NEW MATERIALS FOR INFRARED TRANSMITTING ELECTROOPTIC FILTERS

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Principal Investigator
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A.L. Gentile

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Electrooptic materials  Ternary chalcogenides
IR materials  "Defect" chalcopryites
Binary chalcogenides

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have an EO coefficient an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently.
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During the last quarter, emphasis was placed on the growth of single-crystal CdIn$_2$Te$_4$. Using the published phase equilibrium diagram, the liquid-solid relationships were established for crystal growth. A small single crystal of CdIn$_2$Te$_4$ was grown near the end of the quarter. In addition, synthesis of ZnIn$_2$S$_4$ was started using the constituent elements but failed to go to completion because a sulfide layer formed on top of the molten metals and prevented further reaction with gaseous sulfur.

Quantitative calculations of EO coefficients were made for ternary compounds and showed close agreement with measured results.
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REPORT SUMMARY

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During the last quarter, emphasis was placed on the growth of single-crystal CdIn₂Te₄. Using the published phase equilibrium diagram, the liquid-solid relationships were established for crystal growth. A small single crystal of CdIn₂Te₄ was grown near the end of the quarter. In addition, synthesis of ZnIn₂S₄ was started using the constituent elements but failed to go to completion because a sulfide layer formed on top of the molten metals and prevented further reaction with gaseous sulfur.

Quantitative calculations of EO coefficients, based on the bond charge dielectric theory of Phillips and Van Vechten, were made for ternary compounds and showed good agreement with measured results.
SECTION 1
INTRODUCTION AND SUMMARY

A. PROGRAM OBJECTIVES

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have EO coefficients an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high-melting points or melt incongruently. Our approach will overcome these obstacles. First, we will synthesize 20 polycrystalline samples. Then the dielectric constant of each, at both low and ambient temperatures, will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

B. SUMMARY

During the last quarter, emphasis was placed on the growth of single-crystal CdIn$_2$Te$_4$. Using the published phase equilibrium diagram, the liquid-solid relationships were established for crystal growth. A small single crystal of CdIn$_2$Te$_4$ was grown near the end of the quarter. In addition, synthesis of ZnIn$_2$S$_4$ was started using the consituent elements but failed to go to completion because a sulfide layer formed on top of the molten metals and prevented further reaction with gaseous sulfur.

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SECTION 2

MATERIALS PREPARATION AND CRYSTAL GROWTH

A. CdIn$_2$Te$_4$

Primary emphasis during this quarter was placed on the growth of single-crystal CdIn$_2$Te$_4$, a compound that we previously had reported$^1$ as having a high value for the low-frequency dielectric constant. Using the solid-liquid relationships shown (Figure 1) in the pseudo-binary phase diagram CdTe-In$_2$Te$_3$ as published$^2$ in the literature, we attempted to grow single-crystal material. Melt compositions were selected lying in the composition range covered by the line a–b. In this region, solid CdIn$_2$Te$_4$ (β = solid CdIn$_2$Te$_4$) is in equilibrium with liquid in the temperature range 785°C to 702°C. By selecting a starting composition close to "a," crystals of pure CdIn$_2$Te$_4$ can be grown by lowering the temperature. Below 702°C, however, additional phases begin to solidify and cause a multiphase polycrystalline region to begin to grow, thus preventing further single-crystal growth.

Several runs were made utilizing the conditions discussed above to grow single-crystal CdIn$_2$Te$_4$. Fused quartz crucibles approximately 16 mm in diameter with conical bottoms were used to nucleate single-crystal growth. The sealed, evacuated ampoules were processed in a vertical two-zone Bridgman-like furnace. The ampoule was rotated and vibrational stirring was applied during the growth cycle. As anticipated from the above discussion, several ingots were produced in which the lower (conical-shaped) sections were single phase and, in one case, a single crystal of CdIn$_2$Te$_4$; the upper parts were multiphase and polycrystalline.

X-ray microprobe analysis of the single-phase material showed insignificant variations in composition from nose to tail with an average composition:

- 58% Te
- 29% In
- 13% Cd.
Figure 1. Phase equilibrium diagram for CdTe-In$_2$Te$_3$. 
There are indications from the analysis that the composition is slightly rich in \( \text{In}_2\text{Te}_3 \) and that there is some solid solubility between \( \text{CdIn}_2\text{Te}_4 \) and \( \text{In}_2\text{Te}_3 \). However, our results indicate that the solid solubility line between the regions is more vertical than that reported in Ref. 1 (dashed line in Figure 1) and probably closer to the vertical (dotted) line in Figure 1.

One of the most successful ingots from these runs (Figure 2) yielded a single-crystal section (cone-shaped) as well as the final multiphase section; the boundary between the sections is noted in Figure 2. The tip of the cone appears as-grown and indicates a poor start with nucleation getting underway on an apparent gas void, resulting in a concave interface observed during crystallization. That the crystal grew single under these conditions (see Figure 3, SEM photo of as-grown tip), as confirmed by the growth patterns shown in Figure 3 and by Laue patterns, is very encouraging for future single-crystal growth runs.

Plans for the next quarter include further attempts at single-crystal growth of \( \text{CdIn}_2\text{Te}_2 \) seeking optimum temperature-lowering rates to prevent the crystal from cracking as well as solution from being entrapped to obtain the largest high-quality single crystal for evaluation of its EO properties.

B. \( \text{ZnIn}_2\text{S}_4 \)

During the last quarter, considerable effort was expended to synthesize \( \text{ZnIn}_2\text{S}_4 \) from its constituent elements: \( \text{Zn} \), \( \text{In} \), and \( \text{S} \). A long-term run in which the molten metals were exposed to gaseous sulfur failed to go to completion after several weeks and was aborted. Subsequent observation indicated that a layer of the sulfide had formed on top of the molten metals and prevented further reaction. A second run has gotten underway with added iodine to initiate vapor transport of the solidified species and allow further reaction to take place.
Figure 2. Ingot containing single-crystal CdIn$_2$Te$_4$.
(Region to right of dashed line is single.)
Figure 3. SEM photograph of tip of CdIn$_2$Te$_4$. 
SECTION 3
MATERIALS EVALUATION

A. PROPERTIES OF CdIn$_2$Te$_4$

CdIn$_2$Te$_4$ has been reported$^{3-7}$ to have the following properties:

- **Crystal class**: Tetragonal, $\overline{4}$
- **Band gap**: 0.9 eV
- **Resistivity (r.t.)**: Maximum $10^5$ $\Omega$-cm (n type)  
  Minimum 60 $\Omega$-cm
- **Mobility**: 4000 cm$^2$V$^{-1}$sec$^{-1}$
- **Transmission range**: 1 to 37 $\mu$m
- **Density**: 5.9 g/cm$^3$

Our measurements indicate that the sample we grew has a resistivity of $10^7$ $\Omega$-cm at room temperature. The dielectric constant at 10 kHz was measured to be 456 at room temperature. Low-temperature measurements showed a significant decrease in dielectric constant to 73 at 83$^\circ$K. It is possible that CdIn$_2$Te$_4$ is a ferroelectric slightly below room temperature. Our evaluation to date has not proven that it is, but there is no definite evidence that it is not. This evaluation is continuing, and our results will be discussed in a future report.

B. QUANTITATIVE CALCULATION OF EO COEFFICIENTS

The following represents the work of Professor Amnon Yariv and his graduate student, C. Shih, of the California Institute of Technology. They have applied the bond charge dielectric theory of Phillips and Van Vechten to the calculation of the EO tensor coefficients. Comparisons with experimental values for binary compounds having zincblende and wurtzite structures (as previously reported, Quarterly Report 4) is very good.
Yariv and Shih recently extended the calculations to ternary compounds e.g., LiNbO$_3$, CdIn$_2$Te$_4$, where they also find very good agreement. These results will appear in Table I. A discussion of the calculation appears in the appendix.

We applied the theoretical model for calculating the electrooptic coefficient to the crystal CdIn$_2$Te$_4$. We used the following data:

- Covalent radii (Cd$_{i}$In$_{j}$Te) = 1.405Å
- Structure = 4

Using published data of bond susceptibilities, we calculated the optical dielectric constant $\varepsilon_{\infty} = 7.25$. Using the above data in the equations

$$(r_{ijkl})_{\text{ionic}} = -\varepsilon_{\alpha} \left( \varepsilon_{\text{dc}}^{\varepsilon} - \varepsilon_{\text{ok}}^{\varepsilon} \right) \sum_{\mu} \frac{b_{\mu}^{\varepsilon}}{r} \left[ \left( f_{\mu i} \alpha_{\mu}^{\mu i j k} \right) + \frac{1}{2} \left( \alpha_{\mu}^{\mu i j k} + \alpha_{\mu}^{\mu i j k} \right) \right]$$

$$f = \left( \frac{k_{\varepsilon}}{2} - 1.48 \right) f_{\varepsilon} - 0.02$$

we obtain the result

$$r_{41} = 220 \times 10^{-12} \text{ m/V \pm 30\%}$$

This predicted value is a huge number (roughly 100X that of GaAs and 10X that of LiNbO$_3$). The main difference between this crystal and LiNbO$_3$, as an example, is due to the factor:

$$\frac{\varepsilon_{\text{dc}}^{\varepsilon} - \varepsilon_{\text{k}}^{\varepsilon}}{\varepsilon_{\varepsilon}^{\varepsilon}}$$
Table I. Results for LiNbO₃ and LiTaO₃

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<td>28</td>
<td>43</td>
</tr>
<tr>
<td>$\varepsilon_{dc}^{1,2}$</td>
<td>43</td>
<td>41</td>
</tr>
<tr>
<td>$\varepsilon_{s}^{*}/\varepsilon_{s}$</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>$2r_0$ (Nb-O) (short)</td>
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<td>2.112</td>
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<tr>
<td>$f_i$ (Nb-O) (long)</td>
<td>0.821</td>
<td>0.830</td>
</tr>
<tr>
<td>$-f$ (Ta-O) (short)</td>
<td>0.292</td>
<td>0.241</td>
</tr>
<tr>
<td>$r_{33}$ (Ta-O) (long)</td>
<td>0.282</td>
<td>0.238</td>
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which is equal to 8.55 in CdIn₂Te₄ and to 1.02 in LiNbO₃. It will be very exciting to see if this prediction is actually true.

We also predict a large EO coefficient for ZnIn₂S₄ since it has 3m symmetry so that the form

$$\Sigma_{u} \alpha_{ij}^{u} \delta_{jk}$$

is non-vanishing for $r_{ijj}$. The more numerical prediction awaits the result of measurement of $\varepsilon_{dc}$.
REFERENCES

1. A.L. Gentile et. al., this program, Quarterly Report No. 6, August 1979.


APPENDIX

QUANTITATIVE CALCULATION OF ELECTROOPTIC COEFFICIENTS

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

\[ P_i^{(\omega+\Omega)} = \chi_{ijk}^{(\omega)} E_j^{(\omega)} E_k^{(\Omega)} \]

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 (i.e., they are frequencies above the lattice response but below the optical absorption) has been considered by Levine.\(^1\) He used the localized bond charge model (see Figure A-1(a)) of Phillips and Van Vechten\(^2\) (PV), which attributes the dielectric response of covalent crystals to the localized bond charge resulting in a linear susceptibility:

\[ \chi = \frac{(h\nu_p)^2}{E^2 g} \]

where \( \nu_p \) 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 \( C \) is the heteropolar (ionic) component of the gap energy). Levine starts with the linear dielectric response \( P_i^{(\omega)} = \chi_{ij}^{(\omega)} E_j^{(\omega)} \), taking \( \chi_{ij} \) to be an instantaneous function of the second field \( E_k^{(\Omega)} \). This field causes a change \( \Delta r_\alpha = -\Delta r_\beta \) in the bond charge position, as shown in Figure A-1(a), that oscillates at \( \Omega \). The explicit dependence of \( E_g \) and \( C \) on \( r_\alpha \) given by PV\(^2\) is then used to obtain \( \chi_{ijk} \), where

\[ \chi_{ij} = \chi_{ij}^{(0)} + \Delta \chi_{ij}^{(t)} = \chi_{ij}^{(0)} + 2\chi_{ijk} E_k^{(\Omega)} \cos \Omega t \]

(2)
Figure A-1. The response of ion and bond-change to the applied electric field. In (a) and (b) the frequency of the field is higher than the lattice response. Only the displacement of the bond charge takes place. In (c) and (d) the frequency of the field is lower than the lattice response. It induces the displacement of the bond charge ($\Delta r_\beta$), bondlength elongation ($\Delta d_0$), and bond rotation ($\Delta \beta^\circ$).
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, there is now a contribution to $\chi_{ijk}$ because the crystalline ions are capable of following the field $E_k^{(\Omega)} \cos \Omega t$. This is illustrated in Figure A-1(c and d). In addition to the displacement $\Delta r_\alpha$ of the covalent bond charge, there is now an elongation $\Delta d_\alpha$ of the atomic separation and a rotation $\Theta$ of the bond direction; these are caused by the ionic displacement $\Delta x_k$. $\Delta x_k$ is obtained from "low" frequency dielectric constant measurements and is used to obtain $\Delta d_\alpha$ and $\Delta \Theta$. We use, in the spirit of Levine, the change $\Delta d_\alpha$ to calculate the corresponding change $\Delta \chi \cos \Omega t$ in bond susceptibility. This will give rise to a polarization

$$p_{i}^{(\omega+\Omega)} = \chi_{ijk} E_{j}^{(\omega)} E_{k}^{(\Omega)}.$$ 

A second contribution to $\chi_{ijk}$ is due to the rocking at $\Omega$ of the bond angle ($\Theta = \Theta_\alpha + \Delta \Theta \cos \Omega t$), which yields a dipole component along $i$ at $(\omega+\Omega)$ even when $\Delta d_\alpha = 0$.

In what follows, we will obtain expressions for the ionic contribution to $\chi_{ijk}$, which is due to $\Delta d_\alpha$ and $\Delta \Theta$. Adding this result algebraically to $\chi_{ijk}$ (as measured by second harmonic generation experiments or calculated by Levine) yields the total nonlinear tensor

$$\chi_{ijk} = \chi_{ijk}^{\text{ionic}} + \chi_{ijk}^{\text{elect}}.$$ 

The constants $\chi_{ijk}$ thus determined are those which characterize the linear electrooptic (Pockels) effect. The relationship between the conventionally defined electrooptic tensor $r_{ijk}$ and $\chi_{ijk}$ is (in MKS units)
\begin{equation}
\chi_{ijk} = - \frac{e_i e_j}{2e_o} r_{ijk} .
\end{equation}

We use this procedure below to calculate the tensor $r_{ijk}$ in a number of zincblende and wurtzite crystals. The results are in good agreement with experiments.

The linear susceptibility of a diatomic crystal is given as
\[
\chi = (\hbar \Omega P)^2 / E^2 \tag{Ref. 2}. \]
The ionicity and covalency of the bond are defined as $f_i = C^2 / E^2$ and $f_c = E_h / E_g$, respectively. Values of $E_h$, $C$, $f_c$, and $f_i$ for a large number of crystals are given in Ref. 3. The expressions used in the evaluation of $E_h$ and $C$ are $^{1,2}$

\begin{equation}
E_h \propto r_0^{-s} , \quad s = 2.48
\end{equation}

\begin{equation}
C \propto e^{-k_s r_o} \left( \frac{Z_\alpha}{r_\alpha} - \frac{Z_\beta}{r_\beta} \right) e^2 \tag{5}
\end{equation}

\begin{equation}
r_\alpha = r_\beta = r_o = \frac{d_o}{2}
\end{equation}

where $d_o = r_\alpha + r_\beta$ is the bond length, $r_\alpha, r_\beta$ are the atomic radii, $e^{-k_s r_o}$ is the Thomas-Fermi screening factor, and the proportional factors in $E_h$ and $C$ are independent of bond length and atomic radius.

To consider the crystals with highly unequal atomic radii, a generalized form for $E_h$ was proposed:$^1$

\begin{equation}
E_h^{-2} \propto r_o^{2s} \left[ \frac{(r_\alpha - r_c)^{2s} + (r_\beta - r_c)^{2s}}{2(r_o - r_c)^{2s}} \right],
\end{equation}

where $r_c$ is the average core radius, which is included here since the contribution to the susceptibility in the core region is very small.
The linear macroscopic susceptibility tensor \( \chi_{ij} \) is related to the bond polarizability \( \beta_n \) by

\[
\chi_{ij} = \frac{1}{V} \sum_n \alpha_i \alpha_j \beta_n ,
\]

(7)

where \( V \) is the volume of the unit cell, \( \alpha_{ni} \) is the direction cosine of the bond, \( n \) refers to the individual bond, and the summation is over all the bonds in a unit cell. Although \( PV \) described the macroscopic susceptibility \( \chi \) in terms of the average energy gap, we assume that \( E_h \) and \( C \) should be related to the bond polarizability directly, i.e.,

\[
\beta_n \propto \frac{(\hbar \tilde{\Omega})^2}{E^2}.
\]

The change of bond polarizability due to the applied electric field is

\[
\frac{\Delta \beta}{\beta} = \frac{\Delta (\tilde{\Omega}^2)}{\Omega^2} + \frac{f_c E_h^2}{E^2} \Delta (E_h^{-2}) - 2f_c \frac{\Delta C}{C} .
\]

(8)

When the bond length varies, it is reasonable to assume that the ratio of \( r_\alpha \) to \( r_\beta \) remains constant. With this assumption, the two independent parameters, \( r_\alpha, \beta \), can be transformed into two quantities that relate directly to the macroscopic properties of crystals:

\[
\Delta r_\alpha = \frac{r_\alpha}{d_o} \Delta d_o + \delta
\]

\[
\Delta r_\beta = \frac{r_\beta}{d_o} \Delta d_o - \delta
\]

(9)
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 $n$):

$$
\frac{\Delta \beta}{\beta} = \left\{ \left[ f_i \left( 1 + \frac{k_s r_o}{2} \right) + sf_c - \frac{3}{2} \right] \frac{\Delta d_o}{r_o} 
+ \left[ 4f_i \frac{Z_\alpha + Z_\beta}{Z_\alpha - Z_\beta} + s(2s - 1) \frac{f_c \rho d_o^2}{(r_o - r_c)^2} \right] \frac{\delta}{d_o} \right\},
$$

(10)

where $\rho = (r_\alpha - r_\beta)/(r_\alpha + r_\beta)$. In the first term, $k_s r / 2$ is obtained for the screening wave number, $k_s$ is proportional to $d_o^{-1/2}$ (Ref. 4), and the number $(-3/2)$ is due to the fact that $\Omega_p$ is proportional to $d_o^{-3/2}$. The second term on the right side of Eq. 10 is exactly the same as the expression obtained by Levine in his calculation of the nonlinear optical susceptibility.\(^5\) The first term, which is proportional to $d_o$, 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

$$
\Delta \alpha_{n_1 n_2} = \left( \delta_{i k} - \alpha_{n_1 n_2} \alpha_{n_k} \right) \Delta x_k.
$$

From Eq. 7 we have

$$
\Delta \chi_{ij} = \frac{1}{V} \sum_n \left( \alpha_{n_1 n_2} \Delta \beta_n + \alpha_{n_1 n_2} \Delta \alpha_{n_2 n_1} \Delta \alpha_{n_2} + \alpha_{n_1 n_2} \Delta \alpha_{n_2} \right).
$$

(11)
The complete ionic contribution to the nonlinear susceptibility is thus

$$\Delta \chi_{ij}^{\text{ion}} = \left\{ \sum_n \frac{\beta_n}{V r_0} \left[ f^n \alpha_{ni} \alpha_{nj} \alpha_{nk} + \frac{1}{2} (\alpha_{nk} \delta_{jk} + \alpha_{nj} \delta_{ik}) \right] \right\} \Delta x_k \), (12)$$

where

$$f = f_0 \left( 1 + \frac{kr}{2s} \right) + sf_c = 2.5$$

$$= \left( \frac{kr}{2s} - 1.48 \right) f_0 = 0.02 \). (13)$$

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

$$N e_c^* \Delta x_k = \varepsilon_0 (\varepsilon_r - \varepsilon_\infty) E_k^s$$

where $N$ is the number of pairs of atoms per unit cell, $e_c^*$ is the Callen effective ionic charge, $\varepsilon_r$ is the relative dielectric constant, $\varepsilon_\infty$ is the relative optical permittivity, and $E_k^s$ is the low-frequency electric field component along the $k$ direction.

Using Eq. 3 we obtain the final working expression for the electro-optic tensor:

$$r_{ijkl}^{\text{ion}} = \frac{\varepsilon_0 (\varepsilon_r - \varepsilon_\infty)}{V N e_c^* \varepsilon_r \varepsilon_0} \left\{ \sum_n \frac{\beta_n}{V r_0} \left[ f^n \alpha_{ni} \alpha_{nj} \alpha_{nk} + \frac{1}{2} (\alpha_{ni} \delta_{jk} + \alpha_{nj} \delta_{ik}) \right] \right\}. (15)$$

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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 Eq. 7, and the electrooptic coefficients of zincblende and wurtzite crystals are obtained as follows:

\[
\begin{align*}
\text{zincblende } r_{14}^{\text{ion}} &= 0.3689 \frac{a_0^2 w_f}{e_c/e} \\
\text{wurtzite } r_{33}^{\text{ion}} &= -2 r_{13}^{\text{ion}} = 0.4260 \frac{\gamma_{\text{eff}}^2 w_f}{e_c/e}
\end{align*}
\]

(16) (17)

where $a_0$ is the lattice constant; $a_{\text{eff}} = \sqrt{3} a_0^2 c_0$; $w = (\varepsilon - 1)(\varepsilon_{dc} - \varepsilon)/\varepsilon$; the $r_{ij}$ are in units of $10^{-12}$ m/V; and $a_0$, $a_{\text{eff}}$ are in units Å. Values of the parameters $a_0$, $a_{\text{eff}}$, $w$, $f$, and $f_c$ are listed in Table A-I.

The dependence of the electrooptic coefficients $r_{ijk}^{\text{ion}}$ on the bond geometry is perhaps the most illuminating feature to emerge from this work. This dependence is contained in curly brackets in Eq. 15. For diatomic single-bond crystals, $\beta_n$ is a constant, and the geometrical factor becomes

\[
G_{ijk} = \sum_n \left[ f \alpha_{ni} \alpha_{nj} \alpha_{nk} + \frac{1}{2} (\alpha_{nk} \delta_{jk} + \alpha_{nj} \delta_{ik}) \right].
\]

The factor $f$ is typically $|f| \leq 0.3$. Table A-II contains a listing of these factors for some key directions $(ijk)$ in crystals of the zincblende, wurtzite, and LiNbO$_3$ classes.

It follows immediately that when $\sum_n \alpha_{ni} \neq 0$ the second term in $G_{ijk}$ is an order of magnitude larger than the first one. In such crystals, the ionic contribution to $r_{ijk}$ is about an order of magnitude larger.
Table A-I. Parameters and Results of EO Calculations

<table>
<thead>
<tr>
<th>AB</th>
<th>Zincblende</th>
<th>Wurtzite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GaAs</td>
<td>GaP</td>
</tr>
<tr>
<td>a</td>
<td>5.65</td>
<td>5.45</td>
</tr>
<tr>
<td>$\varepsilon_{dc}$</td>
<td>13.2$^b$</td>
<td>12.0$^c$</td>
</tr>
<tr>
<td>w</td>
<td>0.192</td>
<td>0.284</td>
</tr>
<tr>
<td>f</td>
<td>0.310</td>
<td>0.370</td>
</tr>
<tr>
<td>$g_1$</td>
<td>-0.091</td>
<td>-0.113</td>
</tr>
<tr>
<td>$e_{c}^* / e$</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>r$_{ionic}$</td>
<td>+1.03</td>
<td>+1.53</td>
</tr>
<tr>
<td>r$_{elec}$</td>
<td>-2.73$^h$</td>
<td>-3.20$^i$</td>
</tr>
<tr>
<td>r$_{sum}$</td>
<td>-1.7</td>
<td>-1.7</td>
</tr>
<tr>
<td>r$_{exptl}$</td>
<td>-1.6$^h$</td>
<td>-1.1$^n$</td>
</tr>
</tbody>
</table>

NOTE: $a = a_0$ or $a_{eff}$. r's represent $r_{14}$ (zincblende) and $r_{33}$ (wurtzite) and are in units of $10^{-12}$ m/V. r$_{exptl}$ are measurements with clamped crystals. Their signs have not been determined unless specified.

---

Table A-II. Comparison of the Geometrical Factors Between Zincblende and Wurtzite and LiNbO$_3$

<table>
<thead>
<tr>
<th></th>
<th>Zincblende</th>
<th>Wurtzite</th>
<th>LiNbO$_3$ (Nb-O) Short</th>
<th>LiNbO$_3$ (Nb-O) Long</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma \alpha_{n3}$</td>
<td>0</td>
<td>0</td>
<td>2.849</td>
<td>-4.014</td>
</tr>
<tr>
<td>$\Sigma \alpha_{ni}^2$</td>
<td>16/3</td>
<td>8/3</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$\Sigma \alpha_{n1} \alpha_{n2} \alpha_{n3}$</td>
<td>$16/3 \sqrt{3}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Sigma \alpha_{n1} \alpha_{n3}$ = $\Sigma \alpha_{n2}^2 \alpha_{n3}$</td>
<td>0</td>
<td>-8/9</td>
<td>1.103</td>
<td>-1.109</td>
</tr>
<tr>
<td>$\Sigma \alpha_{n3}^3$</td>
<td>0</td>
<td>16/9</td>
<td>0.642</td>
<td>-1.797</td>
</tr>
<tr>
<td>$\Sigma \alpha_{n2}^3$</td>
<td>0</td>
<td>0</td>
<td>0.396</td>
<td>-0.195</td>
</tr>
</tbody>
</table>
than the electronic term. This is the case in LiNbO$_3$ and LiTaO$_3$. When \( \sum \alpha_n = 0 \), as in zincblende and wurtzite, we have to settle for the smaller term \( \sum_n f_{\alpha} \alpha_n \). This is the main reason why LiTaO$_3$ has \( r_{33} = 30.3 \times 10^{-12} \) m/V, while GaAs and ZnS have \( r_{41} \approx 2 \times 10^{-12} \) m/V.

The effective charge \( e_c^* \) is related to the Szigeti effective charge \( e_s^* \) by

\[
e_c^* = \frac{e_{\infty} + 2}{3e_{\infty}} e_s^*.
\]

The value of \( e_c^* \) varies from 0.2 to 0.4 and seems to be independent of the number of valence electrons. The calculation of \( r_{i,j,k}^{\text{ion}} \) using Eqs. 17 and 18 is shown in Table I as \( r_{i,j,k}^{\text{ionic}} \). The pure electronic contribution is entered as \( r_{i,j,k}^{\text{elec}} \). It is obtained directly from the second harmonic generation coefficient by \( r_{i,j,k}^{\text{elec}} = -\frac{4d_{i,j,k}^2}{\varepsilon^2} \). For most of the crystals in Table I, \( r_{i,j,k}^{\text{ionic}} \) is positive and \( r_{i,j,k}^{\text{elec}} \) is negative. Therefore, the predicted electrooptic coefficients, \( r_{i,j,k}^{\text{theo}} = r_{i,j,k}^{\text{ionic}} + r_{i,j,k}^{\text{elec}} \), involve the algebraic addition of two numbers of comparable values. The only exception is CuCl. Due to the unfilled shell in Cu, the sense of bond polarization in CuCl is different from that in other crystals. For example, excluding valence electrons, As is +5, Ga is +3, and Cl is +7, but Cu is +11. So the signs of \( r_{i,j,k}^{\text{ionic}} \) and \( r_{i,j,k}^{\text{elec}} \) of CuCl are different from those of other crystals. However, since the magnitude of \( r_{i,j,k}^{\text{ionic}} \) is larger than that of \( r_{i,j,k}^{\text{elec}} \) in CuCl, we still obtain a negative electrooptic coefficient for CuCl. Predicted values in Table I show a 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.

We find that the contributions to \( r_{i,j,k} \) from the homopolar part and the heteropolar part are comparable. 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 that will need consideration is $e^*_s$, the effective ionic charge. It was found empirically to be equal to $C/\hbar \omega_p$ in diatomic crystals.\textsuperscript{9} If this relation and

$$e^*_c = \frac{\epsilon_{\infty} + 2}{3\epsilon_{\infty}} e^*_s$$

are valid in the more complex crystals, then our model can be applied to these cases. Present calculations on LiNbO$_3$, LiTaO$_3$, and ternary chalcopyrite crystals are reported in this document (see Table I).
REFERENCES