

## Theory of the Dielectric Constants of Alkali Halide Crystals.

B. G. DICK, JR.,\* AND A. W. OVERHAUSER  
*Cornell University, Ithaca, New York*

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The simple classical theories of the dielectric constants and compressibility of ionic crystals lead to two relations among the experimental quantities from which arbitrary parameters have been eliminated, the Szigeti relations. Neither is satisfied by the data, indicating the inadequacy of these simple theories. The short-range repulsive interaction between ions with closed shell electron configurations is investigated, and an approximate interpretation of the Born-Mayer potential in terms of overlap integrals is developed. These results are applied to the interaction of model ions consisting of rigid charged shells bound to cores by harmonic restoring forces. Using this model, polarization mechanisms neglected in the simple dielectric constant theory, the "short range interaction polarization," and the "exchange charge polarization" are described. Both arise from charge redistributions

occurring when the ions move with resulting changes in electron overlaps. Applied to a crystal, these ion models permit the derivation of generalizations of the Szigeti, Clausius-Mossotti, and Lorenz-Lorentz relations. The  $e^*/e$  of the second Szigeti relation can then be calculated and comparison with the  $e^*/e$  values derived from experimental data imply that the above polarization mechanisms must be at least in part responsible for the deviation of this parameter from unity. The failure of the first Szigeti relation is discussed and attributed to the inadequacy of the treatment of compressibility. The additivity feature of the simple theory and its absence in the refined theory are discussed in relation to the so-called vacuum and crystal ion polarizabilities.

### I. INTRODUCTION

THE simple classical theory of the dielectric constants of ionic crystals<sup>1</sup> considers the following model: The crystal lattice is occupied by polarizable ions in static equilibrium of charge  $\pm Ze$  and polarizability  $\alpha_{\pm}$ . This theory gives expressions for the extrapolated high-frequency dielectric constant  $\epsilon_{\infty}$ , the low-frequency dielectric constant  $\epsilon_0$ , and the characteristic frequency of transverse lattice polarization waves (the restrahlung frequency)  $\omega_0$ :

$$\frac{\epsilon_{\infty}-1}{\epsilon_{\infty}+2} = \frac{4}{3}\pi N(\alpha_+ + \alpha_-), \quad (\text{I.1})$$

$$\frac{\epsilon_0-1}{\epsilon_0+2} = \frac{4}{3}\pi \left[ (\alpha_+ + \alpha_-) + \frac{(Ze)^2}{A} \right], \quad (\text{I.2})$$

$$\bar{M}\omega_0^2 = A - \frac{\frac{4}{3}\pi N(Ze)^2}{1 - \frac{4}{3}\pi N(\alpha_+ + \alpha_-)}. \quad (\text{I.3})$$

Here  $\bar{M}$  is the reduced mass of the positive and negative ions;  $N$  is the number of ion pairs per unit volume; and  $A$  is the harmonic restoring force constant related to the short-range repulsion between the ions which in the simple theory for NaCl type alkali halides is given by  $A = 6R_0/K$ ,  $R_0$  being the nearest neighbor distance and  $K$  the compressibility.

Of the parameters appearing in these expressions  $\bar{M}$ ,  $N$ , and  $Z$  are known if the crystal is specified and is assumed to be completely ionic. The polarizabilities  $\alpha_+$  and  $\alpha_-$  for, say, the alkali metal ions and the halogen ions in alkali halides are known neither in vacuum nor in a crystal environment and are to be regarded as adjustable parameters in the simple classical theory.

Consider the expression for  $\epsilon_{\infty}$ , (I.1). It is a function only of  $N(\alpha_+ + \alpha_-)$ . If it is further assumed that the polarizability of an ion is the same in all crystals then  $\epsilon_{\infty}$  is said to possess the "additivity" property. If the additivity property holds for actual crystals it should be possible, for instance, to find 8 polarizabilities for the ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  which through (I.1) would give the sixteen  $\epsilon_{\infty}$ 's for the NaCl type alkali halides. Tessman, Kahn, and Shockley<sup>2</sup> (TKS) have determined such a set of crystal polarizabilities. These crystal polarizabilities have meaning only insofar as the simple model on which the expressions (I.1), (I.2), and (I.3) are based is valid.

We can use (I.1) to express  $N(\alpha_+ + \alpha_-)$  in terms of  $\epsilon_{\infty}$ . Substituting this  $N(\alpha_+ + \alpha_-)$  into (I.2) and (I.3) we get two expressions from which the adjustable parameters  $\alpha_+$  and  $\alpha_-$  have been eliminated:

$$\epsilon_0 = G[\epsilon_{\infty}, A, N(Ze)^2], \quad (\text{I.4})$$

$$\bar{M}\omega_0^2 = H[\epsilon_{\infty}, A, N(Ze)^2]. \quad (\text{I.5})$$

If  $A$  is expressed in terms of the lattice constant and the compressibility, (I.4) and (I.5) contain experimental quantities only. By eliminating alternately  $A$  or  $N(Ze)^2$  between (I.4) and (I.5) these two relations can be written

$$\bar{M}\omega_0^2(\epsilon_0+2)/(\epsilon_{\infty}+2) = A = 6R_0/K, \quad (\text{I.6})$$

$$\epsilon_0 - \epsilon_{\infty} = (\epsilon_{\infty}+2)^2 [4\pi N(Ze)^2]/9\bar{M}\omega_0^2. \quad (\text{I.7})$$

In this form (I.6) and (I.7) are called the first and second Szigeti relations, respectively (Szigeti<sup>3,4</sup>).<sup>5</sup> The failure of the experimental data to satisfy (I.6) and (I.7) demonstrates the inadequacy of the model on which the classical theory is based.

<sup>2</sup> Tessman, Kahn, and Shockley, *Phys. Rev.* **92**, 890 (1953).

<sup>3</sup> B. Szigeti *Trans. Faraday Soc.* **45**, 155 (1945).

<sup>4</sup> B. Szigeti, *Proc. Roy. Soc. (London)* **A204**, 51 (1950).

<sup>5</sup> In Szigeti's statement, (I.6) has  $A$  replaced by  $6R_0/K$  and (I.7) has  $e$  replaced by  $e^*$ .

\* Present address: Department of Physics, University of Illinois, Urbana, Illinois.

<sup>1</sup> See, for instance, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), Sec. 9.

The first Szigeti relation depends for its validity on both the classical theory of the dielectric constants and the theory of the compressibility which associates  $A$  with experimental data. If we define

$$K^* \equiv 6R_0(\epsilon_\infty + 2)/\bar{M}\omega_0^2(\epsilon_0 + 2),$$

then a comparison of  $K^*$  with the observed compressibility gives a check on the validity of the first Szigeti relation. If the relation were satisfied,  $K^*/K=1$ . Values of  $K^*/K$  derived from the experimental data are listed in Table I. It is seen that deviations of  $K^*/K$  from unity are of both signs and are as great as 34% for RbI.

The second Szigeti relation gives the difference between the high-frequency and the low-frequency or static dielectric constants. It is a relation that does not contain  $A$  and so does not depend in this classical theory on the validity of the theory of the compressibility as did the first Szigeti relation. As is the case with the first Szigeti relation, the second relation is not satisfied by the experimental data. Accordingly Szigeti introduced a quantity  $e^*$  in place of  $e$  in (I.7).  $e^*/e$  is defined by

$$(e^*/e)^2 \equiv 9\bar{M}\omega_0^2(\epsilon_0 - \epsilon_\infty)/4\pi N e^2(\epsilon_\infty + 2)^2, \quad (Z=1).$$

If (I.7) were satisfied,  $e^*/e$  would be unity. The values of  $e^*/e$  derived from experimental data are given in Table I. For the cases given here,  $e^*/e$  is always less than unity.

Whereas the failure of the first Szigeti relation could be due to either the inadequacy of the theory of the dielectric constants and/or the theory of the compressibility, the failure of the second relation demonstrates the inadequacy of the dielectric theory itself. The success of the Born-Mayer equation for the cohesive energy and the fact that the Cauchy relations are approximately satisfied for alkali halides suggest strongly that these crystals are highly ionic in character. This makes it unlikely that the departure of  $e^*/e$  from unity is to be ascribed to a departure from ionicity in these crystals. The suggestion of Mott and Gurney<sup>6</sup>

that overlap alters the Lorentz local field drastically and thus accounts for the failure of the second Szigeti relation has been criticized by Born and Huang<sup>1</sup> and made to appear implausible. It is therefore of interest to know to what extent the departure of  $e^*/e$  from unity can be understood on the basis of a model of an ideally ionic crystal, if it is assumed that the ionic charges are  $\pm e$  and not  $\pm e^*$ . The fact that  $e^*/e$  is less than one for the NaCl-type alkali halides suggests that in these cases, accompanying the electronic polarization of the ions and the polarization due to the displacement of the ions from lattice sites, there is some further polarization of opposite sign which has not been included.

In the classical theory leading to Eqs. (I.1), (I.2), and (I.3) the only agency causing polarization is the effective field at the lattice sites composed of the externally applied field and the field due to the dipoles of the polarized crystal. We shall find that the nearest neighbor short-range repulsive interactions are also responsible for deformations resulting in polarization. These deformations are entirely neglected in the simple classical theory except insofar as they are responsible for the restoring force which limits the ionic displacements. Szigeti, in his paper deducing the second Szigeti relation, suggested that such deformations would cause the deviations of  $e^*/e$  from unity, and Born and Huang present a phenomenological treatment of such distortion dipoles although without investigating the details of their origin. The problem has also been treated by Yamashita<sup>7</sup> and Yamashita and Kurosawa.<sup>8</sup> Yamashita has carried out a quantum mechanical variational calculation of the polarization of LiF and MgO neglecting the positive-ion polarizabilities. Using this calculation as a guide, Yamashita and Kurosawa propose a general theory in which a quadratic form for the energy similar to that used here is employed. However, their general theory in which the polarizability of both  $+$  and  $-$  ions are considered has more parameters than can be evaluated from the experimental data. In the present paper, using the quantum mechanical treatment of the nearest neighbor interaction as a guide, we are led to a simple physical picture of this interaction which allows us to evaluate and estimate quantities which can be identified with the unknown parameters of Yamashita and Kurosawa.

We shall examine in detail a model of an ideal NaCl-type alkali halide crystal with overlapping ions. With a more complicated model than that of the classical theory it is not always possible to accomplish the elimination of all nonexperimental parameters to give simple Szigeti type relations among the experimental data alone. However, we shall be able to derive expressions for  $K^*/K$  and  $e^*/e$  in terms of parameters of the model. The property of additivity which the

TABLE I. Values of  $K^*/K$  and  $e^*/e$  derived from experimental data (Szigeti<sup>3,4</sup>).

	$K^*/K$	$e^*/e$
LiF	1.0	0.87
NaF	0.83	0.93
NaCl	0.99	0.74
NaBr	1.13	0.69
NaI	1.05	0.71
KCl	0.96	0.80
KBr	0.95	0.76
KI	0.99	0.69
RbCl	0.89	0.84
RbBr	0.83	0.82
RbI	0.66	0.89

<sup>6</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), second edition, p. 17.

<sup>7</sup> J. Yamashita, Progr. Theoret. Phys. Japan 8, 280 (1952).

<sup>8</sup> J. Yamashita and J. Kurosawa, J. Phys. Soc. Japan 10, 610 (1955).

simple model possesses will be seen not to hold for more elaborate models. We shall be able to understand, though, why it holds approximately and why Tessen, Kahn, and Shockley were able to find a not too bad "best" set of crystal polarizabilities. The relation of these polarizabilities to vacuum polarizabilities will be given a physical basis on the model.

In Sec. II the short-range interaction between ions is discussed and the magnitude of the exchange charge as a function of internuclear separation is estimated. In Sec. III an ion model is discussed. The implication of this model in the polarization process is treated in Sec. III where two polarization mechanisms neglected in the classical theory are found. These features are incorporated into a theory of the polarization of an ideal crystal in Sec. V.

## II. SHORT-RANGE ION INTERACTIONS

We seek the explanation of the deviation of  $e^*/e$  from unity in the details of the short-range or repulsive interactions between the closed-shell ions of the alkali halide crystals. In this section the interaction of two helium atoms is first discussed, this being the simplest system of two closed-shell atoms. The insight provided by studying this simple case is then applied to more complex ion pairs and an approximate interpretation of the Born-Mayer repulsion potential in terms of overlap integrals is given.

The interaction of two He atoms is studied using a Heitler-London approach<sup>9</sup> in which the atomic wave functions are taken to be products of hydrogen like  $1s$  functions. The effective nuclear charge  $Z'$  in these  $1s$  functions used ultimately in deriving numerical results is  $Z' = 27/16$ , the value for the isolated He atom derived from a variation calculation using a product of  $1s$ -type functions with  $Z'$  as the variation parameter (see Pauling and Wilson<sup>10</sup>).

We wish to calculate the interaction energy  $W$  given by

$$W + E_a^0 + E_b^0 = \langle \Psi_0 | H | \Psi_0 \rangle / \langle \Psi_0 | \Psi_0 \rangle \quad (\text{II.1})$$

as a function of  $R$ . In (II.1),  $E_a^0$  and  $E_b^0$  are the energies of the two He atoms at infinite separation, and  $\Psi_0$  is an antisymmetrized product wave function for the four  $1s$  selectrons.

By treating the integrations and summations of the antisymmetrized wave functions in the standard way, it can be shown that the normalization integral can be expressed as follows:

$$\langle \Psi_0 | \Psi_0 \rangle = (1 - S^2)^2, \quad (\text{II.2})$$

where  $S$  is the overlap integral  $\int u_a(1)u_b(1)d\tau_1$ . The

<sup>9</sup> For closed-shell interactions such as these, the Heitler-London and the molecular orbital schemes are identical. See F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 262.

<sup>10</sup> L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 184.

interaction integral similarly can be written (see Rosen<sup>11,12</sup>)

$$\begin{aligned} \frac{W}{e^2} = & \frac{4 - 2S^2}{(1 - S^2)^2} \int \frac{u_a^2(1)u_b^2(2)}{r_{12}} d\tau_1 d\tau_2 \\ & - \frac{4Z}{1 - S^2} \int \frac{u_a^2(1)}{r_{b1}} d\tau_1 + \frac{Z^2}{R} \\ & - \frac{2 - 4S^2}{(1 - S^2)^2} \int \frac{u_a(1)u_a(2)u_b(1)u_b(2)}{r_{12}} d\tau_1 d\tau_2 \\ & - \frac{4S}{(1 - S^2)^2} \int \frac{u_a(1)u_b(1)u_a^2(2)}{r_{12}} d\tau_1 d\tau_2 \\ & + \frac{4SZ}{1 - S^2} \int \frac{u_a(1)u_b(1)}{r_{b1}} d\tau_1. \end{aligned} \quad (\text{II.3})$$

It is interesting to notice that the interaction energy contains no kinetic energy. The expectation values of the kinetic energy operators in  $H$  all appear as terms in  $E_a^0$  and  $E_b^0$  and not in  $W$ ; thus the interaction of the two helium atoms involves no change in the kinetic energy of the system in this first-order treatment. Lenz and Jensen<sup>13</sup> have treated this problem using Thomas-Fermi atoms and find in that approximation that the origin of the repulsion between rare gas configuration atoms lies in the higher kinetic energy of electrons in the overlap region. The kinetic-energy in the overlap region is considered to be higher because of the increased density there and the operation of the exclusion principle. It seems difficult to reconcile the Thomas-Fermi atom treatment with the Heitler-London treatment. The latter is surely the more realistic.

The terms in (II.3) can be given a simple interpretation in terms of the charge density associated with the wave function  $\Psi_0$ . This charge density is given by

$$\rho(1) = -(|e|/\langle \Psi_0 | \Psi_0 \rangle) \int \Psi_0^* \Psi_0 d\tau', \quad (\text{II.4})$$

where the integration  $d\tau'$  is over all spins and over all space coordinates except one, say coordinate (1). The result of this simple integration is

$$\rho(1) = -[|e|/(1 - S^2)] [2u_a^2(1) + 2u_b^2(1) - 4Su_a(1)u_b(1)]. \quad (\text{II.5})$$

To the first order in  $S^2$  the first two terms, the "electron charge distribution," are

$$\rho_{e1}(1) = -|e|[(1 + S^2)2u_a^2(1) + (1 + S^2)2u_b^2(1)] \quad (\text{II.6})$$

which we see to be the spherically symmetric negative charge distributions of the noninteracting helium atoms

<sup>11</sup> N. Rosen, Phys. Rev. **38**, 255 (1931).

<sup>12</sup> N. Rosen, Phys. Rev. **38**, 2099 (1931).

<sup>13</sup> See P. Gombás, *Die Statistische Theorien des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949), Sec. 18.

TABLE II. Molecular integrals and  $W$  for He-He system. The integrals and  $W$  are given in atomic units.  $\delta = Z'R$ .

$\delta$	$(S_{1s1s})$	$(D_{1s1s1s1s}R)$	$(K_{1s1s}R)$	$(C_{1s1s1s1s}R)$	$(L_{1s1s1s1s}R)$	$(J_{1s1s}R)$	$W$
4	0.09658	0.99785	0.99997	0.018585	0.180830	0.2021	$3.500 \times 10^{-2}$
6	0.04710	0.99956	1.00000	0.0048841	0.0918686	0.1041	$7.467 \times 10^{-3}$
7	0.02219	1.00000	1.00000	0.0011732	0.045765	0.05107	$1.665 \times 10^{-3}$
8	0.01005	1.00000	1.00000				$4.072 \times 10^{-4}$

increased by a factor of  $1+S^2$ . The remaining part, the "exchange charge distribution," to  $O(S^2)$ , is

$$\rho_{\text{ex}}(1) \equiv +|e|4Su_a(1)u_b(1), \quad (\text{II.7})$$

and is seen to be a positive charge distribution which is large where the overlap integrand is large. The charge distribution is thus regarded as the sum of the electron distributions on the atoms increased by a factor  $1+S^2$  and a positive "exchange charge distribution" given by (II.7). The total exchange charge is

$$q_{\text{ex}} \equiv \int \rho_{\text{ex}}(1) d\tau_1 = 4|e|S^2. \quad (\text{II.8})$$

The total electron charge on each atom is  $-(1+S^2)2|e|$ .

With the aid of this picture of the charge distribution, the terms in  $W$  (II.3) can be interpreted. In order, the terms are: the Coulomb interaction between the electron charges on the two atoms; the Coulomb interaction between electron charges and the two nuclei, the electrons on atom  $a$  interacting with nucleus  $b$  and vice versa; the nucleus-nucleus interaction; the exchange charge interaction with itself; the exchange charge-electron charge interaction; and the exchange charge-nuclei interaction.

It remains to calculate the integrals appearing in (II.3) so as to know their relative importance as contributions to  $W$ . These integrals have been expressed in terms of tabulated auxiliary functions by Kotani, Amemiya, and Ishiguro.<sup>14</sup> In the notation of these authors, (II.3) can be written to  $O(S^2)$  with  $Z=2$ , as

$$WR/e^2 = [(4+6S^2)D_{1s1s1s1s}R - 8(1+S^2)K_{1s1s}R + 4] - 2C_{1s1s1s1s}R - 4SL_{1s1s1s1s}R + 8SJ_{1s1s}R, \quad (\text{II.9})$$

when it is noted that  $C_{1s1s1s1s}$  is  $O(S^2)$  and that  $L_{1s1s1s1s}$  and  $J_{1s1s}$  are  $O(S)$ .

These integrals are tabulated in Table II for several values of  $Z'R = \delta$ ,  $R$  in atomic units. The range of  $\delta$  has been chosen to give values of  $S$  similar to the overlap integral magnitudes in crystals (see Löwdin<sup>15</sup>).

The three terms in the square brackets of Eq. (II.9) correspond to the Coulomb interaction of the electron charges and nuclei. Since  $D_{1s1s1s1s}R$  and  $K_{1s1s}R$  are nearly equal to unity in the range considered, this square bracket is nearly equal to  $-2S^2$ . Thus the con-

tribution of the square bracket terms is small, negative, and decreasing in magnitude with increasing  $R$ . This corresponds to a slight attraction arising from the overlap of the charge distributions. The remaining three terms correspond to exchange charge interactions.

Notice that the exchange-exchange and the electron-exchange interactions are attractive while the exchange-nuclei interaction gives a repulsive term. To a very good approximation  $(J_{1s1s}R) \sim 2S$ ,  $(L_{1s1s1s1s}R) \sim 2S$ , and  $(C_{1s1s1s1s}R) \sim 2S^2$  so that we can write

$$W \cong 2S^2e^2/R = eq_{\text{ex}}/2R. \quad (\text{II.10})$$

Thus the exchange charge-nuclei interaction is responsible for the net repulsion between the two helium atoms.

A more precise calculation gives the values of  $W$  listed in Table II. These values are well expressed by the repulsive law

$$W = 4.6 \times 10^{-10} \exp(-\delta/0.688) \text{ ergs.}$$

Slater's calculation<sup>16</sup> using more exact helium wave functions gives

$$W = 7.7 \times 10^{-10} \exp(-\delta/0.695) \text{ ergs.}$$

From Eq. (II.10) we see that if  $W$  is known as a function of  $R$  then we have a way of estimating the magnitude of  $q_{\text{ex}}$ . This method of estimating  $q_{\text{ex}}$  will be of importance in Sec. IV.

Equation (II.10) shows that  $W$  for a pair of helium atoms is proportional to  $q_{\text{ex}}/R$  and depends exponentially on  $R$ . It is plausible to assume that these features are retained in the interaction of pairs of more complex closed shell atoms. Accordingly it is assumed that the short-range interaction energy for such atom pairs can be written

$$W = B \exp(-R/\rho) = \gamma q_{\text{ex}}/R, \quad (\text{II.11})$$

where  $B$ ,  $\rho$ , and  $\gamma$  are constants. The first part of (II.11) is the assumption of the Born-Mayer theory of ionic crystals and that theory evaluates  $B$  and  $\rho$  in terms of the lattice constant and the compressibility.

To evaluate the dimensionless constant  $\gamma$  we need to know  $q_{\text{ex}}$ . Equation (II.8) for the exchange charge of a pair of overlapping helium atoms can be generalized to more complex atoms. If atom  $A$  has occupied states  $u_i (i=1, \dots, n_A)$  and atom  $B$  has occupied states  $u_j (j=1, \dots, n_B)$ , and if both  $A$  and  $B$  have no partially

<sup>14</sup> Kotani, Amemiya, Ishiguro, and Kimura, *Table of Molecular Integrals* (Maruzen Company, Tokyo, 1955).

<sup>15</sup> P. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Uppsala Almqvist and Wiksells, Uppsala, 1948); also Phil. Mag. Suppl. 5, 1 (1956).

<sup>16</sup> J. C. Slater, Phys. Rev. 32, 349 (1928).

filled electron shells then the total exchange charge is

$$q_{\text{ex}} = 2|e| \sum_{i,j} S_{ij}^2, \quad (\text{II.12})$$

where  $S_{ij} = \int u_i(r)u_j(r)d\tau$ .

The overlap integrals  $S_{ij}$  have been evaluated for LiCl and NaCl by Löwdin<sup>15</sup> for a number of internuclear separations. By using these  $S_{ij}$  for separations closest to the measured lattice nearest neighbor distances and the values of  $B \exp(-R_0/\rho)$  from reference 1, values of  $\gamma$  can be deduced. They are 4.2 and 1.4 for LiCl and NaCl, respectively.

Note that (II.11) and (II.12) imply that

$$\sum S_{ij}^2/R \propto \exp(-R/\rho).$$

This relation can be checked by using Löwdin's overlap integrals for LiCl and NaCl. The assumption (II.11) is given support by that fact that a plot of  $\log[(1/R) \sum S_{ij}^2]$  vs  $R$  gives an excellent straight line over the range  $5a_H < R < 6.5a_H$  ( $a_H = 1$  Bohr radius). Furthermore the slope of these lines gives a  $\rho$  of approximately 0.35 Å in good agreement with the values of  $\rho$  deduced by Born and Mayer.<sup>1</sup>

We shall assume that the constant  $\gamma$  is the same for all the lithium halides; also that among the sodium, potassium, and rubidium halides it is the same. One expects the value of  $\gamma$  for the lithium halides to differ from that for the other alkali metal halides since  $\text{Li}^+$  has an  $s$  shell outermost while all the other positive ions— $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ —have  $p$  shells as outer shells.

It is not unreasonable that  $\gamma$  is larger for LiCl than it is for NaCl. The exchange charge is distributed more extensively in the lithium salts where it extends all the way to the lithium nucleus than it is in the sodium, potassium, and rubidium salts where the wave functions of the electrons participating in large overlaps are small near the nucleus. This has the consequence that the exchange-exchange interaction integrals will be considerable larger in the case of the latter salts than for the lithium salts. Since the exchange-exchange term is negative, this consideration leads one to expect that  $\gamma_{\text{NaCl}} < \gamma_{\text{LiCl}}$ .

The principal results of this section are the interpretation of the repulsion in terms of the exchange charge and the approximate relation (II.11).

It will be necessary to consider how the short-range interaction between ions studied in this section is affected by the polarization of the ions. Before considering this problem, a model for the ions themselves will be proposed. Then, in terms of this model, the question of the repulsive interaction between polarized ions will be treated.

### III. ION POLARIZATION MODEL

The polarizabilities of a number of free ions have been calculated by Pauling<sup>17</sup> and Sternheimer.<sup>18</sup> It is

<sup>17</sup> L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

<sup>18</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **107**, 1565 (1957).

desirable to understand the effects arising from the crystalline environment and not to conceal these effects in "crystal polarizabilities" to be assigned to the ions so as to satisfy the relation (I.1). Thus, in the following, the Pauling<sup>19</sup> free-ion polarizabilities will be used since in principle the vacuum polarizabilities should be used as input data. Assuming then that the free-ion polarizabilities are known, a picture of the charge distribution deformations in a polarized ion will be needed. This problem will be treated in terms of an ion model.

In an ion those electrons far from the nucleus, being less tightly bound, are more profoundly affected by the application of an electric field than the inner electrons. Sternheimer has found that the polarizabilities of rare-gas-configuration ions are due almost entirely to the outermost shells. Accordingly a model is used which incorporates this qualitative feature.

The rare-gas-configuration ions are considered as being constituted of an outer spherical shell of  $n$  electrons and a core consisting of the nucleus and the remaining electrons. In an electric field the shell retains its spherical charge distribution but moves bodily with respect to the core. The polarizability is made finite by a harmonic restoring force of spring constant  $k$  which acts between the core and shell. The two unknown parameters  $n$  and  $k$  will be chosen by considering the polarizability and ultraviolet dispersion of a gas of such model ions.

It is easy to show that the polarizability of this model ion in an applied periodic field of angular frequency  $\omega$  is given by

$$\alpha = \alpha_0 [1 - (\omega/\omega_0)^2]^{-1}, \quad (\text{III.1})$$

where  $\alpha_0 = (ne)^2/k$ ,  $\omega_0 = k/nm$ , and  $e$  and  $m$  are the electronic charge and mass. Upon using the Lorentz local field, the static dielectric constant of the gas is given by

$$(\epsilon_0 - 1)/(\epsilon_0 + 2) = \frac{4}{3}\pi N\alpha_0, \quad (\text{III.2})$$

where  $N$  is the number of atoms per unit volume. For nonstatic applied fields with  $\omega \ll \omega_0$ , the dielectric constant is given approximately by

$$\epsilon = \epsilon_0 + m(\epsilon_0 - 1)^2 [4\pi Nne^2]^{-1} \omega^2. \quad (\text{III.3})$$

The static dielectric constants and the frequency dependence of  $\epsilon$  are known for the rare gases<sup>20</sup> and, according to (III.2) and (III.3), suffice to determine  $n$  and  $k$  for these atoms. The values of  $n$  and  $k$  for rare gas atoms calculated in this way are found in Table III.

If only the outer shells moved in polarization, and they did so in the manner assumed in the spring model, then the numbers  $n$  would be  $n_{\text{He}} = 2$ ,  $n_{\text{Ne}} = 6$ ,  $n_{\text{Ar}} = 6$ , etc. The rare gas  $n$ 's of Table III are thus not un-

<sup>19</sup> Using Sternheimer's values for the polarizabilities does not much alter the calculated values of  $(e^*/e)$ .

<sup>20</sup> C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A84**, 13 (1910).

reasonable. The increase in  $n$  for the heavier rare gas atoms suggests that these heavier atoms have more electrons far from the nucleus which can take part in the polarization.

Neither the polarizabilities nor the ultraviolet dispersion data is known for the alkali metal or halogen ions, so that it is not possible to treat them as we have the rare gas atoms. However, for a given rare gas electronic configuration it is reasonable to suppose that the change in polarizability accompanying a change in nuclear charge (e.g., the change in  $\alpha$  from A to  $\text{Cl}^-$ ) will be due mainly to the altered spring constant while  $n$  remains the same. The classical agencies that tend to restore a polarized ion to an unpolarized state are the central field of the nucleus and the electron-electron Coulomb repulsions which tend to make the electrons assume a spherically symmetric distribution. Consider what happens if the nuclear charge of a rare gas atom is increased from  $Z$  to  $Z+1$  without changing the number of electrons. To a first approximation the electron distribution is scaled down in its dimensions by a factor  $Z/(Z+1)$ . The decrease of size of the electron distribution puts the electrons both closer to the nucleus and to one another and therefore increases the effectiveness of the restoring agencies which appear in the spring model in the spring constant  $k$ . Therefore it will be assumed that the number of shell electrons  $n$  will be the same as that of the rare gas atom with the same electronic configuration. The spring constants  $k$  will then be determined from the Pauling polarizabilities on the assumption that these are good estimates of the vacuum free-ion polarizabilities. These  $n$  and  $k$  are given in Table III.

Using the physical insight into the repulsive interaction provided by the discussion of Sec. II and the ion model outlined above, the problem of the repulsive interaction of polarized rare gas configuration ions can be discussed.

Consider for simplicity the case of two helium atoms differently polarized as shown in Fig. 1.

TABLE III. Some data for rare gas atoms and derived quantities for isoelectronic ions.

Atom or ion	Pauling <sup>a</sup> polarizability ( $10^{-24}$ cm <sup>3</sup> )	TKS <sup>b</sup> polarizability ( $10^{-24}$ cm <sup>3</sup> )	$n$ Spring model	$k$ ( $10^7$ cgs)
He	0.201		2.24	5.77
$\text{Li}^+$	0.029	0.03	2.24	3.39
$\text{F}^-$	1.04	0.652	4.8	0.511
Ne	0.390		4.8	1.36
$\text{Na}^+$	0.179	0.41	4.8	2.97
$\text{Cl}^-$	3.66	2.97	8.7	0.477
A	1.62		8.7	1.08
$\text{K}^+$	0.83	1.33	8.7	2.10
$\text{Br}^-$	4.77	4.17	9.9	0.474
Kr	2.46		9.9	0.91
$\text{Rb}^+$	1.98	1.98	9.9	1.62
$\text{I}^-$	7.10	6.44	11.3	0.412
Xe	3.99		11.3	0.736

<sup>a</sup> See reference 17.

<sup>b</sup> See reference 2.

X Shell Centers

● Cores

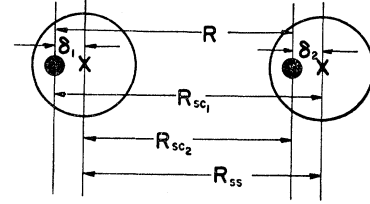


FIG. 1. Core and shell configurations for the interaction of two differently polarized helium atoms.

The short-range interaction energy can be estimated in the same way as was used to write (II.9) in the approximate form (II.10) except that  $R_{ss}$ ,  $R_{sc1}$ , and  $R_{sc2}$  must be used as denominators where before all the denominators were  $R$ . For instance, for the electron-core interaction the distance entering in the denominator of the estimate of the corresponding term will be  $R_{sc1}$  or  $R_{sc2}$  in the polarized state (Fig. 1) where it was  $R$  in the unpolarized state.  $S^2$  is clearly a function of  $R_{ss}$ . Thus:

$$W \cong -\frac{6S^2}{R_{ss}} + 4S^2 \left( \frac{1}{R_{sc1}} + \frac{1}{R_{sc2}} \right). \quad (\text{III.4})$$

But

$$R_{sc1} = R_{ss} - \delta_1,$$

$$R_{sc2} = R_{ss} - \delta_2.$$

Expand in powers of  $\delta_1/R_{ss}$ ,  $\delta_2/R_{ss}$  to get

$$W \cong \frac{2S^2}{R_{ss}} + \frac{4S^2}{R_{ss}} \left( \frac{\delta_1 + \delta_2}{R_{ss}} \right) + \dots \cong B \exp(-R_{ss}/\rho). \quad (\text{III.5})$$

Since the deformations of ions in the state of polarization are very small compared with the lattice separations that are encountered, we can neglect the second term.

In using this spring model, the alteration of the repulsion due to polarization of the atoms will be estimated using (III.5). Knowing the state of polarization of the ions and the separation of the ion cores we can deduce  $R_{ss}$ ; the short-range interaction energy is then given by  $B \exp(-R_{ss}/\rho)$  rather than by  $B \exp(-R/\rho)$ . Thus the repulsion between ions is to be regarded as acting between the shells and not the cores. This modification constitutes the first improvement of the present theory over the simple classical theory.

#### IV. SHORT-RANGE INTERACTION POLARIZATION MECHANISMS

From the discussion of the short-range interactions of the ions that has preceded, we can now deduce two polarization mechanisms which are neglected in the simple classical model of Sec. I.

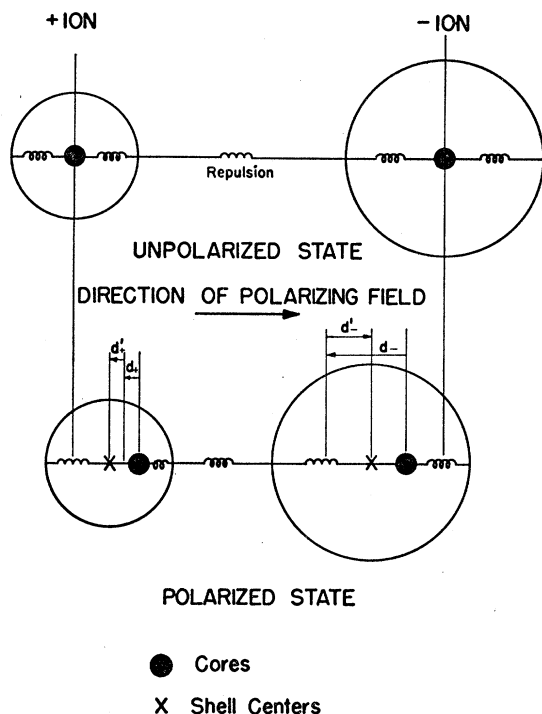


FIG. 2. The short-range interaction polarization.  $d_{\pm}$  are the displacements of the shells with respect to the cores in the absence of repulsion between the ions.  $d'_{\pm}$  are the additional shell displacements resulting from repulsion.

### Short-Range Interaction Polarization

First consider what happens due to the short-range interaction when pairs of ions are moved together as is the case in that polarization of a crystal due to the motion of the positive and negative ions. As we have seen, the shells of the ions repel one another and tend to become displaced with respect to the ion cores because of this repulsion. This is equivalent to a polarization of the ions. The restoring spring between the shell and the core is in general weaker in the negative ion than it is in the positive ion, and hence one would expect the polarization of the negative ion due to the repulsion of the shells to exceed that of the positive ion if the shell charges were the same. Referring to Fig. 2, we see that the polarization due to the short-range interaction is in the direction of the applied field for the positive ion and against the direction of the field for the negative ion. If the negative-ion "short-range interaction polarization" exceeds that of the positive ion, it is seen that there is a resulting net dipole per ion pair directed opposite to the applied field. Whether it will in fact be a net dipole directed opposite to the field depends, of course, both on the spring constants  $k$  and on the shell charges  $ne$ . For the NaCl-type alkali halides, the polarization due to this mechanism is indeed negative, as we shall see. As discussed in Sec. I, this is the sort of contribution to the polarization that serves to reduce  $e^*/e$  to values less than unity. The short-range inter-

action polarization arises from a coupling of the ionic displacement polarization and the electronic polarization of the ions, a coupling beyond that which exists because of the Lorentz field.

### Exchange Charge Polarization<sup>21</sup>

There is another sort of polarization which is a consequence of the overlap of the ions and the resulting exchange charge. When the repelling ions are moved with respect to one another there is a change in the overlap integrals and a consequent change in the exchange charge distribution. This change is responsible for the repulsive force between the ions at short distances. In a crystal the displacement of the ions in the polarization process causes such redistributions of exchange charge and the resulting forces cause the ionic displacement polarization to be finite. Associated with these charge redistributions is a net dipole moment per unit volume. This will be called the "exchange charge polarization."

Consider a chain of ions in a NaCl-type alkali halide crystal in equilibrium (no field) with their associated exchange charges (Fig. 3).

Except for the end members of this chain, each ion in the crystal is surrounded by six nearest neighbors which are dissimilar to itself. The end members of the chain have only five nearest neighbors. There is an exchange charge between each pair of ions, and the ions have acquired increased negative charges from the electrons "excavated" to make the exchange charge. Although, of course, the exchange charges are distributed throughout some region they are represented schematically by squares in Fig. 3. Only those exchange charges along the line of the chain are shown. The charge magnitudes associated with the ions and the exchange charges are shown. The end atoms differ from the interior ones by a charge of magnitude  $|q/2|$ .

Now consider the crystal in a polarized state with the positive-ion shells displaced relative to the negative-ion shells by a distance  $x$ . Figure 4 shows a line of ions in such a crystal. The center of exchange charge  $q_1$  is a distance  $\xi$  from the negative-ion shell center and  $q_2$  is a distance  $\eta$  from the point halfway between the negative-ion shell centers. The dotted circles are ions in one of the four adjacent lines of ions. The exchange charges  $q_3$

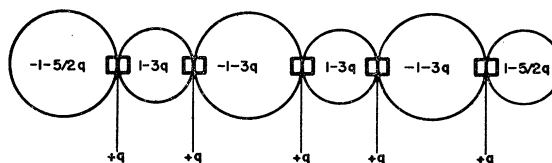


FIG. 3. Chain of positive and negative ions in an unpolarized crystal, showing exchange and electron charge magnitudes and positions. The large circles represent negative ions.

<sup>21</sup> After the completion of this work we have received an unpublished manuscript from P. W. Anderson in which this exchange charge polarization effect is treated. Our results and those of Anderson on this effect are in good agreement.

are a horizontal distance  $\xi$  from the equilibrium positions  $0, R_0, 2R_0, \dots, nR_0, \dots$ . Except for the ends of the chain the charges on the positive (small) and negative (large) ions are  $1 - \frac{1}{2}(q_1 + q_2) - 2q_3$  and  $-1 - \frac{1}{2}(q_1 + q_2) - 2q_3$ , respectively. The positive ion at the right end of the chain of Fig. 4 has a charge  $1 - \frac{1}{2}q_2 - 2q_3$  and the negative ion on the left end has a charge  $-1 - \frac{1}{2}q_1 - 2q_3$ . The distance  $x$  is the displacement of the positive-ion shell relative to the negative-ion shell and so includes the electronic polarizability of the ions.

Each row of  $q_3$ 's is shared by two rows of ions. There are four rows of them surrounding each row of ions, so there should be two rows of  $q_3$ 's associated with each line of ions in counting up the total dipole moment of the crystal. This, of course, includes too many rows of  $q_3$ 's since it neglects absence of them at the surfaces. It is correct, however, to order  $1/(N^{\frac{1}{2}})$  where  $N$  is the number of ion pairs in the crystal.

From (II.11) we can calculate  $q_1, q_2$ , and  $q_3$ :

$$q_1 = q_0 - gx, \quad (IV.1)$$

where

$$q_0 = (R_0 B)(\gamma e)^{-1} \exp(-R_0/\rho),$$

$$g = q_0(\rho^{-1} - R_0^{-1}).$$

Similarly

$$q_2 = q_0 + gx, \quad (IV.2)$$

$$\begin{aligned} P = & q_1 \{ \xi + [\xi + 2R_0] + \dots + [\xi + 2R_0(N-1)] \} \\ & + q_2 \{ [R_0 + \eta] + [(R_0 + \eta) + 2R_0] + \dots + [(R_0 + \eta) + 2R_0(N-2)] \} \\ & + [1 - \frac{1}{2}q_1 - \frac{1}{2}q_2 - 2q_3] \{ [R_0 + x] + [(R_0 + x) + 2R_0] + \dots + [(R_0 + x) + 2R_0(N-2)] \} \\ & + [-1 - \frac{1}{2}q_1 - \frac{1}{2}q_2 - 2q_3] \{ 2R_0 + 4R_0 + \dots + 2R_0(N-2) \} + [1 - \frac{1}{2}q_1 - 2q_3] \{ R_0 + x + 2R_0(N-1) \} \\ & + 2q_3 \{ \xi + [\xi + R_0] + \dots + [\xi + (2N-1)R_0] \}. \quad (IV.4) \end{aligned}$$

Performing the arithmetic sums in (IV.4) and using (IV.1), (IV.2), and (IV.3), we have for the dipole moment per ion pair (dropping terms of order  $1/N$ )

$$\begin{aligned} P/N = & gx(\eta - \xi) \\ & + q_0(\xi + \eta - 3x - R_0 + 4\xi) + R_0 + x, \quad (IV.5) \end{aligned}$$

where the first term is the dipole due to changes in the magnitude of the exchange charges, the second term is the dipole due to the movement of the exchange charges, and the third term is the dipole of the chain of positive and negative ions. This third term is exactly canceled by a similar term in the neighboring chain in the crystal. The last term is the polarization due to the displacement of the ion shells. The first two terms constitute the "exchange charge polarization" per ion pair:

$$P_{\text{exch}}/N = gx(\eta - \xi) + q_0(\xi + \eta - 3x - R_0 + 4\xi). \quad (IV.6)$$

By taking care, as has been done, to treat the end ions of the chain correctly (and this is essential if  $P_{\text{exch}}/N$  is to be unambiguous), the dipole moment per ion pair calculated using a chain starting on the left with a positive ion is exactly the same as (IV.6).

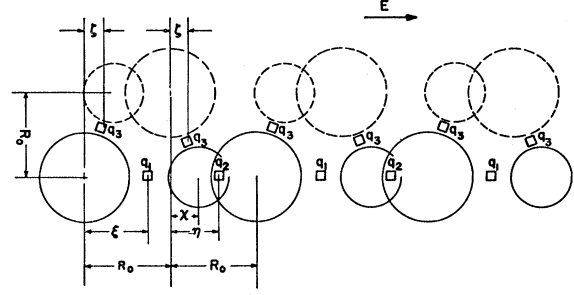


FIG. 4. Chain of positive and negative ions in a polarized crystal, showing exchange charge magnitudes and positions. (Exchange charge polarization.)

and

$$q_3 = q_0 + O(x^2). \quad (IV.3)$$

We need carry the expressions for these exchange charges only to  $O(x)$ , as we shall see in Sec. V.

We now calculate the dipole moment of the line of charges of Fig. 4. Since the net charge of this line with the two associated lines of  $q_3$ 's is zero, the choice of origin is arbitrary. It is chosen to be at the negative-ion shell center at the left end. The dipole moment  $P$  for a line of  $N$  ion pairs with associated exchange charges is<sup>22</sup>

If it is assumed that initially, before the application of the electric field  $E$ , the exchange charge centers are at the points of tangency of the spheres possessing the Zachariasen radii  $r_+$  and  $r_-$  (Kittel<sup>23</sup>) and further that the exchange charge center moves so as to keep the ratio of its distances to the two ion shell centers the same after polarization as before, then

$$\begin{aligned} \xi &= r_- + r_- x / R_0, \\ \eta &= r_+ + r_- x / R_0, \\ \xi &= r_- x / R_0. \end{aligned} \quad (IV.7)$$

The Zachariasen, Pauling, and Goldschmidt ionic radii are very nearly the same for the ions considered here with the exception of  $\text{Li}^+$ . In the case of  $\text{Li}^+$  the Zachariasen radius has a value which lies between the Goldschmidt and Pauling radii and is arbitrarily chosen for use here. Substituting these expressions for  $\xi, \eta, \zeta$

<sup>22</sup> The dipole moment due to the ion core displacements is not included in this expression since it is simply an additive term not of interest here.

<sup>23</sup> Charles Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition.



TABLE IV. Values of the parameters. The  $D/e$  (in units of  $10^{-2}$ ) are calculated by using (IV.9), where  $r_+ - r_-$  is set equal to the difference of the Zachariasen ionic radii in the calculation of  $D/e$  and  $r_+ - r_-$  is set equal to  $-R_0$  in calculating  $(D/e)_{\text{extreme}}$ . Here, as in the other calculations throughout, the Born-Mayer parameters  $B$  and  $\rho$  used are those given in reference 1, p. 26.  $\gamma$  is deduced for the various salts in Sec. II.  $A$  is given by  $6R_0/K$ , where  $R_0$  is the nearest neighbor distance and  $K$  is the compressibility from reference 1, p. 26.  $\lambda$ ,  $\mu$ , and  $\nu$  in terms of  $D$  and of quantities to be found in Table III are given by Eqs. (V.19) and (V.12).  $\lambda$ ,  $-\mu/e$  and  $\nu/e^2$  are given in cgs units.  $e^*/e$  and  $(e^*/e)_{\text{extreme}}$  in the seventh and eighth columns were calculated by using (V.31) with  $e' = e + D$  and  $e' = e + D_{\text{extreme}}$ , respectively. The  $(e^*/e)_{\text{obs}}$  are from Table I.

	$D/e$ ( $10^{-2}$ )	$(D/e)_{\text{extreme}}$ ( $10^{-2}$ )	$A$ ( $10^4$ ergs/cm $^2$ )	$\lambda \times 10^7$	$-\mu/e \times 10^6$	$\nu/e^2 \times 10^6$	$e^*/e$	$(e^*/e)_{\text{extreme}}$	$(e^*/e)_{\text{obs}}$
LiF	-1.36	-4.20	9.79	2.29	0.883	0.464	0.91	0.88	0.87
LiCl	-1.47	-3.34	4.35	2.43	1.77	1.60	0.92	0.90	...
LiBr	-1.61	-2.83	3.82	2.44	2.03	2.08	0.91	0.90	...
LiI	-1.77	-3.52	3.00	2.76	2.69	3.12	0.90	0.88	...
NaF	-1.58	-10.43	6.34	2.29	0.778	0.529	0.93	0.86	0.93
NaCl	-3.30	-11.2	3.80	2.43	1.66	1.67	0.91	0.84	0.74
NaBr	-3.78	-11.5	3.43	2.45	1.93	2.15	0.89	0.82	0.69
NaI	-4.28	-11.4	2.66	2.77	2.58	3.18	0.89	0.83	0.71
KF	0.00	-11.4	4.70	2.43	0.526	0.811	0.98	0.87	...
KCl	-1.87	-12.2	3.25	2.57	1.41	1.95	0.93	0.84	0.80
KBr	-2.38	-12.4	2.88	2.59	1.68	2.43	0.93	0.84	0.76
KI	-3.08	-12.6	2.42	2.90	2.33	3.46	0.91	0.82	0.69
RbF	+0.609	-11.4	4.02	2.58	0.326	1.06	1.05	0.88	...
RbCl	-1.23	-12.2	2.89	2.72	1.21	2.19	0.95	0.84	0.84
RbBr	-1.72	-12.3	2.54	2.73	1.48	2.68	0.92	0.83	0.82
RbI	-2.50	-10.7	1.97	3.05	2.13	3.71	0.93	0.85	0.89

into (IV.6), we get

$$P_{\text{exch}}/N = x(r_+ - r_-)q_0(R_0 - 4\rho)/\rho R_0. \quad (\text{IV.8})$$

Note that for  $r_+ < r_-$  this is opposite to the direction of the field. Since the Zachariasen radii of negative ions do, for the salts of Table I, exceed those of the positive ions, we see that the exchange charge polarization also contributes toward making  $e^*/e < 1$ . It is convenient to define the exchange charge polarization coefficient  $D$  by writing (IV.8) as

$$P_{\text{exch}}/N = [(r_+ - r_-)B \times \exp(-R_0/\rho)(R_0 - 4\rho)/\rho\gamma e]x \equiv Dx. \quad (\text{IV.9})$$

Using the values of  $r_+$  and  $r_-$  given in reference 23, p. 81;  $B \exp(-R_0/\rho)$ ,  $\rho$ , and  $R_0$  from reference 1, p. 26; and  $\gamma$  from Sec. II, we can then calculate values for  $D/e$ . They are listed in Table IV. All the  $D$ 's are negative except that for KF which is zero and that for RbF which is positive. The values labeled  $(D/e)_{\text{extreme}}$  are calculated on the assumption that the exchange charge is at the center of the positive ion. These values will be useful in estimating how much alteration in the calculated of  $e^*/e$  is to be expected if  $q_{\text{exch}}$  were in fact located nearer the positive ion core than it has been assumed to be.

The assumptions that go into the calculation of  $D$  are rather rough. They are

(1) Assumption of the relation between exchange charge and the interaction energy, Eq. (II.11).

(2) The relation of the interaction energy parameters  $B$ ,  $\rho$  to the compressibility and lattice constant. (See Sec. V.)

(3) The assumption as to the position of the center of exchange charge.

(4) The proportional motion of the exchange charge.

Because of the compounded uncertainty of these assertions it would not be surprising if  $D$  as listed in Table IV were incorrect by more than a factor of two.

## V. POLARIZATION OF CRYSTAL MODELS

We are now ready to incorporate the model ions which we have discussed in Sec. III into a model crystal. We consider a NaCl-type lattice with positive and negative ions at the lattice sites of interlocking face-centered-cubic lattices omitting phonons. It will be the procedure here to find the Lagrangian of this system polarized in an applied electric field on the assumption of long polarization waves in the lattice. The solution of Lagrange's equations of motion will then allow us to calculate the dielectric constants of the model.

It will suffice to consider the electric field applied in the direction of a crystal axis since the dielectric properties of a cubic crystal are isotropic.

Consider a state of polarization of such a crystal made of spring model ions in the presence of an applied field. The field and the polarization are assumed to be constant over a region including very many lattice sites. As shown in Fig. 5, in the state of polarization the ion cores are displaced distances  $x_+$  and  $x_-$  from the lattice sites in the direction of the applied field (the  $X$  axis). The shells are displaced distances  $d_+$  and  $d_-$  from the cores. These  $x$ 's and  $d$ 's will be the generalized coordinates in the Lagrangian formulation of the problem. We seek the kinetic energy  $T$  and the potential energy  $V$  of this system. The potential energy has three parts:

$V_e$ , the electrostatic energy;  $V_{sr}$ , the short-range interaction energy; and  $V_{se}$ , the self-energy of the polarized ions, i.e., the restoring spring energies of the ions. Thus the Lagrangian can be written:

$$L = T - (V_e + V_{sr} + V_{se}). \quad (\text{V.1})$$

### Electrostatic Energy $V_e$

In calculating the electrostatic energy of the polarized crystal model, the charge distribution is expanded in multipoles about the lattice sites. Since we will be interested in the potential energy only to second order in the applied field and since  $x_+$ ,  $x_-$ , and  $d_+$ ,  $d_-$  will be of first order in the applied field, multipoles of higher order than quadrupoles need not be considered. About a positive-ion site the multipoles due to the positive-ion core and shell include a monopole  $+e$ , a dipole directed along the positive  $x$  axis of magnitude  $ex_+ - n_+ed_+$ , and a quadrupole which is of second order in the applied field and has only an  $xx$  component. Here  $n_+$  is the number of electrons on the shell of the positive ion. The uniformly charged spheres of the spring model are very convenient for the calculation of these multipoles since they can be replaced by point charges. About a negative ion site there are a monopole  $-e$ , an  $x$  axis directed dipole of magnitude  $-ex_- - n_-ed_-$ , and a quadrupole which is of second order in the applied field.

In order to write down the electrostatic energy of these multipoles, we must know the electrostatic potential at and near to the lattice sites. For charges distributed axially, as in this case, the energy of interaction of the distribution with the local field is

$$P^1 V_{\text{loc}} + P^2 \frac{\partial V_{\text{loc}}}{\partial x} + \frac{1}{2} P^4 \frac{\partial^2 V_{\text{loc}}}{\partial x^2},$$

where  $P^1$ ,  $P^2$ , and  $P^4$  are the monopole, dipole, and quadrupole moments, respectively. The local field is the sum of the applied field plus that field due to the

multipoles other than those at the lattice site in question. The latter field for the case of a transverse polarization wave, of wavelength long compared to the lattice constant and short compared with the size of the dielectric sample, is, in the Lorentz approximation, composed of the Lorentz field  $4\pi P/3$  and the depolarizing field. In this case the macroscopic field appearing in Maxwell's equations is the sum of the applied field and the depolarizing field.

Consider first the energy of the multipoles in the macroscopic field. The monopole contribution is zero when summed over the crystal because of the electrical neutrality of every plane of lattice points perpendicular to the macroscopic field on which the potential due to the macroscopic field is constant. Considering the macroscopic field as being uniform, the field has no gradient and the quadrupole energy of interaction with the macroscopic field is also zero. This leaves only the dipoles with nonvanishing energy of interaction with the macroscopic field.

Of the interaction of the multipoles with one another we need retain only those contributions of, at most, second order in the displacements. Thus only the monopole-monopole, monopole-dipole, monopole-quadrupole, and dipole-dipole interactions need be considered.

The monopole-monopole interaction energy is independent of the displacements or the applied field since piezoelectric effects are absent in crystals with center-of-inversion symmetry (such as alkali halides). Thus the monopole-monopole contribution to the potential energy in the Lagrangian is merely an additive constant, the Madelung energy.<sup>24</sup> The monopole-dipole term is zero since the field at a lattice site due to the monopoles in a cubic array is zero.

The monopole-quadrupole term is given by  $\frac{1}{2} P^4 (\partial^2 V / \partial x^2)$ , where  $V$  in this expression is the potential due to positive and negative monopole charges distributed on a NaCl lattice. Since in a cubic crystal  $\partial^2 V / \partial x^2 = 0$  at a lattice site, the quadrupole-monopole interaction also vanishes.

Thus the electrostatic potential energy of the polarized crystal reduces to just that due to the interaction of the point dipoles with the macroscopic field and with one another. The dipole moment per ion pair due to displacements  $x_+$  and  $d_+$  is

$$e(x_+ - x_-) - n_-ed_- - n_+ed_+.$$

This does not include the exchange charge polarization per ion pair, which is given by

$$D(x_+ + d_+ - x_- - d_-),$$

<sup>24</sup> This is true even when one considers the increased electronic charge on the ions which comes to them from the exchange charge region. This alteration of the ionic charge from unity is given by  $\Delta q = -\frac{1}{2}q_1 - \frac{1}{2}q_2 - q_3 = -2q_0 = \text{constant}$ . (The notation is that of Sec. IV.) Since  $\Delta q$  is a constant, the correction for it in the Madelung energy is independent of the ionic displacements, and the Madelung energy thus corrected is still merely an additive constant in the electrostatic energy of the crystal.

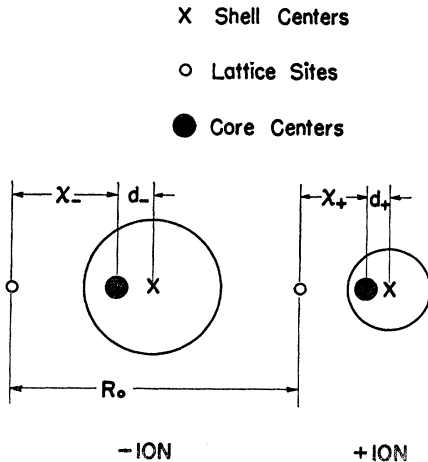


FIG. 5. The generalized coordinates used in expressing the Lagrangian of the model crystal.

where  $D$  is defined in Eq. (IV.9) and  $x_+ + d_+ - x_- - d_-$  is, in terms of the generalized coordinates, the displacement of the positive-ion shell relative to the negative-ion shell.

The exchange charge dipoles are not well represented as point dipoles but arise from extended distributions of charge. The interaction of these exchange charge dipoles with the macroscopic field, with the "point dipoles" of the polarization of the ions and the displacement polarizations, and with one another is a complicated problem. Here it will be assumed that the exchange charge polarization is to be incorporated exactly as the usual dipoles are; that is, it is assumed that they contribute to and experience the same local field as they would if they were point dipoles at the lattice sites. The expression (V.31) for  $e^*/e$  that results from the present analysis can be shown to be quite insensitive to considerable variation of the local field. Thus we write the total dipole per ion pair,  $p$ , as

$$p = e(x_+ - x_-) - n_-ed_- - n_+ed_+ + D(x_+ + d_+ - x_- - d_-). \quad (V.2)$$

$P = Np$  is the dipole moment per unit volume, where  $N$  is the number of ion pairs per unit volume. The potential energy of the dipole (V.2) in the macroscopic field is  $-pE_{\text{mac}}$ . The local field due to the other dipoles is the Lorentz field  $(4\pi/3)Np$  (we are considering long transverse polarization waves in the lattice). The dipole-dipole interaction energy per ion pair is then

$$-\frac{1}{2}(4\pi N p^2/3) \equiv -\frac{1}{2}Cp^2. \quad (V.3)$$

The  $\frac{1}{2}$  is included to avoid counting each dipole-dipole interaction twice. It has here been convenient to introduce the notation

$$C \equiv 4\pi N/3. \quad (V.4)$$

We have, finally, an expression for  $V_e$ :

$$V_e = -pE_{\text{mac}} - \frac{1}{2}Cp^2 \quad (V.5)$$

per ion pair.

### Short-Range Interaction Energy

The short-range interaction is the origin of another contribution to the potential energy of the polarized crystal. The relative displacement of the positive and negative ion shells is given by  $x = (x_+ + d_+ - x_- - d_-)$  so that, per ion pair, the short-range interaction energy is given to the lowest order in  $x$  by

$$V_{sr} = \frac{1}{2}Ax^2 + \text{constant} \quad (V.6)$$

where

$$A \equiv 2B \exp(-R_0/\rho)(R_0 - 2\rho)/R_0\rho^2. \quad (V.7)$$

Notice that this term involves a cross term between the  $x_{\pm}$ 's and  $d_{\pm}$ 's and thus couples the ion displacement polarization with the electron cloud polarization of the ions. The short-range interaction polarization is therefore built into the Lagrangian that we are constructing.

Also, note that  $A$  is related to the compressibility according to the Born-Mayer theory and given by  $6R_0/K$ .

### Self-Energies of the Ions

According to the spring model, the self-energy of per ion pair is

$$V_{ee} = \frac{1}{2}k_+d_+^2 + \frac{1}{2}k_-d_-^2, \quad (V.8)$$

where  $k_+$  and  $k_-$  are those spring constants given in Table IV.

### Kinetic Energy

We neglect the kinetic energy of the electrons, that is to say, the kinetic energy of the shells. This assumption is valid so long as we only consider applied fields with frequencies well below the ultraviolet dispersion region of the crystal. In that frequency region the phenomena are such that the spring model would be inadequate in any case. Thus we write the kinetic energy per ion pair

$$T = \frac{1}{2}M_+\dot{x}_+^2 + \frac{1}{2}M_-\dot{x}_-^2, \quad (V.9)$$

where  $M_+$  and  $M_-$  are the ion masses.

The Lagrangian (V.1) per ion pair, using (V.5), (V.6), (V.8), and (V.9), is

$$L = \frac{1}{2}M_+\dot{x}_+^2 + \frac{1}{2}M_-\dot{x}_-^2 + pE_{\text{mac}} + \frac{1}{2}Cp^2 - \frac{1}{2}Ax^2 - \frac{1}{2}k_+d_+^2 - \frac{1}{2}k_-d_-^2. \quad (V.10)$$

Written explicitly in terms of the generalized coordinates, (V.10) becomes

$$L = \frac{1}{2}M_+\dot{x}_+^2 + \frac{1}{2}M_-\dot{x}_-^2 + [e'(x_+ - x_-) - \beta_-d_- - \beta_+d_+]E_{\text{mac}} + \frac{1}{2}C[e'(x_+ - x_-) - \beta_-d_- - \beta_+d_+]^2 - \frac{1}{2}A(x_+ + d_+ - x_- - d_-)^2 - \frac{1}{2}k_+d_+^2 - \frac{1}{2}k_-d_-^2, \quad (V.11)$$

where terms containing  $E_{\text{mac}}$  and  $C$  have been simplified using the definitions:

$$\begin{aligned} (e + D) &\equiv e', \\ n_-e + D &\equiv \beta_-, \\ n_+e - D &\equiv \beta_+. \end{aligned} \quad (V.12)$$

We now consider Lagrange's equations of motion,

$$\frac{\partial}{\partial t} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0.$$

Multiply the  $x_-$  and  $x_+$  equations, respectively, by  $M_+$  and  $M_-$  and subtract. This yields the equation

$$\bar{M}d^2X/dt^2 = e'E_{\text{mac}} + Ce'^2X - Ce'(\beta_-d_- + \beta_+d_+) - AX - A(d_+ - d_-), \quad (V.13)$$

where

$$\bar{M} = M_+M_-(M_+ + M_-)^{-1}, \quad (V.14)$$

and

$$X = x_+ - x_- \quad (\text{V.15})$$

This is merely a conversion to coordinates expressing the relative motion of the positive and negative ions. The motion of the center of mass is not of interest here.

Assuming that  $E_{\text{mac}}(t) = E_{\text{mac}} e^{i\omega t}$ ,  $X(t) = X e^{i\omega t}$ , and  $d_{\pm}(t) = d_{\pm} e^{i\omega t}$ , then Eq. (V.13) becomes Eq. (V.16). This equation with the  $d_+$  and  $d_-$  Lagrange equations of motion give the three equations

$$(-\bar{M}\omega^2 - Ce'^2 + A)X + (Ce'\beta_- - A)d_- + (Ce'\beta_+ + A)d_+ = e'E_{\text{mac}}, \quad (\text{V.16})$$

$$-(Ce'\beta_- - A)X + (C\beta_-^2 - k_- - A)d_- + (C\beta_- \beta_+ + A)d_+ = \beta_- E_{\text{mac}}, \quad (\text{V.17})$$

$$-(Ce'\beta_+ + A)X + (C\beta_+ \beta_- + A)d_- + (C\beta_+^2 - k_+ - A)d_+ = \beta_+ E_{\text{mac}}, \quad (\text{V.18})$$

which must be solved for  $x$ ,  $d_+$ , and  $d_-$ .

It is useful to define the following quantities:

$$\begin{aligned} \lambda &\equiv 1/k_+ + 1/k_-, \\ \mu &\equiv \beta_+/k_+ - \beta_-/k_-, \\ \nu &\equiv \beta_+^2/k_+ + \beta_-^2/k_-. \end{aligned} \quad (\text{V.19})$$

Then we have, by a straightforward calculation,

$$\Delta X/k_+ k_- E_{\text{mac}} = A e' \lambda + e' + A \mu, \quad (\text{V.20})$$

$$\Delta d_-/E_{\text{mac}} = \bar{M}\omega^2 [k_+ \beta_- + A(\beta_+ + \beta_-)] + A k_+ (e' - \beta_-), \quad (\text{V.21})$$

$$\Delta d_+/E_{\text{mac}} = \bar{M}\omega^2 [k_- \beta_+ + A(\beta_+ + \beta_-)] - A k_- (e' + \beta_+), \quad (\text{V.22})$$

where  $\Delta$ , the determinant of the coefficients of (V.16), (V.17), and (V.18), is given by

$$\Delta/k_+ k_- = [(A - Ce'^2) - AC(\lambda^2 + 2e'\mu + \nu)] - \bar{M}\omega^2 [(1 + A\lambda)(1 - C\nu) + AC\nu^2]. \quad (\text{V.23})$$

The polarization per unit volume,  $P = N(e'X - \beta_- d_- - \beta_+ d_+)$ , can be written in terms of these quantities. Further, we can write an expression for the dielectric susceptibility which is defined by the equation  $P = \chi E_{\text{mac}}$ . Comparing the resulting expression for  $\chi$  with the infrared dispersion relation

$$\chi = [\chi_0 - \chi_\infty (\omega/\omega_0)^2] [1 - (\omega/\omega_0)^2]^{-1}, \quad (\text{V.24})$$

we can identify the following expressions:

$$\chi_0 = -\frac{3}{4\pi} \frac{e'^2 + A(\lambda e'^2 + 2\mu e' + \nu)}{(A - Ce'^2) - AC(\lambda e'^2 + 2\mu e' + \nu)}, \quad (\text{V.25})$$

$$\chi_\infty = -\frac{3}{4\pi} \frac{\nu + A(\lambda\nu - \mu^2)}{(1 + A\lambda)(1 - C\nu) + AC\mu^2}, \quad (\text{V.26})$$

$$\bar{M}\omega_0^2 = \frac{(A - Ce'^2) - AC(\lambda e'^2 + 2\mu e' + \nu)}{(1 + A\lambda)(1 - C\nu) + AC\mu^2}. \quad (\text{V.27})$$

With these we can construct generalizations of the two Szigeti relations and the Clausius-Mossotti, Lorenz-Lorentz equations.

The generalized first Szigeti relation is

$$\bar{M}\omega_0^2(\epsilon_0 + 2)/(\epsilon_\infty + 2) = A(1 + A\lambda)^{-1} \equiv 6R_0/K^*. \quad (\text{V.28})$$

The generalized second Szigeti relation is

$$\begin{aligned} \epsilon_0 - \epsilon_\infty &= \left( \frac{\epsilon_\infty + 2}{3} \right)^2 \frac{4\pi N}{\bar{M}\omega_0^2} \left\{ e' \left[ \frac{1 + A(\lambda + \mu/e')}{1 + A\lambda} \right] \right\} \\ &\equiv 4\pi N(e^*)^2(\epsilon_\infty + 2)^2/9\bar{M}\omega_0^2. \end{aligned} \quad (\text{V.29})$$

According to (V.28) and (V.29), we have

$$K^*/K = 1 + A\lambda, \quad (\text{V.30})$$

$$e^*/e = (e'/e)[1 + (A\mu/e')(1 + A\lambda)^{-1}]. \quad (\text{V.31})$$

$A$  is defined in Eq. (V.7),  $\lambda$  and  $\mu$  are given by Eqs. (V.19), and  $e'$  is defined in (V.12).

All of the parameters that occur in the expressions (V.30) and (V.31) have been estimated so that estimates of  $e^*$  and  $K^*$  can be made on the basis of the present model.

The generalized Clausius-Mossotti and Lorenz-Lorentz relations are

$$(\epsilon_0 - 1)(\epsilon_\infty + 2)^{-1} = \frac{4}{3}\pi N(e'^2/A + \lambda e'^2 + 2\mu e' + \nu), \quad (\text{V.32})$$

and

$$(\epsilon_\infty - 1)(\epsilon_\infty + 2)^{-1} = \frac{4}{3}\pi N[\nu - A\mu^2/(1 + A\lambda)]. \quad (\text{V.33})$$

In Table IV are given values of  $e^*/e$  calculated using both  $D/e$  and  $(D/e)_{\text{extreme}}$ . For the assumptions which yield the values of  $D/e$  given in the first column of Table IV, the short-range interaction polarization mechanism contributes somewhat more to the deviation of  $e^*/e$  from unity than the exchange charge polarization mechanism. The slight difference in the relative importance of the mechanisms is reversed for the case in which  $(D/e)_{\text{extreme}}$  is used.

The predicted values of  $e^*/e$  are seen to be too high for the most part, though they follow in general, with less extreme changes, the trends of the observed values of  $e^*/e$ . The values omitted from the observed  $e^*/e$  column are missing because the reststrahlung frequencies for these salts are apparently unknown. It is regrettable that  $\omega_0$  is not known for RbF since for this salt the model predicts  $e^*/e > 1$ . The crudeness of the many approximations makes the rather poor numerical agreement of the calculated and observed  $e^*/e$  not surprising. However, it seems very convincing that the mechanisms discussed in Sec. IV, the short-range interaction polarization and the exchange charge polarization, are responsible for at least part of the deviation of  $e^*/e$  from unity.

An idea of how much improvement in the value of  $e^*/e$  could be expected from assuming  $q_{\text{exch}}$  to be nearer

the positive ion than supposed in the present calculation is furnished by  $(e^*/e)_{\text{extreme}}$ . These values for  $e^*/e$  are calculated on the assumption that the exchange charge is at the positive-ion core, certainly an upper bound on the displacement of the position of the exchange charge toward the positive ion. It is seen that these extreme values are rather close to the observed values except in the cases of very low  $e^*/e$ : NaCl, NaBr, NaI, KBr, KI. Of course, this is not the only manner in which  $D$  might be altered; for instance, the values used for  $\gamma$  may be in error.

The calculations of  $e^*/e$  and  $K^*/K$  have been carried out with an entirely different ion model than the spring model described above. In this alternative model, the ion is again regarded as a shell and core though in this case the shell is fixed with respect to the core. The electron density on the shell in the presence of a time-varying electric field is taken to be proportional to  $(1+\sigma \cos\theta)$  when the field is applied in the  $\theta=0$  direction.  $\sigma$  is calculated to first order in the electric field. The restoring force in this case is the Coulomb interaction of the charges on the shell. In this "tidal model" the undetermined parameters are the radius of the shell and the number of electrons on it. These are determined from the experimental data for the rare gas atoms and the Pauling polarizabilities in the same manner that  $k$  and  $n$  were determined for the spring model. All of the features and mechanisms that have been described for the spring model can be given an interpretation in terms of this tidal model, and on this basis values for  $e^*/e$  and  $K^*/K$  can be deduced. The results for the two ion models are in close agreement, the spring model giving slightly smaller values for  $e^*/e$  than the tidal model. It is interesting that the two models which differ considerably in their details should give such similar values for  $e^*/e$ , and the fact that they do suggests that the underlying physical arguments have some validity.

With regard to the additivity property, we note from Table IV that  $A\mu^2/[V(1+A\lambda)] \sim 10^{-4}$  in cgs units. Hence the Lorenz-Lorentz equation can be written to a good approximation as

$$(\epsilon_\infty - 1)(\epsilon_\infty + 2) \cong \frac{4}{3}\pi N \nu = \frac{4}{3}\pi N [(\beta_-^2/k_-) + (\beta_+^2/k_+)].$$

Thus, although the generalized Lorenz-Lorentz equation (V.33) does not strictly admit the assumption of the additivity property for  $\epsilon_\infty$ , it does so approximately.  $\beta_-^2/k_-$  and  $\beta_+^2/k_+$  are crystal polarizabilities which differ from the vacuum polarizabilities in the same way as the TKS polarizabilities differ from the Pauling or free-ion polarizabilities. For one has

$$\begin{aligned} \beta_-^2/k_- &= (n_-e + D)^2/k_- < (n_-e)^2/k_- \\ &= \text{Pauling polarizability of } - \text{ ion;} \\ \beta_+^2/k_+ &= (n_+e - D)^2/k_+ > (n_+e)^2/k_+ \\ &= \text{Pauling polarizability of } + \text{ ion.} \end{aligned}$$

Quantitatively  $D$  is too small to account for the difference between the TKS and the Pauling polarizabilities.

Now consider the predictions of  $K^*$  given by the model. Equation (V.30) predicts  $K^*/K$  values slightly greater than one, whereas the experimental values of Table I differ from unity by as much as 34% and show both positive and negative deviations. It is interesting to notice that this difficulty is more or less unrelated to the disagreement between experiment and the present theory with regard to  $e^*/e$ . For instance, if the exchange charge polarization parameter  $D$ , the magnitude of which is rather doubtful, were greater in magnitude it would tend to improve the theoretical prediction of  $e^*/e$ , and it is likely that improvement in the theoretical  $e^*/e$  lies in this direction as we have seen in the calculation of  $(e^*/e)_{\text{extreme}}$ .  $K^*/K$ , however, does not depend on  $D$  at all.

Since the first Szigeti relation is quite insensitive to the polarization mechanisms introduced in our model, as evidenced by the small deviations from unity predicted by (V.30), it seems likely that an explanation of the deviations of  $K^*$  from  $K$  is more to be sought in the theory relating  $A$  with the elastic constants than in the dielectric theory.

$A$  is related to the parameters of the Born-Mayer potential, and these parameters have been determined on the assumption that only the nearest neighbor repulsive interactions and the Coulomb interactions of point monopoles are present in the crystal. The failure of the Cauchy relations even for alkali halides indicates that this assumption is in error. It is clear that the Born-Mayer potential derived in the absence of other interactions than these will not necessarily be an accurate representation of the nearest neighbor interactions. The Born-Mayer parameters will then give an erroneous value for  $A$  which is related only to the nearest neighbor interactions. Among the neglected interactions are clearly the next nearest neighbor interactions. Also, using the picture furnished by the model of the crystal containing exchange charges we see that in this model the interactions of these small charges should be included. When the crystal is strained these exchange charges move and change in magnitude. The interaction of ions  $A$  and  $B$ , say, and their associated exchange charges will depend on the magnitude and positions of these associated exchange charges. These magnitudes and positions are determined by the positions of the neighbors nearest to  $A$  and  $B$ . Thus the interaction of  $A$  and  $B$  depends on the configuration of ions other than  $A$  and  $B$  and hence the presence of the exchange charges gives a "many-body" character to the interaction of the ions in the crystal. This probably corresponds to Löwdin's "S-energy" contributions in the theory of the cohesive energy and elastic constants of the alkali halides. The "S-energy" or "many-body" contribution to  $c_{12}$  and  $c_{44}$  is as great as 30% of the electrostatic contribution according to Löwdin. The many-body effects are there-

fore not negligible, and the values of  $A$  used here are somewhat in error.

Instead of using the static lattice bulk moduli and lattice constants to evaluate the Born-Mayer potential parameters, as would be correct, the room temperature values of  $K$  and  $R_0$  were used. It is estimated that the static lattice compressibility is about 10% lower than the observed room temperature compressibility and that the lattice constant of the static lattice is a few percent lower than the observed room temperature value.<sup>1</sup> This correction will be neglected here, such a refinement being unwarranted by other approximations in the theory.

### SUMMARY

The results of this study may be briefly summarized as follows: The mechanisms of polarization described in Sec. IV must be responsible for at least part of the deviations of  $\epsilon^*/\epsilon$  from unity. These mechanisms also give a qualitative explanation of the deviations of the so-called crystal polarizabilities from the free-ion polarizabilities. The explanation of the deviations of  $K^*/K$  from unity is to be sought in a more sophisticated theory of the elastic constants than that used here. The model of the short-range repulsive interaction in terms of the exchange charge introduces many-body forces into a Born-Mayer type model of the crystal.

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## Study of Reactor-Irradiated $\alpha$ - $\text{Al}_2\text{O}_3$ <sup>†</sup>

J. J. ANTAL, *Ordnance Materials Research Office, Watertown, Massachusetts, and Brookhaven National Laboratory, Upton, New York*

AND

A. N. GOLAND, *Brookhaven National Laboratory, Upton, New York*

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Studies are presented here on reactor-irradiated alpha aluminum-oxide single crystals. These are a continuation of the use of long-wavelength neutron transmission for determining the concentration and types of defects produced in solids by high-energy particle irradiation. The material exhibited crystallographic stability to fast-neutron irradiation at temperatures  $<40^\circ\text{C}$ , and the results indicate a total number of defects approximately 40 times less than that predicted by current theories. Correlation with macroscopic density changes is good. Examination of the wavelength dependence of the neutron scattering indicated that the damage may be partly Al-O vacancy pairs at room temperature. Annealing of the material produced no decrease in the concentration of defects from room temperature to  $400^\circ\text{C}$ , a steady decrease from  $400^\circ\text{C}$  to  $1250^\circ\text{C}$ , and nonuniform changes in neutron scattering and visually observable optical coloring beyond  $1250^\circ\text{C}$ . Annealing at a temperature of  $1800^\circ\text{C}$  did not remove the coloring, although the density returned to its pre-irradiation value.

### I. INTRODUCTION

SOME earlier experiments concerning the use of neutron spectroscopy for the determination of point defects in irradiated graphite<sup>1</sup> gave promising results. The experiments to be described here are primarily a continuation of this work. The technique is simply a measurement of the scattering of long-wavelength neutrons by crystallographic defects in a solid. It is unique in its ability to give a direct measure of the number of defects in a material without an undue number of assumptions. As a result of the low neutron intensity which is presently available for wavelengths greater than 4 or 5 angstroms, only concentrations of defects of 0.1% or greater are readily detectable. For the same reason the experiment must be restricted to materials which have a low capture cross section and a high bound-atom coherent scattering cross section, and which will retain large numbers of defects at tempera-

tures where irradiation and examination are possible. It was expected that the strong, mostly ionic bonding in  $\alpha$ -aluminum oxide (corundum) would lead to retention of defects at the temperatures available for this irradiation (always less than  $40^\circ\text{C}$ ). Also, the low capture cross sections of the constituent nuclei made this a favorable material. As explained in the next section, complicating features of this material are its complex crystal structure and its diatomic nature.

### II. BASIC CONSIDERATIONS

#### A. Neutron Transmission

(1) *Monatomic material.*—If one considers the scattering of slow neutrons by isolated, randomly arranged point defects in a crystal lattice, for wavelengths sufficiently long that Bragg scattering is not possible, the atomic fraction of such defects is simply<sup>1</sup> given by

$$f = \sigma_d / \sigma_a.$$

Here,  $\sigma_d$  is the cross section per atom for scattering by

<sup>†</sup> Work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> Antal, Weiss, and Dienes, *Phys. Rev.* **99**, 1081 (1955).