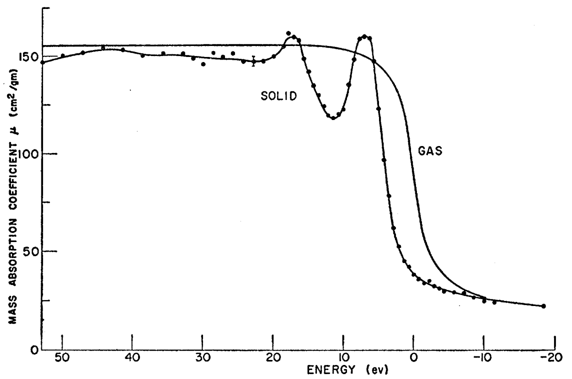

FIG. 4. Mass absorption coefficient of gaseous and solid krypton in the region of the *K*-absorption edge at 0.86 A.

to 40 ev from the absorption edge. Figure 4 shows the corresponding result for krypton. The Kossel lines in the gas absorption spectrum are unresolved, as observed previously.[6] However, as before, the zero of the energy scale has been assigned by analyzing the edge into component lines approaching a series limit.[6] Two principal maxima are seen in the solid krypton spectrum. The mass absorption coefficients were computed as for argon by fitting the observed data to the known absorption coefficients at energies far from the absorption discontinuity. The uncertainty in the plotted points is approximately ± 2 cm^2/g.

Richtmyer[7] has shown that x-ray transitions involving a continuum or band of energy levels having a sharply defined edge will result in an emission or absorption edge structure of arc tangent shape. Figure 2 shows such calculated arc tangent points fitted to the observed solid argon spectrum. The sharp initial rise at the absorption edge is clearly too high to be accounted for wholly by such transitions. It appears that x-ray-induced transitions into the *p*-symmetry states in the conduction band of solid argon exhibit strong resonances for energies 1 or 2 ev less than the ionization energy of the isolated argon atom. This result is in good agreement with present ideas concerning the formation of excitation states near the lower edge of the conduction band in x-ray excited solids.

The initial rise at the absorption edge of solid krypton, although displaced 4 ev to greater energies than the ionization potential of the isolated atom, also shows the steep slope to be expected on the basis of exciton theory.

---

[6] C. H. Shaw, Phys. Rev. **57**, 877 (1940).

[7] Richtmyer, Barnes, and Ramberg, Phys. Rev. **46**, 843 (1934).

PHYSICAL REVIEW VOLUME 113, NUMBER 2 JANUARY 15, 1959

Effective Ionic Charge in Alkali Halides

JACQUE E. HANLON AND A. W. LAWSON
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received September 22, 1958)

An expression is derived for the effective charge in the Born-Szigeti equation for the dielectric constant of ionic crystals with the NaCl structure. The derivation is based on a coupled oscillator model in which the lattice vibrations are coupled to the electronic motions within the ions. The deviation of the ionic charge from its nominal value is found to be proportional to the difference in electronic polarizability between the positive and negative ions. Agreement between theory and experiment is satisfactory. Secondary effects on the index of refraction and the reststrahl frequency are calculated. The model is in semiquantitative agreement with the observed dipole moments of alkali halide molecules.

INTRODUCTION

THE dielectric constant of an ionic crystal at low frequencies exceeds its value at optical frequencies owing to the lattice distortion produced by the application of an electric field. The contribution of a lattice of rigid ions was first estimated by Born,[1] who derived for an NaCl type crystal the relation

$$\epsilon - n^2 = 3Le^2/\mu\Omega_t^2 v, \tag{1}$$

where ϵ is the static dielectric constant, n the index of refraction, v is the volume of a unit cell, e the ionic charge, L the Lorentz factor, μ is the reduced mass of a neutral ion pair, and Ω_t is the infrared, angular resonance frequency for transverse electric waves of infinite wavelength.

At optical frequencies, where the ionic displacement is negligibly small compared to the electronic displacement, we may write

$$n^2 - 1 = (\alpha_0/v)(Ln^2 - L + 4\pi), \tag{2}$$

where n is the index of refraction and α_0 is the polarizability of a unit cell in the lattice. It is customary to assume that polarizabilities are additive so that for a diatomic crystal such as NaCl

$$\alpha_0 = \alpha_0^+ + \alpha_0^-, \tag{3}$$

---

[1] M. Born, Physik. Z. **19**, 539 (1918).

where α_0^+ and α_0^- are, respectively, the polarizabilities of the positive and negative ion in the lattice. Although this assumption cannot be rigorous, it is known empirically to be a good approximation.

Szigeti[2] has modified Eq. (1) to take account of the fact that the long-range interaction of the transverse waves contributes an additional electronic polarization. In the limit of zero short-range forces, the Lorentz theorem holds and $L=4\pi/3$; but in fact short-range forces in ionic crystals are considerable and Szigeti takes this into account by replacing the electronic charge e by an effective charge e^*. The resulting formula is in this case

$$\epsilon-n^2=\frac{4\pi}{v}\left(\frac{n^2+2}{3}\right)^2\frac{e^{*2}}{\mu\Omega_t^2}. \tag{4}$$

When there is no optical polarization and the short-range forces vanish, this formula reduces to Eq. (1).

An equation essential to Szigeti's derivation of Eq. (4) is

$$\Omega_t^2=\left(\frac{n^2+2}{\epsilon+2}\right)\Omega_S^2. \tag{5}$$

In Eq. (5), Ω_S is the angular resonance frequency for mechanical vibration in a sphere of radius small compared with the wavelength of the vibration. For this case Lorentz has shown that the long-range interaction vanishes for a cubic lattice, i.e. the Lorentz field vanishes. Equation (5) was first given by Lyddane, Sachs, and Teller.[3]

For crystals with the NaCl type structure, with which we shall be exclusively concerned in this discussion, it may be shown[4] that

$$\mu\Omega_S^2=6a(c_{44}-c_{12}+\beta), \tag{6}$$

where β is the bulk modulus, and c_{44} and c_{12} are the usual elastic constants. Equation (6) is approximate, since it is derived on the basis of a nearest neighbor model. When the forces are central, Cauchy's relation $c_{44}=c_{12}$ must hold and Eq. (6) is correspondingly simplified, reducing to the equation given by Szigeti.[2]

In the case of the alkali halides, which are good ionic crystals, i.e., homopolar bonding may be neglected, it might be expected that $e^*=1$ in Eq. (4). However, it is found necessary to take $0.7<e^*<1$ in order to obtain agreement with experiment. In the case of NaCl, for instance, if e^* is set equal to the electronic charge, the lattice contribution to the dielectric constant is overestimated by a factor of two. The purpose of this paper is to present a semiclassical model which essentially removes this discrepancy.

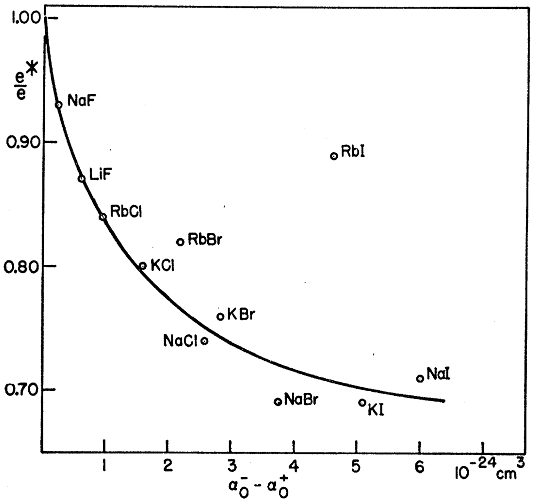

FIG. 1. The correlation between effective charge and difference in polarizabilities of the negative and positive ions.

It is known from the work of Szigeti,[3] and also that of Born and Huang,[5] that factors affecting the value of e^* are (1) overlap, (2) distortion of the ions, and (3) the noncentrality of the forces. Only the short-range forces affect e^* since the long-range interaction between the electric field and the lattice is properly taken into account by Eq. (5).

Yamashita[6] has published a quantum-mechanical theory of the effect of overlap on e^*. The results of this theory are very sensitive to the choice of wave functions and, according to Lundquist,[4] certain terms in the energy have been omitted. The latter has also derived an expression for e^* which depends on the amount of overlap and the noncentrality of the forces. His result is expressed in terms of the lattice spacing and the elastic constants c_{12} and c_{44}. We do not feel that it is clear from his work that the e^* which he discusses is the same as that used by Szigeti. It is pointed out in reference 3 that e^* depends on the geometry considered. In any case, the numerical success of his equation is only fair.

The point of view developed below is based on an empirical observation that the values of e^* satisfying Eq. (4) correlate very well with the difference between the polarizabilities of the positive and negative ions. This correlation is exhibited in Fig. 1. It suggests that the value of e^* is predominantly determined by the distortion of the ions (in excess of that produced by the electric field) arising from their displacement in the lattice due to an electric field. For example, consider a NaCl molecule in an external electric field. Each ion will be polarized by the field in its direction. However, the positive and negative ions will also move relatively closer. Their electron shells will mechanically repel one another, resulting in a relative shift of each electron

---

[2] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949); Proc. Roy. Soc. (London) **A204**, 51 (1950).

[3] Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941).

[4] S. O. Lundquist, Arkiv Fysik **9**, 435 (1955).

[5] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).

[6] J. Yamashita, Progr. Theoret. Phys. Japan **8**, 280 (1952).

cloud with respect to its nucleus. This shift corresponds to an additional polarization. In the positive ion this mechanical polarization enhances the electrical polarization, but in the negative ion it detracts. Similar effects occur in a lattice. According to our model, such mechanical polarization, which is proportional to the nuclear displacement, contributes to e^*. In the ensuing sections we shall proceed to formulate this point of view quantitatively.

MECHANICAL *VERSUS* ELECTRICAL POLARIZABILITY

We shall assume that only the outer electrons of the ions contribute to the polarization. In the alkali halides, all the ions, except lithium, have outer shells with the same electronic configuration, i.e., two s electrons and six p electrons. This configuration is nearly spherically symmetric. Now consider an electric field E_x applied to such an ion along the x axis. Then, the induced polarization p_x will be given by

$$P_x=2E_x\sum_{s,p}\sum_{k}\frac{\langle 0|ex|k\rangle\langle k|ex|0\rangle}{h\nu_{0k}},\quad (\nu_{\text{exp.}}\ll\nu_{0k}),\quad (7)$$

where $h\nu_{0k}$ is the difference in energy between the ground state and the kth excited state. $\sum_{s,p}$ indicates that we must sum over all the s and p electrons. The corresponding expression for α_E, the polarizability, may be written in analogy with the classical expression,

$$\alpha_E=\sum_{\iota}\frac{e^2}{k_\iota}=\sum_{\iota}\frac{e^2}{m\omega_\iota^2},\quad (8)$$

where k_ι is an effective spring constant of the ιth electron which is equal to the electronic mass m times the square of an optical absorption frequency ω_ι.

For our closed shell configuration, we may write approximately

$$\alpha_E\cong\frac{2e^2}{m\omega_p^2}+\frac{2e^2}{m\omega_s^2},\quad (9)$$

corresponding to the fact that we may expect the major contribution to come from the two s electrons and from two of the six p electrons. The basis for this approximation may be seen by choosing the orientation of our spherically symmetrical ion so that two of the loops of the p wave functions lie along the direction of the field. The contributions from the p functions along the y and z directions will be much less than that from the two in the direction of the field. The contributions from these electrons and the two s electrons will be comparable because the major portions of their radial distribution functions are almost congruent. If $\omega_s^2=\omega_p^2$, Eq. (9) would correspond to an effective number of electrons $Z=4$. Actually $\omega_s^2=2\omega_p^2$ and $Z=3.5$ for the Cl^- ion according to an analysis by Mayer[7] of the ultraviolet absorption spectrum of the alkali halides.

Consider now the ion entering a repulsive field of force of which the potential is V. Then this potential will perturb the wave functions of the ion and a mechanical polarization will be produced which is given by

$$P_M=2\sum_{s,p}\sum_{k}\frac{\langle 0|V|k\rangle\langle k|ex|0\rangle}{h\nu_{0k}}.\quad (10)$$

The matrix element $\langle 0|V|k\rangle$ will in general be larger than $\langle 0|ex|k\rangle$ because our potential for a repulsive force between ions will vary as a high power of x (or exponentially). Accordingly, the mechanical polarization for a given force $F=eE$ applied to an electron will in general be larger than the corresponding electrical polarization. This fact may also be seen crudely as follows. A uniform spring of weight W hanging in a vertical position extends an amount equivalent to $W/2$ applied in a concentrated form at its lower end.

For the mechanical polarizability, i.e., the polarization per unit mechanical force applied to the *ion*, we have, corresponding to Eq. (8),

$$\frac{1}{\alpha_M}=\frac{2m\omega_s^2}{4ef_s}+\frac{2m\omega_p^2}{4ef_p},\quad \alpha_M\cong\frac{2ef}{m\omega_s^2+m\omega_p^2},\quad (11)$$

where the f_ι may be taken as equal for the s and p electrons in an outer shell because their radial distribution functions are almost congruent. Equation (11) differs from Eq. (8) because it seems more reasonable to expect the s and p electrons to be displaced by the same distance in a potential varying as strongly with distance as does the repulsive force rather than assume that the force acts equally on all electrons.

If in Eq. (9) and Eq. (11) we take $\omega_s^2=\omega_p^2$, then we obtain

$$\alpha_M/\alpha_E=f/Ze\approx f/4e,\quad (12)$$

Z is the effective number of electrons contributing to the polarizability and is approximately 4. Equation (12) is not seriously affected by choosing $\omega_s^2=2\omega_p^2$. In this case the effective value of Z is 4.5 instead of 4. Because the form of Eq. (10) is determined by the fact that the parallel springs supporting the external force F all deflect the same amount in order to minimize the strain energy, a simplified model is suggested for the ion. We think of the ion as consisting of a spherical shell of effective charge $-Z$ surrounding an incompressible core of charge $+Z$. Their centers are connected by a spring of stiffness $K_E=Zm\omega^2$.

Then, the pertinent useful equations for this model are

$$\alpha_E=Z^2e^2/K_E,\quad (13)$$

$$\alpha_M=\frac{Ze}{K_M}=\frac{fZe}{K_E}=\frac{f\alpha_E}{Ze}.\quad (14)$$

---

[7] J. E. Mayer, J. Chem. Phys. 1, 270 (1933).

MECHANICAL EQUATIONS OF MOTION

We shall neglect electronic masses in comparison with nuclear masses. Consider a diatomic ionic lattice composed of ions of mass M^+ and M^-. Let $r_n^\pm$ denote the displacements of the nuclei and associated inner electronic shells. Let $r_s^\pm$ denote the displacements of the centers of the outer shells whose effective charges are Z^+ and Z^-, respectively.

In the nearest neighbor approximation for the NaCl structure, the equations of motion are

$$-M^+\omega^2 r_n^+ = -K_M^+(r_n^+ - r_s^+), \tag{15}$$

$$-m^+\omega^2 r_s^+ = K_M^+(r_n^+ - r_s^+) - 2k_{ss}(r_s^+ - r_s^-) \cong 0, \tag{16}$$

$$-m^-\omega^2 r_s^- = K_M^-(r_n^- - r_s^-) + 2k_{ss}(r_s^+ - r_s^-) \cong 0, \tag{17}$$

$$-M^-\omega^2 r_n^- = -K_M^-(r_n^- - r_s^-), \tag{18}$$

where

$$2k_{ss} = \mu\Omega_S^2, \tag{19}$$

and the condition

$$M^+r_n^+ + m^+r_s^+ + M^-r_n^- + m^-r_s^- = 0. \tag{20}$$

The solution of the foregoing equations for the resonant frequency Ω_R is

$$\frac{1}{\mu\Omega_R^2} = \frac{1}{\mu\Omega_S^2} + \frac{1}{K_M^+} + \frac{1}{K_M^-}, \tag{21}$$

where $\mu\Omega_S^2$, the spring constant in a lattice of rigid ions, is given by Eq. (6).

It is immediately apparent from Eqs. (15)–(21) that we suggest that the prominent contribution to the deviation of e^* from e is the displacement of the shell centers from the nuclei. The resulting lattice may in a first approximation still be considered composed of dipoles but with modified moments. The argument is carried through for the case of zero Lorentz field, so the Ω_R obtained for the frequency must be compared with Szigeti's Ω_S. The long-range terms are assumed to be already taken into account by using Szigeti's formulation.

EFFECTIVE IONIC CHARGE

We note that e^* in Eq. (4) is defined by Szigeti by the equation

$$\mathbf{p} = e^*(\mathbf{r}_n^+ - \mathbf{r}_n^-)/v. \tag{22}$$

In the shell model, we have

$$\mathbf{p} = e\{(\mathbf{r}_n^+ - \mathbf{r}_n^-) - Z^+(r_s^+ - r_n^+) - Z^-(r_s^- - r_n^-)\}/v. \tag{23}$$

Using the equations of motion to eliminate r_s^+ and r_s^-, we find

$$\mathbf{p} = e\left[1 + \left(\frac{Z^+}{K_M^+} - \frac{Z^-}{K_M^-}\right)\mu\Omega_R^2\right](r_n^+ - r_n^-)/v. \tag{24}$$

Comparing Eq. (24) with Eq. (22), and using Eq. (14), we have

$$e^* = e\left[1 - \left(\frac{\alpha_E^-}{Z^-} - \frac{\alpha_E^+}{Z^+}\right)\frac{f\mu\Omega_R^2}{e^2}\right]. \tag{25}$$

If we assume $Z^- = Z^+ \cong 4$, the correlation between e^*/e and $(\alpha^- - \alpha^+)$ presented in Fig. 1 is thus explained. A more detailed discussion of Eq. (25) is given below.

OPTICAL POLARIZABILITY

To obtain simply a formula for α_0 from our equations of motion, we apply a static field E and set $r_n^- = r_n^+ = 0$. Using f to take into account the difference between the effect of mechanical and electrical forces, i.e., the effective nondistributed force per charge of an electric field E is E/f, we have

$$Z^+eE = -K_E^+r_s^+ + 2k_{ss}f(r_s^- - r_s^+), \tag{26}$$

$$Z^-eE = -K_E^-r_s^- + 2k_{ss}f(r_s^+ - r_s^-). \tag{27}$$

Utilizing the fact that the induced moment $\mathbf{p}$ per unit cell is given by

$$\mathbf{p} = \mathbf{p}^+ + \mathbf{p}^- = (\alpha_0^+ + \alpha_0^-)\mathbf{E} = Z^+er_s^+ + Z^-er_s^-, \tag{28}$$

we find

$$\begin{aligned} \alpha_0^+ &= \alpha_E^+\left[1 + \frac{2k_{ss}f}{K_E^-}\frac{Z^-}{Z_R}\right]\Big/\left[1 + \frac{2k_{ss}f}{K_R}\right], \\ \alpha_0^- &= \alpha_E^-\left[1 + \frac{2k_{ss}f}{K_E^+}\frac{Z^+}{Z_R}\right]\Big/\left[1 + \frac{2k_{ss}f}{K_R}\right], \end{aligned} \tag{29}$$

where

$$1/K_R = 1/K_E^+ + 1/K_E^-, \tag{30}$$

and

$$1/Z_R = 1/Z^+ + 1/Z^-. \tag{31}$$

If, in Eq. (29), we assume $Z = Z^+ = Z^-$, then to a first approximation we have

$$\begin{aligned} \alpha_E^+ &= \alpha_0^+[1 - \mu\Omega_R^2 f(\alpha_E^- - \alpha_E^+)/Z^2e^2], \\ \alpha_E^- &= \alpha^{0-}[1 + \mu\Omega_R^2 f(\alpha_E^- - \alpha_E^+)/Z^2e^2], \end{aligned} \tag{32}$$

where α_0^+ and α_0^- have been estimated by Tessman *et al.*[8] by a least-squares fit to the observed indices of refraction.

We note that Eq. (32) may be rewritten as

$$\begin{aligned} \alpha_E^+ &= \alpha_0^+\left[1 - \frac{1}{Z}\left(1 - \frac{e^*}{e}\right)\right], \\ \alpha_E^- &= \alpha_0^-\left[1 + \frac{1}{Z}\left(1 - \frac{e^*}{e}\right)\right]. \end{aligned} \tag{33}$$

Knowing α_0 and e^* for a crystal, we may now determine $\alpha_E^\pm$ by an iterative procedure. Starting with LiF, where the polarizability of the Li^+ ion may be taken as equal to its free ion value[9] of 0.03×10^{-24} cm^3,

---

[8] Tessman, Kahn, and Shockley, Phys. Rev. **92**, 890 (1953).

[9] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

TABLE I. Polarizabilities in units of 10^{-24} cm^3.

	$\alpha_E^{\pm}$ [$Z=4$. Eqs. (2) and (33) iterated.]	$\alpha_0^{\pm}$	$\alpha_0^{\pm}$ Tessman *et al.*[a]
Li^+	(0.03)	(0.03)	0.03
Na^+	0.27	0.28	0.26
K^+	1.09	1.16	1.20
Rb^+	1.62	1.69	1.80
F^-	0.90	0.88	0.76
Cl^-	3.15	3.00	2.97
Br^-	4.42	4.11	4.13
I^-	6.55	6.09	6.20

[a] See reference 8.

we estimate α_E^- for the F^- ion. This value is now used in conjunction with the observations on NaF to determine α_E^+ for Na^+ ion and so on. In this manner, the values of $\alpha_E^{\pm}$ for all the ions may be calculated. In certain cases, the calculation is redundant and several values are obtained independently for certain ions, e.g., 4.41 and 4.43 for Br^-, 6.40 and 6.70 for I^-, and 1.62 twice for Rb^+, all in units of 10^{-24} cm^3. Average values of $\alpha_E^{\pm}$ and $\alpha_0^{\pm}$ are given in Table I where the values for $\alpha_0^{\pm}$ estimated by Tessman *et al.* are also given for comparison. The agreement is good although we should emphasize that from the point of view presented here $\alpha_E^{\pm}$ should be approximately constant in going from compound to compound and not $\alpha_0^{\pm}$ as assumed by Tessman, Kahn, and Shockley. Strictly $\alpha_E^{\pm}$ must vary somewhat from compound to compound because the environment of the ion is varied.[9]

ESTIMATE OF e^*

Using the values of $\alpha_E^{\pm}$ given in Table I and the experimental values of $\mu\Omega_R^2$, we may now proceed to calculate e^* from Eq. (24). Such a procedure is open to objection, however, since $\alpha_E^{\pm}$ has been calculated using the experimental values of e^* to avoid the necessity of estimating f.

We note that Eq. (33) may be recast as follows:

$$(\alpha_E^- - \alpha_E^+) = (\alpha_0^- - \alpha_0^+)\left[1+\frac{1}{Z}\left(1-\frac{e^*}{e}\right)\right]. \quad (34)$$

TABLE II. Calculated and observed values of $1-e^*/e$.

	$10^{-23}\times(\mu\Omega_R^2/e^2)$	$\alpha_0^+ + \alpha_0^-$ (10^{-24} cm^3)	$(1-e^*/e)_{\mathrm{calc}}$[a]	$(1-e^*/e)_{\mathrm{calc}}$[b]	$(1-e^*/e)_{\mathrm{obs}}$[c]
LiF	3.50	0.91	0.13	0.15	0.13
NaF	3.44	1.16	0.09	0.11	0.07
NaCl	1.71	3.26	(0.26)	(0.26)	0.26
NaBr	1.35	4.39	0.30	0.29	0.31
NaI	1.14	6.26	0.39	0.37	0.29
KCl	1.54	4.17	0.15	0.17	0.20
KBr	1.36	5.29	0.23	0.24	0.24
KI	1.09	7.39	0.31	0.31	0.31
RbCl	1.45	4.71	0.09	0.12	0.16
RbBr	1.34	5.92	0.17	0.20	0.18

[a] $Z=4$, $f/Z=0.53$, α_0.
[b] $Z=4$, $f/Z=0.53$, α_E.
[c] From data quoted by B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

Inserting Eq. (34) in Eq. (25), we obtain after rearranging

$$\left(1-\frac{e^*}{e}\right)=\frac{f\mu\Omega_R^2[\alpha_0^- - \alpha_0^+]/Ze^2}{1-f\mu\Omega_R^2[\alpha_0^- - \alpha_0^+]/Z^2e^2}. \quad (35)$$

If f and Z are known e^* may be calculated from this equation using the independent values of α_0^- and α_0^+ estimated in reference 8. As before, we take $Z=4$. The value of f is then determined by forcing Eq. (35) to give the correct value of e^* for one salt, say NaCl. The calculated value of e^* for the other salts should then agree with the observed values. The agreement is shown in Fig. 2 and must be considered very good in view of all the approximations introduced. The agreement is better for KCl and RbCl if the interated values of $\alpha_E^{\pm}$ are used but worse for the fluorides. The values of $1-e^*$ obtained by both methods are given in Table II. The relatively large errors in $1-e^*$ do not lead to such large errors in the dielectric constant ϵ which is tabulated in Table III. Repeated reiteration of e^* would lead to a better distribution of the error but has not been carried out because the errors in the basic data are not uniformly distributed. It will be noted that the two sources of experimental data on the dielectric constant differ more from each other on the average than either differs from the calculated values, excepting NaI. The better agreement of the calculated values with the set "obs I" is due to the fact that f was fixed by the value of ϵ for NaCl given in that set.

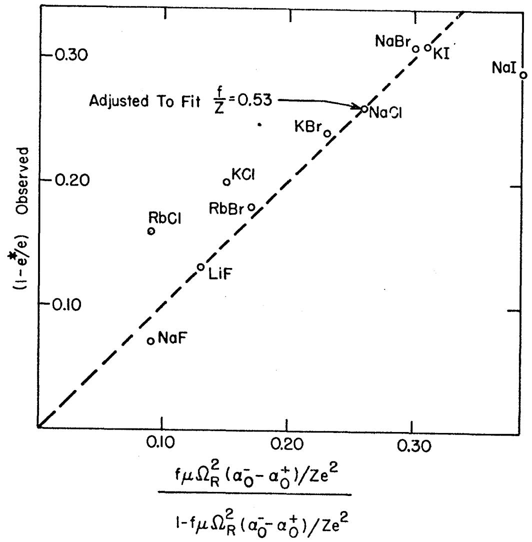

FIG. 2. The calculated and observed values of effective charge. For the calculation, Eq. (35) is used with $Z=4$, $\alpha_0^{\pm}$ is taken from reference 8, and f is determined by fitting one salt, NaCl, to the theoretical slope.

RESTSRAHL FREQUENCY AND THE ELASTIC CONSTANTS

Because of the coupling between the electronic frequencies and the lattice frequency, Ω_R does not depend solely on the properties of the lattice as does Ω_S but also on the polarizabilities in a way determined by Eq. (21). In this model we must replace Ω_S in Eq. (5) by Ω_R, substituting for Ω_S in Eq. (21) its value from Eq. (6). In this way we obtain to a first approximation an equation for Ω_t, in a NaCl structure, namely

$$\mu\Omega_t^2=\frac{n^2+2}{\epsilon+2}\left[\frac{6a(\beta+c_{44}-c_{12})}{1+6a(\beta+c_{44}-c_{12})f(\alpha_E^{+}+\alpha_E^{-})/Z^2e^2}\right]. \quad (36)$$

A convenient way to compare this formula with experiment is to compute the compressibility χ in terms of $\mu\Omega_t^2$, etc. and compare χ with the observed value. Following this procedure, we find

$$\chi=6a[1+R-S]/\mu\Omega_R^2, \quad (37)$$

where

$$R=(c_{44}-c_{12})\chi, \quad (38)$$

and

$$S=f\mu\Omega_R^2(\alpha_E^{+}+\alpha_E^{-})/Z^2e^2. \quad (39)$$

The quantities $6a/\mu\Omega_R^2$, R, S, and χ_{obs} are given in Table IV. The agreement is not altogether satisfactory. We believe that the discrepancies arise from (1) inaccuracies in the measurement of $c_{44}-c_{12}$, (2) the fact that Lundquist's theory is only applicable at 0°K, and (3) the neglect of other than nearest neighbor interactions in the derivation of Eq. (6). The term R arises from the failure of Cauchy's relation in the lattice, i.e., the noncentral interactions. Herpin[10] has shown that dipole coupling terms in a simple cubic lattice do not contribute to the elastic constants but that the quantity $c_{12}-c_{44}$ determined by the quadrupole coupling is of the same order of magnitude as terms involving $\alpha^{\pm}$ squared neglected above. For this reason alone, Eq. (37) must be regarded as a very crude approximation.

It is perhaps appropriate to remark here that one should be able to compute both the temperature and pressure coefficients of ϵ from Eq. (4), Eq. (37), and experimental data. If one assumes that $de^*/dP=de^*/dT=0$, the agreement is quite satisfactory. An attempt to show that these conditions are approximately satisfied proved futile because of the uncertainties in the temperature and pressure variation of $c_{44}-c_{12}$. The data suggest, however, that in Eq. (37) R should be replaced by R' where

$$R'=(c_{44}-c_{12}+2P)\chi, \quad (40)$$

where P is hydrostatic pressure, in accordance with the generalized Cauchy relation given by Love.[11] No proof of Eq. (40) is given.

TABLE III. Calculated and observed values of static dielectric constant.

	Obs. I[a]	Obs. II[b]	Calc.
LiF	9.27	8.90	9.3
NaF	6.0	5.10	5.8
NaCl	5.62	5.87	(5.6)
NaBr	5.99	6.38	6.1
NaI	6.60	7.26	5.6
KCl	4.68	4.85	5.0
KBr	4.78	4.89	4.8
KI	4.94	5.09	4.9
RbCl	5	4.92	5.6
RbBr	5	4.87	5.0

[a] Obs. I: quoted by B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).
[b] Obs. II: S. Haussühl, Z. Naturforsch. **12A**, 445 (1957).

INFRARED SPECTRA

In an analysis of the infrared spectra of alkali halides, Rice and Klemperer[12] have shown that the dipole moments of the molecules cannot be explained by using Pauling's free ion polarizabilities.[4] To get the observed moments, they used Pauling's positive ion polarizabilities and arbitrarily adjusted α^- to satisfy the relation

$$d=ea-(\mu^{+}+\mu^{-}), \quad (41)$$

where d is the net dipole moment, a is the nuclear spacing, and μ^+ and μ^- are the electronic moments whose sum is given by

$$\mu^{+}+\mu^{-}=\frac{(\alpha^{-}+\alpha^{+})a^4e+4\alpha^{-}\alpha^{+}ea}{a^6-4\alpha^{-}\alpha^{+}}. \quad (42)$$

The individual electronic moments of the ions are determined by solving simultaneously the equations

$$\begin{aligned}\mu^{+}&=\alpha^{+}e/a^2+2\alpha^{+}\mu^{-}/a^3,\\ \mu^{-}&=\alpha^{-}e/a^2+2\alpha^{-}\mu^{+}/a^3.\end{aligned} \quad (43)$$

TABLE IV. Comparison of observed and calculated compressibilities in 10^{-6} cm²/kg.

	$6a/\mu\Omega_R^2$	R[a]	S	Calc. χ	Obs. χ
LiF	1.5	0.26	+0.04	1.8	1.5
NaF	1.72	0.18	0.05	1.95	2.07
NaCl	4.14	0.04	0.07	4.01	4.18
NaBr	5.56	−0.01	0.08	5.06	4.98
NaI	7.28	−0.03	0.09	6.40	6.94
KCl	5.12	+0.02	0.08	4.81	5.33
KBr	6.22	+0.01	0.09	5.72	6.56
KI	8.27	−0.01	0.11	7.29	8.37
RbCl	5.80	−0.02	0.09	5.16	6.52
RbBr	6.47	−0.01	0.10	5.76	7.78

[a] Adiabatic elastic constants from S. Haussühl, Z. Krist. **110**, 67 (1958). These values have been converted to isothermal values to obtain R.

---

[10] A. Herpin, J. phys. radium **14**, 611 (1953).

[11] A. E. H. Love, *Mathematical Theory of Elasticity* (Cambridge University Press, Cambridge, 1934), p. 620.

[12] S. A. Rice and W. Klemperer, J. Chem. Phys. **27**, 573 (1957).

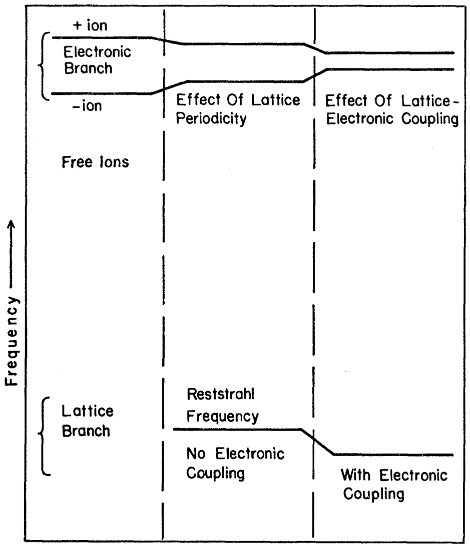

FIG. 3. Schematic level diagram.

We suggest that both the positive and negative ions are affected by the mechanically induced moments of the repulsive force R acting between the two ions in the molecule. Accordingly, we propose to replace Eq. (43) by the set

$$\begin{aligned}\mu^+&=\alpha_p{}^+e/a^2+2\alpha_p{}^+\mu^-/a^3+\gamma\alpha_p{}^+R/e,\\ \mu^-&=\alpha_p{}^-e/a^2+2\alpha_p{}^-\mu^+/a^3-\gamma\alpha_p{}^-R/e.\end{aligned}\tag{44}$$

In the foregoing pair of equations, the subscript p on α designates the use of the free-ion polarizabilities. The repulsive force is given by

$$R=e^2/a^2+2e(\mu^++\mu^-)/a^3+6\mu^-\mu^+/a^4.\tag{45}$$

The quantity γ is equal to f'/Z', where primes have been used to distinguish the quantities for the molecular values from the unprimed quantities used in the lattice case.

In zero-order approximation, we find

$$\mu^++\mu^-=[(\alpha_p{}^++\alpha_p{}^-)-\gamma(\alpha_p{}^--\alpha_p{}^+)]e/a^2.\tag{46}$$

Physically, the repulsive force increases the effective α^+ and decreases α^-.

By using Eq. (44) in conjunction with Eq. (45), we may estimate the values of γ which give agreement with observed nuclear spacings and dipole moments. The results are given in Table V. In general, the value of γ tends to be lower than that found for the lattice case. The lower values of γ can be caused by lower values of f' and higher values of Z'. We believe that both factors play a role. Since the electric field is nonuniform, we believe f' tends to be less than f. The closer distance of approach in molecular cases tends to make Z' greater than Z. A good deal of the scatter, we believe, arises from experimental error and the use of free-ion polarizabilities for the ions in the molecule. The most rewarding result of the calculation is the fact that CsF has a value of γ consistent with those for the other molecules even though this molecule has a positive-ion polarizability greater than the negative-ion polarizability, which causes the sign of the correction term to change.

TABLE V. Values of γ for alkali halide molecules from Eqs. (44) and (45). Experimental data from Rice and Klemperer.[a]

	a(A)	$\alpha_p{}^+(A^3)$	$\alpha_p{}^-(A^3)$	μ (Debye units)	γ
CsF[b]	2.43	2.95	1.04	(7.61)	0.25
NaCl	2.361	0.18	3.66	8.5	0.15
KCl	2.667	0.83	3.66	10.48	0.42
CsCl	2.906	2.95	3.66	10.40	0.35
LiBr	2.17	0.03	4.77	6.19	0.08
KBr	2.821	0.83	4.77	10.41	0.20
LiI	2.39	0.03	7.20	6.64	0.11

[a] See reference 12.
[b] The value of γ for CsF was computed from $d\mu/dr=7.77$ Debye units/A. The value computed from μ is 0.46.

SUMMARY

In a crystal lattice, the electron cloud of an ion is distorted by its neighbors. In a NaCl-type lattice, this distortion produces no net electric moment when the ion is in its equilibrium position. However, when an ion is not on an equilibrium position, a polarization proportional to the restoring force is produced. If the displacement of the ions is produced by an electric field, the distortion moment in the positive ion produced by the neighbors adds to the moment induced by the field; in the negative ion it subtracts. Because, in most ionic crystals with a NaCl structure, the negative ion is more easily distorted than the positive ion, the net distortion moment per unit cell tends to decrease the polarization in the crystal, leading to an "effective" ionic charge less than unity. The qualitative energy level scheme is given in Fig. 3. On condensing into a lattice, the frequencies of the negative ion are pushed up and those of the positive ion only slightly affected.[9] The coupling between the lattice and electronic modes due to the shell-shell repulsions considered here cause the "frequency" of the positive ion to decrease, of the negative ion to increase, and of the restrahl vibration to decrease.

A similar effect appears to take place in ionic molecules.

ACKNOWLEDGMENTS

The authors are indebted to the Office of Naval Research and the industrial sponsors of the Institute for the Study of Metals for financial support of this investigation.*

---

* *Note added in proof.*—Since this article was submitted for publication, a paper on the same subject by B. J. Dick, Jr., and A. W. Overhauser has appeared [Phys. Rev. **112**, 90 (1958)]. Although the two approaches are similar, the models treated are not the same and, consequently, the conclusions are somewhat different.