due to the latter acting on the former. Alternatively, we may also regard the effect of the overlap as equivalent to a reduction of the effective charge on the ions from  $e$  to  $e^* < e$  (Fröhlich 1949).

The second observation concerns the method ~~used by Ramanathan (1947), and~~ referred to in the Introduction, for calculating the frequencies of some of the simple modes of oscillation of these crystals on the basis of certain specified force-constants between the atoms. Since these constants are not known functions of the distance of separation between the interacting atoms, the method is not capable of giving information regarding the anharmonicity of the oscillations, in which we are specially interested in this paper. Even in the calculation of the frequencies by this method, since no attempt is made to distinguish between the contributions to the force-constants from electrostatic interaction and from other types of interaction, ~~or in other words since~~ <sup>and</sup> the electric charges

on the ions are not <sup>therefore</sup> invoked explicitly in calculating the forces between them, any cooperative effect of the electric charges, like the polarization of the medium ~~as a whole~~ that may accompany the oscillation, is completely overlook<sup>ed</sup> in this method. When such a polarization occurs, as in the lattice oscillation of the alkali halides considered in this paper, the effect of the polarization field on the restoring forces acting on the ions, and thence on the frequency of the oscillation, as we have seen, can be quite large.

We shall have more to say on the force constants between the atoms in alkali halide crystals when we calculate the frequencies of some of the other modes of oscillation of these crystals in Part II.

9. THE  $r^4$  TERM IN EXPRESSION (9) FOR POTENTIAL ENERGY

The contribution to the potential energy from the polarization of the medium is confined, as we have seen, to the  $r^2$  term. But both the repulsion and the Coulomb interactions will contribute to the  $r^4$  term. It will be seen from (17), (21) and (22) that this term is of the form

$$\underline{f} r^4 = \underline{b} r^4 + \underline{c} r^4 (\underline{l}^4 + \underline{m}^4 + \underline{n}^4), \quad \text{we (35)}$$

and is thus a function of the direction of the relative displacement  $\underline{r}$  of the two lattices.

As in the calculation of the  $r^2$  term, in the present case also, it will be convenient to consider separately the contributions from the repulsion and the electrostatic interactions, and denote them by the subscripts 1 and 2 respectively, so that

$$\underline{b} = \underline{b}_1 + \underline{b}_2 \quad \text{we} \quad (36)$$

and

$$\underline{c} = \underline{c}_1 + \underline{c}_2 \quad \text{we} \quad (37)$$

Considering the repulsion interactions first, and adopting for them the exponential law (6), and ignoring interactions except between nearest neighbours, we obtain from (17)

$$\underline{b}_1 = \frac{\alpha e^2}{d^5} \left\{ \frac{\delta^3 + 2\delta^2 + 9\delta + 9}{48} - \frac{\delta^3 + 6\delta^2 + 15\delta + 15}{16} \sigma \right\} \quad \text{Sigma} \quad (38)$$

$$\underline{c}_1 = -\frac{\alpha e^2}{d^5} \left\{ \frac{\delta^3 + 6\delta^2 + 15\delta + 15}{48} (1 - 5\sigma) \right\} \quad \text{we} \quad (39)$$

respectively.

In the NaCl type, in which the immediate neighbours are six, at  $(\pm d, 0, 0)$ , etc.,

$$\sigma = 1/3, \quad \text{we} \quad (40)$$

whence (38) and (39) reduce to

$$\underline{b}_1 = -\frac{\alpha e^2}{d^5} \left\{ \frac{2\delta^2 + 3\delta + 3}{24} \right\} \quad \text{we} \quad (41)$$

$$\underline{c}_1 = \frac{\alpha e^2}{d^5} \left\{ \frac{\delta^3 + 6\delta^2 + 15\delta + 15}{72} \right\} \quad \text{we} \quad (42)$$

respectively.

Similarly in the CsCl type, in which the nearest neighbours are eight, at  $(\pm d/\sqrt{3}, \pm d/\sqrt{3}, \pm d/\sqrt{3})$ ,

$$\sigma = 1/9, \quad \text{we} \quad (43)$$

and the values of  $\underline{b}_1$  and  $\underline{c}_1$  are given by

$$\underline{b}_1 = \frac{\alpha e^2}{d^5} \left\{ \frac{\delta^3 + 6\delta + 6}{72} \right\} \quad \text{we} \quad (44)$$

$$\underline{c}_1 = -\frac{\alpha e^2}{d^5} \left\{ \frac{\delta^3 + 6\delta^2 + 15\delta + 15}{108} \right\} \quad \text{we} \quad (45)$$

In calculating the corresponding contributions  $\underline{b}_2$  and  $\underline{c}_2$  from the Coulomb interactions, which are long-range ones, we have naturally to include many more of the negative ions surrounding the positive ion at  $(x, y, z)$ . Substituting  $-e^2/R$  for  $\psi(R)$  in (17), and putting

$$\underline{R}_0/d = \Delta, \quad \text{we} \quad (46)$$

we obtain

*Sigma*  
*Cap. delta*

$$b_2 = -\frac{21}{16} \frac{e^2}{d^5} \sum \left\{ n, \frac{1-5\sigma}{\Delta^5} \right\} \quad \text{or} \quad (47)$$

$$c_2 = \frac{35}{16} \frac{e^2}{d^5} \sum \left\{ n, \frac{1-5\sigma}{\Delta^5} \right\} \quad \text{or} \quad (48)$$

The values of  $n$ ,  $\Delta$  and  $\sigma$  will naturally vary from one group to another, and their values for the different groups of negative ions surrounding any given positive ion in the crystal are given in Table II.

TABLE II

$n$	$\Delta^2$	Typical co-ordinates	$\sigma$	$n(1-5\sigma)/\Delta^5$
<b>NaCl Type</b>				
6	1	$\underline{d}, 0, 0$	1/3	-4.000
8	3	$\underline{d}, \underline{d}, \underline{d}$	1/9	0.228
24	5	$\underline{2d}, \underline{d}, 0$	17/75	-0.057
24	9	$\underline{2d}, \underline{2d}, \underline{d}$	11/81	0.032
6	9	$\underline{3d}, 0, 0$	1/3	-0.016
24	11	$\underline{3d}, \underline{d}, \underline{d}$	83/363	-0.009
24	13	$\underline{3d}, \underline{2d}, 0$	97/507	0.002
Total				-3.82
$D = d/\sqrt{3}$				
<b>CsCl Type</b>				
8	1	$\underline{D}, \underline{D}, \underline{D}$	1/9	3.556
24	11/3	$\underline{3D}, \underline{D}, \underline{D}$	83/363	-0.133
24	19/3	$\underline{3D}, \underline{3D}, \underline{D}$	163/1083	0.059
8	27/3	$\underline{3D}, \underline{3D}, \underline{3D}$	1/9	0.015
24	27/3	$\underline{5D}, \underline{D}, \underline{D}$	209/729	-0.043
<del>24</del> 48	35/3	$\underline{5D}, \underline{3D}, \underline{D}$	<del>101707/367515</del>	0.004
Total				3.46

*rules*

*split fraction*

101/525

It will be seen from the last column of Table II that  $n(1-5\sigma)/\Delta^5$  decreases rapidly with increase of  $\Delta$ , and the value of  $\sum \left\{ n(1-5\sigma)/\Delta^5 \right\}$ , appearing in (47) and (48), in which the summation extends over all the surrounding/

surrounding groups, is therefore calculated easily. Its value is -3.82 for crystals of the NaCl type, and 3.46 for those of the CsCl type. Using these values, those of  $b$  and  $c$  can be calculated with the help of (47) and (48) respectively. The values of  $b = b_1 + b_2$  and of  $c = c_1 + c_2$  thus calculated are entered in columns (2) and (3) of Table III.

Table III<sup>3</sup>

*theta*

*Cap. theta*

Crystals	$b \times 10^{-20}$	$c \times 10^{-20}$	$f_{100} \theta \times 100$	$f_{111} \theta \times 100$	$\bar{f} \theta \times 100$	$(n)/100$
<u>NaCl type</u>						
LiF	-2.72	7.03	6.5	-0.6	2.3	22 44
NaF	-2.20	5.84	3.3	-0.2	1.2	32 64
KF	-1.52	4.21	2.4	-0.1	0.9	36 72
RbF	-1.35	3.80	2.1	-0.1	0.8	35 70
CsF	-1.28	3.79	2.0	0	0.8	35 70
LiCl	-1.29	3.43	4.1	-0.3	1.5	29 58
NaCl	-1.18	3.26	2.4	-0.1	0.9	32 64
KCl	-0.90	2.60	1.8	0	0.7	35 70
RbCl	-0.84	2.47	1.5	0	0.6	34 68
LiBr	-1.12	3.01	3.7	-0.2	1.4	31 62
NaBr	-1.02	2.89	2.0	-0.1	0.7	33 66
KBr	-0.81	2.39	1.5	0	0.6	34 68
RbBr	-0.74	2.23	0.2	0	0.5	34 68
LiI	-0.98	2.78	3.2	-0.1	1.2	30 60
NaI	-0.89	2.62	1.8	0	0.7	33 66
KI	-0.71	2.20	1.5	0	0.6	31 62
RbI	-0.66	2.08	1.0	0	0.6	32 64
<u>CsCl type</u>						
CsCl	1.39	-1.34	0.1	1.3	0.4	21 42
CsBr	1.30	-1.24	0.1	0.9	0.8	22 44
CsI	1.23	-1.16	0.1	0.8	0.5	22 44

Now the extreme values of  $\sum l^4$  are

$$\sum l^4 = 1$$

when the direction of oscillation is along any of the cubic axes, i.e. along (1 0 0), etc., and

$$\sum l^4 = 1/3$$

when it is along any of the long diagonals of the cube, i.e. along (1 1 1), etc., and its average value, taken over all directions, is given by

$$\overline{\sum l^4} = 3/5$$

The corresponding extreme values of  $f$  (see (35)) are

$$f_{100} = b + c \quad \dots \quad (49)$$

and

$$f_{111} = b + c/3 \quad \dots \quad (50)$$

and its average value is

$$\overline{f} = b + 3c/5 \quad \dots \quad (51)$$

### 10. ENERGY LEVELS OF THE ANHARMONIC OSCILLATOR

The energy levels of an anharmonic oscillator of the above type are given by\*

$$W_n = (n + 1/2) h \nu_0 + 3 h^2 f (2n^2 + 2n + 1) / (64 \pi^4 \mu^2 \nu_0^2) \quad \dots \quad (52)$$

which may be written in the form

$$W_n = h \nu_0 [n + 1/2 + (n^2 + n + 1/2) f \theta], \quad \dots \quad (53)$$

where

$$\theta = 3h / (32 \pi^4 \mu^2 \nu_0^3) \quad \dots \quad (54)$$

and  $f \theta$  is a measure of the anharmonicity of the oscillator, which ~~and~~ varies, as we have seen, with the direction of the oscillation. In these expressions we may use for  $\nu_0$  the value of  $\nu$  given in Table I.

The "first differences" between the energy levels will be given by

$$W_{n+1} - W_n = h \nu_0 + 2(n+1) f \theta h \nu_0, \quad \dots \quad (55)$$

and the "second differences" by  $2 f \theta h \nu_0$  (which is a constant) for example we thus obtain from (53) (43)

\* See, for example, Ta-You-Wu (1946) and Pauling & Wilson (1935).

See also J.W. Edwards 1946 p. 48.

$$\nu_2 = (\underline{W}_2 - \underline{W}_0) / \underline{h} = 2\nu_0 + 6\nu_0 \underline{f} \theta, \quad \text{or} \quad (56)$$

$$\nu_1 = (\underline{W}_1 - \underline{W}_0) / \underline{h} = \nu_0 + 2\nu_0 \underline{f} \theta, \quad \text{or} \quad (57)$$

so that the ratio of the frequency  $\nu_2$  of the first overtone (second harmonic) to twice the frequency of the fundamental is given by

$$\Delta = \nu_2 / (2\nu_1) = 1 + \underline{f} \theta. \quad \text{or} \quad (58)$$

The frequency of the octave will obviously vary with the direction of the oscillation, unlike the frequency of the fundamental.

The two extreme values of the anharmonicity factor  $\underline{f} \theta$  are given in columns (4) and (5) of Table III<sup>3</sup>, which give us a measure of the spread of the spectrum of the octave on either side of twice the frequency of the fundamental.

The anharmonicities of the oscillations of several diatomic molecules have been studied in detail both theoretically and experimentally. There are two features that distinguish them from the anharmonicities of the lattice oscillations of the alkali halides. In the first place the main term determining the anharmonicity in diatomic molecules is the  $r^3$  term, whereas in <sup>the</sup> alkali halides it is the  $r^4$  term, the  $r^3$  term being absent. The sign of the anharmonic factor in diatomic molecules is negative, i.e. the energy levels come closer together as  $n$  increases, and the Condon Parabola tends to widen out as one moves to high energy levels. In the lattice oscillations, on the other hand, the anharmonicity factor varies with the direction of oscillation, from large positive to small negative values.

From the values of the anharmonicity factor  $\underline{f} \theta$  entered in Table III<sup>3</sup> it will be seen that its magnitude decreases as we proceed from the fluorides to the iodides, and again from the lithium salts to the corresponding salts of caesium.

11

II. INFLUENCE OF THE ANHARMONICITY OF THE SPECIFIC HEAT

For linear oscillators having an anharmonicity of the above type, the specific heat at constant volume at sufficiently high temperatures, will be given by (Born <sup>and Brody</sup> ~~Meyer~~ 1921)

$$c_v = k(1 - T/\Theta), \quad (59)$$

where

$$\Theta = 8\pi^4 \mu^2 \nu_0^4 / (3fk) \quad (60)$$

The significance of  $\Theta$  is that the specific heat at constant volume of an assemblage of such linear anharmonic oscillators will fall from its theoretical value k per oscillator characteristic of harmonic oscillators, by 1% per

$\Theta$  / 100 degrees rise in temperature. Using for f its average value, namely,  $\bar{f} = b + 3c/5$ , the values of  $\Theta$

~~100~~ have been calculated and are entered in the last column of Table III.

We naturally need to know similarly the anharmonicities of all the other normal modes of oscillation of these crystals, before we can correlate them with the observed temperature variation of  $c_v$  (of these crystals.) On the observational side also, only rough estimates of  $c_v$  are available, and those too for one crystal, namely sodium chloride. Direct measurements naturally give the specific heat at atmospheric pressure, and in order to calculate from these data the specific heat at constant volume, one needs to know the compressibilities of the crystal at these very high temperatures, whereas the available compressibility measurements are at ordinary temperatures only and only very rough estimates can be made by extrapolation. Using such extrapolated values for the compressibility of sodium chloride, Eucken <sup>and</sup> Dannöhl (1934) find that  $c_v$  attains nearly the theoretical value characteristic of an assemblage of harmonic oscillators at above

300° C,

Cap theta

cap theta

cap. theta

Cap. theta

300°C, and then falls off almost linearly by about one sixth in 500°C. This would correspond roughly to an effective value of 3000°C for  $\omega$ , which is of the same sign, and of the same order of magnitude, and of the same sign, as that calculated for the lattice oscillations.

We shall resume this discussion after the anharmonicities of all the other modes of oscillation have also been calculated.

We wish to thank Mr. K.S. Sarma and Mr. K.D. Baveja for helpful discussions.

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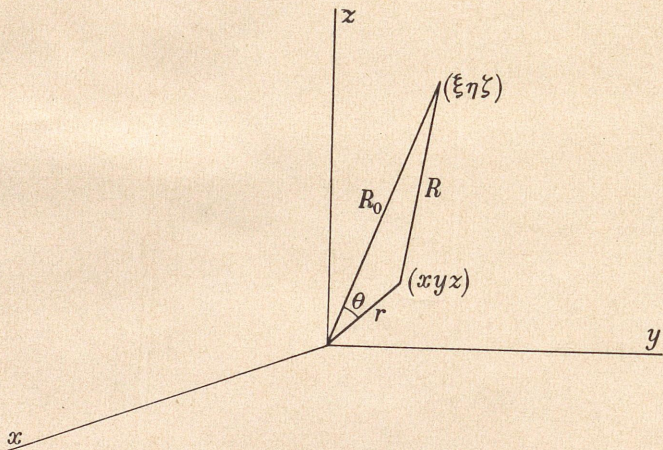
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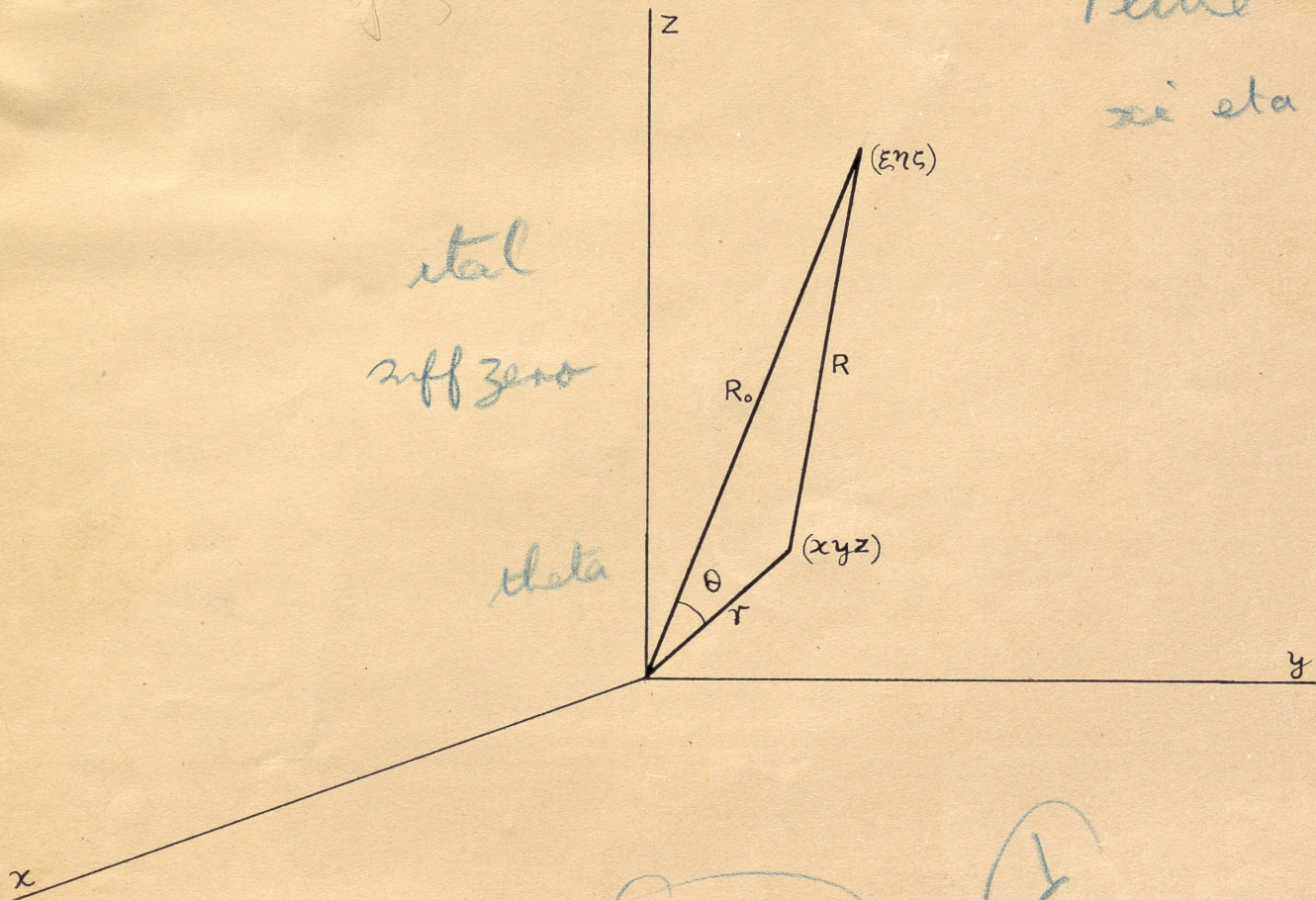


Fig 1.

1/2