

Dielectric Theory of Tetrahedral Solids: Application to Ternary Compounds with Chalcopyrite Structure*

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The Phillips-Van Vechten dielectric theory of binary tetrahedral compounds and Levine's bond-charge model are formulated in terms of macroscopically defined linear and nonlinear bond polarizabilities. This formulation allows the determination of the linear and nonlinear optical properties of tetrahedral solids. As an illustration, the case of ternary compounds with chalcopyrite structure is considered. Theoretical and experimental results are in good agreement.

According to the theory of Phillips and Van Vechten¹⁻³ (PVV), the dielectric constant ϵ of an elementary (A) or binary (AB) compound with tetrahedral coordination⁴ is

$$\epsilon_{AB} = 1 + D_{AB} [\hbar\Omega_p / E_g(AB)]^2, \quad (1)$$

where

$$\begin{aligned} E_g^2(AB) &= H^2(AB) + C^2(AB), \\ C(AB) &= 1.5e^2(Z_A/r_A - Z_B/r_B) \exp[-\frac{1}{2}k_s(r_A + r_B)], \\ H(AB) &\propto (r_A + r_B)^{-2.5}. \end{aligned}$$

The correcting factor D_{AB} is introduced³ to take into account the contribution of the core electrons. Z_A and r_A are the valence number and covalent radius,⁵ respectively, of element A; Ω_p and k_s are the plasma frequency and the Thomas-Fermi screening constant, respectively, calculated for a free-electron gas with a density of four electrons per atomic volume.

The polarization induced by an external field \vec{E} in such a material is therefore

$$\vec{P} = \frac{16}{V} (2a_0)^3 E_0^2 \frac{D_{AB}}{E_g^2(AB)} \vec{E}, \quad (2)$$

where V is the volume of the unit cell, $a_0 = \hbar^2 / me^2$, and $E_0 = me^4 / 2\hbar^2$.

In a very different and more classical approach, the linear susceptibility tensor χ_{ij} ⁽¹⁾ can be calculated from the linear microscopic polarizability tensor α_{ij} of the bond. For a bond with axial symmetry the only nonvanishing elements of α_{ij} are α_{\parallel} and α_{\perp} . The calculation of the bond polarizabilities proceeds as follows.^{6,7} One assumes first that the local field \vec{E}_{10c} is constant over a bond and is the same for all directions. Taking then a common value W_{\parallel} for all the energies $W_i - W_0$ in the Kramers-Heisenberg dispersion formula $\alpha_{\parallel}(0) = 4e^2 \sum_{i \neq 0} |z_{0i}|^2 / (W_i - W_0)$ and in the Thomas-Kuhn sum rule $(2m/\hbar^2) \sum_{i \neq 0} (W_i - W_0)$

$\times |z_{0i}|^2 = 1$, one obtains

$$\alpha_{\parallel} \simeq (2a_0)^3 E_0^2 / W_{\parallel}^2. \quad (3)$$

z is parallel to the bond axis; 0 and i correspond, respectively, to the ground state and to an excited state; and $(2m/\hbar^2)W_{\parallel} \simeq (|z_{00}|^2 - |z_{0i}|^2)^{-1}$. α_{\perp} and W_{\perp} are defined by changing z into x or y . It should be noted that these approximations are very similar to those leading to Eq. (1) in Penn's work⁸. It is convenient to introduce the two scalar invariants associated with the irreducible components of α_{ij} : the average linear polarizability $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$, and the linear polarizability anisotropy $\partial\alpha = (\alpha_{\parallel} - \alpha_{\perp})/3$. The average linear polarizability can now be written as

$$\alpha = (2a_0)^3 \frac{E_0^2}{W^2}, \quad \frac{3}{W^2} = \frac{1}{W_{\parallel}^2} + \frac{2}{W_{\perp}^2}. \quad (4)$$

The polarization induced by an external field \vec{E} in a crystal with diamond, sphalerite, or ideal wurtzite structure (which are built up from a single type of bond) is

$$\vec{P} = \frac{16}{V} \alpha \vec{E}_{10c} = \frac{16}{V} (2a_0)^3 \frac{E_0^2}{W^2} \vec{E}_{10c} \quad (5)$$

Comparison of formulas (2) and (5) leads to the following interpretation of the PVV theory: *The dielectric constant of a tetrahedrally coordinated solid can be calculated as if each bond sees only the applied field and has an average polarizability $\alpha_{AB}^* = (2a_0)^3 E_0^2 D_{AB} / E_g^2(AB)$ which is macroscopically defined.* This is equivalent to saying that the local field effects are automatically taken into account by assigning to W the value E_g determined by PVV to fit the experimental dielectric constant.

A macroscopically defined bond nonlinear susceptibility $\beta^* = \beta_{\parallel}^*$ can be calculated from Levine's bond-charge model.^{9,10} It is found that

$$\beta^* = (C^* + \rho^*) (\alpha^* / E_g)^2, \quad (6)$$

where

$$C^* = 12 \frac{Z_A + Z_B}{(r_A + r_B)^2} \frac{e^2}{q} \exp[-\frac{1}{2}k_s(r_A + r_B)]C,$$

$$\rho^* = \frac{80H^2}{q(r_A + r_B)^2} (r_A - r_B)$$

are functions of the bond charge $q = -2e/\epsilon$ (ϵ is the dielectric constant of the material). Let us define for a microscopic dipole an analog of Miller's¹¹ Δ that describes the total acentricity of the bond,

$$\delta^* = \beta^*/\alpha^{*3} = (C^* + \rho^*)E_0^{-2}(2a_0)^{-3}. \quad (7)$$

We are now in a position to calculate the dielectric properties of a tetrahedral crystal. The crystallographic axes are XYZ , and V is the volume of the unit cell. Let $(xyz)^{(s)}$ be the axes associated with the bond s .¹² (The variable index s covers the different bonds of a unit cell.) Then

$$\begin{aligned} \chi_{av}^{(1)} &= \frac{1}{3}(\chi_{XX} + \chi_{YY} + \chi_{ZZ}) = V^{-1} \sum_s \alpha_s^*, \\ \partial\chi^{(1)} &= \frac{1}{6}(2\chi_{ZZ} - \chi_{XX} - \chi_{YY}) \\ &= V^{-1} \sum_s \frac{1}{2}(3 \cos^2\theta_{zz}^{(s)} - 1) \partial\alpha_s^*, \\ \chi_{XYZ}^{(2)} &\simeq V^{-1} \sum_s \beta_s^* \cos\theta_{zz}^{(s)} \cos\theta_{zY}^{(s)} \\ &\quad \times \cos\theta_{zX}^{(s)}. \end{aligned} \quad (8)$$

If the material has a small birefringence then Miller's Δ is

$$\begin{aligned} \Delta_{XYZ} &\simeq \frac{1}{2} \chi_{XYZ}^{(2)} / (\chi_{av}^{(1)})^3 \\ &= \frac{1}{2} V^2 \sum_s \eta_s \delta_s^* \cos\theta_{zz}^{(s)} \cos\theta_{zY}^{(s)} \cos\theta_{zX}^{(s)}, \end{aligned}$$

where we have introduced the weight of a bond, $\eta_s = (\alpha_s^* / \sum_s \alpha_s^*)^3$.

As an illustration of the above theory let us consider the case of ternary compounds (ABC_2) with chalcopyrite structure. These compounds are attractive materials for nonlinear optics since one expects that they have, like binary compounds, high nonlinear susceptibilities.¹³ The birefringence is high enough to allow phase matching¹⁴ as has recently been demonstrated for $AgGaS_2$.¹³ More than fifty ternary compounds have been reported. However, high optical quality crystals are difficult to grow.

The chalcopyrite cell can be built up from two sphalerite cells.⁴ The distortion with respect to two superposed sphalerite cells can be characterized by two parameters τ and σ :

$$\tau = 2 - c/a, \quad \sigma = 4x - 1,$$

where c and a are the cell parameters, x is the

abscissa in units of a of the anion C in crystallographic position¹⁵ d ; the cations A and B are in positions a and b , respectively. Equations (8) give immediately

$$\chi_{av}^{(1)} = \frac{16}{V} (2a_0)^3 E_0^2 \left[\frac{D_{AC}}{E_s^2(AC)} + \frac{D_{BC}}{E_s^2(BC)} \right],$$

$$\begin{aligned} \partial\chi^{(1)} &= \frac{1}{3}(\chi_e - \chi_0) \\ &= -(16/3V)[(\tau + \sigma)\partial\alpha_{BC}^* + (\tau - \sigma)\partial\alpha_{AC}^*], \end{aligned}$$

$$\begin{aligned} \Delta_{14} &= \frac{1}{6\sqrt{3}} \left(\frac{V}{16} \right)^2 \left[\left(\frac{\alpha_{AC}^*}{\alpha_{AC}^* + \alpha_{BC}^*} \right)^3 \delta_{AC}^* \right. \\ &\quad \left. + \left(\frac{\alpha_{BC}^*}{\alpha_{AC}^* + \alpha_{BC}^*} \right)^3 \delta_{BC}^* \right], \end{aligned}$$

where use has been made of $\cos\theta_{zz}^{(s)} \cos\theta_{zY}^{(s)} \times \cos\theta_{zX}^{(s)} = (3\sqrt{3})^{-1}$ to the second order in τ and σ .

The PVV theory deals with the isotropic part of the dielectric constant and therefore with the isotropic part of the bond polarizability. In order to include the anisotropic part of the bond polarizability the theory could be extended by defining macroscopically the anisotropic part of the dielectric constant from experimental measurements, as has been done for ϵ . There is at the moment insufficient experimental information to allow such an extension.

In Table I we compare the theoretical refractive index with experimental values for nine ternary compounds for which measurements have been reported. The agreement is very encouraging. For the only material whose nonlinear susceptibility has been measured, $AgGaS_2$, the agreement is very good:

$$\Delta_{cal} = 2.4 \times 10^{-6} \text{ esu}, \quad \Delta_{meas} = 2.5 \times 10^{-6} \text{ esu}.$$

The theory can be used in materials research to predict those materials which are likely to be of

Table I. Experimental and calculated refractive index.

Compound	n_{exp}	n_{calc}
ZnSiP ₂	3.1	3
ZnSiAs ₂	3.1	3.4
ZnSnP ₂	2.9	3.2
CdGeP ₂	3.6	3.2
CdGeAs ₂	3.4	3.5
CdSnAs ₂	3.7	3.6
AgGaS ₂	2.4	2.5
CuAlS ₂	2.4	2.5
CuAlSe ₂	2.6	2.8

Table II. Calculated average index and Miller's Δ for thirty ternary compounds.

Compound	Optical gap eV	$\tau = 2 - c/a$ (10^{-3})	$\sigma = 4x - 1$ (10^{-3})	average index	Miller's Δ (10^{-6} esu)
ZnSiP ₂	2 - 2.5	67	76	3	+ 1,7
ZnSiAs ₂	1.6 - 2.2	58		3.4	+ 3.3
ZnGeP ₂	1.8 - 2.4	35	56	3,1	+ 1,5
ZnGeAs ₂	0.6 - 0.85	34	56	3,5	+ 3.2
ZnSnP ₂	1.3 - 1.5	0	- 44	3,2	- 0.3
ZnSnAs ₂	0.6 - 0.75	0	- 44	3.6	+ 1
CdSiP ₂	2.2 - 2.4	163		3.1	+ 1.2
CdSiAs ₂	1.6	152		3.5	+ 2.7
CdGeP ₂	1.7 - 1.8	123	132	3.2	+ 1.2
CdGeAs ₂	0.4 - 0.55	112	144	3.5	+ 2.8
CdSnP ₂	1.15 - 1.5	50		3.1	- 0.1
CdSnAs ₂	0.25 - 0.3	43	44	3.6	+ 1.2
CuAlS ₂	3.3	39	8	2.5	+ 2.4
CuAlSe ₂	2.5	55	4	2.8	+ 4
CuAlTe ₂	0.9	25	0	3.3	+ 7.2
CuGaS ₂		42	0	2.5	+ 2.7
CuGaSe ₂	0.95 - 1.65	40	0	2.8	+ 4.4
CuGaTe ₂	0.8 - 1	13	0	3.3	+ 8.1
CuInS ₂	1.2	- 5	- 20	2.6	+ 1.9
CuInSe ₂	0.85 - 1.05	- 1	- 15	2.9	+ 3.4
CuInTe ₂	0.95	- 6	- 9	3.4	+ 6.6
AgAlS ₂		198	20	2.5	+ 2
AgAlSe ₂	0.7	195	8	2.8	+ 3.5
AgAlTe ₂	0.55	122	4	3.3	+ 6.6
AgGaS ₂	2.7	214	12	2.5	+ 2.4
AgGaSe ₂	1.65	177	8	2.8	+ 4
AgGaTe ₂	1.1	103	4	3.3	+ 7.4
AgInS ₂	1.9	80	0	2.5	+ 2
AgInSe ₂	1.2	84	0	2.8	+ 3.5
AgInTe ₂	0.95	38	0	3.4	+ 6.4

interest. To illustrate this point we indicate in Table II the calculated average refractive index and Miller's Δ along with the optical gap and parameters τ and σ . The only data used for this calculation are the crystallographic parameters and the covalent radii⁵ of elements.

As for the mean energy gap, the ionicity $f_i(AB) = [C(AB)/E_g(AB)]^2$ should be seen as an intrinsic parameter of a bond in a solid. This interpretation allows the study of bonds which could not ap-

pear in binary compounds. As an example let us consider four compounds ZnSiP₂, ZnGeP₂, CdSiP₂, and CdGeP₂ built up from combinations of the four bonds ZnP, CdP, SiP, and GeP. In Table III are given the mean energy gap, the ionicity, the average polarizability, and the total acentricity of the four bonds calculated in the different compounds. There is a slight variation of the bond ionicity from one crystal to another due to the change of the screening constant. By con-

Table III. Parameters defining a bond in a ternary compound.

Bond	Compound	Mean energy gap (eV)	Ionicity $f_i = C^2/E_g^2$	Average linear polarizability (Å^3)	Total acentricity (10^{41} esu)
ZnP	ZnSiP ₂	6.9	0.53	4.9	2.7
	ZnGeP ₂	7	0.54	4.8	3
CdP	CdSiP ₂	6.1	0.58	6.7	0.4
	CdGeP ₂	6.2	0.59	6.5	0.6
SiP	ZnSiP ₂	5.4	0.13	7.4	1.5
	CdSiP ₂	5.4	0.14	7.3	1.7
GeP	ZnGeP ₂	5.2	0.17	8.8	0.9
	CdGeP ₂	5.3	0.18	8.7	1.1

trast the bond charge and consequently the bond total acentricity are more sensitive to the environment.

The above formulation gives a unified description of the dielectric properties of tetrahedral solids. The only data needed for calculations are the crystallographic parameters and the PVV tetrahedral covalent radii of elements. The theory can easily be applied to more complicated structures like stannite, enargite, or famatinite. The case of defect structures which may involve nonbounded electron pairs should be considered more carefully.

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Note added in proof.—Additional data have been recently published on CdSnP₂ [J. L. Shay and E. Buehler, Phys. Rev. Lett. **26**, 506 (1971)] and on ZnGeP₂ [G. D. Boyd, E. Buehler, and F. G. Storz, Appl. Phys. Lett. **18**, 301 (1971)]. The experimental results, $n(\text{CdSnP}_2) = 3.1$, $n(\text{ZnGeP}_2) = 3.1$, and $\Delta(\text{ZnGeP}_2) = 0.85 \pm 0.35$, are in good agreement with our calculations (see Table II).

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¹J. C. Phillips, Phys. Rev. Lett. **19**, 415 (1967).

²J. C. Phillips, Phys. Rev. **166**, 832 (1968), and **168**, 905, 912 (1968).

³J. A. Van Vechten, Phys. Rev. **182**, 891 (1969), and **187**, 1007 (1969).

⁴E. Parthe, *Crystal Chemistry of Tetrahedral Structures* (Gordon and Breach, New York, 1964).

⁵J. A. Van Vechten and J. C. Phillips, Phys. Rev. B **2**, 2160 (1970).

⁶J. P. Vinti, Phys. Rev. **41**, 813 (1932).

⁷C. Flytzanis and J. Ducuing, Phys. Rev. **178**, 1218 (1969).

⁸D. R. Penn, Phys. Rev. **128**, 2093 (1962).

⁹B. F. Levine, Phys. Rev. Lett. **22**, 787 (1969).

¹⁰B. F. Levine, Phys. Rev. Lett. **25**, 440 (1970).

¹¹R. C. Miller, Appl. Phys. Lett. **5**, 17 (1964).

¹²C. Jeggo and G. D. Boyd, J. Appl. Phys. **41**, 2741 (1970).

¹³D. S. Chemla, P. J. Kupecek, D. S. Robertson, and R. C. Smith, Opt. Commun. **3**, 29 (1971).

¹⁴N. A. Goryunova, L. B. Zlatkin, and E. K. Ivanov, J. Phys. Chem. Solids **31**, 2557 (1970).

¹⁵*International Table for X Ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch Press, Birmingham, England, 1952).