Quantitative Calculation of Electro-Optic Coefficients of Diatomic Crystals

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The bond-charge dielectric theory of Phillips and Van Vechten is applied to the calculation of the electro-optic tensor coefficients. The agreement of the theoretical predictions with experimental values in the case of zinc blende and wurtzite crystals is very good.

The second-order nonlinear optical response of asymmetric crystals is usually represented by the relation

\[ P_i^{(2)} = \chi_{ijk} E_j^{(2)} E_k^{(2)} \]

between the amplitude of the induced polarization at \( \omega + \Omega \) and the inducing field amplitudes at \( \omega \) and \( \Omega \). The case when both \( \omega \) and \( \Omega \) are optical frequencies, that is, frequencies above the lattice response but below optical absorption, has been considered by Levine.\(^1\) He used the localized bond-charge model [see Fig. 1(a)] of Phillips and Van Vechten\(^2\)\(^,\)\(^3\) (PV) which attributes the dielectric response of covalent crystals to the localized bond charge resulting in a linear susceptibility:

\[ \chi = (\hbar \Omega_{p})^2 / E_{g}^2. \]

(1)

Here \( \Omega_p \) is the plasma frequency due to valence electrons and \( E_g \), the effective energy gap, is given by \( E_g^2 = E_h^2 + C^2 \), where \( E_h \) is the homopolar component and \( C \) the heteropolar (ionic) component of the energy gap. Levine starts with the linear dielectric response \( P_i^{(1)} = \chi_{ij} E_j^{(1)} \), taking \( \chi_{ij} \) to be an instantaneous function of the second field \( E_s^{(2)} \). This field causes a change \( \Delta \sigma / \Omega \) in the bond charge position, as shown in Fig. 1(b), which oscillates at \( \Omega \). The explicit dependence of \( E_h \) and \( C \) on \( r_a \) given by PV is then used to obtain \( \chi_{ijk} \), where

\[ \chi_{ijkl} = \chi_{ij}^{(1)} + \Delta \chi_{ij}^{(1)}(t) \]

\[ = \chi_{ij}^{(1)} + 2 \chi_{ijk} E_k^{(2)} \cos \Omega t. \]

(2)

If the frequency \( \Omega \) is below the lattice response region (we will refer to it in this case as "low"), then in addition to the purely electronic nonlinear response described above we now have a contribution to \( \chi_{ijk} \) due to the fact that now the crystal ions are capable of following the field \( E_s^{(2)} \cos \Omega t \). This is illustrated in Figs. 1(c) and 1(d). In addition to the displacement \( \Delta \sigma_a \) of the covalent bond charge we now have an elongation \( \Delta d_0 \) of the atomic separation as well as a rotation \( \Delta \theta \) of the bond axis, both caused by the ionic displacement \( \Delta X_a \). \( \Delta X_b \) is obtained from "low"-frequency dielectric constant measurements and is used to determine \( d_0 \) and \( \Delta \theta \). We use, in the spirit of Levine,\(^1\) the change \( \Delta d_0 \) to calculate the corresponding change \( \Delta X \cos \Omega t \) in bond susceptibility. This will give rise to a polarization \( P_i^{(2)} = \chi_{ijk} E_j^{(2)} E_k^{(2)} \).

A second contribution to \( \chi_{ijk} \) is due to the rocking at \( \Omega \) of the bond angle (\( \theta = \theta_0 + \Delta \theta \cos \Omega t \)) which yields a dipole component along the direction \( i \) at \( (\omega + \Omega) \) even when \( \Delta d_0 = 0 \).

In what follows we will obtain expressions for the ionic contributions to \( \chi_{ijk} \) which are due to \( \Delta d_0 \) and \( \Delta \theta \). When the result is added algebraically to \( \chi_{ijk} \) \( \text{elec} \), as measured by second-harmonic-generation experiments or calculated by Levine,\(^1\) the result is the total nonlinear tensor \( \chi_{ijk} = \chi_{ijk}^{\text{ionic}} + \chi_{ijk}^{\text{elec}} \). The constants \( \chi_{ijk} \) thus determined are those which characterize the linear electro-optic (Pockels) effect. The relationship between the conventionally defined electro-optic tensor \( r_{1jk} \) and \( \chi_{ijk} \) is

\[ r_{1jk} = -\left( \epsilon_0 / \epsilon_0 \right) \chi_{ijk} \text{elec}. \]

(3)

The linear susceptibility of a diatomic crystal
is given as $\chi = (h\Omega)^2/E^2$. The ionicity and covalency of the bond are defined as $f_i = C^2/E_i^2$, $f_e = C_i^2/E_e^2$. The expressions used in the evaluation of $E_h$ and $C$ are:

$$E_h \propto r_{o}^{-s}, \quad s = 2.48, \quad (4)$$

$$C \propto \exp(-k r_{o})(Z_{a}/r_{a} - Z_{b}/r_{b})e^2, \quad (5)$$

$$r_{a} \propto r_{b} \propto r_{o} = d_{o}/2, \quad (6)$$

where $d_{o} = r_{a} + r_{b}$ is the bond length, $r_{a}, r_{b}$ are the atomic radii, and $\exp(-k r_{o})$ is the Thomas-Fermi screening factor. In order to consider crystals with highly unequal atomic radii, a generalized form for $E_h$ was proposed as

$$E_h \propto r_{o}^{2s} \frac{(r_{a} - r_{b})^{2s} + (r_{b} - r_{a})^{2s}}{2(r_{o} - r_{c})^{2s}}, \quad (7)$$

where $r_{c}$ is the average core radius.

The linear macroscopic susceptibility tensor $\chi_{ij}$ is related to the bond polarizability $\beta_n$ by

$$\chi_{ij} = V^{-1} \sum \alpha_n \alpha_n \beta_n, \quad (8)$$

where $V$ is the volume of unit cell, $\alpha_n$ is the direction cosine of the $n$th bond, and the summation is over all the bonds in a unit cell. Although PV describe the macroscopic susceptibility $\chi$ in terms of the average energy gap, we assume that $E_h$ and $C$ are also related to the bond polarizability directly, i.e.,

$$\beta_n \propto (h\Omega)^2/E_e^2. \quad (9)$$

When the bond length varies, it is reasonable to assume that the ratio of $r_{a}$ and $r_{b}$ remains constant. With this assumption, the two independent parameters, $r_{a}, r_{b}$, can be transformed into two quantities which relate directly to the macroscopic properties of crystals:

$$\Delta r_{a} = (r_{a}/d_{o}) \Delta d_{o} + \delta$$

$$\Delta r_{b} = (r_{b}/d_{o}) \Delta d_{o} - \delta$$

where $\delta$ is the displacement of the bond charge in the case of no bond elongation, $\Delta d_{o} = 0$. From Eqs. (5), (6), (8), and (9), the change of bond polarizability is obtained as (here we drop the bond index $n$)

$$\frac{\Delta \beta}{\beta} = \left[f_i \left(1 + \frac{k r_{o}}{2}\right) + sf_e - \frac{3}{2}\right] \Delta d_{o} + \left[4f_i \frac{Z_a + Z_b}{Z_a - Z_b} + S(2s - 1) \frac{f_e \rho d_{o}^2}{(r_{o} - r_{c})^3} \right] \delta, \quad (10)$$

where $\rho = (r_{a} - r_{b})/(r_{a} + r_{b})$. In the first term, $k r_{o}/2$ is obtained because the screening wave number $k_s$ is proportional to $d_{o}^{-1/2}$, and the number $-3/2$ is because $\Omega_0$ is proportional to $d_{o}^{-3/2}$. The second term on the right-hand side of (10) is identical to that obtained by Levine in his calculation of the nonlinear optical susceptibility. The first term, which is proportional to $\Delta d_{o}$, is thus the ionic contribution of a single bond due to bond stretching.

The rotational contribution can be obtained by considering the changes in bond direction cosines. These are related to the ionic displacement $\Delta x_k$ by $\Delta \alpha_{nl} = (\delta_l - \alpha_{nl}) \Delta x_k$.

From (7) we have

$$\Delta \chi_{ij} = V^{-1} \sum \alpha_n \alpha_n \Delta \alpha_{nl} + \Delta \alpha_{nl} \alpha_{nl} \beta_n + \alpha_{nl} \Delta \alpha_{nl} \beta_n). \quad (11)$$

The complete ionic contribution to the nonlinear susceptibility is thus

$$\Delta \chi_{ij}^{\text{ion}} = \left[\sum \beta_n / \sqrt{r_{o}} \left[f \alpha_n \alpha_n \alpha_n + \frac{1}{2} (\alpha_n \delta_{lh} + \alpha_n \delta_{lk})\right] \right] \Delta x_k, \quad (12)$$

where

$$f = f_i \left[1 + \frac{1}{2} (k r_{o}) + s f_e - 2.5 = \left(\frac{1}{2} k r_{o}\right) - 1.48\right] f_i - 0.02, \quad (13)$$

$\Delta x_k$ is related to the dielectric constant of the crystal as

$$N e_0 \varepsilon e^{\text{ion}} = e_0 (e_{dc'} - e_{\omega'}) |E_k|, \quad (14)$$

where $N$ is the number of pairs of atoms per unit cell, $e_0$ is the Callen effective ionic charge, $e_{dc'}$ is the relative dielectric constant, $e_{\omega'}$ is the relative optical permittivity, and $E_k$ is the low-frequency electric-field component along the $k$ direction.

Using (3) we obtain the final working expression for the ionic component of the electro-optic tensor:

$$\gamma_{ijk}^{\text{ion}} = \frac{e_0 (e_{dc'} - e_{\omega'})}{V N e_0 e_{j} (e_{dc'}/e_{j})} \left[\sum \beta_n / \sqrt{r_{o}} \left[f \alpha_n \alpha_n \alpha_n + \frac{1}{2} (\alpha_n \delta_{lh} + \alpha_n \delta_{lk})\right] \right]. \quad (15)$$
TABLE I. Comparison of calculated and measured electro-optic coefficients (clamped) of zinc blende ($r_{ij}$) and wurtzite ($r_{ij}$) crystals (in units of $10^{-12}$ m/V). The signs of $r_{ijkl}$ have not been determined except where specified.

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>GaP</th>
<th>ZnSe</th>
<th>ZnS</th>
<th>ZnTe</th>
<th>CuCl</th>
<th>ZnS</th>
<th>CdS</th>
<th>CdSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{ij}^{\lambda}$</td>
<td>13.2</td>
<td>12.0</td>
<td>9.1</td>
<td>8.3</td>
<td>10.1</td>
<td>7.5</td>
<td>8.7</td>
<td>9.5</td>
<td>10.2</td>
</tr>
<tr>
<td>$f$</td>
<td>-0.09</td>
<td>-0.11</td>
<td>-0.16</td>
<td>-0.18</td>
<td>-0.12</td>
<td>-0.21</td>
<td>-0.18</td>
<td>-0.16</td>
<td>-0.15</td>
</tr>
<tr>
<td>$e e^\ast /e$</td>
<td>0.20</td>
<td>0.23</td>
<td>0.33</td>
<td>0.35</td>
<td>0.26</td>
<td>0.27</td>
<td>0.35</td>
<td>0.41</td>
<td>0.36</td>
</tr>
<tr>
<td>$r_{1ijk}$</td>
<td>+1.03</td>
<td>+1.53</td>
<td>+2.64</td>
<td>+2.93</td>
<td>+2.07</td>
<td>+5.56</td>
<td>+3.63</td>
<td>+3.80</td>
<td>+3.61</td>
</tr>
<tr>
<td>$r_{2ijk}$</td>
<td>-2.73</td>
<td>-3.20</td>
<td>-4.68</td>
<td>-4.77</td>
<td>-6.41</td>
<td>+2.66</td>
<td>-5.63</td>
<td>-6.71</td>
<td>-7.40</td>
</tr>
<tr>
<td>$r_{3ijk}^\lambda$</td>
<td>-1.7</td>
<td>-1.7</td>
<td>-2.0</td>
<td>-1.8</td>
<td>-4.3</td>
<td>-2.9</td>
<td>-2.0</td>
<td>-2.9</td>
<td>-3.8</td>
</tr>
<tr>
<td>$r_{ijkl}^\lambda$</td>
<td>-1.5</td>
<td>-1.1</td>
<td>2.0</td>
<td>1.6</td>
<td>4.3</td>
<td>-2.4</td>
<td>1.8</td>
<td>2.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>


For wurtzite crystals, we neglect the small distortion from the perfect tetragonal structure. $\beta_n$ can be expressed in terms of the measured macroscopic susceptibility $\chi$ as in (7), and the electro-optic coefficients of zinc blende and wurtzite crystals are obtained as follows: zinc blende,

$$r_{14}^{\text{ion}} = 0.3689 a_0^2 w / (e^\ast / e);$$

wurtzite,

$$r_{33}^{\text{ion}} = -2r_{13}^{\text{ion}} = 0.4260 a_0^2 w / (e^\ast / e),$$

where $a_0^2 = \sqrt{3} a_0 c_0$, $a_0$ and $c_0$ are the lattice constants, $w = (e - 1) / (e^\ast - e) / e^2$, and $r_{ij}$ are in units of $10^{-12}$ m/V. $a_0$ and $a_{ij}$ are in angstroms. Values of the parameters $e_0^\ast$, $f$, $e^\ast$ are listed in Table I.

The dependence of the electro-optic coefficients $r_{ijkl}^{\text{ion}}$ on the bond geometry is perhaps the most illuminating feature to emerge from this work.

This dependence is contained in curly brackets in (15). For diatomic single-bond crystals $\beta_n$ is a constant and the geometrical factor becomes

$$G_{ijh} = \left[ \sum_n f a_n^\lambda a_n^\lambda a_n^\lambda + \frac{1}{2} (a_n^\lambda b_n^\lambda + a_n^\lambda b_n^\lambda) \right].$$

The factor $f$ is typically $|f| \approx 0.3$. Table II contains a listing of these factors for some key directions (ijk) in crystals of the zinc blende, wurtzite and LiNbO$_3$ classes. It follows immediately that when $\sum n a_n^\lambda \neq 0$ the second term in $G_{ijh}$ is an order of magnitude larger than the first one. In such crystals the ionic contribution to $r_{ijkl}$ is about an order of magnitude larger than the electronic term. This is the case in LiNbO$_3$ or LiTaO$_3$. When $\sum n a_n^\lambda = 0$, as in zinc blende and wurtzite, we have to settle for the smaller term $\sum n f a_n^\lambda a_n^\lambda a_n^\lambda$. This is the main reason why LiTaO$_3$ has $r_{33} = 30.3$

<table>
<thead>
<tr>
<th></th>
<th>Zinc blende</th>
<th>Wurtzite</th>
<th>LiNbO$_3$</th>
<th>(Nb-O)$_{\text{short}}$</th>
<th>(Nb-O)$_{\text{long}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_b^{-1} \Sigma a_{3}$</td>
<td>0</td>
<td>0</td>
<td>0.475</td>
<td>-0.669</td>
<td></td>
</tr>
<tr>
<td>$n_b^{-1} \Sigma a_{3}^2$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td></td>
</tr>
<tr>
<td>$n_b^{-1} \Sigma a_{3} a_{3}$</td>
<td>$0$</td>
<td>$-\frac{1}{3}$</td>
<td>0.184</td>
<td>-0.185</td>
<td></td>
</tr>
<tr>
<td>$n_b^{-1} \Sigma a_{3}^3$</td>
<td>0</td>
<td>$\frac{1}{3}$</td>
<td>0.107</td>
<td>-0.300</td>
<td></td>
</tr>
</tbody>
</table>
The effective charge \( e^* \) is related to the Szeged effective charge \( e_s^* \) by \( e_s^* = \left( \frac{e^*}{e} \right) \). The value of \( e_s^*/e \) varies from 0.2 to 0.4 and seems to be independent of the number of valence electrons. The calculated values of \( r_{\text{ion}}^{\text{th}} \) using (17) and (18) are shown in Table I as \( r_{\text{ion}} \). The pure electronic contribution is entered as \( r_{\text{elec}} \). It is obtained directly from the experimentally determined second-harmonic-generation coefficient by \( r_{13} = -4d_{13}/\epsilon^2 \). For most of the crystals in Table I, \( r_{\text{ion}} \) is positive and \( r_{\text{elec}} \) is negative. Therefore, the predicted electro-optic coefficients, \( r_{\text{sum}}^{\text{th}} = r_{\text{ion}} + r_{\text{elec}} \), involve the algebraic addition or cancellation of two numbers of comparable values. The only exception is CuCl. Because of the unfilled shell in Cu, the sense of bond polarization in CuCl is different from that in other crystals. The signs of \( r_{\text{ion}} \) and \( r_{\text{elec}} \) of CuCl are thus different from others. However, the magnitude of \( r_{\text{ion}} \) is larger than that of \( r_{\text{elec}} \) in CuCl. We still obtain a negative electro-optic coefficient for CuCl. The predicted values in Table I are in good agreement with experiment. The worst case is GaP. It is interesting to note that the electronic contribution is about double the ionic contribution. This is in excellent agreement with the experimental observation.\(^8\)

We intend to extend this model to complex crystals with different point-group symmetries. The generalization of the bond parameters used above to multibond crystals has already been considered. The one parameter which will need added thought is \( e^* \), the effective ionic charge. It was found empirically to be equal to \( C/e\omega \) in diatomic crystals.\(^9\) If this relation and \( e_s^* = \left( \frac{e^*}{e} \right) \) are valid in the more complex crystals, then our model can be applied to these cases. Calculations now in progress on KHPO, LiNbO, LiTaO, and ternary chalcogenide crystals will be reported separately.

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\(^{1}\) Consultant: Hughes Research Laboratories, Malibu, Cal. 90265.


\(^{7}\) H. B. Callen, Phys. Rev. 75, 1394 (1949).


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**Interfacial Reaction and Schottky Barrier in Metal-Silicon Systems**

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Electronic states at the metal-silicon interface have previously been postulated in order to explain the pinning of the Fermi level, and the origin of these states has been a matter of some dispute. We propose here that in a reactive interface, such as the interface between Si and transition metals, physical properties of the interface are related to an interfacial layer, and that the relationship is manifest through the correlation between Schottky barrier height and eutectic temperature.

The theory of the Schottky barrier is an important subject concerning solid interfaces and is relevant to applications in microelectronics.\(^{1,2}\) The classical theory of Schottky assumes that at the interface between a metal and a semiconductor the Fermi levels should match up. This produces