

## A Theory of Dielectric Polarization in Alkali-Halide Crystals

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A theory of dielectric polarization is described in which each ion in an alkali-halide crystal is considered as a separate entity capable of being distorted internally by an electric field. Three stiffness coefficients suffice to describe the interaction between the local electric field and the polarizable ion. The Lorentz internal field is shown to be valid for this calculation. Optical and dielectric polarizabilities per molecule and infra-red absorption frequencies in alkali-halide crystals calculated by this method are shown to be in substantial agreement with experiment. Electronic polarizabilities of free (gaseous) ions are also calculated, and a novel "pseudo-piezoelectric" effect is predicted.

### I. INTRODUCTION

It seems intuitively obvious that the dielectric properties of a solid material should be determined uniquely by the properties of the atoms or ions of which it is made, and by the way in which they are arranged. In respect to the atomic arrangement, the alkali-halide crystals are the simplest ionic solids and their pertinent dielectric and optical properties have generally been known for seventeen years. An interpretation of ionic polarization is now proposed which is inherently simple, explains all the experimental data to a good approximation and does not go beyond classical mechanical principles.

In order to study a single ion independently of the crystal, it is necessary to construct an imaginary boundary around it and to replace forces which formerly existed between particles inside the boundary and those outside by corresponding forces between the internal particles and the boundary. In this way a relation can be found between the forces acting on an ion and the distortion produced thereby. This relation may be expressed by three stiffness coefficients or "springs" connected between the nucleus, the electron cloud, and the boundary. All of these springs are necessary to explain the experimental results.

### II. DISTORTION OF IONS BY ELECTRIC FIELDS

The arrangement and size of ions in ionic crystals are generally studied in the absence of an electric field by

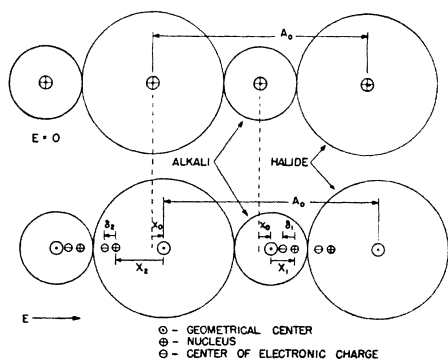


FIG. 1. Ionic arrangement in neutral crystal (upper diagram) and in polarized crystal (lower diagram) showing nuclear and electronic displacements.

x-ray diffraction methods. In this way, it is determined, for example, that a sodium chloride crystal has a cubic unit cell with face-centered symmetry containing four ions of each type and having an edge 5.629 angstroms in length. This is the distance from the center of one sodium ion to the next, with a chlorine ion in between.

It is convenient to think of each ion as a separate individual which just touches its neighbors. Then it is an experimental fact that the points of contact so defined between a given ion and its neighbors in the crystals being considered determine a sphere. This is what is meant by the spherical boundary of an ion. In crystals of the sodium chloride type it follows that the edge of the unit cube is equal to the sum of the diameters of the alkali and halide ions (if they do touch). From the regularity in the observed lattice spacings, it is found that each ion has very nearly the same diameter in different kinds of crystals.

When an electric field of ordinary magnitude is applied to an alkali-halide crystal, the ions are internally distorted, but their external spherical shape and size (as defined by the points of contact) as well as their arrangement are unaffected. This conclusion follows directly from the same symmetry considerations which are employed to prove the absence of the first-order piezoelectric effect. Since the ionic boundaries are not deformed by an electric field, there is no loss in generality for the present problem by considering the boundaries to be rigid spheres. A more complicated (non-rigid) ionic model would be needed if elastic deformation were to be considered in addition to electrical polarization.

In order to describe the internal distortion of an ion, it will be necessary to consider the relative displacements of certain reference points. The center of the spherical boundary is such a point. It is the center of charge, mass, etc., of the unpolarized ion and the geometrical center of the polarized ion. The position of the nucleus is another such point, which would be at the center in the unpolarized ion, but is displaced a distance  $X$  to one side of the center in the polarized ion. The third point is the center of charge of the electron cloud including all electrons, even those closely bound to the nucleus. In the unpolarized ion, the center of electronic

charge coincides with the position of the nucleus, but in the polarized ion, it is displaced a distance  $\delta$  to one side of the nucleus.

These three points and the displacements  $X$  and  $\delta$  for each of the two types of ions in an alkali-halide crystal are shown schematically in Fig. 1. A row of ions in an unpolarized crystal (upper diagram) is compared with a similar row of ions in a polarized crystal (lower diagram). The distance  $X_0$ , indicated in this figure, represents a displacement of the whole system of boundaries from its equilibrium position. Such a displacement is possible because, though rigid, the system of boundaries is not necessarily fixed in space. In this figure, positive vectors are drawn to the right.

### III. EQUATIONS OF MOTION

The individual ion is distorted because forces operate on its component parts. The forces causing the distortion are due to the action of the local electric field on charge carriers. These forces are opposed by restoring forces depending on the magnitude of the ionic distortion. For simplification, the forces and displacements are to be considered small enough so that a relation analogous to Hooke's law is obeyed. In other words, the restoring forces are assumed proportional to the displacements. Three constants of proportionality  $b$ ,  $c$ , and  $f$  are then needed to express the forces between the nucleus, the electron cloud and the ionic boundary due to their relative displacements. The equations for the total forces are given below.

#### 1. Force on nucleus:

$$F_n = -bX + c\delta + peF_i, \quad (1)$$

where  $pe$  is the charge on the nucleus and  $F_i$  is the electrostatic field at the center of the ion.

#### 2. Force on electron cloud:

$$F_e = -c\delta - f(X + \delta) - neF_i, \quad (2)$$

where  $n$  is the total number of electrons and  $e$  is the electronic charge.

#### 3. Force on boundary (due to internal distortion):

$$F_b = bX + f(X + \delta). \quad (3)$$

Equation (2) involves the proposition that the average electric field effective in displacing the electron

TABLE I. Tentative ionic parameters.

|    | A      | B<br>(A <sup>2</sup> ) | C<br>(A <sup>2</sup> ) |
|----|--------|------------------------|------------------------|
| Li | —      | 0                      | 0                      |
| Na | 2.075  | 1.4                    | 1.97                   |
| K  | 1.501  | 8.1                    | 11.44                  |
| Rb | 1.769  | 9.9                    | 14.63                  |
| Cs | 1.277  | 16.0                   | 33.69                  |
| F  | -0.867 | 35.2                   | 11.05                  |
| Cl | -0.702 | 75.6                   | 37.25                  |
| Br | -0.678 | 87.4                   | 52.54                  |
| I  | -0.614 | 109.2                  | 79.90                  |

cloud is that at the center of the ion, or rather the field that would exist at this point if the ion itself were absent. The electric field in the space vacated by the ion is extremely unhomogeneous due to the close proximity of charged particles. However, in any such space where Laplace's equation is valid, the average potential on the surface of a sphere is equal to that at its center. Similarly, the average over the spherical surface of any Cartesian component of the potential gradient is equal to that at the center. If the distribution of electron probability density in the ion is uniform over each such concentric sphere, then the average field effective in causing electron polarization is that at the center. The assumption of radial symmetry follows from the picture of spherical ions adopted earlier.

The dipole moment induced on a given ion is obtained by multiplying the charge on each part of the ion by its total displacement in space from its initial or equilibrium position.

$$\begin{aligned} \mu_i &= pe(X + X_0) - ne(X + \delta + X_0) \\ &= e(p - n)(X + X_0) - ne\delta. \end{aligned} \quad (4)$$

The mass of the electron cloud is negligible relative to that of the nucleus, hence the force on the electron cloud is effectively zero throughout the frequency range to be considered. Thus, Eq. (2) can be used to eliminate one of the variables, namely:

$$\delta = (-fX - neF_i)/(c + f). \quad (5)$$

Substituting this value of  $\delta$  in Eqs. (1), (3), and (4), gives:

$$\left. \begin{aligned} F_n &= -\frac{bc + cf + fb}{c + f}X + \left(p - \frac{cn}{c + f}\right)eF_i \\ F_b &= \frac{bc + cf + fb}{c + f}X - \frac{nf}{c + f}eF_i \\ \mu_i &= \left(p - \frac{cn}{c + f}\right)eX + (p - n)eX_0 + \frac{n^2}{c + f}e^2F_i \end{aligned} \right\} \quad (6)$$

The form of these equations as well as all subsequent calculations can be greatly simplified by substituting three new parameters in place of the ionic stiffnesses  $b$ ,  $c$ , and  $f$ . The new parameters are defined in terms of the old in the following way:

$$\left. \begin{aligned} A &= p - cn/(c + f) \\ B &= e^2/\xi_0 \cdot (c + f)/(bc + cf + fb) \\ C &= e^2/\xi_0 \cdot n^2/(c + f) \end{aligned} \right\} \quad (7)$$

where  $\xi_0$  is the permittivity of free space.

The fundamental equations then take the following form:

$$\left. \begin{aligned} F_n &= -1/B \cdot (e^2/\xi_0)X + AeF_i \\ F_b &= 1/B \cdot (e^2/\xi_0)X - (A - p + n)eF_i \\ \mu_i &= AeX + (p - n)eX_0 + C\xi_0F_i \end{aligned} \right\} \quad (8)$$

Equations (8) are helpful in explaining the significance

TABLE II. Comparison of experimental and theoretical data for alkali-halide crystals.

|      | 1                  | 2     | 3            | 4                      |                           | 5                      |                           | 6                         |                              | 7                      |                           | 8                      |                           | 9 |  | 10 | 11    |
|------|--------------------|-------|--------------|------------------------|---------------------------|------------------------|---------------------------|---------------------------|------------------------------|------------------------|---------------------------|------------------------|---------------------------|---|--|----|-------|
|      | $V$                | $K$   | $n$          | $\alpha_D$             |                           | $\alpha_e$             |                           | $\lambda_A$               |                              | $\alpha_{sol}$         | $\alpha_g$                |                        |                           |   |  |    |       |
|      | ( $\text{\AA}^3$ ) |       | (Na-D light) | exp ( $\text{\AA}^3$ ) | theor. ( $\text{\AA}^3$ ) | exp ( $\text{\AA}^3$ ) | theor. ( $\text{\AA}^3$ ) | exp ( $\times 10^{-6}$ m) | theor. ( $\times 10^{-6}$ m) | exp ( $\text{\AA}^3$ ) | theor. ( $\text{\AA}^3$ ) | exp ( $\text{\AA}^3$ ) | theor. ( $\text{\AA}^3$ ) |   |  |    |       |
| LiF  | 16.21              | 9.27  | 1.391        | 35.7                   | 37.5                      | 11.55                  | 11.05                     | 32.6                      | 32.3                         |                        |                           |                        |                           |   |  |    | 11.7  |
| LiCl | 33.74              | 11.05 | 1.662        | 77.9                   | 74.5                      | 37.45                  | 37.25                     | 49.4                      | 49.4                         | 43.5                   |                           |                        |                           |   |  |    | 44.0  |
| LiBr | 41.36              | 12.1  | 1.784        | 97.6                   | 92.7                      | 52.26                  | 52.54                     | 55.5                      | 55.5                         | 61.1                   |                           |                        |                           |   |  |    | 61.6  |
| LiI  | 54.00              | 11.03 | 1.955        | 124.7                  | 121.1                     | 78.52                  | 79.90                     | 57.2                      | 57.2                         | 93.4                   |                           |                        |                           |   |  |    | 96.2  |
| NaF  | 24.65              | 6.0   | 1.326        | 46.2                   | 45.5                      | 14.92                  | 14.98                     | 40.6                      | 40.6                         |                        |                           |                        |                           |   |  |    | 15.8  |
| NaCl | 44.59              | 5.62  | 1.544        | 81.1                   | 82.5                      | 42.23                  | 41.81                     | 61.1                      | 61.6                         | 45.9                   |                           |                        |                           |   |  |    | 48.0  |
| NaBr | 52.95              | 5.99  | 1.641        | 99.3                   | 100.7                     | 57.32                  | 57.20                     | 74.7                      | 74.1                         | 64.1                   |                           |                        |                           |   |  |    | 65.7  |
| NaI  | 67.46              | 6.60  | 1.774        | 131.7                  | 129.1                     | 84.41                  | 84.82                     | 85.5                      | 85.5                         | 96.3                   |                           |                        |                           |   |  |    | 100.3 |
| KF   | 38.07              | 6.05  | 1.362        | 71.6                   | 67.2                      | 25.33                  | 25.14                     |                           | 48.5                         | 24.7                   |                           |                        |                           |   |  |    | 26.0  |
| KCl  | 61.86              | 4.68  | 1.490        | 102.2                  | 104.2                     | 53.65                  | 53.36                     | 70.7                      | 70.8                         | 58.1                   |                           |                        |                           |   |  |    | 58.3  |
| KBr  | 71.42              | 4.78  | 1.560        | 119.5                  | 122.4                     | 69.29                  | 69.00                     | 88.3                      | 88.3                         | 74.5                   |                           |                        |                           |   |  |    | 76.0  |
| KI   | 87.67              | 4.94  | 1.667        | 149.4                  | 150.8                     | 97.92                  | 97.27                     | 102.0                     | 101.8                        | 107.3                  |                           |                        |                           |   |  |    | 110.5 |
| RbF  | 44.85              | 5.91  | 1.398        | 83.6                   | 83.1                      | 32.47                  | 31.97                     |                           | 53.4                         | 31.9                   |                           |                        |                           |   |  |    | 32.9  |
| RbCl | 69.93              | 5.0   | 1.494        | 119.8                  | 120.1                     | 61.07                  | 61.85                     | 84.8                      | 84.8                         | 63.4                   |                           |                        |                           |   |  |    | 65.2  |
| RbBr | 80.50              | 5.0   | 1.553        | 137.9                  | 138.3                     | 77.28                  | 77.76                     | 114.0                     | 113.7                        | 81.0                   |                           |                        |                           |   |  |    | 82.9  |
| RbI  | 98.30              | 5.0   | 1.647        | 168.4                  | 166.7                     | 107.19                 | 106.64                    | 129.5                     | 135.4                        | 113.3                  |                           |                        |                           |   |  |    | 117.4 |
| CsF  | 54.22              |       | 1.478        |                        | 97.3                      | 46.03                  | 46.59                     |                           | 48.1                         |                        |                           |                        |                           |   |  |    | 46.4  |
| CsCl | 69.43              | 7.20  | 1.642        | 140.4                  | 134.3                     | 75.23                  | 75.31                     | 102.0                     | 101.1                        | 76.1                   |                           |                        |                           |   |  |    | 78.7  |
| CsBr | 78.95              | 6.51  | 1.698        | 153.2                  | 152.5                     | 91.33                  | 91.09                     | 134.0                     | 135.1                        | 94.3                   |                           |                        |                           |   |  |    | 96.3  |
| CsI  | 94.94              | 5.65  | 1.788        | 173.2                  | 180.8                     | 120.40                 | 119.72                    |                           | 155.9                        |                        |                           |                        |                           |   |  |    | 130.9 |

of the new ionic parameters. According to this interpretation,  $Ae$  would be a sort of effective charge on the nucleus, while the remaining charge  $-(A-p+n)e$  would be appropriately linked with the boundary. The parameter  $B$ , which has the dimensions of polarizability or volume, would be a measure of the displacement of the nucleus relative to the boundary for a given force between them.

If the boundary of an ion is restrained from moving, and if likewise its nucleus is held fixed, then only the inner electrons can move and the dipole moment is  $C\xi_0F_i$ , which corresponds to a polarizability,  $C$ . If the nucleus is released, the polarizability is increased by an amount proportional to the square of the nuclear charge times the parameter  $B$ . Then, the total polarizability is  $A^2B+C$ . Similarly, if only the nucleus is held fixed, the corresponding polarizability will be  $(A-p+n)^2B+C$ . A more detailed derivation of the polarizabilities is given in the next section.

A set of values of the parameters  $A$ ,  $B$ , and  $C$  for alkali and halide ions is given in Table I. These values were obtained by successive approximations in order to achieve the most consistent agreement between experimental data and theoretical calculations. In order to resolve a certain indefiniteness in the absolute scale of values, the parameters  $B$  and  $C$  for lithium were arbitrarily set equal to zero. This should have a minimum effect on the results for other ions since the values for lithium are obviously much smaller, if different from zero.

#### IV. POLARIZABILITIES OF IONS IN CRYSTALS

In alkali-halide crystals, the subscripts 1 and 2 will be used to differentiate between the parameters of the

alkali ion and the halide ion respectively. Then:

$$p_1 = n_1 + 1; \quad p_2 = n_2 - 1. \quad (9)$$

The equations of motion of the crystal comprise two sets of equations similar to (8), one set for each type of ion. Since  $X_0$  is the same for both types of ion, it does not appear in the expression for the total dipole moment per molecule.

$$\mu = \mu_1 + \mu_2 = e(A_1X_1 + A_2X_2) + \xi_0F_i(C_1 + C_2). \quad (10)$$

The polarizability  $\alpha$  is by definition the constant ratio of the dipole moment  $\mu$  to the internal field  $F_i$ , divided by  $\xi_0$ .

$$\alpha = (\mu/\xi_0F_i) = (e/\xi_0F_i)(A_1X_1 + A_2X_2) + C_1 + C_2. \quad (11)$$

If the displacements are sinusoidal functions of time with a frequency  $\omega/2\pi$ , the force on the nucleus is:

$$F_n = ma = m(d^2/dt^2)(X + X_0) = -\omega^2m(X + X_0), \quad (12)$$

where  $m$  is the mass of the nucleus and  $a$  its acceleration.

At very low frequencies, the forces on the nucleus are nearly balanced so that the first part of Eq. (8) can be set equal to zero for each ion. Then:

$$X_1 = A_1B_1(\xi_0F_i/e); \quad X_2 = A_2B_2(\xi_0F_i/e). \quad (13)$$

The dielectric polarizability,  $\alpha_D$ , valid at very low frequencies, is derived by substituting (13) in (11).

$$\alpha_D = (A_1^2B_1 + C_1) + (A_2^2B_2 + C_2). \quad (14)$$

Equation (14) indicates that the dielectric polarizability is an additive function expressible as a sum of polarizabilities of the separate ions.

The values of dielectric polarizability of alkali-halide

crystals calculated by means of this equation are shown in column 5 of Table II.

At wave-lengths in the range of visible light, the frequency is so high that the inertia of the nuclei effectively prevents them from moving, so that:

$$X_1 + X_0 = 0; \quad X_2 + X_0 = 0,$$

$$\text{or} \quad X_1 = X_2 = -X_0. \quad (15)$$

Since the system of ionic boundaries has no mass, the combined force on it per molecule must equal zero. Or:

$$F_{b1} + F_{b2} = 1/B_1 \cdot (e^2/\xi_0)X_1 - (A_1 - 1)eF_1 + 1/B_2 \cdot (e^2/\xi_0)X_2 - (A_2 + 1)eF_2 = 0. \quad (16)$$

From this, one obtains:

$$X_1 = X_2 = \frac{A_1 + A_2}{1/B_1 + 1/B_2} \cdot \frac{\xi_0 F_i}{e}. \quad (17)$$

The electronic polarizability,  $\alpha_e$ , so called because electrons are the only particles which move, is derived by substituting (17) in (11).

$$\alpha_e = \frac{(A_1 + A_2)^2}{1/B_1 + 1/B_2} + C_1 + C_2. \quad (18)$$

Since the boundaries have some freedom of motion, this electronic polarizability is greater than  $C_1 + C_2$ , which corresponds to the hypothetical example of fixed boundaries. Equation (18) indicates that the electronic polarizability is not a strictly additive function since the first term involves cross products of the ionic parameters. However, this term is relatively small and the resulting departure from additivity is too slight to be observed experimentally.

Values of electronic polarizability calculated by means of Eq. (18) are shown in column 7 of Table II.

#### V. POLARIZABILITIES OF FREE IONS

It was formerly thought that the electronic polarizabilities of ions in crystals were smaller than those for ions in aqueous solutions.<sup>1</sup> Values of electronic polarizability of ions in solution were calculated by assuming the Lorentz value of internal field and were compared with theoretical polarizabilities of free ions calculated from data on the Stark effect.<sup>2</sup> Subsequent work by Böttcher<sup>3</sup> indicated that it was necessary to correct the Lorentz field to account for the interaction between a dissolved ion and its surroundings. When this was done the electronic polarizabilities of ions in solution were found to be more nearly equal to those of ions in crystals. So far no one has measured the polarizability of a "free" ion; however, it is now possible to calculate such polarizabilities from the data on solid crystals. Oddly enough, the resulting values turn out to be almost

precisely equal to the original polarizabilities of ions in solution calculated by the Lorentz field assumption.

The polarizability of an unconstrained ion can be calculated by setting the force on its boundary equal to zero.

$$F_b = 1/B \cdot (e^2/\xi_0)X - (A - p + n)eF_i = 0. \quad (19)$$

Then:

$$X = (B/e)(A - p + n)\xi_0 F_i. \quad (20)$$

At optical frequencies  $X + X_0 = 0$ , since the nucleus does not move. The dipole moment is derived from Eq. (8).

$$\mu_i = [B(A - p + n)^2 + C]\xi_0 F_i. \quad (21)$$

The polarizability of an alkali-halide ion pair is then obtained by adding the individual dipole moments and dividing by  $\xi_0 F_i$ .

$$\alpha_p = B_1(A_1 - 1)^2 + C_1 + B_2(A_2 + 1)^2 + C_2. \quad (22)$$

The electronic polarizability  $\alpha_p$  of a pair of free (gaseous) ions has been calculated for each of the alkali-halides by using Eq. (22). These results are given in column 11 of Table II. For comparison, the polarizabilities  $\alpha_{sol}$  of ionized molecules in dilute aqueous solutions as reported by Heydweiller<sup>4</sup> for the wave-length of sodium light are given in column 10. The conversion factor from his units to ours is  $3/L \times 10^{24} = 4.981$ , where  $L$  is Loschmidt's number and there are  $10^{24}$  cubic angstroms per cubic centimeter.

#### VI. THE INTERNAL FIELD

In order to derive a relation between polarizability and dielectric constant or index of refraction, it is first necessary to establish the relation between the applied or macroscopic field  $E$  and the local field  $F_i$  which exists at the center of an ion in the crystal—or would exist there if the ion were removed without disturbing its neighbors. This calculation was originally carried out by Lorentz,<sup>5</sup> who assumed that the external field set up by a polarized ion was the same as that from a point dipole at its center.

The local field at a given position in a homogeneous crystal may be thought of as composed of four components. Of these,  $F_0$  is the static field at equilibrium resulting from the Coulomb forces of the various charged particles making up the crystal. This component has been discussed in a previous paper<sup>6</sup> and has been shown to be zero at the centers of ions in the crystals under consideration.

The second component is just the applied field  $E$ , which needs no further comment.

The third component is the change in the Coulomb field due to displacement of charged particles from their equilibrium positions including only those particles

<sup>1</sup> K. Fajans and G. Joos, *Zeits. f. Physik* **23**, 1 (1924).

<sup>2</sup> L. Pauling, *Proc. Roy. Soc. A*, **114**, 181 (1927).

<sup>3</sup> C. J. F. Böttcher, *Rec. des Trav. Chim.* **65**, 19 (1946).

<sup>4</sup> A. Heydweiller, *Physik. Zeits.* **26**, 526 (1925).

<sup>5</sup> H. A. Lorentz, *Theory of Electrons*, Note 55, (B. G. Teubner, Leipzig, 1916), second edition, p. 308.

<sup>6</sup> S. Roberts, *Phys. Rev.* **76**, 1215 (1949).

which are outside a sphere concentric with the ion in question, but of relatively large radius. This component is generally conceded to be  $P/3\xi_0$ , as derived by Lorentz and others, where  $P$  is the total polarization or dipole moment per unit volume.

Most of the discussion centers around the remaining term which is the change in the Coulomb field due to the displacement of charged particles (or induced dipoles) within the sphere. Lorentz found that this term vanishes in certain cubic crystals.

His calculation is based on the assumption of cubic symmetry with respect to each ionic position. A consequence of this symmetry requirement is that if the rectangular coordinates of the center of any one ion are  $(a, b, c)$  relative to any second ion, then there are two more ions like the first whose coordinates are  $(b, c, a)$  and  $(c, a, b)$ . Only the "diagonal cubic" types of crystals have this degree of symmetry. These include NaCl, CaCl,  $\text{CaF}_2$ , and ZnS.

The  $Z$  component of field at the origin due to a  $Z$  oriented dipole of strength  $\mu$  located at the position  $(X, Y, Z)$  is:

$$E_z = -\mu/4\pi\xi_0 \cdot (X^2 + Y^2 - 2Z^2)/(X^2 + Y^2 + Z^2)^{5/2}. \quad (23)$$

If one adds the components of field due to three equal dipoles at positions  $(a, b, c)$ ,  $(b, c, a)$ , and  $(c, a, b)$ , the result is evidently zero. Hence, one may conclude that there is no net contribution to the field at the center by all dipoles at a given distance from the ion in question in crystals having diagonal cubic symmetry. From this, it is also clear that the field component due to all dipoles within the sphere must vanish.

The external field of an ion may not necessarily be considered equivalent to that produced by a single point dipole at its center. In this event the ion needs to be represented by an assembly of point dipoles distributed throughout the space it occupies. In view of the spherical concept of the ion, it seems appropriate to assume that the dipoles are arranged inside in a manner at least consistent with cubic symmetry. In this, as in the previous example, the field at the center vanishes due to all polarized ions within the sphere.

Since only the second and third components of the internal field are non-vanishing, it may be expressed in the form derived by Lorentz.

$$F_i = E + P/3\xi_0. \quad (24)$$

In actual fact, it is not so simple to prove that the induced dipoles should be arranged inside the ion according to cubic symmetry. If true, this seems to imply a certain rigidity of the electron structure in which electrons are arranged in concentric spherical shells (or equivalent) which are displaced in relative position but not distorted in shape by the electric field. This is related to the previous assumption, based on the absence

<sup>7</sup> M. Born and M. Goepfert-Mayer, *Handbuch der Physik* (1933), second edition, Vol. 24, No. 2, p. 625.

of a piezoelectric effect, that the spherical boundaries of ions are not distorted in shape by an electric field.

### VII. DIELECTRIC CONSTANTS AND INDICES OF REFRACTION

The Lorentz internal field given by Eq. (24) is used in calculating the relations between the polarizabilities and the dielectric constant and index of refraction. If  $V$  is the volume per molecule in the crystal lattice, the total dipole moment per unit volume is:

$$P = \mu/V = \alpha\xi_0 F_i / V = (\alpha\xi_0/V)E + (\alpha/3V)P = [\xi_0\alpha/(V - \alpha/3)]E. \quad (25)$$

Then, at low frequencies,  $\alpha_D$  may be determined from measurements of the dielectric constant,  $K$ .

$$K = 1 + P/\xi_0 E = (V + \frac{2}{3}\alpha_D)/(V - \frac{1}{3}\alpha_D),$$

or:

$$\alpha_D = 3V(K - 1)/(K + 2). \quad (26)$$

This is the Clausius-Mosotti equation.

The corresponding equation relating the electronic polarizability to the optical index of refraction is that attributed to Lorentz and Lorenz.

$$\alpha_e = 3V(n^2 - 1)/(n^2 + 2), \quad (27)$$

where  $n$  is the index of refraction.

The molecular volumes  $V$  of the alkali-halide crystals are calculated from the lattice constants compiled by Wyckoff.<sup>8</sup> The results are given in column 1 of Table II. The dielectric constants as compiled by Hojendahl<sup>9</sup> are listed in column 2. The indices of refraction for Na-D light as reported by Spangenberg<sup>10</sup> are listed in column 3. From these experimental data, values of dielectric polarizability  $\alpha_D$  and electronic polarizability  $\alpha_e$  are calculated by means of Eqs. (26) and (27). These results are shown in columns 4 and 6 respectively.

### VIII. INFRA-RED ABSORPTION FREQUENCIES

The frequency, or wave-length, in the infra-red dispersion spectrum which seems to have been measured with greatest accuracy is that of maximum absorption. The experimental wave-length data for alkali-halide crystals reported by Barnes<sup>11</sup> are given in column 8 of Table II. At this frequency,  $\omega_A/2\pi$ , the dielectric constant or index of refraction is theoretically infinite and the applied field  $E$  vanishes corresponding to a finite polarization. Then, from Eq. (24):

$$E = F_i - P/3\xi_0 = F_i - \mu/3\xi_0 V = 0,$$

or:

$$\mu = 3V\xi_0 F_i. \quad (28)$$

Then from Eq. (10):

$$A_1 X_1 + A_2 X_2 = (3V - C_1 - C_2)\xi_0 F_i / e. \quad (29)$$

<sup>8</sup> R. W. G. Wyckoff, *Crystal Structures, Section I* (Interscience Publications, Inc., New York, 1948).

<sup>9</sup> K. Hojendahl, *Kgl. Danske Vid. Sels., Math.-Fys. Medd.* **16** (2), 59 (1938).

<sup>10</sup> K. Spangenberg, *Zeits. f. Krist.* **57**, 494 (1923).

<sup>11</sup> R. B. Barnes, *Zeits. f. Physik* **75**, 723 (1932).

The forces on the nuclei are derived from Eqs. (8) and (12).

$$\left. \begin{aligned} F_{n1} &= -1/B_1 \cdot (e^2/\xi_0)X_1 + A_1 eF_i \\ &= -\omega_A^2 m_1 (X_1 + X_0) \\ F_{n2} &= -1/B_2 \cdot (e^2/\xi_0)X_2 + A_2 eF_i \\ &= -\omega_A^2 m_2 (X_2 + X_0) \end{aligned} \right\} \quad (30)$$

Eliminating  $X_0$  and solving for  $\omega_A^2$  gives:

$$\omega_A^2 = \frac{\left( \frac{X_1}{m_1 B_1} - \frac{X_2}{m_2 B_2} \right) \frac{e^2}{\xi_0} - \left( \frac{A_1}{m_1} - \frac{A_2}{m_2} \right) eF_i}{X_1 - X_2} \quad (31)$$

By solving Eqs. (16) and (29) for  $X_1$  and  $X_2$ , substituting these values in (31) and by using Eqs. (14) and (18) for  $\alpha_D$  and  $\alpha_e$  to simplify the result, one finally obtains:

$$\begin{aligned} \omega_A^2 &= \frac{e^2(3V - \alpha_D)(1/m_1 + 1/m_2)}{\xi_0(3V - \alpha_e)(B_1 + B_2)} \\ &= \frac{e^2(n^2 + 2)(1/m_1 + 1/m_2)}{\xi_0(K + 2)(B_1 + B_2)}. \end{aligned} \quad (32)$$

The corresponding wave-length is:

$$\lambda_A = 2\pi c/\omega_A, \quad (33)$$

where  $c$  is the velocity of light.

Wave-lengths calculated by this method are shown in column 9 of Table II. In this calculation, more consistent results were obtained by using the experimental values of  $\alpha_D$  and  $\alpha_e$ , or  $n$  and  $K$ , rather than the theoretical values. This is further evidence that the small deviations between theory and experiment are of real significance.

Equation (32) indicates that  $(B_1 + B_2)$  may be calculated from observable properties of the crystal. Hence this equation leads to a second additivity relation, the first being the additivity of dielectric polarizabilities. A third additivity relation may be derived from Eqs. (14) and (18).

$$[(B_1 + B_2)(\alpha_D + \alpha_e)]^\dagger = A_1 B_1 - A_2 B_2. \quad (34)$$

### IX. THE PSEUDO-PIEZOELECTRIC EFFECT

A novel physical phenomenon is predicted by a further extension of the present theory. This is the "pseudo-piezoelectric" effect, which is similar to the ordinary piezoelectric effect in that it is a linear electro-mechanical phenomenon, but it differs in that it does not depend on crystalline anisotropy. In comparison with the ordinary piezoelectric effect, in which statically balanced forces applied to a crystal induce electric fields within it, a statically unbalanced force or acceleration is found to have the same effect on the isotropic crystals considered here.

In order to calculate the magnitude of the effect, the electric field will be considered which is set up in a

crystal by raising its acceleration from zero to a uniform value " $a$ ." The surfaces of the crystal are to be electrically open, that is, no charge may flow to or from the surfaces from an external circuit. In this case, the electric field in the crystal turns out to be proportional to the acceleration.

$$E = \rho a, \quad (35)$$

where  $\rho$  is a new parameter equal to the following expression.

$$\rho = (m_1 A_1 B_1 + m_2 A_2 B_2) / e(\frac{2}{3}\alpha_D + V). \quad (36)$$

The electric field produced by an acceleration equivalent to gravity in a sodium iodide crystal is, for example,  $-5.52$  microvolt per meter according to the theory. In most of the alkali halides, the sign of the effect is negative. This is a result of the fact that the halide ions, having negative effective nuclear charges  $Ae$ , are the most highly polarizable. In view of the small magnitude of the effect, no attempt has been made to confirm it experimentally. However, if this were done, it would afford an independent means of testing the theory.

### X. ADDITIONAL COMMENTS

The success in interpreting experimental results indicates that the theoretical assumptions are approximately valid in the case of alkali-halide crystals. However, these initial assumptions may be subject to certain limitations when applied to other types of crystals. For example, in many less symmetrical crystals, there are ions which are not in electrostatic equilibrium, hence  $F_0$  is not zero. Such an ion may be distorted so much by this residual field that the relation between field strength and dipole moment is no longer linear. Owing to such a saturation effect the polarizability would be reduced. Experimental data for a number of crystals in this category are discussed in a previous paper.<sup>6</sup>

Since the theoretical derivation is based on the idea of contact between rigid spherical boundaries, it seems a little surprising that the experimental results should be consistent even in the case of certain lithium-halide crystals in which the lithium ions do not touch their neighbors. Evidently some other mechanism is needed to account for the constraint imposed on the lithium ions.

There would be a different complication in the case of piezoelectric crystals of the cubic ZnS type, since there would be relative motion between the respective ionic boundaries. These relative motions could be prevented by "clamping" the crystal, although this distinction probably makes little practical difference, since the clamped dielectric constant is only slightly different from that of the free crystal.

The foregoing theory was developed because existing theories did not explain the additivity of dielectric polarizabilities reported previously.<sup>6</sup> The author is indebted to Dr. F. E. Williams for urging him to find such an explanation. He also wishes to acknowledge the helpful discussions with Dr. M. H. Hebb.