

Pockels Effect in Zinc-Blende-Structure Ionic Crystals*

ROBERT L. KELLY

Research Laboratories, General Motors Corporation, Warren, Michigan†

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When a static electric field is applied to a crystal there are changes in its optical properties. The Pockels effect is a change in the optical dielectric tensor which is proportional to the applied field strength. By generalizing Huang's theory of the linear dielectric properties of an ionic crystal, we have obtained a non-linear equation for the polarization of a zinc-blende-type ionic crystal. This equation has been used to obtain an expression for the electro-optic coefficient. The calculated values of the electro-optic coefficient for ZnS and CuCl agree satisfactorily with the experimentally determined values.

I. INTRODUCTION

THE electro-optic effect may be regarded as a change in the optical dielectric tensor of a crystal upon the application of a static electric field. When this change is linear in the applied field strength it is called the linear electro-optic or Pockels effect. Ionic crystals of the zinc-blende structure are perhaps the simplest crystals which exhibit the Pockels effect. The linear dielectric properties of these crystals are described by Huang's¹ well-known macroscopic equations [Eqs. (1) and (2)]. In the following section we will discuss Huang's equations and their relation to his microscopic model of an ionic lattice. In Sec. III we derive a non-linear polarization equation for a zinc-blende-type crystal using techniques similar to Huang's. This equation is then used to obtain an expression for the electro-optic coefficient. Actually, several expressions are obtained on the basis of several slightly different models. Our theoretical results are compared with experiment in Sec. IV.

II. THE HUANG MODEL

Huang¹ has shown that the macroscopic equation of motion and the macroscopic polarization equation for the long-wavelength optical vibrations of a diatomic ionic lattice with tetrahedral symmetry have the following general form:

$$\frac{d^2\mathbf{w}}{dt^2} = b_{11}\mathbf{w} + b_{12}\mathbf{E}, \quad (1)$$

$$\mathbf{P} = b_{21}\mathbf{w} + b_{22}\mathbf{E}, \quad (2)$$

where

$$b_{12} = b_{21}, \quad (3)$$

and

$$\mathbf{w} = (\bar{M}/v)^{1/2}(\mathbf{u}^+ - \mathbf{u}^-). \quad (4)$$

In Eqs. (1) and (2) \mathbf{E} and \mathbf{P} are the local macroscopic

electric field and the local macroscopic polarization within the crystal. In Eq. (4) \bar{M} is the reduced mass of the two kinds of ions in the crystal, v is the volume per ion pair, and \mathbf{u}^+ (\mathbf{u}^-) is the displacement of the positively (negatively) charged sublattice from its equilibrium position. Huang² has also carried out a simultaneous solution of Eqs. (1) and (2) and Maxwell's equations. This solution shows that the coefficients of Eqs. (1) and (2) are related to the infrared dispersion frequency ω_0 , the low-frequency ($\omega \ll \omega_0$) dielectric constant ϵ_0 , and the high-frequency ($\omega \gg \omega_0$) dielectric constant ϵ_∞ in the following way:

$$b_{11} = -\omega_0^2, \quad (5)$$

$$b_{12} = b_{21} = [(\epsilon_0 - \epsilon_\infty)/4\pi]^{1/2}\omega_0, \quad (6)$$

$$b_{22} = (\epsilon_\infty - 1)/4\pi. \quad (7)$$

A basic limitation on Eqs. (1) and (2) is that they are only valid for frequencies well below the lowest electronic transition frequency in the crystal. Thus the dielectric constant is ϵ_∞ only for frequencies in the range $\omega_0 \ll \omega \ll E_g/\hbar$ where E_g is the energy gap.

Equations (1)–(7) are macroscopic equations, and their validity is not dependent on the validity of any specific microscopic model. However, Huang¹ has also derived Eqs. (1) and (2) on the basis of a specific microscopic model for an ionic lattice. This derivation yields expressions for the coefficients of Eqs. (1) and (2) in terms of the parameters of the model, and thus implies certain relations between the macroscopic quantities ω_0 , ϵ_0 , and ϵ_∞ and the model parameters. We will follow a quite similar procedure in Sec. III of this paper, but the specific macroscopic quantity of interest here is the electro-optic coefficient. In order to establish our notation and to set the context for Sec. III we will now review Huang's derivation of the polarization equation [Eq. (2)] from his microscopic model. The model used is an array of interacting atomic ions. Each ion may be displaced and polarized by the others, but they all retain their individuality. We are only concerned with those optical vibrations whose wavelength is much larger than the lattice constant so, from a microscopic point of view, we may regard all the

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† Present address: Department of Physics, University of California, Berkeley, California.

¹ K. Huang, Report L/T239 of The British Electrical and Allied Industries Research Association, 1950 (unpublished). The material in this report is also contained in Ref. 3 which is more accessible.

² K. Huang, Proc. Roy. Soc. (London) A208, 352 (1951).

positive ions as having the same displacement and dipole moment and similarly for the negative ions. For convenience we will choose a coordinate system whose origin lies at the lattice site of a positive ion and discuss the polarization of the positive sublattice in terms of this particular ion. A similar procedure may then be carried out for the negative sublattice.

The dipole moment of the positive ion at the origin, \mathbf{p}^+ , will consist of a part $q\mathbf{u}^+$ due to displacement of its charge q , and a part \mathbf{p}_{el}^+ due to electronic polarization. The electronic polarization arises as a response to the electric field acting on the ion, the so-called effective field. This field may be conveniently separated into a long-range part and a short-range part. The net long-range field acting on any ion in the crystal is $\mathbf{E} + (4\pi/3)\mathbf{P}$.³ The short-range part of the effective field arises from ions in the immediate vicinity of the origin, and it is to be expected that this field will not be uniform over the volume of the ion at the origin. Huang uses a uniform-field approximation in which the actual short-range field is replaced by its value at the origin. It is shown in Sec. III that the same results may be obtained by evaluating the effective field at any point within a small neighborhood of the origin. With this approximation we can now write the dipole moment of a positive ion as

$$\mathbf{p}^+ = q\mathbf{u}^+ + \mathbf{p}_{el}^+, \quad (8)$$

$$\mathbf{p}_{el}^+ = \alpha^+ \mathbf{E}_{eff}^+, \quad (9)$$

$$\mathbf{E}_{eff}^+ = \mathbf{E} + (4\pi/3)\mathbf{P} + \mathbf{E}_{sr}^+, \quad (10)$$

$$\mathbf{E}_{sr}^+ = \sum_{l \neq 0} \mathbf{E}_l(0), \quad (11)$$

where α^+ is the polarizability of a positive ion, \mathbf{E}_{eff}^+ is the effective field acting on a positive ion, \mathbf{E}_{sr}^+ is the short-range part of \mathbf{E}_{eff}^+ , and $\mathbf{E}_l(0)$ is the field of the l th ion evaluated at the origin.

We wish to evaluate the total polarization, $\mathbf{P} = (\mathbf{p}^+ + \mathbf{p}^-)/v$, only through terms linear in \mathbf{w} and \mathbf{E} [as in Eq. (2)]. Thus we may evaluate \mathbf{E}_{sr}^+ by a multipole expansion of $\mathbf{E}_l(0)$ in which only the monopole and dipole terms are retained. In this approximation \mathbf{E}_{sr}^+ vanishes identically in a lattice of tetrahedral symmetry.^{3,4} \mathbf{E}_{sr}^- is defined in a completely analogous way, and it also vanishes. Thus the total polarization becomes,

$$\mathbf{P} = \frac{1}{v} \left\{ q(\mathbf{u}^+ - \mathbf{u}^-) + (\alpha^+ + \alpha^-) \left(\mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right) \right\}. \quad (12)$$

³ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).

⁴ The individual terms in \mathbf{E}_{sr}^+ do not decrease rapidly with increasing distance from the origin, in fact $\sum_{l \neq 0} |\mathbf{E}_l(0)|$ diverges. However, it is not really a misnomer to call \mathbf{E}_{sr}^+ short range because the nonvanishing quadrupole part of the sum does converge absolutely. Equation (17) shows that the nonvanishing part of \mathbf{E}_{sr}^+ converges more rapidly than $\int d\mathbf{r} r^{-2}$ at large distances.

Comparing Eqs. (2) and (12) one obtains

$$b_{21} = \frac{q}{(\bar{M}v)^{1/2}} \left(1 - \frac{4\pi}{3} \frac{\alpha^+ + \alpha^-}{v} \right)^{-1}, \quad (13)$$

$$b_{22} = \left(\frac{\alpha^+ + \alpha^-}{v} \right) \left(1 - \frac{4\pi}{3} \frac{\alpha^+ + \alpha^-}{v} \right)^{-1}. \quad (14)$$

Combining Eqs. (7) and (14) one obtains the Clausius-Mossotti relation

$$\alpha^+ + \alpha^- = \frac{3}{4\pi} \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right) v. \quad (15)$$

Combining Eqs. (6), (13), and (15) one obtains the Szigeti⁵ relation

$$q = (\bar{M}v)^{1/2} \omega_0 \left(\frac{3}{\epsilon_\infty + 2} \right) \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2}. \quad (16)$$

III. THE ELECTRO-OPTIC COEFFICIENT

In this section we will derive nonlinear polarization equations using straightforward extensions of Huang's techniques, and then use these equations to obtain expressions for the electro-optic coefficient. It is well known that Eqs. (15) and (16) are not satisfied experimentally if q , α^+ , and α^- are interpreted as the free ionic charge and free ionic polarizabilities. All questions concerning the origin of these discrepancies will be sidestepped here by using a phenomenological model in which Eqs. (15) and (16) are taken to be the defining equations of $\alpha^+ + \alpha^-$ and q . In order to obtain a nonlinear polarization equation we will retain quadrupole terms in the multipole expansion of $\mathbf{E}_l(0)$. This gives

$$\mathbf{E}_{sr}^+ = \frac{1}{2} \sum_{l \neq 0} \mathbf{Q}_l : \left(9\mathbf{I} \frac{\mathbf{R}_l}{R_l^5} - 15 \frac{\mathbf{R}_l \mathbf{R}_l \mathbf{R}_l}{R_l^7} \right), \quad (17)$$

where \mathbf{I} is the unit dyadic, \mathbf{R}_l is the lattice vector of the l th ion, and \mathbf{Q}_l is the quadrupole tensor of the l th ion (\mathbf{Q}^+ or \mathbf{Q}^-).

$$\mathbf{Q}_l = \int d^3r \rho_l(\mathbf{r}) (\mathbf{r} - \mathbf{R}_l) (\mathbf{r} - \mathbf{R}_l), \quad (18)$$

where $\rho_l(\mathbf{r})$ is the charge density of the l th ion. The double dot product of two dyads is defined to be

$$\mathbf{ab} : \mathbf{cd} = (\mathbf{a} \cdot \mathbf{d})(\mathbf{b} \cdot \mathbf{c}). \quad (19)$$

In order to carry out the sum in (17) we will introduce a specific coordinate system. The zinc-blende lattice consists of two interpenetrating fcc lattices. The origin is chosen to lie at a positive ion site; three more positive ions in the unit cube of the positive fcc sublattice lie at $(a, 0, 0)$, $(0, a, 0)$, and $(0, 0, a)$ where a is the lattice

⁵ B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1949).

TABLE I. Calculated values of $a_{\mathcal{R}}$.

| $\frac{R_1}{a}$ | $\frac{R_2}{a}$ | $\frac{R_3}{a}$ | $\frac{R}{a}$ | $a_{\mathcal{R}}$ |
|-----------------|-----------------|-----------------|---------------|-------------------|
| 1/4 | 1/4 | 1/4 | 0.43 | 328.4482 |
| 1/4 | 1/4 | -3/4 | 0.83 | -31.3155 |
| 1/4 | 3/4 | 3/4 | 1.09 | 13.8713 |
| 1/4 | 1/4 | 5/4 | 1.30 | 2.2527 |
| 3/4 | 3/4 | -3/4 | 1.30 | -4.0549 |
| 1/4 | 3/4 | -5/4 | 1.48 | -2.7250 |
| 1/4 | 5/4 | -3/4 | 1.48 | -2.7250 |
| 3/4 | 3/4 | 5/4 | 1.64 | 3.9773 |
| 1/4 | 1/4 | -7/4 | 1.79 | -0.3405 |
| 1/4 | 5/4 | 5/4 | 1.79 | 1.2161 |
| 1/4 | 3/4 | 7/4 | 1.92 | 0.6134 |
| 1/4 | 7/4 | 3/4 | 1.92 | 0.6134 |
| 3/4 | 5/4 | -5/4 | 1.92 | -2.1907 |
| 3/4 | 3/4 | -7/4 | 2.05 | -1.1792 |
| 1/4 | 5/4 | -7/4 | 2.17 | -0.4414 |
| 1/4 | 7/4 | -5/4 | 2.17 | -0.4414 |
| 5/4 | 5/4 | 5/4 | 2.17 | 0.1051 |

constant. The negative fcc sublattice is displaced from the positive one by an amount $(a/4, a/4, a/4)$. For our purposes we may specify the symmetry properties of the zinc-blende lattice as follows³: If there is an ion at lattice site (R_1, R_2, R_3) there will be identical ions at $(R_1, -R_2, -R_3)$, $(-R_1, R_2, -R_3)$, $(-R_1, -R_2, R_3)$ and at eight more sites obtained from these four by cyclic permutation of the indices. We denote such a set of ions by \mathcal{R} . If (R_1, R_2, R_3) is invariant under some of the operations of the tetrahedral point group there will be less than twelve ions in \mathcal{R} , e.g., there are only four nearest neighbors. We let $n_{\mathcal{R}}$ be the number of ions in \mathcal{R} .

Using these definitions we can easily carry out the sum in Eq. (17). The term involving \mathbf{I} has the same geometrical structure as the monopole field and therefore vanishes. Summing the other term over a particular set \mathcal{R} one obtains

$$\sum_{\mathbf{R} \text{ in } \mathcal{R}} \frac{\mathbf{R}\mathbf{R}\mathbf{R}}{R^3} = \frac{n_{\mathcal{R}}}{R^3} \mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 \boldsymbol{\beta}, \quad (20)$$

where $\boldsymbol{\beta}$ is a third-rank dyadic given by

$$\boldsymbol{\beta} = \hat{x}\hat{y}\hat{z} + \hat{x}\hat{z}\hat{y} + \hat{y}\hat{x}\hat{z} + \hat{y}\hat{z}\hat{x} + \hat{z}\hat{x}\hat{y} + \hat{z}\hat{y}\hat{x}. \quad (21)$$

In the positive fcc sublattice there will be, for every set \mathcal{R} , a set $-\mathcal{R}$ generated from $(-R_1, -R_2, -R_3)$. The contributions of \mathcal{R} and $-\mathcal{R}$ to (17) will cancel, so only negative ions contribute to \mathbf{E}_{sr}^+ . Summing (20) over sets \mathcal{R} of negative ions we finally obtain

$$\mathbf{E}_{\text{sr}}^+ = -\frac{1}{2}(A/a^4)\mathbf{Q}^- : \boldsymbol{\beta}, \quad (22)$$

where

$$A = 15a^4 \sum_{\mathcal{R}} \frac{n_{\mathcal{R}}}{R^3} \mathbf{R}_1 \mathbf{R}_2 \mathbf{R}_3 = \sum_{\mathcal{R}} a_{\mathcal{R}} \quad (23)$$

and $\sum_{\mathcal{R}^-}$ means a sum over sets of negative ions only. Similarly,

$$\mathbf{E}_{\text{sr}}^- = \frac{1}{2}(A/a^4)\mathbf{Q}^+ : \boldsymbol{\beta}. \quad (24)$$

The sum in (23) has been carried out through tenth nearest negative neighbors with the result

$$A \approx 306. \quad (25)$$

The calculated values of $a_{\mathcal{R}}$ are given in Table I. No estimate of the truncation error has been made, but it is probably not appreciable.

In order to obtain a macroscopic polarization equation we must be able to write \mathbf{E}_{sr}^+ and \mathbf{E}_{sr}^- in terms of \mathbf{w} and \mathbf{E} . For definiteness let us again consider the positive ion at the origin and evaluate this ion's quadrupole tensor. From (18) we have

$$\begin{aligned} \mathbf{Q}^+ &= \int d^3r \rho_0(\mathbf{r}) [\mathbf{u}^+ + (\mathbf{r} - \mathbf{u}^+)] [\mathbf{u}^+ + (\mathbf{r} - \mathbf{u}^+)] \\ &= \int d^3r \rho_0(\mathbf{r}) [\mathbf{u}^+ \mathbf{u}^+ + \mathbf{u}^+ (\mathbf{r} - \mathbf{u}^+) + (\mathbf{r} - \mathbf{u}^+) \mathbf{u}^+ \\ &\quad + (\mathbf{r} - \mathbf{u}^+) (\mathbf{r} - \mathbf{u}^+)] \\ &= q\mathbf{u}^+ \mathbf{u}^+ + \mathbf{u}^+ \mathbf{p}_{\text{el}}^+ + \mathbf{p}_{\text{el}}^+ \mathbf{u}^+ + \mathbf{Q}_{\text{el}}^+, \end{aligned} \quad (26)$$

where \mathbf{Q}_{el}^+ is the electronic quadrupole tensor. Similarly,

$$\mathbf{Q}^- = -q\mathbf{u}^- \mathbf{u}^- + \mathbf{u}^- \mathbf{p}_{\text{el}}^- + \mathbf{p}_{\text{el}}^- \mathbf{u}^- + \mathbf{Q}_{\text{el}}^-. \quad (27)$$

In order to include the electronic quadrupoles it is necessary to introduce new phenomenological parameters into our equations. This will be done presently, but for the time being the electronic quadrupoles will be neglected. The electronic dipoles in (26) and (27) need only be evaluated to first order in \mathbf{w} and \mathbf{E} ,

$$\mathbf{p}_{\text{el}}^+ = \alpha^+ \left(\mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right) = \alpha^+ \left(1 + \frac{4\pi}{3} b_{22} \right) \mathbf{E} + \frac{4\pi}{3} \alpha^+ b_{21} \mathbf{w}, \quad (28)$$

$$\mathbf{p}_{\text{el}}^- = \alpha^- \left(1 + \frac{4\pi}{3} b_{22} \right) \mathbf{E} + \frac{4\pi}{3} \alpha^- b_{21} \mathbf{w}. \quad (29)$$

Finally, \mathbf{u}^+ and \mathbf{u}^- may be expressed in terms of \mathbf{w} by using Eq. (4) and imposing the condition that the center of mass of the crystal is at rest,

$$M^+ \mathbf{u}^+ + M^- \mathbf{u}^- = 0. \quad (30)$$

Collecting these results, Eqs. (22) and (24) may be written as

$$\begin{aligned} \mathbf{E}_{\text{sr}}^+ &= \frac{A}{a^4} \left\{ \left(\frac{q\bar{M}v}{2(M^-)^2} + \frac{4\pi b_{21} \alpha^- (\bar{M}v)^{1/2}}{3M^-} \right) \mathbf{w}\mathbf{w} \right. \\ &\quad \left. + \frac{\alpha^- (\bar{M}v)^{1/2}}{M^-} \left(1 + \frac{4\pi b_{22}}{3} \right) \mathbf{w}\mathbf{E} \right\} : \boldsymbol{\beta}, \end{aligned} \quad (31)$$

$$\begin{aligned} \mathbf{E}_{\text{sr}}^- &= \frac{A}{a^4} \left\{ \left(\frac{q\bar{M}v}{2(M^+)^2} + \frac{4\pi b_{21} \alpha^+ (\bar{M}v)^{1/2}}{3M^+} \right) \mathbf{w}\mathbf{w} \right. \\ &\quad \left. + \frac{\alpha^+ (\bar{M}v)^{1/2}}{M^+} \left(1 + \frac{4\pi b_{22}}{3} \right) \mathbf{w}\mathbf{E} \right\} : \boldsymbol{\beta}. \end{aligned} \quad (32)$$

The polarization may now be expressed as

$$\begin{aligned} \mathbf{P} &= \frac{1}{v} \left\{ q(\mathbf{u}^+ - \mathbf{u}^-) + (\alpha^+ + \alpha^-) \left(\mathbf{E} + \frac{4\pi}{3} \mathbf{P} \right) \right. \\ &\quad \left. + \alpha^+ \mathbf{E}_{\text{sr}}^+ + \alpha^- \mathbf{E}_{\text{sr}}^- \right\} \\ &= b_{21} \mathbf{w} + b_{22} \mathbf{E} + \frac{1}{v} \left(1 - \frac{4\pi}{3} \frac{\alpha^+ + \alpha^-}{v} \right)^{-1} \\ &\quad \times (\alpha^+ \mathbf{E}_{\text{sr}}^+ + \alpha^- \mathbf{E}_{\text{sr}}^-) \\ &= b_{21} \mathbf{w} + b_{22} \mathbf{E} + (\eta \mathbf{w} \mathbf{w} + \gamma \mathbf{w} \mathbf{E}) : \mathfrak{B}, \end{aligned} \quad (33)$$

where

$$\begin{aligned} \eta &= \frac{A}{2} \left(\frac{a}{\bar{M}} \right)^{1/2} \omega_0 (\epsilon_0 - \epsilon_\infty)^{1/2} \left\{ \frac{1}{4(\pi)^{1/2}} \right. \\ &\quad \times \left(\frac{\alpha^+ / a^3}{(M^- / \bar{M})^2} + \frac{\alpha^- / a^3}{(M^+ / \bar{M})^2} \right) \\ &\quad \left. + \frac{8(\pi)^{1/2}}{9} (\epsilon_\infty + 2) \frac{\alpha^+ \alpha^-}{a^6} \right\}, \end{aligned} \quad (34)$$

$$\gamma = \frac{2A}{9} \left(\frac{a}{\bar{M}} \right)^{1/2} (\epsilon_\infty + 2)^2 \frac{\alpha^+ \alpha^-}{a^6}. \quad (35)$$

We have used Eqs. (6), (7), (15), (16), and $v = a^3/4$ to write η and γ in the forms given by Eqs. (34) and (35).

In order to obtain an expression for the electro-optic coefficient from Eq. (33) we put $\mathbf{E} = \mathbf{E}_0 + \mathfrak{C}$, where \mathbf{E}_0 is large and static and \mathfrak{C} is small and oscillatory. \mathfrak{C} is assumed to have a frequency in the range $\omega_0 \ll \omega \ll E_0/\hbar$ so it gives rise to no ion motion and we may put $\mathbf{w} = \mathbf{w}_0$, where \mathbf{w}_0 is large and static. Finally, we put $\mathbf{P} = \mathbf{P}_0 + \mathfrak{B}$, where \mathbf{P}_0 is large and static and \mathfrak{B} is small and oscillatory. Substituting these expressions for \mathbf{E} , \mathbf{w} , and \mathbf{P} into Eq. (33) and linearizing in \mathfrak{C} and \mathfrak{B} we obtain

$$\mathfrak{B} = b_{22} \mathfrak{C} + \gamma \mathbf{w}_0 \mathfrak{C} : \mathfrak{B}. \quad (36)$$

We will neglect departures from linearity in the static dielectric behavior of the crystal and put

$$\mathbf{w}_0 = -\frac{b_{12}}{b_{11}} \mathbf{E}_0 = -\frac{1}{\omega_0} \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2} \mathbf{E}_0. \quad (37)$$

The electric displacement associated with \mathfrak{B} and \mathfrak{C} is

$$\mathfrak{D} = \mathfrak{C} + 4\pi \mathfrak{B} = \epsilon_\infty(\mathbf{E}_0) \cdot \mathfrak{C}, \quad (38)$$

where

$$\epsilon_\infty(\mathbf{E}_0) = \epsilon_\infty \mathbf{I} + \frac{4\pi\gamma}{\omega_0} \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2} \mathfrak{d} \quad (39)$$

$$\mathfrak{d} = \mathfrak{B} \cdot \mathbf{E}_0 = \begin{pmatrix} 0 & E_{0,z} & E_{0,y} \\ E_{0,z} & 0 & E_{0,x} \\ E_{0,y} & E_{0,x} & 0 \end{pmatrix} \quad (40)$$

$\epsilon_\infty(\mathbf{E}_0)$ is the high-frequency dielectric tensor in the presence of an applied static field. The inverse dielectric tensor (through terms linear in \mathbf{E}_0) is given by

$$\epsilon_\infty^{-1}(\mathbf{E}_0) = \epsilon_\infty^{-1} \mathbf{I} - \frac{4\pi\gamma}{\epsilon_\infty^2 \omega_0} \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2} \mathfrak{d}. \quad (41)$$

The electro-optic coefficient for the zinc-blende lattice is defined in the following way⁶

$$\epsilon_\infty^{-1}(\mathbf{E}_0) = \epsilon_\infty^{-1} \mathbf{I} - r_{41} \mathfrak{d}. \quad (42)$$

Comparing Eqs. (41) and (42) and using Eq. (35) for γ we obtain

$$r_{41} = \frac{4(\pi)^{1/2}}{9} A \left(\frac{a}{\bar{M}} \right)^{1/2} \frac{(\epsilon_0 - \epsilon_\infty)^{1/2} (\epsilon_\infty + 2)^2 \alpha^+ \alpha^-}{\omega_0 \epsilon_\infty^2 a^6}. \quad (43)$$

The above expression for r_{41} does not include the contribution of the electronic quadrupoles. In order to evaluate this contribution we will employ the shell model of Dick and Overhauser.⁷ In this model each ion consists of a rigid core which moves with the nucleus and a rigid spherical shell which may be displaced with respect to the core. The shell represents the electrons which participate in electronic polarization; the displacement of the shell with respect to core gives rise to this polarization. Let the charge and the radius of the shell of a positive (negative) ion be $-q_s^+$ ($-q_s^-$) and R^+ (R^-), respectively. If the center of the shell of a positive ion is displaced an amount \mathbf{d} from the nucleus one has in this model

$$\mathbf{p}_{\text{el}}^+ = -q_s^+ \mathbf{d}, \quad (44)$$

$$\mathbf{Q}_{\text{el}}^+ = -\frac{q_s^+(R^+)^2}{3} \mathbf{I} - q_s^+ \mathbf{d} \mathbf{d} = -\frac{q_s^+(R^+)^2}{3} \mathbf{I} - \frac{\mathbf{p}_{\text{el}}^+ \mathbf{p}_{\text{el}}^+}{q_s^+}. \quad (45)$$

Similarly,

$$\mathbf{Q}_{\text{el}}^- = -\frac{q_s^-(R^-)^2}{3} \mathbf{I} - \frac{\mathbf{p}_{\text{el}}^- \mathbf{p}_{\text{el}}^-}{q_s^-}. \quad (46)$$

These expressions are now to be included in \mathbf{Q}^+ and \mathbf{Q}^- when evaluating \mathbf{E}_{sr}^- and \mathbf{E}_{sr}^+ . The terms involving R^+ and R^- do not contribute because $\mathfrak{B} : \mathbf{I} = 0$; the electronic dipoles need only be evaluated to first order as in Eqs. (28) and (29). The resulting polarization equation is

$$\mathbf{P} = b_{21} \mathbf{w} + b_{22} \mathbf{E} + \{ (\eta + \eta_1) \mathbf{w} \mathbf{w} + (\gamma + \gamma_1) \mathbf{w} \mathbf{E} + \xi_1 \mathbf{E} \mathbf{E} \} : \mathfrak{B}, \quad (47)$$

⁶ In the literature (see, for example, Ref. 8) the defining equation of r_{41} is conventionally taken to be $\epsilon_\infty^{-1}(\mathbf{E}_0) = \epsilon_\infty^{-1} \mathbf{I} + r_{41} \mathfrak{d}$ but the crystallographic coordinate system in which the equation is written is not completely specified. If we make the coordinate transformation $\hat{x}' = -\hat{y}$, $\hat{y}' = -\hat{x}$, $\hat{z}' = -\hat{z}$ then

$\mathfrak{d} = E_{0,x}(\hat{y}\hat{z} + \hat{z}\hat{y}) + E_{0,y}(\hat{x}\hat{z} + \hat{z}\hat{x}) + E_{0,z}(\hat{x}\hat{y} + \hat{y}\hat{x})$
 $= -E_{0,y}(\hat{x}'\hat{z}' + \hat{z}'\hat{x}') - E_{0,x}(\hat{y}'\hat{z}' + \hat{z}'\hat{y}') - E_{0,z}(\hat{y}'\hat{x}' + \hat{x}'\hat{y}') = -\mathfrak{d}'$

and Eq. (42) may be written in the conventional way.

⁷ B. Dick and A. Overhauser, Phys. Rev. **112**, 90 (1958).

where

$$\eta_1 = \frac{32\pi^{3/2}}{81} A \left(\frac{a}{\bar{M}} \right)^{1/2} \omega_0 (\epsilon_0 - \epsilon_\infty)^{1/2} (\epsilon_\infty + 2)^2 \frac{\alpha^+ \alpha^-}{a^6} \times \left(\frac{\alpha^-/a^3}{S^-} - \frac{\alpha^+/a^3}{S^+} \right), \quad (48)$$

$$\gamma_1 = \frac{32\pi}{81} A \left(\frac{a}{\bar{M}} \right)^{1/2} (\epsilon_\infty + 2)^3 \frac{\alpha^+ \alpha^-}{a^6} \left(\frac{\alpha^-/a^3}{S^-} - \frac{\alpha^+/a^3}{S^+} \right), \quad (49)$$

$$\xi_1 = \frac{8(\pi)^{1/2}}{81} A \left(\frac{a}{\bar{M}} \right)^{1/2} \frac{1}{\omega_0 (\epsilon_0 - \epsilon_\infty)^{1/2}} \frac{(\epsilon_\infty + 2)^4}{a^6} \frac{\alpha^+ \alpha^-}{a^6} \times \left(\frac{\alpha^-/a^3}{S^-} - \frac{\alpha^+/a^3}{S^+} \right), \quad (50)$$

$$S^+ = q_s^+/q, \quad S^- = q_s^-/q. \quad (51)$$

We may derive an expression for the electro-optic coefficient from (47) in the same way that (43) was obtained from (33). The result is

$$r_{41} = \frac{4\pi}{\epsilon_\infty^2} \left[\frac{(\gamma + \gamma_1)}{\omega_0} \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2} + 2\xi_1 \right] = r_{41}' \left[1 + \frac{16\pi (\epsilon_0 + 2)(\epsilon_\infty + 2)}{9 (\epsilon_0 - \epsilon_\infty)} \left(\frac{\alpha^-/a^3}{S^-} - \frac{\alpha^+/a^3}{S^+} \right) \right], \quad (52)$$

where r_{41}' is the value of the electro-optic coefficient given by Eq. (43).

As a final consideration we will investigate the effect of evaluating the effective field acting on an ion at some point other than its lattice site. The effective field acting on the l th ion will be evaluated at $\mathbf{R}_l + \mathbf{r}_l$ where $\mathbf{r}_l = \mathbf{r}^+$ for all positive ions and $\mathbf{r}_l = \mathbf{r}^-$ for all negative ions. In order to facilitate an expansion of the polarization in powers of \mathbf{w} and \mathbf{E} we will take \mathbf{r}^+ and \mathbf{r}^- to be of first order in these quantities. To second order in \mathbf{w} and \mathbf{E} we have

$$\mathbf{E}_{sr}^+ = \sum_{l \neq 0} (\mathbf{E}_l(0) + \mathbf{r}^+ \cdot \nabla \mathbf{E}_l(0) + \frac{1}{2} \mathbf{r}^+ \mathbf{r}^+ : \nabla \nabla \mathbf{E}_l(0)). \quad (53)$$

Performing a multipole expansion of $\mathbf{E}_l(0)$ one obtains

$$\mathbf{E}_{sr}^+ = - (A/a^4) \left(\frac{1}{2} \mathbf{Q}^- - \mathbf{r}^+ \mathbf{p}^- - \frac{1}{2} q \mathbf{r}^+ \mathbf{r}^+ \right) : \boldsymbol{\beta} \quad (54)$$

and similarly,

$$\mathbf{E}_{sr}^- = (A/a^4) \left(\frac{1}{2} \mathbf{Q}^+ - \mathbf{r}^- \mathbf{p}^+ + \frac{1}{2} q \mathbf{r}^- \mathbf{r}^- \right) : \boldsymbol{\beta}. \quad (55)$$

Notice that the short-range part of the effective field still vanishes to first order in \mathbf{w} and \mathbf{E} as mentioned in Sec. II. \mathbf{r}^+ and \mathbf{r}^- cannot be chosen uniquely on the basis of the model we have used thus far; a meaningful choice would certainly involve new phenomenological parameters. In the following section it will be seen that

TABLE II. Quantities used in the calculations of r_{41} .

| | CuCl | ZnS |
|-------------------|-----------------------------------|-----------------------------------|
| \bar{M} | 37.79×10^{-24} g | 32.06×10^{-24} g |
| a | 5.406 Å | 5.409 Å |
| ω_0 | 3.56×10^{13} sec $^{-1}$ | 5.71×10^{13} sec $^{-1}$ |
| ϵ_0 | 10 | 8.3 |
| ϵ_∞ | 3.57 | 5.07 |
| α^- | 2.974 Å 3 | 4.9 Å 3 |
| q_s^- | 8.7e | 8.7e |
| q_s^+ | 18e | 18e |

Eqs. (43) and (52) agree reasonably well with the existing experimental data. In view of this the introduction of new phenomenological parameters at this point seems to be an unnecessary elaboration of our model. We give below the result of a calculation in which

$$\mathbf{r}^+ = \mathbf{u}^+, \quad \mathbf{r}^- = \mathbf{u}^-. \quad (56)$$

This serves to indicate the sensitivity of the expression for r_{41} to the choice of \mathbf{r}^+ and \mathbf{r}^- . The result is

$$r_{41} = r_{41}' \left[2 + \frac{16\pi (\epsilon_0 + 2)(\epsilon_\infty + 2)}{9 (\epsilon_0 - \epsilon_\infty)} \left(\frac{\alpha^-/a^3}{S^-} - \frac{\alpha^+/a^3}{S^+} \right) \right]. \quad (57)$$

IV. COMPARISON WITH EXPERIMENT

In this section we will compare our theoretical results with experimentally determined values of the electro-optic coefficients of ZnS⁸⁻¹⁰ and CuCl.^{11,12} We have calculated theoretical values of r_{41} for these materials using Eqs. (43), (52), and (57). The quantities used in the calculations are listed in Table II. The lattice constants were taken from Wyckoff¹³; ω_0 , ϵ_0 , and ϵ_∞ were taken from Born and Huang,³ Tessman, Kahn, and Shockley¹⁴ (TKS) have determined the polarizabilities of ions in crystals from experimental data. They give polarizabilities for the halide ions both at the sodium D line ($\lambda = 5893$ Å) and in the limit of long wavelength ($\lambda = \infty$). The $\lambda = \infty$ limit corresponds to our requirement that $\omega \ll E_0/\hbar$. For $\alpha(\text{Cl}^-)$ we have used the TKS polarizability for Cl^- in an alkali chloride at $\lambda = \infty$. TKS give no value for $\alpha(\text{S}^{--})$ at $\lambda = \infty$, but S^{--} has the same electronic configuration as Cl^- and the polarizabilities of Cl^- at $\lambda = 5893$ Å and $\lambda = \infty$ differ by less than 1%. We have assumed that $\alpha(\text{S}^{--})$ and $\alpha(\text{Cl}^-)$ are similar in this respect, and in Table II we list the TKS polarizability of S^{--} in ZnS at $\lambda = 5893$ Å. $\alpha(\text{Cu}^+)$ and $\alpha(\text{Zn}^{++})$ were calculated from

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¹² C. West, J. Opt. Soc. Am. **43**, 335 (1953).

¹³ R. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), 2nd ed., Vol. 1.

¹⁴ J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

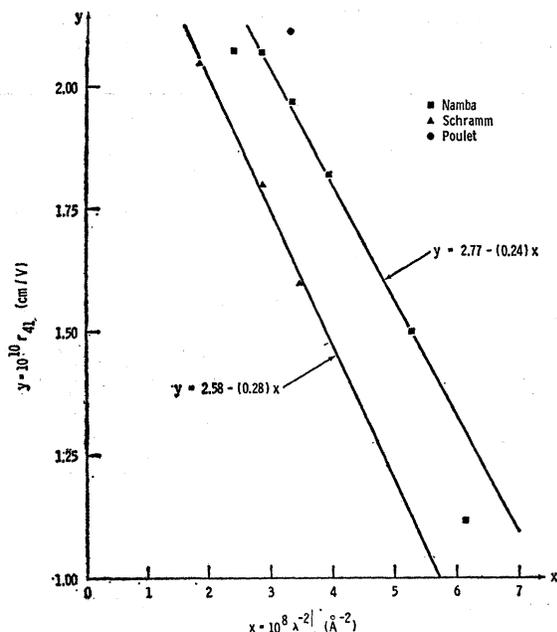


FIG. 1. Wavelength dependence of r_{41} in ZnS.

Eq. (15). Dick and Overhauser⁷ estimate that $q_s^- = 8.7e$ for ions with a $3s^2p^6$ electronic configuration, such as Cl^- and S^{--} . We have taken $q_s^+ = 18e$ because both Cu^+ and Zn^{++} have a $3s^2p^6d^{10}$ configuration. This may well be an overestimate (e.g., it may be that only the d electrons participate in polarization), but it is unlikely to be an underestimate. The results of the calculations are as follows: Eq. (43) gives

$$r_{41}(\text{ZnS}) = 1.89 \times 10^{-10} \text{ cm/V}, \quad (58)$$

$$r_{41}(\text{CuCl}) = 8.65 \times 10^{-10} \text{ cm/V}; \quad (59)$$

Eq. (52) gives

$$r_{41}(\text{ZnS}) = 2.28 \times 10^{-10} \text{ cm/V}, \quad (60)$$

$$r_{41}(\text{CuCl}) = 9.57 \times 10^{-10} \text{ cm/V}; \quad (61)$$

Eq. (57) gives

$$r_{41}(\text{ZnS}) = 4.18 \times 10^{-10} \text{ cm/V}, \quad (62)$$

$$r_{41}(\text{CuCl}) = 18.2 \times 10^{-10} \text{ cm/V}. \quad (63)$$

The values of $r_{41}(\text{ZnS})$ measured by Namba,⁸ Poulet,⁹ and Schramm¹⁰ are plotted in Fig. 1 and those of Namba and Schramm are extrapolated to $\lambda = \infty$. r_{41} is linear in λ^{-2} as would be expected since the polarizabilities are linear in λ^{-2} in regions of normal optical dispersion. Namba's values extrapolate to 2.8×10^{-10} cm/V and Schramm's to 2.6×10^{-10} cm/V. Sterzer, Blattner, and Minitier¹¹ and West¹² have measured the half-wave retardation voltage for the longitudinal electro-optic effect in CuCl using visible light; both obtained 6.2 kV which corresponds to $r_{41}(\text{CuCl}) = 6 \times 10^{-10}$ cm/V. The author is not aware of any measurements of $r_{41}(\text{CuCl})$ as a function of wavelength.

The agreement between Eq. (60) and the experimental value of $r_{41}(\text{ZnS})$ at $\lambda = \infty$ is quite satisfactory. Some of the discrepancy between the theoretical and experimental values of $r_{41}(\text{ZnS})$ can certainly be attributed to the fact that ZnS is not a strictly ionic crystal. The experimental data on CuCl is not sufficient to assess the relative accuracy of Eqs. (59) and (61), but both are probably better than (63). Equations (58)–(61) indicate that the electronic quadrupoles are not primarily responsible for the magnitude of r_{41} , but that they do give a non-negligible contribution. Equations (62) and (63) indicate that r_{41} is rather sensitive to the choice of \mathbf{r}^+ and \mathbf{r}^- . In view of this it is indeed fortuitous that good results are obtained with $\mathbf{r}^+ = \mathbf{r}^- = 0$.

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