

## Local-field effects and birefringence in II-IV-V<sub>2</sub> chalcopyrite crystals

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We present a new analysis of the birefringence of chalcopyrite crystals, which uses the irreducible components of the susceptibility and polarizability tensors. This analysis shows that the major part of the crystal birefringence is due to local-field anisotropy rather than to the bond optical anisotropy. Contradictions encountered formerly between the dielectric-theory approach and the molecular-orbital approach are explained.

### INTRODUCTION

Ternary compounds with chalcopyrite structure have recently received a great deal of interest because of their applications in nonlinear optics<sup>1</sup> and semiconductor physics.<sup>2</sup> Chalcopyrite crystals belong to the family of tetrahedrally coordinated compounds. Their structure derives from the sphalerite structure by the splitting of the cation sublattice into two different sublattices.

It is a well-known technique in nonlinear optics to use the birefringence to achieve phase-matched<sup>3</sup> frequency mixing. Consequently, and as far as nonlinear optics is concerned, the most interesting specific property of chalcopyrite compounds, among the tetrahedrally coordinated crystals, is their natural birefringence.<sup>1,4</sup> Most of the dielectric properties of chalcopyrite compounds, including their average refractive indices<sup>5</sup> and their second- and third-order nonlinear optical susceptibilities,<sup>6,7</sup> are now rather well understood. But so far, there has been no correct theory of their birefringence. The average refractive indices of chalcopyrite compounds have been correctly accounted for by the generalization to multibonds tetrahedral crystals<sup>5</sup> of Phillips dielectric theory.<sup>8</sup> Using this generalization, Chemla<sup>9</sup> and Lind and Grand<sup>10</sup> have found in the case of II-IV-V<sub>2</sub> compounds some correlations between the birefringence and the crystallographic parameters. However, their analysis implies that the II-V bi-atomic bonds must have a parallel polarizability smaller than the perpendicular polarizability. This result is in absolute contradiction with the precise calculations of the bond polarizabilities in these compounds given by Scholl and Tang.<sup>11</sup>

In this paper we present a new analysis of the birefringence of the chalcopyrite crystals, based on the use of the irreducible components of the

susceptibility and polarizability tensors.<sup>9</sup> This analysis puts forward the difference of symmetry of the local-field contribution in the average refractive index and in the birefringence. One of the consequences of our analysis is to eliminate the contradiction formerly found between the molecular-orbital approach<sup>11</sup> and the dielectric-theory approach.<sup>9,10</sup>

### I. LOCAL-FIELD EFFECTS ON THE BIREFRINGENCE

The optical anisotropy reflects the structural anisotropy of chalcopyrite crystals. The difference of atomic interactions along the optic axis and perpendicular to it results in a tetragonal compression which can be measured by a dimensionless quantity  $\tau = 2 - c/a$ , where  $c$  and  $a$  are the crystallographic cell parameters. The chalcopyrite structure exhibits another anisotropy. The elementary building block of the structure is a tetrahedron formed by the anion  $C$  surrounded by two cations of the  $A$  type and two cations of the  $B$  type (Fig. 1). The anion is not situated at its center. It is pulled towards a couple of cations on one type along a plane perpendicular to the optic axis. This displacement can be measured by another dimensionless quantity  $\sigma = 4x - 1$ , where  $x$  defines the coordinate of the anion in the crystallographic cell in unit  $a$ . The relationships among the various geometrical quantities in the chalcopyrite cell are given in Appendix A.

In the transparency domain of the crystal, the linear polarizability tensors of the various bonds are second-rank symmetric tensors, which have two irreducible components,<sup>9</sup> a scalar which describes the average polarizability of the bond and a deviator which represents the optical anisotropy of the bond. In the case of a system with axial symmetry, the decomposition of the polarizability tensor in irreducible parts is obvious,<sup>9</sup>

$$\vec{\alpha} = \begin{pmatrix} \alpha_{\perp} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\parallel} \end{pmatrix} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp}) \begin{pmatrix} +1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -2 \end{pmatrix}. \quad (1)$$

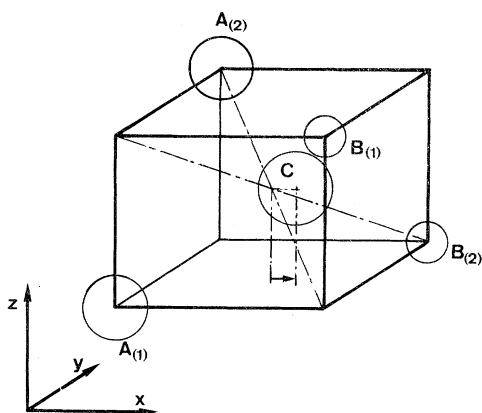


FIG. 1. Elementary building block of the chalcopyrite structure. An anion  $C$  surrounded by two cations  $A$  and two cations  $B$  at the vertices of an irregular tetrahedron.

Equation (1) leads us to introduce the two quantities  $\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$  and  $\delta\alpha = \frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp})$ . Due to the special symmetry of the bond, the deviator has only one independent component which transforms as the spherical harmonic  $Y_2^0$ .

It was shown in Ref. 5 that Phillips dielectric theory is equivalent to a microscopic-bond-polarizabilities approach for the scalar  $\alpha$ , using the Kramers-Heisenberg dispersion formula, Vinti approximation,<sup>12</sup> and assuming that all the local field effects can be included in the definition of the mean energy gap  $E_g$ , i. e., in  $\alpha$ . In the same paper, it was noticed that if the polarizability anisotropy  $\delta\alpha$  could also be defined in a way which include the local-field effects, then the birefringence of chalcopyrite crystals  $ABC_2$  should be written

$$\Delta n = n_e - n_o = \frac{32\pi}{nV} \left[ \frac{1}{2}(3 \cos^2 \theta^{(+)} - 1) \delta\alpha^{(+)} + \frac{1}{2}(3 \cos^2 \theta^{(-)} - 1) \delta\alpha^{(-)} \right], \quad (2)$$

where the  $AC$  bond is denoted by (+) and the  $BC$  bond by (-);  $\theta^{(\pm)}$  is the angle between the bonds axis and the crystal optic axis.

In the case of the  $\Pi$ -IV- $V_2$  compounds, Abrahams and Bernstein<sup>13</sup> have shown that the tetrahedra centered at the IV atoms are regular with a very good accuracy. To the first order in the structural quantities, one has  $\frac{1}{2}(3 \cos^2 \theta^{(\pm)} - 1) = -\frac{1}{3}(\tau \pm \sigma)$ . The regularity of the IV- $V_4$  tetrahedra implies that  $\tau = \sigma$ , and consequently,  $\Delta n = -64\pi\tau\delta\alpha^{(+)} / 3nV$ .

This expression can be used to establish correlations between crystals involving the same  $\Pi$ -V bonds  $(nV \Delta n / \tau)_{ABC_2} = (nV \Delta n \tau)_{AB'C_2}$ . Such a relationship was applied by Chemla<sup>9</sup> and also by Lind and Brant.<sup>10</sup> The numerical values they deduced from it are rather inaccurate but they give the right order of magnitude. A more important result of

this approach is that since all  $\Pi$ -IV- $V_2$  compounds known to date have a positive birefringence ( $n_e > n_o$ ) and are all compressed ( $c < 2a$ ),  $\delta\alpha^{(+)}$  should be negative. This result is quite surprising and in contradiction with molecular-orbital calculation, performed by Scholl and Tang<sup>11</sup> on the same compounds showing that  $\delta\alpha^+$  is positive.

This contradiction indicates clearly that it is not possible to define macroscopically a quantity such as  $\delta\alpha$ , or in other words, that the local-field contribution to the birefringence is completely different of that to the average refractive index.

The local field varies very rapidly over the unit cell. Only very heavy self-consistent quantum-mechanical calculations<sup>14</sup> can handle correctly the problem. In the semiconductors that we consider, the electrons are only partially localized. During their motion over the bonds, they probe the average microscopic field. We can therefore use a simplified approach and assume that the local field is constant over an elementary  $(A_{(2)}-C-B_{(2)})$  tetrahedron. Since it is the sum of all the fields radiated by the dipoles of the crystal when excited by an applied field, it can be described by a tensor equation  $\vec{\mathcal{E}}^{loc} = \vec{f} \vec{\mathcal{E}}$ , where  $f$  is a tensor having at least the crystal symmetry. For chalcopyrite crystal  $\vec{f}$  has three nonzero elements which are in the crystallographic axes  $f_{ZZ} = f_{\parallel}$  and  $f_{XX} = f_{YY} = f_{\perp}$ . In order to calculate the nonzero components of the crystal susceptibility tensor, it is necessary to sum up the contributions of all the dipoles induced in the unit cell. The detail of the calculation is given in Appendix B. The two invariants associated with the susceptibility tensor are

$$\chi = \frac{1}{3}(\chi_e + 2\chi_o) = \frac{1}{V} \sum_s [f\alpha^{(s)} + \delta f \delta\alpha^{(s)} (3 \cos^2 \theta^{(s)} - 1)], \quad (3a)$$

$$\Delta\chi = \frac{1}{3}(\chi_e - \chi_o) = \frac{1}{V} \sum_s [\delta f \alpha^{(s)} + (f + \delta f) \delta\alpha^{(s)} (3 \cos^2 \theta^{(s)} - 1)/2]. \quad (3b)$$

In these equations the superscript (s) is used to label the different bonds in the unit cell.  $f = \frac{1}{3}(f_{\parallel} + 2f_{\perp})$ , and  $\delta f = \frac{1}{3}(f_{\parallel} - f_{\perp})$  are the invariants associated with the tensor  $\vec{f}$ .

The physical interpretation of Eqs. (3a) and (3b) are the following. First, because of the bond anisotropy, the bond dipole is different whether the applied field is parallel or perpendicular to its axis. In addition, the bonds are arranged in the crystal in an anisotropic fashion and the sum of the fields radiated by all the bonds in the crystal results in the field on the unit tetrahedron. This field is different according to the direction of the applied field with respect to the crystal axes. A

TABLE I. Isotropic- and anisotropic-local-field correction for five chalcopyrite II-IV-V<sub>2</sub> compounds.

Compound	Bond	$\alpha$	$\delta\alpha$	$\tau$	$\chi$	$3\Delta\chi$	$f$	$\delta f$																																										
CdGeAs <sub>2</sub>	CdAs	8.12	1.24	0.113	0.94	0.098	1.77	0.074																																										
	GeAs	5.02	1.05						CdGeP <sub>2</sub>	CdP	7.02	1.4	0.123	0.74	0.015	1.41	0.023	GeP	4.59	1.38	ZnSiAs <sub>2</sub>	ZnAs	6.02	0.62	0.057	0.74	0.027	1.48	0.021	SiAs	4.7	1.32	ZnSiP <sub>2</sub>	ZnP	5.27	0.97	0.067	0.70	0.059	1.88	0.064	SiP	3.68	0.9	ZnGeP <sub>2</sub>	ZnP	5.34	1.03	0.038	0.70
CdGeP <sub>2</sub>	CdP	7.02	1.4	0.123	0.74	0.015	1.41	0.023																																										
	GeP	4.59	1.38						ZnSiAs <sub>2</sub>	ZnAs	6.02	0.62	0.057	0.74	0.027	1.48	0.021	SiAs	4.7	1.32	ZnSiP <sub>2</sub>	ZnP	5.27	0.97	0.067	0.70	0.059	1.88	0.064	SiP	3.68	0.9	ZnGeP <sub>2</sub>	ZnP	5.34	1.03	0.038	0.70	0.038	1.42	0.044	GeP	4.52	1.31						
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very important consequence is to be noted. *Even if the bonds were all isotropic* ( $\delta\alpha^{(s)}=0$ ), *the crystal would be still birefringent as a whole because of the anisotropic ordering of the bonds* ( $\delta f \neq 0$ ).

From the point of view of irreducible tensors, the form of Eq. (6) can be explained as follows. Each of the three tensors  $\vec{\chi}$ ,  $\vec{\alpha}$ ,  $\vec{f}$  is the sum of two irreducible components, a scalar whose weight is  $J=0$  and a deviator whose weight is  $J=2$ . In the product of two irreducible tensors of weight  $J_1$  and  $J_2$  appear tensors of weight  $|J_1 - J_2|$ ,  $|J_1 - J_2 + 1|$ , ...,  $|J_1 + J_2|$ . So that  $\chi$  comes from  $\alpha f$  and  $\delta\alpha\delta f$ , while  $\Delta\chi$  comes from  $\alpha\delta f$ ,  $f\delta\alpha$ , and  $\delta\alpha\delta f$ . The angular factors are explained as follows: The tensor  $\chi$  and  $f$  are expressed in the crystal axis; only  $\alpha$  has to be transformed from the microscopic frame to the macroscopic one. In this transformation, the scalar  $\alpha$  is invariant and the deviator  $\delta\alpha$  is just multiplied by the Legendre polynomial  $P_2(\theta)$ .

Let us particularize Eqs. (5) to the case of II-IV-V<sub>2</sub>.

$$\chi = (16/V)[f(\alpha^{(+)} + \alpha^{(-)}) - \frac{4}{3}\tau \delta\alpha^{(+)} \delta f], \quad (4a)$$

$$\Delta\chi = (16/V)[\delta f(\alpha^{(+)} + \alpha^{(-)}) - \frac{2}{3}\tau \delta\alpha^{(+)} (f + \delta f)]. \quad (4b)$$

As expected, the deviator part of  $\vec{\alpha}^{(-)}$  does not appear because of its special orientation. But the IV-V bonds contribute to the birefringence not only through their contribution to the local-field tensor, but also by their average polarizability  $\alpha^{(-)}$ , which is multiplied by  $\delta f$ . Equation (4b) therefore explains why there is no simple correlation among the birefringence of different compounds involving the same II-V bonds, conversely to what could be deduced from Eq. (2). For most of these compounds, the tetragonal compression is small ( $0 \leq \tau \leq 0.17$ ) and the deviator  $\delta\alpha$  is small (but not negligible) in front of the scalar. It is therefore possible to write with a good accuracy

$$\chi = (16/V)f(\alpha^{(+)} + \alpha^{(-)}). \quad (5)$$

This shows that as far as average refractive indices are concerned, it is possible to define macroscopically an average polarizability  $\alpha^* = f\alpha$  which automatically includes the local-field effects. This result justifies *a posteriori* our generalization of Phillip's theory to chalcopyrite crystals.<sup>5</sup> Conversely, for the birefringence it is impossible to include the whole local-field effects in the definition of some bond optical anisotropy.

In order to evaluate the anisotropy of local field which can explain the observed II-IV-V<sub>2</sub> crystals birefringence, we consider now five compounds whose refractive indices have been experimentally measured. We use Scholl and Tang<sup>11</sup> bond polarizabilities to calculate the two local field contributions  $f$  and  $\delta f$  from the experimental refractive indices. The numerical values are displayed in Table I. The average local-field factors are of the order of 1.5; if we were dealing with completely delocalized electrons,  $f$  should be equal to one, and for completely ionic compounds it should be close to the Lorentz correction  $f_L = \frac{1}{3}(n^2 + 2) \approx 4$ . The value we obtain shows the covalent character of the bonding in these crystals. As for the  $\delta f$ , a very small anisotropy of the local fields ( $\delta f/f < 5 \times 10^{-2}$ ) is sufficient to account for the positive birefringence. This is due to the fact that *the local-field anisotropy contribution is multiplied by the sum of the bonds average polarizabilities and represents the major part of the birefringence of the crystal*. The bond polarizability anisotropy has a small contribution since it is always multiplied by the geometrical factor  $P_2(\theta)$ . The former contradiction among the signs of  $\Delta\chi$  and  $\delta\alpha$  is eliminated. Even in compressed crystals ( $c < 2a$ ), a very small local-field anisotropy can overcome the bond anisotropy contribution and produce a positive birefringence.

It is, however, interesting to understand why a slightly compressed geometry exhibit a positive local-field anisotropy (i. e.,  $\delta f > 0$ ). Such a tendency is easily explained from elementary electrostatics

theory. The local-field factor inside an ellipsoidal cavity whose semiaxes are  $a_1$ ,  $a_2$ ,  $a_3$  may be found from consideration of boundary-value problems in electrostatics; these are<sup>15</sup>  $f_I = 1 + (n^2 - 1)A_I$ , where

$$A_I = \frac{a_1 a_2 a_3}{2} \int_0^\infty \frac{ds}{(s + a_1^2)[(s + a_1^2)(s + a_2^2)(s + a_3^2)]^{1/2}}. \quad (6)$$

For a spheroidal cavity ( $a_1 = a_2 = a_3 = a$ ) well suited to describe a cubic crystal, one has  $A_I = \frac{1}{3}$ , and  $f_I = \frac{1}{3}(n^2 + 2)$  is the Lorentz local-field correction. The chalcopyrite geometry may be approximated by an oblate ellipsoidal cavity whose semiaxes are chosen to reproduce the tetragonal compression,  $a_1 = a_2 = a$ ,  $a_3 = a(1 - \tau/2)$ . An elementary calculation gives to the first order in  $\tau$ ,  $A_1 = A_2 = \frac{1}{3} - \frac{1}{15}\tau$  and  $A_3 = \frac{1}{3} + \frac{1}{15}2\tau$ . The two invariants associated with the local-field tensor  $f$  are

$$f_{c_{av}} = f_L = (n^2 + 2)/3, \quad (7a)$$

$$\delta f_{c_{av}} = (n^2 - 1)\tau/15. \quad (7b)$$

The scalar remains exactly equal to the cubic Lorentz correction, whereas the anisotropy of the local-field tensor is positive and proportional to  $\tau$ . This simplified model shows that a slight compression on a cubic crystal tends to increase the local field along the direction of compression and decrease the local field perpendicular to it. Although the Lorentz correction only applies in the case of ionic compounds and does not give correct results in the case of the semiconductors that we consider, it is interesting to see how the local-field anisotropy deduced from Eq. (7b) compare with the values of Table I. We find  $\delta f_{c_{av}}(\text{CdGeAs}_2) = 0.09$ ,  $\delta f_{c_{av}}(\text{CdGeP}_2) = 0.07$ ,  $\delta f_{c_{av}}(\text{ZnSiAs}_2) = 0.035$ ,  $\delta f_{c_{av}} \times (\text{ZnSiP}_2) = 0.038$ ,  $\delta f_{c_{av}}(\text{ZnGeP}_2) = 0.022$ . These values are of course different from those calculated from the birefringence; however, they agree surprisingly within 60%, indicating that this approach is quite sensible.

It is worth noting that the correlation among the birefringence of the II-IV-V<sub>2</sub> crystals involving the same II-V bonds although inaccurate is not accidental.<sup>9,10</sup> It is very likely that the local-field anisotropy is proportional to  $\tau$ , as in Eq. (7b). The birefringence can then be written  $\Delta n = K\tau/nV$  [see Eq. (4b)]; where  $K$  is some quantity which should not vary too much for a family of related compounds. Therefore,  $\tau/nV$  is a useful scanning factor for a rough estimate.

#### CONCLUSION

We have given a new analysis of chalcopyrite crystals birefringence, which shows that the major part of the crystal-optical anisotropy is due to the anisotropy of the local field which reflects the

ordering of the bonds in the structure. Conversely to what was formerly stressed, the bond anisotropy has a small influence on the birefringence. In the case of II-IV-V<sub>2</sub> compounds where numerical calculations are possible, a local-field anisotropy as low as 5% is sufficient to explain the positive birefringence and to eliminate the contradiction encountered formerly. The compression of a cubic structure has on the birefringence two effects opposite; one is positive on the local-field anisotropy and the other is negative on the bond orientations. The birefringence results from a delicate balance between two competing factors, and it is very likely that only a very sophisticated theory can account for it.

#### APPENDIX A

The elementary building block of chalcopyrite structure is an irregular tetrahedron  $A_{(2)}-C-B_{(2)}$  (Fig. 1). The coordinates of the atoms are given in the following table.

Atom	X	Y	Z
$A_{(1)}$	0	0	0
$A_{(2)}$	0	$a/2$	$c/4$
$B_{(1)}$	$a/2$	0	$c/4$
$B_{(2)}$	$a/2$	$a/2$	0
C	$x$	$a/4$	$c/8$

The interatomic distances are

$$d^{(\pm)2} = \frac{1}{16}a^2[1 + (1 - \frac{1}{2}\tau)^2 + (1 \pm \sigma)^2] \\ \approx \frac{1}{16}a^2(3 - \tau \pm 2\sigma).$$

The cosines of the angles between the bonds axes and the crystal optic axis are  $\cos^2\theta^{(\pm)} = (Z^{(\pm)}/d^{(\pm)})^2$ , so that the Legendre polynomials are

$$P_2(\theta^{(\pm)}) = \frac{1}{2}(3\cos^2\theta^{(\pm)} - 1) = -\frac{1}{3}(\tau \pm \sigma).$$

#### APPENDIX B

Let us label the crystallographic axes  $XYZ$  and the bond axes  $x^{(s)}y^{(s)}z^{(s)}$ , where the superscript (s) covers all the bonds in the unit cell. The susceptibility tensor and the local field are defined according to

$$P_I = \chi_{IJ} \mathcal{E}_J, \quad \mathcal{E}_I^{loc} = f_{IJ} \mathcal{E}_J. \quad (B1)$$

The irreducible invariant of any symmetric second-rank tensor  $\bar{t}$  are

$$t = \frac{1}{3}(t_{ZZ} + t_{YY} + t_{XX}), \quad \delta t = \frac{1}{6}(2t_{ZZ} - t_{YY} - t_{XX}).$$

In the microscopic axes the bond dipole is  $p_i^{(s)} = \alpha_{ij}^{(s)} \mathcal{E}_j^{loc}$ . The only nonvanishing elements of  $\alpha^{(s)}$  are

$$\alpha_{11}^{(s)} = \alpha_{zz}^{(s)}, \quad \alpha_{11}^{(s)} = \alpha_{xx}^{(s)} = \alpha_{yy}^{(s)}.$$

The transformation from the microscopic axes

to the crystal axes of the bond dipole can be written

$$P_I^{(s)} = \cos\theta_{II}^{(s)} \cos\theta_{JJ}^{(s)} \alpha_{ij}^{(s)} f_{JK} \delta_K,$$

where  $\theta_{II}^{(s)}$  is the angle between the  $I$  crystal axis and the  $i^{(s)}$  bond axis.

Since the tensors  $\vec{f}$  and  $\vec{\chi}$  are diagonal, the only

nonvanishing elements of  $\chi$  are of the following form:

$$\chi_{XX} = \frac{1}{V} \sum_s \cos^2\theta_{Xi}^{(s)} \alpha_{ii}^{(s)} f_{XX},$$

which results in Eqs. (3a) and (3b).

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