

NATIONAL PHYSICAL LABORATORY OF INDIA

SIR K. S. KRISHNAN, F.R.S.  
DIRECTOR

HILLSIDE ROAD  
NEW DELHI

*Mss. sent by  
air mail.*

12th September 1951

The Assistant Secretary,  
The Royal Society,  
Burlington House,  
Piccadilly, London W 1.

Dear Sir,

Herewith I am enclosing the typescripts  
of a paper by Dr. S.K.Roy and me, entitled  
" The Frequencies and the Anharmonicities of  
The Normal Modes of Oscillation of Alkali Halide  
Crystals

II. Low Frequency Acoustic Modes "

for consideration for publication in the Proceed-  
ings of the Royal Society, A Series. If the paper  
is accepted for publication, the proofs may kindly  
be sent to my address.

Yours faithfully,

*USR*

Encl: Typescripts of  
paper and 3 copies  
of synopsis.

Proof recd on 16<sup>11</sup>/<sub>51</sub>  
+ recd of regd air-  
mail on 17<sup>11</sup>/<sub>51</sub>

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The Royal Society  
Burlington House  
London W. 1

17 September 1951

IN SO FAR AS THE WORK REPORTED IN THE PAPER COMMUNICATED BY YOU MAY HAVE BEEN CARRIED OUT IN OR ON BEHALF OF A GOVERNMENT RESEARCH ESTABLISHMENT, WILL YOU KINDLY STATE IN WRITING WHETHER THE AGREEMENT OF THE DEPARTMENT CONCERNED HAS BEEN OBTAINED TO PUBLICATION OF THE PAPER.

*J. C. Martin*

Assistant Secretary

THE ROYAL SOCIETY.

*J. C. Martin*

*Assistant Secretary*

Received

1 MS.

Figures

Plates (Photographs, etc.)

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The Royal Society  
Burlington House  
London W. 1

17 September 1951

Sir,

The paper communicated by you to the Royal Society, entitled The frequencies and the anharmonicities of the normal modes of oscillation of alkali halide crystals. II. The low frequency acoustic modes.

has been safely received.

Yours faithfully,

*D. C. Martin*

*Assistant Secretary*

Received

1 MS.

Figures

Plates (Photographs, etc.)

Proc Roy Soc Aropy No blocks

285 Report A216

THE FREQUENCIES AND THE ANHARMONICITIES OF  
THE NORMAL MODES OF OSCILLATION OF ALKALI HALIDE CRYSTALS  
II. LOW-FREQUENCY ACOUSTIC MODES

By Sir K.S. Krishnan, F.R.S., and Sanat Kumar Roy, Ph.D.,  
National Physical Laboratory of India, New Delhi

(Received 17 September 1951)

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Abstract

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In the present Part are deduced, on the basis of Born's model, expressions for the frequency and the ratio of the amplitudes of the alkali and the halide ions in an alkali halide crystal, for any general normal mode of oscillation of the crystal. The results are applied in detail to the special case of low-frequency acoustic modes. Since the amplitudes of the two ions are not in general the same, there is a resultant electric polarization of the medium accompanying the oscillations, and consequently a polarization field. The force acting on an ion due to this field is found to be comparable with the force of interaction with the other ions, not only in the optical branch, in which the displacements of adjacent positive and negative ions are in opposite directions and in which, therefore, the polarization is large, but also in general in the acoustic branch, in which their displacements are in the same direction. A detailed calculation, however, shows that for low frequency acoustic modes, though the ratio of the amplitudes of the two ions is affected by the polarization field, the frequency remains completely unaffected by it.

The expressions deduced for the frequencies of the acoustic modes give us also the velocities of propagation of the corresponding acoustic waves, and since the latter are already known in terms of the elastic constants of the crystal, we obtain, incidentally, simple expressions for these constants. The elastic constants so calculated are found to agree with observation.

Unlike the principal oscillations of the crystal dealt with in Part I, these low-frequency <sup>acoustic modes</sup> ~~oscillations~~ have negligible anharmonicity.

1. INTRODUCTION *crs*

*←* In Part I of this paper (Krishnan <sup>&</sup> and Roy 1951) the oscillation of the lattice of positive ions in alkali halide crystals with respect to the lattice of negative ions, was discussed in ~~some~~ detail, on the basis of the simple Born model. Among other results it was ~~not~~ found that the electric polarization of the crystal that accompanies the oscillation, plays an important part in determining its frequency. The force acting on any given ion, due to this polarization field, is comparable in magnitude with the force due to its interactions with the other ions. For example, in sodium chloride crystal, the force due to the polarization is nearly half that due to the interactions with the other ions, and, being in opposite direction to the latter, is almost of the same magnitude as the resultant force.

The model enables us also to calculate the anharmonicity of this oscillation, since the expression for the potential energy of the crystal contains, in addition to the prominent term proportional to the square of the relative displacement of the two lattices, ~~and~~ which <sup>term</sup> determines the frequency, also a term proportional to its fourth power. The latter term, unlike the square term, varies with the direction of the displacement, and hence the anharmonicity, unlike the frequency, varies with the direction of the oscillation.

In the present ~~part~~ are deduced, on the basis of the same model, general expressions for the frequency and the ratio of the amplitudes of the positive and the negative ions, for any general normal mode of oscillation of the alkali halide crystal. The results are applied in detail to the special case of low-frequency acoustic modes.

These and other modes of oscillation of the alkali

halide crystal, have been discussed previously by several authors, and particularly by Kellermann (1940). But the present treatment is in some ways much simpler, and yields some new results of interest.

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2. THE POTENTIAL ENERGY OF AN ION DISPLACED BY AN ELASTIC WAVE IN THE CRYSTAL

~~section title~~  
etc

lambda-delta

Consider an alkali halide crystal of the NaCl type, and propagation in it of a plane elastic wave of wave length  $\lambda$ , and consider one of the three principal directions of displacement of the ions in the crystal associated with this wave, the displacements being small in comparison with the distance  $d$  between neighbouring ions. Choosing as the coordinate axes the cubic axes of the crystal, and as the origin the equilibrium position of an alkali ion, we denote by  $l_{mn}$  the direction-cosines of the wave-normal, and by  $L_{MN}$  the direction-cosines of the displacements, and by  $r_m$  the displacement at any given instant  $t$  of an ion  $m$  whose equilibrium position corresponds to the coordinates  $(\xi_m, \eta_m, \zeta_m)d$ , where  $\xi_m, \eta_m, \zeta_m$  are integers. Let  $\psi(R)$  be the energy of interaction between any two ions separated by a distance  $R$ . For simplicity  $\psi(R)$  may be assumed, as in Part I of this Paper, to be of the form

lmn

xi, eta, zeta

$$\psi(R) = \pm \frac{e^2}{R} + A e^{-R/\rho}, \quad (1)$$

where the second term on the right-hand side represents the repulsion interaction between the ions, and the first term the electrostatic interaction between the  $m$  ions, the + or the - sign being chosen according as the second ion, say  $n$ , is of the same type as the first, or is different. It will be the former when  $(\xi_n + \eta_n + \zeta_n) - (\xi_m + \eta_m + \zeta_m)$  is even, and the latter when it is odd.  $e$  in the first term denotes the electronic charge.

The repulsion interactions, which are of short range, are regarded in this paper as confined to the nearest neighbours only, and hence we use in (1) single constant  $A$  and  $\rho$  which refer to the interactions between near ions of the opposite types only. <sup>Other</sup> ~~The~~ <sup>like those</sup> interactions of the van der Waals type between the dipoles induced in the ions, are also

neglected.

Considering now the interactions between the various ions in the crystal, all of which have been displaced appropriately to correspond to the same instant  $t$ , we obtain for the potential energy of the crystal

$$U = \frac{1}{2} \sum_m \sum_{\substack{n \\ m \neq n}} \psi_{mn} \quad (2)$$

where  $\psi_{mn}$  is used for brevity in place of  $\psi(R_{mn})$ .

Let us denote by  $U_m$  the potential energy involved in displacing one of the ions, say ion  $m$ , from its equilibrium position to the position appropriate to time  $t$ , the other ions being displaced synchronously from their respective equilibrium positions to the positions corresponding to  $t$ .  $U_m$  can be readily obtained, except for a constant term independent of the displacements, in which we are not at present interested, by putting

$$U_m = \int_0^{r_m} \left( \frac{\partial U}{\partial r_m} \right) dr_m \quad (3)$$

in which while differentiating  $U$  with respect to  $r_m$  all the other displacements are kept constant, whereas in the integration all the displacements are increased from 0 to their final value characteristic of time  $t$ , synchronously with  $r_m$ ; i.e. before integrating, all the other displacements  $r_n$  occurring in the expression for  $\frac{\partial U}{\partial r_m}$  are expressed in terms of  $r_m$  and the appropriate differences in phase between them, so that for the purpose of this integration  $\frac{\partial U}{\partial r_m}$  may be regarded as a function of  $r_m$  only.

In obtaining the differential coefficient  $\frac{\partial U}{\partial r_m}$  occurring in (3) we may, therefore, omit straightaway all those terms in expression (2) for  $U$  that obviously do not involve  $r_m$ , and rewrite (3) in the simpler form

$$U_m = \int_0^{r_m} \frac{\partial}{\partial r_m} \left[ \sum_{\substack{n \\ n \neq m}} \psi_{mn} \right] dr_m \quad (4)$$

### 3. EXPANSION AS A POWER SERIES

Now the interaction energy  $\psi$  between the alkali ion near the origin and any other ion at a distance  $R$  from it may be expressed in the form of a Taylor expansion

$$\psi(R) = \psi(R_0) + r(\partial\psi/\partial r)_{r=0} + (r^2/2!)(\partial^2\psi/\partial r^2)_{r=0} + \dots, \quad (5)$$

where  $r$  is the displacement of the former ion, with respect to the latter. In view of the relation

$$R^2 = R_0^2 + r^2 - 2QR_0r, \quad \dots \dots (6)$$

in which  $Q$  is the cosine of the angle between the directions of  $r$  and  $R_0$ , <sup>in which therefore</sup> and  $R \rightarrow R_0$  as  $r \rightarrow 0$ , we may express the differential coefficients of  $\psi$  with respect to  $r$  at  $r = r_0$  in terms of the differential coefficients of  $\psi$  with respect to  $R$ , at  $R = R_0$ . We shall, for simplicity, designate the latter coefficients by  $\psi'$ ,  $\psi''$ ,  $\psi'''$ , ... . Obviously

$$(\partial\psi/\partial r)_{r=0} = -Q\psi',$$

$$\begin{aligned} (\partial^2\psi/\partial r^2)_{r=0} &= (1-Q^2)\psi'/R_0 + Q^2\psi'' \\ &= F, \text{ say,} \end{aligned}$$

$$\begin{aligned} (\partial^3\psi/\partial r^3)_{r=0} &= 3Q(1-Q^2)(\psi'/R_0^2 - \psi''/R_0) - Q^3\psi''' \\ &= G, \text{ say,} \end{aligned} \quad (7)$$

$$\begin{aligned} (\partial^4\psi/\partial r^4)_{r=0} &= 3(1-Q^2)(5Q^2-1)(\psi'/R_0^3 - \psi''/R_0^2) \\ &\quad + 6Q^2(1-Q^2)\psi'''/R_0 + Q^4\psi^{iv} \\ &= H, \text{ say,} \end{aligned}$$

where

$$Q = (L\xi + M\eta + N\zeta) / (\xi^2 + \eta^2 + \zeta^2)^{1/2}. \quad (8)$$

Since  $\psi_{mn}$  can thus be expressed as a power series in  $r_{mn}$ ,  $U_m$  also, as we shall show presently, can be expressed as a power series in  $r_m$ , and in particular  $U_0$ , the potential energy of the alkali ion <sup>near</sup> the origin as a power series in  $r_0$ .

4. INTERACTION OF AN ION WITH A PAIR CENTRO-SYMMETRIC TO IT

As a first step towards expressing  $U_0$  as a power series in  $r_0$ , we shall confine attention to the interaction between the alkali ion near the origin and the pair of ions at  $\pm (\xi_n, \eta_n, \zeta_n)d$  respectively, and designated  $n$  and  $n'$  respectively,  $n'$  being the inverse of  $n$  with respect to the origin. Now choosing the positive direction of the displacement to be the same for all the ions, and the positive direction of  $R_{on}$  to be from the origin to the lattice point  $n$  under consideration, one can readily see that  $Q_{on}$  and  $Q_{on'}$  are of the same magnitude, but have opposite signs. Hence putting  $Q_{on} = -Q_{on'} = Q$ , and denoting by  $\psi_0$  the value of  $\psi_{on}$  when both the ions  $o$  and  $n$  are in their equilibrium positions, we obtain

$$\begin{aligned} \psi_{on} + \psi_{on'} &= 2\psi_0 - Q\psi' \left[ (r_0 - r_n) - (r_0 - r_{n'}) \right] \\ &\quad + (F/2!) \left[ (r_0 - r_n)^2 + (r_0 - r_{n'})^2 \right] \\ &\quad + (G/3!) \left[ (r_0 - r_n)^3 - (r_0 - r_{n'})^3 \right] \\ &\quad + (H/4!) \left[ (r_0 - r_n)^4 + (r_0 - r_{n'})^4 \right] + \dots \end{aligned} \quad (9)$$

Now the amplitudes of the alkali and the halide ions will in general be different. Denoting by  $q$  the ratio of the latter amplitude to the former, and by  $\phi_{on}$  the difference in phase of the elastic wave at the ions  $o$  and  $n$ , we obtain

$$\left. \begin{aligned} r_n/r_0 &= q e^{-i\phi_{on}} \\ r_{n'}/r_0 &= q e^{i\phi_{on}} \end{aligned} \right\}, \quad \dots \quad (10)$$

in which  $q$  will be unity if  $n$  and  $n'$  are alkali ions, but otherwise will, in general, be different from unity, and will be positive in the acoustic branch in which the displacements of adjacent positive and negative ions are in the same direction, and will be negative in the optical branch in which the displacements of the two ions are in opposite directions.  $\phi_{on}$  will evidently be equal

to  $2\pi\kappa\Delta_{on}$ , where  $\kappa = 1/\lambda$ , and  $\Delta_{on}$  is the path difference between o and n, and is given by

$$\Delta_{on} = (\ell \xi_n + m \eta_n + n \zeta_n) d. \quad (11)$$

In other words,  $\Delta_{on}$  is the projection of  $\underline{R}_o$  on the wave-normal.

Now equation (4) for  $\underline{U}_o$  may be written in the form

$$\underline{U}_o = \sum \int_0^{\tau_o} \frac{\partial}{\partial \tau_o} (\psi_{on} + \psi_{on'}) d\tau_o, \quad \dots (12)$$

in which the summation extends over all pairs  $nn'$ . The differential coefficient appearing in it may be obtained by differentiating (9) with respect to  $\tau_o$ , remembering that in this operation  $\tau_n$  and  $\tau_{n'}$  are to be treated as constants independent of  $\tau_o$  (see remarks at the end of ~~Section~~<sup>§</sup> 2). The coefficient thus obtained will naturally involve  $\tau_n$  and  $\tau_{n'}$  in addition to  $\tau_o$ . Now by substituting for  $\tau_n$  and  $\tau_{n'}$  from (10), we can express the integrand as a function of  $\tau_o$  alone, and thus obtain  $\underline{U}_o$  as a function of  $\tau_o$ , or, to be more precise, as a power series in  $\tau_o$ .

5. THE  $\tau_o^2$  TERM IN THE EXPRESSION FOR  $\underline{U}_o$  AND THE EFFECT OF THE POLARIZATION FIELD

In expression (12) for  $\underline{U}_o$  we shall consider separately the terms that involve the different powers of  $\tau_o$ , and take first the  $\tau_o^2$  term, which is the first non-vanishing term. Now

$$\begin{aligned} \frac{\partial}{\partial \tau_o} (\psi_{on} + \psi_{on'}) &= F [2\tau_o - (\tau_n + \tau_{n'})] \\ &= 2F\tau_o [1 - q \cos \varphi_{on}], \end{aligned} \quad (13)$$

and hence

$$\int_0^{\tau_o} \frac{\partial}{\partial \tau_o} (\psi_{on} + \psi_{on'}) d\tau_o = F\tau_o^2 (1 - q \cos \varphi_{on}). \quad (14)$$

In equations (13) and (14), as in (10),  $q$  <sup>is to</sup> ~~should~~ be put equal to unity whenever  $nn'$  are alkali ions, i.e. are of the same type as the ion at the origin. Hence the  $\tau_o^2$  term in expression (12) for  $\underline{U}_o$  will be given by

$$a_{1,0} r_0^2 = \frac{r_0^2}{2} \left[ \sum_1 F(1 - q \cos \varphi_{on}) + \sum_2 F(1 - \cos \varphi_{on}) \right], \quad (15)^*$$

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in which  $\sum_1$  denotes summation over all the ions for which  $\delta = \xi + \eta + \zeta$  is odd, and similarly  $\sum_2$  denotes summation over all the ions for which  $\delta$  is even.

If  $m_1$  be the mass of the alkali ion,  $-2a_1/m_1$  will obviously be the acceleration of the ion per unit displacement under the interaction forces under consideration. If these were all the forces acting on the ion,  $2a_1/m_1$  should be equal to the square of the frequency of oscillation of the ion, and therefore of the elastic waves.

In Part I of ~~this paper~~, we showed that the interactions  $\psi$  between the ions, on the basis of which we have calculated  $a_1$ , do not include the effects of any cooperative phenomena <sup>on</sup> like the electric polarization of the crystal that may accompany the oscillations. Such a polarization obviously accompanies what are usually described as polar oscillations of the crystal, in which the displacements of adjacent positive and negative ions are in opposite directions. The oscillation of the lattice of positive ions with respect to the lattice of negative ions, is a special case of such polar oscillations and is characterized by  $k=0$  and hence by a homogeneous polarization, i.e. polarization that is the same throughout the medium. In Part I, ~~of this paper~~, in which this case was discussed in detail, it was found that the force acting on any ion due to the polarization field is comparable in

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\*Equation (14) refers to the interaction between the alkali ion near the origin and the pair of ions  $n$  and  $n'$ . Hence in obtaining the potential energy  $U_0$  of the ion 0, due to interactions with all <sup>the</sup> other ions, we have to sum up the effects of all such pairs  $nn'$ . In (15), however, for convenience in doing the summations, we have regarded the ion  $n$  and its inverse  $n'$  separately, and to rectify the double counting thus introduced, we have inserted the multiplying factor

$\frac{1}{2}$  on the right-hand side of (15).

~~NaCl chloride~~

magnitude with the force due to interaction with the surrounding ions. In NaCl for example, it is roughly half of the latter, and being opposed to it, is of nearly the same magnitude as the resultant restoring force. It was also found that any polarization induced in the ions by the displacement of the electrons with reference to the corresponding nuclei, does not contribute to the force acting on an ion and tending to displace the ion as a whole.

The polarization field plays an important part in <sup>many</sup> ~~some~~ of the other modes of oscillation too of the alkali halide crystal, and will be discussed in detail elsewhere. We shall merely note here the following <sup>results</sup> which are relevant to our present purpose.

(1) Even when the polarization of the medium is not quite homogeneous, the polarization field acting on an ion may be nearly as large as when it is homogenous, but will now depend markedly on whether the displacements of the ions that produce the polarization are longitudinal or transverse to the direction of the gradient of the polarization, i.e., to the wave-normal.

(2) Considering elastic waves having their wave-normals along  $[111]$  such a polarization occurs not only for the optical branch, in which the displacements of adjacent positive and negative ions are in opposite directions, but also for the acoustic branch in which the displacements are in the same direction, because the magnitudes of the displacements of the two ions are different as a result of the difference in their masses. For a given amplitude of one of the ions, the polarization <sup>u</sup> ~~this~~ produced will of course be much smaller than in the corresponding optical branch, but the frequencies involved now are also ~~more~~ correspondingly smaller, and hence the polarization fields acting on the ions will still remain comparable with the forces of interaction between the ions displaced from their respective equilibrium positions by the acoustic wave.

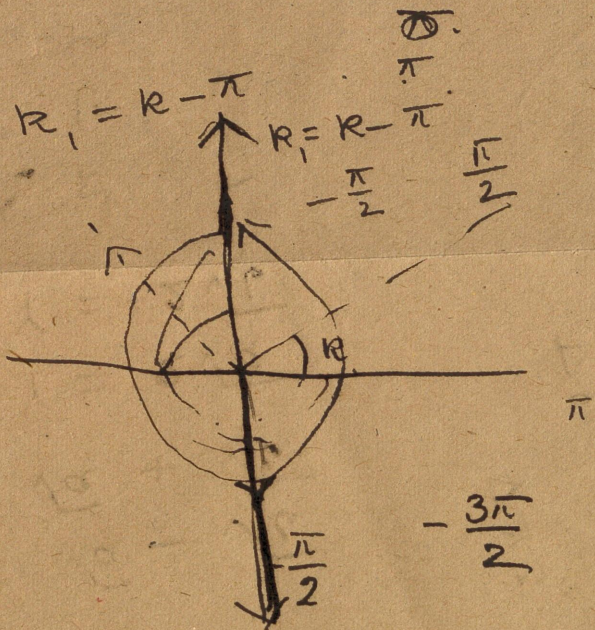
~~New the polarization of the medium per unit volume,~~

When  $k$  is small in comparison with  $1/d$ , <sup>and</sup> the polarization is nearly homogeneous over regions covering a large number of ions. The polarization per unit volume in the neighbourhood of the origin will then be given by  $Ne(1-q)r_0$ , where  $N$  is the number of ion pairs per unit volume; the direction of the polarization will naturally be that of the direction of displacement of the ions under the elastic wave. (Consistently with the finding in Part I, we neglect here the polarization due to the electronic displacements, as distinguished from the polarization due to the relative displacements of the positive and <sup>the</sup> negative ions, since the former polarization does not affect the <sup>i</sup>displacements of the ions, in which alone we are interested here.) Hence the extra force due to the polarization field acting on the alkali ion near the origin, and tending to restore it to its equilibrium position, can be put equal to  $\mu Ne^2(1-q)r_0$ , and the corresponding contribution to the potential energy  $U_0$  of this ion will be given by  $-(1/2)\mu Ne^2(1-q)r_0^2$ , in which  $p$  is the polarization factor, which will depend on whether the direction of the polarization is along or transverse to the direction of the gradient of the polarization, i.e., whether the displacements under the elastic wave, that cause the polarization, are longitudinal or transverse. In the latter case  $p$  will evidently have the Lorentz value  $4\pi/3$ , for the same reason for which the usual Lorentz treatment of dielectric polarization is applicable not only for an incident static electric field, but also for the field of an electromagnetic wave whose wave-length is much longer than the interatomic distance, as is the case with the elastic waves that we are considering now.

Even when  $k$  is not small, the extra potential energy of the ion near the origin due to the polarization produced in the medium by the elastic wave, may still be put equal to  $-(1/2)\mu Ne^2(1-q)r_0^2$ , <sup>( $\mu$  will not be merely the polarization factor, and its)</sup> in which ~~the~~ value of  $p$  will now depend not only on whether the displacements are longitudinal or transverse, but also on the magnitude of  $k$  in relation to  $1/d$ , but can ~~however~~, be calculated.

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this to the right-hand side of (15) we obtain for the  $r_0^2$  term in the expression for  $U_0$ , which determines the frequency of the mode, the value

$$\frac{r_0^2}{2} \left[ \Sigma F - \Sigma_2 (F \cos \varphi_{on}) - \mu N e^2 (1-q) - q \Sigma_1 (F \cos \varphi_{on}) \right]. \quad (16)$$

Equating this to  $(1/2) m_1 \omega^2 r_0^2$ , and putting

$$\Sigma_1 (F \cos \varphi_{on}) = c_1 \quad (17)$$

and

$$\Sigma F - \Sigma_2 (F \cos \varphi_{on}) - \mu N e^2 = g, \quad (18)$$

we obtain

$$q = \frac{g - m_1 \omega^2}{c_1 - \mu N e^2} \quad (19)$$

By shifting the origin of the coordinate system from the equilibrium position of an alkali ion, where we have located it at present, to that of a halide ion, we obtain similarly

$$\frac{1}{q} = \frac{g - m_2 \omega^2}{c_1 - \mu N e^2} \quad (20)$$

in which  $m_2$  is the mass of the halide ion, and  $\Sigma_1$  and  $\Sigma_2$  occurring in the expressions for  $c_1$  and  $g$  denote as before summations over all odd and even values respectively of  $\delta$ .

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6. EXPRESSIONS FOR THE FREQUENCY AND THE RATIO OF THE AMPLITUDES OF THE TWO IONS

For any given value of  $R$ , which determines the phase differences  $\varphi$  of the elastic wave between the ions, one may eliminate either  $q$  or  $\omega^2$  from (19) and (20), and thus obtain

$$m_1 m_2 \omega^4 - (m_1 + m_2) g \omega^2 + g^2 - (c_1 - \mu N e^2)^2 = 0, \quad (21)$$

whence

$$\omega^2 = \frac{(m_1 + m_2) g \pm \sqrt{(m_1 - m_2)^2 g^2 + 4 m_1 m_2 (c_1 - \mu N e^2)^2}}{2 m_1 m_2}, \quad (22)$$

and similarly

$$\underline{m}_2 (c_1 - \underline{\mu} N e^2) \underline{q}^2 + (\underline{m}_1 - \underline{m}_2) \underline{g} \underline{q} - \underline{m}_1 (c_1 - \underline{\mu} N e^2) = 0, \quad (23)$$

whence

$$\underline{q} = - \frac{(\underline{m}_1 - \underline{m}_2) \underline{g} \mp \sqrt{(\underline{m}_1 - \underline{m}_2)^2 \underline{g}^2 + 4 \underline{m}_1 \underline{m}_2 (c_1 - \underline{\mu} N e^2)^2}}{2 \underline{m}_2 (c_1 - \underline{\mu} N e^2)} \quad \dots (24)$$

In both (22) and (24) the upper sign corresponds to the acoustic branch of the elastic <sup>modes,</sup> waves, and the lower sign to the optical branch.

over

### 7. PARTICULAR CASE WHEN $\underline{R}$ IS SMALL

Let  $\underline{u}$  be the distance up to which the electrostatic interactions between ions, which are of long range, remain significant, and let  $\underline{R}$  be sufficiently small that  $\cos \varphi = \cos 2\pi \underline{R} \Delta$  can be put equal to  $1 - \frac{\varphi^2}{2}$  even when  $\Delta$  is as large as  $\underline{u}$ . Expression (24) for  $\underline{q}$  then reduces to

$$\underline{q} = 1 - \frac{1}{2} \frac{\underline{m}_1 - \underline{m}_2}{\underline{m}_1 + \underline{m}_2} \frac{\Sigma (F \varphi_{on}^2)}{\Sigma_1 F - \underline{\mu} N e^2} \quad \dots (25)$$

in the acoustic branch, and to

$$\underline{q} = - \frac{\underline{m}_1}{\underline{m}_2} \left( 1 + \frac{1}{2} \frac{\underline{m}_1 - \underline{m}_2}{\underline{m}_1 + \underline{m}_2} \frac{\Sigma (F \varphi_{on}^2)}{\Sigma_1 F - \underline{\mu} N e^2} \right) \quad \dots (26)$$

in the optical branch. Similarly, expression (22) for  $\omega$  reduces to

$$\omega^2 = \frac{\Sigma (F \varphi_{on}^2)}{\underline{m}_1 + \underline{m}_2} \quad \dots (27)$$

in the acoustic branch and to

$$\omega^2 = \frac{\Sigma_1 F - \underline{\mu} N e^2}{\underline{\mu}} + \frac{\Sigma_2 (F \varphi_{on}^2)}{2 \underline{\mu}} - \frac{\Sigma (F \varphi_{on}^2)}{\underline{m}_1 + \underline{m}_2} \quad \dots (28)$$

in the optical branch, where

$$\frac{1}{\underline{\mu}} = \frac{1}{\underline{m}_1} + \frac{1}{\underline{m}_2} \quad \dots (29)$$

In the special case when  $\underline{R} \rightarrow 0$ ,

$$\underline{q} \rightarrow 0 \quad \square \text{ or } \square - \frac{\underline{m}_1}{\underline{m}_2} \quad \dots (30)$$

The first value corresponds obviously to an acoustic wave of infinite wave-length, for which the amplitudes of the two ions will naturally be the same, and the second value to the oscillations of the lattice of the alkali ions with respect to <sup>the lattice</sup> that of the halide ions, in which their

will

displacements would naturally be in opposite directions, and the amplitudes inversely proportional to their respective masses. Similarly, when  $k \rightarrow 0$

omega

$$\omega^2 \rightarrow 0 \text{ or } \omega^2 = (\sum_i F_i - hNe^2) / \mu, \quad (31)$$

the first value in (31) referring to the acoustic, and the second to the optical branch. In the latter case, in which the polarization is homogenous,  $h = 4\pi/3$ , and is independent of the direction of the displacement of the lattice of positive ions with respect to the lattice of the negative ions. This expression for the optical frequency is identical with that obtained in Part I, where too it was found to be independent of the direction of displacement.

8. LONG ACOUSTIC WAVES: VELOCITIES AND AMPLITUDES

From now on we shall confine our attention to low-frequency acoustic modes, and postpone to later parts of this paper the consideration of the other modes.

It will be readily seen from the expressions derived in the previous section that the ratio of the amplitudes is considerably influenced by the polarization field, in both the acoustic and the optical branches, and the frequency too in the optical branch. But the frequency of long acoustic waves, as is evident from (27), remains completely unaffected by the polarization field. This result is significant, since otherwise the validity of the well-known Christoffel relations between the elastic constants and the velocities of propagation of long acoustic waves for different directions of the wave-normal, and <sup>(the corresponding) directions</sup> of displacement, which we need to use in the next section, will be disturbed. One can understand in a general way how in the case of long acoustic waves this happens, in spite of the restoring force acting on an ion due to the polarization field, being still quite large and comparable with the force due to the interactions. The frequencies of the oscillations of adjacent positive and negative ions

which are determined jointly by the interactions with all the surrounding ions and the polarization field, have naturally to be identical, and this is secured by a suitable <sup>automatic</sup> adjustment in the crystal of the relative amplitudes of the two ions. The relative <sup>a</sup> amplitudes and in general the frequencies also will, therefore, depend very much on whether the polarization field is present or not. In the case of low-frequency acoustic modes, however, unlike in other modes, it happens that the condition that the frequencies of the neighbouring ions remain equal in spite of the extra polarization forces, incidentally ensures that these frequencies remain quite unaffected by these extra forces, the whole effect of these extra forces being now confined to changing the relative amplitudes of the two ions.

Now expression (27) for  $\omega^2$  for low-frequency acoustic modes of vibration of the crystal leads to the following expression for the velocities of propagation  $v$  of the corresponding long acoustic waves in the crystal, namely,

$$\underline{D}v^2 = \underline{N} \Sigma (\underline{F} \Delta_{on}^2), \quad (32)$$

in which  $\underline{D}$  is density of the crystal, and is given by

$$\underline{D} = \underline{N} (\underline{m}_1 + \underline{m}_2). \quad (33)$$

The calculation of the velocities of long acoustic waves thus reduces, on Born's model, to evaluating  $\Sigma (\underline{F} \Delta_{on}^2)$ . It becomes particularly simple when, as in the case of propagation along  $[100]$ ,  $[110]$  and  $[111]$ , the acoustic waves can be regarded as longitudinal and transverse respectively. The restriction of the calculation to these special cases does not involve any loss of generality, since for any given general direction of the wave-normal the directions of the displacements and the corresponding velocities of propagation can be obtained from the data for these particular directions.

Since  $\underline{h}$  is known, the ratio of the amplitudes of

of the two ions can also be calculated for the above directions of the wave-normal.

9. EVALUATION OF  $\Sigma(F\Delta^2)$

We now proceed to calculate  $\Sigma(F\Delta^2)$  for these special directions. (For convenience we are dropping the subscripts from  $\Delta$ .) The summation can be done conveniently in two stages, as similar summations were done in Part I. In a cubic crystal of the alkali halide type, corresponding to every lattice point  $(\xi, \eta, \zeta)$  there are others whose coordinates are obtained by the various permutations of  $\pm\xi, \pm\eta, \pm\zeta$ . Their number  $\tau$  when all the three coordinates are different and different from zero, will be 48, and otherwise will be smaller. For any such group of ions round the origin,  $|R_0|$  will remain the same, and hence the average value of  $F\Delta^2$  taken over all the ions in the group, which we shall denote by  $\overline{F\Delta^2}$ , can be calculated easily, and hence the contribution to  $\Sigma(F\Delta^2)$  from all the ions in this group, namely,  $\tau(\overline{F\Delta^2})$ . The summation can then be extended over all such groups.

Moreover, in expression (7) for  $F$  we may separate the contributions from the electrostatic and the repulsion interactions by substituting for  $\psi$  given by (1) either the first or the second term only, and thus get separately the contributions to  $\Sigma(F\Delta^2)$  from the electrostatic and the repulsion interactions. The repulsion interactions being of short range may be restricted to the six immediate neighbours only, whereas in the electrostatic case we have to include interactions over a much wider range.

In order to calculate the average value of  $F\Delta^2$  taken over all the ions in any particular group, i.e., over all the ions whose coordinates may be obtained by the

permutations of  $(\pm\xi, \pm\eta, \pm\zeta)d$ , we merely require the average values of the following functions of these coordinates, all of which are readily obtained. Putting

$$\xi^2 + \eta^2 + \zeta^2 = S, \quad (34)$$

we obtain

$$\left. \begin{aligned} \overline{\xi^2} &= S/3; \quad \overline{\xi\eta} = 0; \quad \overline{(\xi+\eta+\zeta)^2} = 3\overline{\xi^2} = S; \\ \overline{(\xi+\eta)^2} &= \overline{(\xi-\eta)^2} = 2S/3; \quad \overline{\xi^2\eta^2} = S^2/6 - \overline{\xi^4}/2; \\ \overline{(\xi^2-\eta^2)^2} &= -S^2/3 + 3\overline{\xi^4}; \quad \overline{(\xi+\eta)^4} = S^2 - \overline{\xi^4}; \\ \overline{(\xi+\eta+\zeta)^4} &= 3S^2 - 6\overline{\xi^4}. \end{aligned} \right\} \quad (35)$$

The results of the calculation are entered in Table 1.

The first column in the Table gives the direction of the wave-normal, and the second the direction of the displacement. The third column gives the contribution to  $\sum(F\Delta^2)$  from repulsion interaction, which, being restricted to the six immediate neighbours, is readily calculated, and needs no comment. Following the notation used in Part I the repulsion interaction is expressed in terms of  $\frac{d}{\rho} \left( \frac{d}{\rho} \right)$ .

delta  $\delta = \frac{d}{\rho}$ .

rho

*le.*  
~~Sodium chloride~~  
alpha chi

Table 1 NaCl type

Direction of wave-normal	displacement	Repulsion interaction $\Sigma(F\Delta^2)/(e^2/d)$	Electrostatic interaction				in terms of elastic constants
			$F\Delta^2 = (-1)^s (e^2/d) (A s^{-3/2} + B s^{-5/2})$	$\Sigma(F\Delta^2) = (-1)^s \frac{e^2}{d} (a + b)$			
			A	B	a	b	
T	[100]	$\alpha \delta/3$	$-\xi^2$	$3\xi^4$	1/3	-1	$c_{11}$
[100]	[010]	$-\alpha/3$	"	$3\xi^2\eta^2$	-1/6	1/2	$c_{44}$
#	[001]						
T	[110]	$\alpha(\delta-1)/6$	$-(\xi+\eta)^2/2$	$3(\xi+\eta)^4/4$	-5/12	1/4	$(c_{11}+c_{12}+2c_{44})/2$
[110]	[1\bar{1}0]	"	"	$3(\xi^2-\eta^2)^2/4$	7/12	-3/4	$(c_{11}-c_{12})/2$
#	[001]	$-\alpha/3$	"	$3(\xi^2+\eta^2)\zeta^2/2$	-1/6	1/2	$c_{44}$
T	[111]	$\alpha(\delta-2)/9$	$-(\xi+\eta+\zeta)^2/3$	$(\xi+\eta+\zeta)^4/3$	-2/3	2/3	$(c_{11}+2c_{12}+4c_{44})/3$
[111]	$\perp^r$ to [111]	"	"	$(\xi+\eta+\zeta)^2\alpha^2$	1/3	-1/3	$(c_{11}-c_{12}+c_{44})/3$

centre ~~lines~~  
on point of  
braces

The calculation of the electrostatic contribution, however, presents certain features of interest. Considering the interaction between the alkali ion at  $o$  with any particular ion  $n$  whose coordinates are  $(\xi, \eta, \zeta)d$ , we find that the value of  $F\Delta^2$  can be expressed in the form

$$(F\Delta^2) = (-1)^s (A s^{-3/2} + B s^{-5/2}) (e^2/d), \quad (36)$$

where  $A$  and  $B$  are functions of the coordinates, <sup>elec. term.</sup> which vary and also with the direction of the wave-normal and of the displacement. The values of  $A$  and  $B$  for different directions are entered in columns 4 and 5 of the Table. Now the average values of  $A$  and  $B$  for the group of ions whose coordinates are obtained by the permutation of  $(\pm\xi, \pm\eta, \pm\zeta)d$  are found to have the form  $a s$  and  $b(\xi^4 + \eta^4 + \zeta^4)$  respectively, and hence the average

value of  $(F\Delta^2)_{elec.}$  taken over the group can be expressed in the form

$$(\overline{F\Delta^2})_{elec.} = (-1)^s \left[ \underline{a} \underline{S}^{-1/2} + \underline{b} (\xi^4 + \eta^4 + \zeta^4) \underline{S}^{-5/2} \right] (e^2/d), \quad (37)$$

where a and b are found to be independent of the coordinates and therefore have the same value for all the groups. (They, however, depend on the direction of the wave-normal and of the displacement.) We are thus led to the important result that the net electrostatic contribution from all the ions to  $\sum (F\Delta^2)$  is as though each ion contributed just two terms, both unique, one to the series  $(e^2/d)a\alpha$  and the other to the series  $(e^2/d)b\chi$ , where

$$\alpha = -\sum (-1)^s (\xi^2 + \eta^2 + \zeta^2)^{-1/2}, \quad (38)$$

$$\chi = -\sum (-1)^s (\xi^4 + \eta^4 + \zeta^4) (\xi^2 + \eta^2 + \zeta^2)^{-5/2}, \quad (39)$$

in which  $\xi \eta \zeta$  take all integral values except  $\xi = \eta = \zeta = 0$ .

In other words, the electrostatic part of  $\sum (F\Delta^2)$  can be expressed in the form

$$\sum (F\Delta^2)_{elec.} = (\underline{a}\alpha + \underline{b}\chi) e^2/d, \quad (40)$$

in which a and b are known functions of the direction of propagation and of displacement. The values of a and b for the principal directions are entered in columns 6 and 7 of Table 1.

$\alpha$  can be readily identified as the well-known Madelung series, and  $\chi$  also is a known series (see, for example, Löwdin, 1948 a and b). Their values are  $\alpha = 1.75$  and  $\chi = 3.14^*$

## 10. EXPRESSIONS FOR THE ELASTIC CONSTANTS

As is well known, for any given direction of the wave-normal of an acoustic wave in a cubic crystal, the three directions of displacement, and the corresponding velocities, can be readily calculated in terms of the known elastic constants  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  with the help of

\*Both  $\alpha$  and  $\chi$  have been computed numerically to seven places of decimals;  $\alpha = 1.747,557,8$ ;  $\chi = 3.138,555,8$  (Löwdin 1948 b).

Christoffel relations. (See, for example, Love 1944)

The values of  $Dv^2$  thus obtained in terms of the elastic constants are entered in the last column of Table 1.

At the same time, we have in equation (32), namely,

$$Dv^2 = N \Sigma (F\Delta^2) = \Sigma (F\Delta^2) / (2d^3),$$

an expression for  $Dv^2$  for crystals of the NaCl type, in terms of  $\alpha$ ,  $\chi$  and  $\delta$ , all of which are known. From a comparison of these two values of  $Dv^2$  we obtain expressions for the elastic constants of the crystal in terms of  $\alpha$ ,  $\chi$ ,  $\delta$ , and also the contributions to these constants from the electrostatic and the repulsion interactions separately.

The data entered in Table 1 offer nine relations between the elastic constants, and  $\alpha$ ,  $\chi$  and  $\delta$ . ~~Four~~ <sup>Three</sup> of these relations are identical, and any three of the remaining <sup>six</sup> ~~five~~ will enable us to calculate the three elastic constants, or rather to calculate  $c_{11}$  and  $c_{12}$  and to verify the Cauchy relation, namely,  $c_{12} = c_{44}$ , which we should expect the crystal to satisfy on the basis of the model adopted by us, in which both the repulsion and the Coulomb forces are "central". The ~~two~~ <sup>three</sup> extra relations offer an effective check on our calculation. rho

We shall denote the contributions to  $c_{11}$  from the repulsion and the electrostatic interactions by  $p_{11}$  and  $\epsilon_{11}$  respectively, and similarly the contributions to  $c_{12}$  by  $p_{12}$  and  $\epsilon_{12}$ , and to  $c_{44}$  by  $p_{44}$  and  $\epsilon_{44}$  respectively. Their values are entered in Table 2, and are expressed in terms of  $\frac{4}{3}e^2/(12d^4)$ .

epsilon

Table 2. NaCl type

	11	12	44
$\epsilon$	$2\alpha - 6\chi$	$-5\alpha + 3\chi$	$-\alpha + 3\chi$
$\rho$	$2\alpha\delta$	$2\alpha$	$-2\alpha$
$C = \epsilon + \rho$	$2\alpha(\delta+1) - 6\chi$	$-3\alpha + 3\chi$	$-3\alpha + 3\chi$

epsilon  
rho

It will be seen immediately (1) that the Cauchy relation is verified,  $c_{12}$  being equal to  $c_{44}$ , though the components  $\epsilon_{12}$  and  $\rho_{12}$  are not separately equal to  $\epsilon_{44}$  and  $\rho_{44}$  respectively; and (2) that the compressibility

beta

$$\beta = 3/(c_{11} + 2c_{12}) = 18d^4/\{e^2\alpha(\delta-2)\} \quad (41)$$

is the same as the value  $9d/\{Ne^2\alpha(\delta-2)\}$  obtained in Part I (equation (7)), from direct considerations (in view of the relation  $N = 1/(2d^3)$  for the NaCl type of crystals that we are now considering).

The values of the elastic constants obtained here agree with those calculated <sup>by</sup> Kellermann on the basis of the same model. His expressions, however, involve more complicated series than  $\chi$ . It should also be mentioned here that the values of  $\epsilon_{12}$  and  $\rho_{12}$ , and of  $\epsilon_{44}$  and  $\rho_{44}$  obtained by Kellermann differ from the corresponding values obtained by us.

The numerical values of the elastic constants calculated from <sup>the</sup> above expressions which obviously refer to very low temperatures, are entered in Table 3, along with the observed values wherever available. The values of  $\delta$  used in the calculation are those given by Pauling (1928) and used by us in Part I of this paper, and are entered in column 2 of the Table. The agreement <sup>of the elastic constants</sup> between the calculated and the observed values is satisfactory.

It will also be seen from the Table <sup>3</sup> that in the NaCl type of crystal, the elastic constant  $c_{12} = c_{44}$ , as calculated on Born's simple model, depends on the lattice constant  $d$  only, and is inversely proportional to its fourth power. This result is verified by observation. This result, however, does not apply to the CsCl type, as we shall see presently.\*

\* A preliminary report of the results on the elastic constants has been communicated to Nature

Table 3. ✓

The elastic constants are expressed in  $10^{11}$  dynes/cm<sup>2</sup>

Crystals	$d_0$ (in Å)	$\delta$ (Pauling)	$c_{11}$		$c_{12} = c_{44}$		$c_{44}$	
			Cal.	Obs.	Cal.	Obs.	Obs.	
<u>NaCl type</u>								
LiF	2.01	7.0	10.7	9.8	4.9	5.2		
NaF	2.31	8.0	8.5		2.8			
KF	2.67	9.0	6.1		1.6			
RbF	2.82	9.5	5.4		1.3			
CsF	3.00	10.5	5.1		1.0			
LiCl	2.57	8.0	5.5		1.8			
NaCl	2.81	9.0	5.0	4.8	1.3			
KCl	3.14	10.0	3.9	3.9	0.8	0.8	0.7	
RbCl	3.27	10.5	3.6		0.7			
LiBr	2.75	8.5	4.8		1.4			
NaBr	2.98	9.5	4.3	(3.3)	1.0	1.3		
KBr	3.29	10.5	3.5	3.4	0.7	0.6	0.6	
RbBr	3.43	11.0	3.4		0.6			
LiI	3.00	9.5	4.2		1.0			
NaI	3.23	10.5	3.8		0.7			
KI	3.53	11.5	3.1	2.7	0.5	0.4		
RbI	3.66	12.0	2.8		0.4			
<u>CsCl type</u>								
CsCl	3.56	11.5	5.0		0.1			
CsBr	3.71	12.0	4.6		0.2			
CsI	3.95	13.0	3.5		0.2			

CsCl

at least of these  
 The experimental values of the elastic constants have been taken from Bridgman (1929), Voigt (1928), Huntington (1947), Galt (1948) and Ramachandran (1949)

11. THE ELASTIC CONSTANTS FROM STEADY DISPLACEMENTS

? part

Our main interest in the present paper is the calculation of the frequencies and the amplitudes of the acoustic modes of oscillation in the crystal and their harmonicities, on the simple Born Model, and the expressions obtained for the frequencies are used, incidentally, by making  $\kappa$  small, to give us the elastic constants. If our main purpose had been to calculate the elastic constants of the alkali halides, we could have calculated directly the potential energy associated with certain specific homogeneous strains produced in the crystal, and thence evaluated the elastic constants; for example,  $C_{11} - C_{12}$  in increasing slightly the distances between the ions along the  $x$ -axis and decreasing simultaneously by the same amount the distances along the  $y$ -axis, those along the  $z$ -axis remaining unaltered, and  $C_{44}$  by a shearing strain in a plane parallel to two of the cubic axes. In general, for a cubic crystal, adopting the usual Voigt notation (Voigt, 1928), and denoting by  $\alpha_1, \alpha_2, \alpha_3$  the three tension components of the strain tensor, and by  $\alpha_4, \alpha_5, \alpha_6$  the sheer components, and expressing the energy  $E$  per unit volume of the crystal in terms of the strains

$$E = \frac{1}{2} \sum_{ij} c_{ij} \alpha_i \alpha_j, \quad \dots \quad (42)$$

we obtain

$$c_{ij} = c_{ji} = \frac{\partial^2 E}{\partial \alpha_i \partial \alpha_j} \quad \dots \quad (43)$$

The calculation of  $E$  involves, as mentioned just now, the same technique as used in the earlier parts of this paper, and leads naturally to the same expressions for the elastic constants as obtained here from the velocities of acoustic waves of long wave-lengths.

? sections  
? part

12. ALKALI HALIDES OF THE CsCl TYPE

Though the discussion till now has been made to refer explicitly to the NaCl type of alkali halides, most of it will apply equally well to the CsCl type also. Choosing again as the origin the equilibrium position of an alkali ion, the <sup>ci.</sup>coordinates of all the other ions will now be given by  $(\xi, \eta, \zeta) d/\sqrt{3}$ , where, as before,  $d$  is the distance between neighbouring ions, and  $\xi, \eta, \zeta$  are integers, but are now either all of them odd, in which case they refer to a halide ion, or all of them even, in which case they refer to an alkali ion. The number of ion pairs  $N$  per unit volume will now be given by  $3\sqrt{3}/(8d^3)$ , instead of by the value  $1/(2d^3)$  characteristic of the NaCl type. The contribution to  $\sum (F\Delta^2)$  from the repulsion interactions will <sup>also</sup> be different, since the number of nearest neighbours is now 8 instead of 6, and so ~~also~~ will be the contributions from the electrostatic interactions. The latter, however, can still be expressed in the form

$(\underline{a}\alpha' + \underline{b}x')e^2/d$ , where  $\underline{a}' = \underline{a}\sqrt{3}$  and  $\underline{b}' = \underline{b}\sqrt{3}$ , in which  $\underline{a}$  and  $\underline{b}$  have the same values as for NaCl (see Table I) and

$$\alpha' = -\sum (-1)^{\xi+\eta+\zeta} (\xi^2 + \eta^2 + \zeta^2)^{-1/2} \quad \dots (44)$$

$$x' = -\sum (-1)^{\xi+\eta+\zeta} (\xi^4 + \eta^4 + \zeta^4) (\xi^2 + \eta^2 + \zeta^2)^{-5/2} \quad \dots (45)$$

chi

Though  $\alpha'$  and  $x'$  have the same form as  $\alpha$  and  $x$ , they are really different from them, since  $\xi, \eta, \zeta$  do not now take all integral values as before, but are restricted to where they are all odd, or are all even. ( $\xi = \eta = \zeta = 0$  is excluded in both the cases).  $\alpha'$  is obviously the Madelung constant for the CsCl type of crystal, and has been calculated by several investigators (see in particular Shermann, 1932) and is equal to 1.018.

It should be remembered here that the Madelung constant used in Part I for the CsCl type of crystal, namely,  $\alpha = 1.763$ , is defined by

$$-\alpha/d = \sum (-1)^s/R,$$

where R is the distance of the ion from the origin and is equal to  $s^{1/2} \times d/\sqrt{3}$ . Hence our  $\alpha' = 1.763/\sqrt{3}$ .

The series  $\chi'$ , however, does not seem to have been studied, but can be evaluated in the following manner. The CsCl type of crystal is body-centred cubic, with two ions in the unit cell. If we divide the crystal into such unit cells and calculate in the usual manner the contributions from such cells to  $\chi'$ , the terms are found to converge very slowly, and one needs to take contributions from several thousand cells before <sup>even</sup> the second decimal place could be decided with certainty. This method of cubic summation, which is usually adopted for the computation of such series, is not, therefore, helpful in the present case. There is, however, an alternative <sup>choice</sup> ~~method~~ of the elementary cells, which we find on trial to give terms that are much more rapidly convergent. Choosing as before the equilibrium position of an alkali ion as the origin, consider the cube of eight halide ions immediately surrounding it. The ~~eight~~ <sup>of the cube</sup> corners will correspond in our notation to  $\xi \eta \zeta = \pm 1, \pm 1, \pm 1$ . Join the origin to any three adjacent corners of this cube, say, 111, 1-11, 11-1. The parallelepiped formed with these three lines as the adjoining edges will form a suitable unit cell with one ion at each of its corners, half of them positive, and the other negative. By considering these eight ions forming the corners of such a cell as forming a group, and regarding every alternate cell as unoccupied, one can calculate readily the contributions from these cells to  $\chi'$ , and they are found, after the first few terms, to converge <sup>fairly</sup> rapidly. Detailed calculations have been made by this method by Mr. K.D. Baveja and Mr. Gyan Mohan in this laboratory, and will be published elsewhere. We shall merely

chi

quote here the final result of their computation, namely,

$$\chi' = -1.70 - 1.08$$

Coming back to the calculation of  $\Sigma(F\Delta^2)$  and thence of the elastic constants of alkali halides of the CsCl type, on the Born Model, the results obtained are given in Table 4, and are expressed in terms of  $e^2/(16d^4)$ .

Table 4. CsCl type

	11	12	44
<i>epsilon</i> $\epsilon$	$6\alpha' - 18\chi'$	$-15\alpha' + 9\chi'$	$-3\alpha' + 9\chi'$
<i>rho</i> $\rho$	$2\alpha'(\delta - 2)$	$2\alpha'(\delta + 4)$	$2\alpha'(\delta - 2)$
$\underline{c = \epsilon + \rho}$	$2\alpha'(\delta + 1) - 18\chi'$	$\alpha'(2\delta - 7) + 9\chi'$	$\alpha'(2\delta - 7) + 9\chi'$

Here again though  $\underline{c_{12}} = \underline{c_{44}}$  as should be expected, the contributions to  $\underline{c_{12}}$  from the repulsion and the electrostatic interactions, namely  $\rho_{12}$  and  $\epsilon_{12}$ , are not separately equal to  $\rho_{44}$  and  $\epsilon_{44}$  respectively.

Further

$$\beta = 3/(\underline{c_{11}} + 2\underline{c_{12}}) = 8d^4/\{e^2\alpha'(\delta - 2)\}, \quad (46)$$

which is the same as the value obtained in equation (7) of Part I from direct considerations.

### 13. THE ANHARMONICITIES OF THE LOW FREQUENCY ACOUSTIC MODES

Coming back to expression (12) for  $U_0$  (see also (9)) we shall now consider the terms in it that involve higher powers of  $\underline{r_0}$  than  $\underline{r_0^2}$ . These terms will evidently determine the anharmonicity of the oscillation, in the same manner in which the  $\underline{r_0^2}$  term determines the frequency. The  $\underline{r_0^4}$  term, which we shall consider first, will be given by

$$\underline{h r_0^4} = \Sigma \int_0^{r_0} \frac{\partial}{\partial r_0} \left[ \frac{H}{4!} \left\{ (\underline{r_0} - \underline{r_n})^4 + (\underline{r_0} - \underline{r_{n'}})^4 \right\} \right] d\underline{r_0}, \quad (47)$$

where  $\underline{H}$  has the value defined by (8) and where, while differentiating with respect to  $\underline{r}_0$ ,  $\underline{r}_n$  and  $\underline{r}_{n'}$  are to be treated as constants, whereas before integrating, both  $\underline{r}_n$  and  $\underline{r}_{n'}$  are to be expressed in terms of  $\underline{r}_0$ . Doing so, we obtain for the coefficient of  $\underline{r}_0^4$

$$\underline{h} = \sum \left[ \frac{\underline{H}}{4!} (1 - 3q \cos \varphi + 3q^2 \cos 2\varphi - q^3 \cos 3\varphi) \right], \quad (48)$$

where the summation extends over all the ions.

For the low frequency modes, for which  $\cos \varphi$  can be put equal to  $1 - \varphi^2/2$ ,  $q$  is given by (25), which we may rewrite for convenience in the form

$$q = 1 - \underline{W} \underline{\kappa}^2, \quad (49)$$

where the second term is of the same order of magnitude as  $\varphi^2$ . After some simple reductions, we find that the terms in (44) that are independent of  $\varphi$  cancel each other out, and that the first ~~non-vanishing~~ non-vanishing term corresponds to

$$\underline{h} = - \sum_i \left( \frac{\underline{H}}{8} \underline{W} \underline{\kappa}^2 \varphi^2 \right), \quad (50)$$

and is of the <sup>same</sup> order of magnitude as  $\sum (\underline{H} \varphi^4)$ .

There is thus an essential difference between the optical modes and the low-frequency acoustic modes. In the optical branch, the coefficients of the  $\underline{r}_0^2$  and  $\underline{r}_0^4$  terms in the expression for potential energy are of the order of  $\sum \underline{F}$  and  $\sum \underline{H}$  respectively, and the ratio of the latter to the former is of the order of  $10^{-16} \text{ cm}^2$ . In other words, the  $\underline{r}_0^4$  term will become comparable with the  $\underline{r}_0^2$  term only when the amplitude becomes as large as an <sup>angstrom</sup>  $\underline{r}_0$ , which may be taken as a rough measure of the anharmonicity.

On the other hand, for the low-frequency acoustic modes that we are now considering, the  $\underline{r}_0^2$  and <sup>the</sup>  $\underline{r}_0^4$  terms are of the order of  $\sum (\underline{F} \varphi^2)$  and  $\sum (\underline{H} \varphi^4)$  respectively. The ratio of the latter to the former will now be of a lower order of magnitude than for the optical modes, lower

by a factor  $\varphi^2$ .

The calculation of the  $r_0^3$  term is slightly more complicated, but here again, the coefficient is of the order of  $\varphi^3$ .

Hence for the low-frequency acoustic modes, the anharmonicities are of a lower order of magnitude than for the optical branch, and will be the smaller the lower the frequency and quite insignificant.

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We wish to thank Mr, K.D.Baveja and Mr, Gyan Mohan for undertaking the numerical computation of the series  $\chi'$ , and for making available to us their results.

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By Air mail

26th October 1951

The Assistant Secretary,  
The Royal Society,  
Burlington House,  
London W 1.

Dear Sir,

About a month ago, I communicated a paper by me and Dr. S.K. Roy entitled THE FREQUENCIES AND THE ANHARMONICITIES OF THE NORMAL MODES OF OSCILLATION OF ALKALI HALIDE CRYSTALS (II) LOW FREQUENCY ACOUSTIC MODES for consideration for publication in the Proceedings of the Royal Society.

After communicating the paper, I found a numerical error in the value of one of the constants used in the paper. I shall be glad if you will kindly get the following corrections made in the paper:

1. Page 21, Table 3. <sup>the</sup> entries under  $C_{11}$  cal. for the last three crystals (namely CsCl, CsBr, CsI) should read

4.0	<u>instead of</u>	5.0
3.5	"	4.6
2.8	"	3.5

Similarly entries under  $C_{12}$   $C_{44}$  cal. should read

0.6	<u>instead of</u>	0.1
0.6	"	0.2
0.6	"	0.2

2. Page 25 second line from the top should read

1.08	<u>instead of</u>	1.70
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Yours faithfully,

*Ugru*

11 DEC 1951

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The Royal Society

Burlington House

London W.1

8 NOV 1951

Dear Sir,

I have to inform you that the paper No. A 216  
by Sanat Kumar Roy and yourself  
which you communicated to the Society has been accepted for  
publication in the Proceedings/~~Transactions~~.

Galley proofs will be sent for your approval in due  
course. If you require the proofs to be read by any person other  
than yourself, please let me know the name and address to which  
they should be sent.

Yours faithfully,

D. C. Martin

Assistant Secretary