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Nonlinear Optical Susceptibilities of Covalent Crystals

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The two-band quantum-mechanical model of Phillips and Van Vechten is applied to the calculation of the second-order susceptibility. The theory contains no adjustable parameters and gives the correct sign and reasonable agreement with measured magnitudes of second-harmonic coefficients for nine zinc-blende crystals.

Recently Phillips and Van Vechten[1] (hereafter called PV) have applied the Phillips theory[2,3] of the dielectric constant (also called the "dielectric theory of electronegativity") to the second- and third-order susceptibilities of zinc-blende and wurtzite structure crystals. From their presentation it is clear that the theory is capable of giving order-of-magnitude agreement with the measured $|\chi^{(2)}|$. It can not account for the measured $|\chi^{(3)}|$ in Si, Ge, or GaAs, but this has been explained by Van Vechten and Aspnes[4] who have shown that a "Franz-Keldysh" mechanism is dominant for $\chi^{(3)}$ in semiconductors having a sufficiently small direct gap. In this paper the PV theory for $\chi^{(2)}$ will be reformulated to eliminate an objectionable approximation made by PV, and to bring out clearly just how the theory predicts the sign of $\chi^{(2)}_{123}$ (the only nonvanishing component) in zinc-blende crystals. Wurtzite crystals will not be discussed here.

At zero frequency the linear ($\chi^{(1)}$) and second-order ($\chi^{(2)}$) susceptibilities are defined by

$$P_i = \sum_j \chi^{(1)}_{ij} E_j + \sum_{jk} \chi^{(2)}_{ijk} E_j E_k + \cdots \, , \qquad (1)$$

where $\vec{E}$ is the macroscopic electric field and $\vec{P}$ is the macroscopic electric polarization. We consider only the electronic contribution to $\chi^{(1)}$ and $\chi^{(2)}$ and ignore the contribution of the infrared lattice vibration[5] which is negligible at optical frequencies. Adler[6] has shown that the electrons can be considered localized within cells which are small compared to optical wavelengths and large compared to atomic dimensions. The linear polarizability $\vec{\alpha}$ and second-order polarizability $\vec{\beta}$ of a single cell can be written[6,7]

$$\alpha_i = \sum\nolimits'_{\nu} (2e^2/\hbar\omega_\nu) |\langle 0|\hat{\mathrm{R}}_i|\nu\rangle|^2 \, , \qquad (2)$$

$$\beta_{ijk} = \sum_{\nu\mu}{}'' \langle 0|e\hat{R}_i|\nu\rangle\langle\nu|e\hat{R}_j|\mu\rangle\langle\mu|e\hat{R}_k|0\rangle \hbar^{-2}\omega_\nu^{-1}\omega_\mu^{-1}$$
$$+ (ijk \rightarrow ikj) + (ijk \rightarrow jik) \, , \qquad (3)$$

where the ground electronic state $|0\rangle$ is taken to be at zero energy, $\hbar\omega_\nu$ is the energy of state $|\nu\rangle$, the primed sum omits the ground state, and

$$e\hat{\vec{\mathrm{R}}} \equiv e\sum \vec{r} - e\langle 0|\sum \vec{r}|0\rangle \qquad (4)$$

is the total electric moment operator. The coordinates ijk refer to principal axes of $\vec{\alpha}$. Implicit in (2) and (3) is the assumption that $\vec{E}$ is constant over the cell (the electric dipole approximation). Although the macroscopic field can be assumed constant there is in general a microscopic *local-field correction*[8] having the periodicity of the crystal. If this local-field correction is neglected the susceptibilities are

$$\chi^{(1)} = N\alpha, \quad \chi^{(2)} = N\beta \, , \qquad (5)$$

where N^{-1} is the cell volume.

It is not necessary here to go into the question of the validity of neglecting local-field corrections, since (5) can be regarded as exact if (2) and (3) refer to a suitable macroscopic model for the electrons. We use the model introduced by PV based on Phillips dielectric theory[2,3] and, with no additional assumptions or parameters, proceed to calculate $\chi^{(2)}$ for this model. According to this model each valence electron in a zinc-blende crystal is described macroscopically by a quantum-mechanical model with two states and a single coordinate ξ measured along the covalent bond. Each electron contributes the polarizability

$$\alpha_\xi = (2e^2/\hbar\omega_{ab})\,|\langle a|\xi|b\rangle|^2 \,, \tag{6}$$

where a, b represent the antibonding and bonding (ground) states, respectively. It follows that the isotropic linear susceptibility is

$$\chi^{(1)} = (64e^2/3a^3\hbar\omega_{ab})\,|\langle a|\xi|b\rangle|^2 \,, \tag{7}$$

where a is the edge of the unit cube in the crystal. The factor 3^{-1} in (7) arises because each bond in this model can only polarize along the bond direction. This is a feature of the model in disagreement with the prevailing view of the covalent bond, but there seems to be no way of avoiding it without giving up the elegance and simplicity of the two-state (Pauli matrix) formalism.

According to the Phillips dielectric theory $\chi^{(1)}$ can be written

$$\chi^{(1)} = \frac{ne^2\hbar^2/m}{E_g^2} \,, \tag{8}$$

where $n = 32a^{-3}$ is the electron density and E_g is an effective energy gap for transitions to the conduction band. Furthermore

$$E_g^2 = E_h^2 + C^2 \,, \tag{9}$$

where E_h is the effective gap for a hypothetical homopolar crystal of the same lattice constant, and the ionicity gap C is due to the antisymmetric part of the electron potential. These gaps have been tabulated by Van Vechten[3] for all crystals of the diamond, zinc-blende, wurtzite, and rocksalt structures for which data on $\chi^{(1)}$ are available. The f-sum rule for the assumed model requires

$$(2m\omega_{ab}/\hbar)\,|\langle a|\xi|b\rangle|^2 = 1 \,. \tag{10}$$

It follows that (7) and (8) agree if

$$3(\hbar\omega_{ab})^2 = E_g^2 \,, \tag{11}$$

and it then follows that

$$|\langle a|\xi|b\rangle|^2 = (3^{1/2}/64)(a^3/e^2)\,E_g\,\chi^{(1)} \,. \tag{12}$$

This relation was not used by PV.

It follows from (3) that each electron contributes the second-order polarizability

$$\beta_{\xi\xi\xi} = (3e^3/\hbar^2\omega_{ab}^2)\,|\langle a|\xi|b\rangle|^2[\langle a|\xi|a\rangle - \langle b|\xi|b\rangle] \,. \tag{13}$$

Let ξ be measured as shown in Fig. 1 from the midpoint of the bond toward the V atom in a III-V compound (or the VI atom in a II-VI compound); then

$$\chi_{123}^{(2)} = (32/3^{3/2}a^3)\,\beta_{\xi\xi\xi} \tag{14}$$

in accordance with the usual convention[9] on coordinates in zinc-blende crystals.

The model is now constructed as follows: Consider a homopolar crystal (no antisymmetric potential) with electron eigenvalues $\pm(E_h/2\sqrt{3})$ and eigenstates $|b_0\rangle$, $|a_0\rangle$. In the basis $|b_0\rangle$, $|a_0\rangle$ the homopolar-model Hamiltonian is

$$H_0 = (2\sqrt{3})^{-1}\begin{bmatrix} -E_h & 0 \\ 0 & E_h \end{bmatrix} . \tag{15}$$

Now let there be an antisymmetric potential $V_a(\xi)$ sketched in Fig. 1, and let

$$C \equiv 2\sqrt{3}\langle b_0|\,V_a(\xi)\,|a_0\rangle \,. \tag{16}$$

The heteropolar Hamiltonian in the basis $|b_0\rangle$, $|a_0\rangle$ is then

$$H = (2\sqrt{3})^{-1}\begin{bmatrix} -E_h & C \\ C & E_h \end{bmatrix} \tag{17}$$

having eigenvalues $\pm(E_g/2\sqrt{3})$. Note that $E_h > 0$, $E_g > 0$, but C may have either sign. Nevertheless we shall see that the theory uniquely determines the sign of $\beta_{\xi\xi\xi}$ in (13). The eigenstates of H are

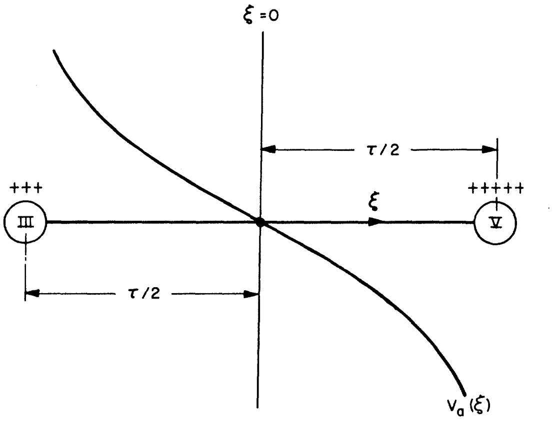

FIG. 1. Coordinate ξ is measured from the midpoint of the bond toward the V atom, or the VI atom in a II-VI crystal. The antisymmetric potential $V_a(\xi)$ is related to the ionicity gap C in (9).

$$|b\rangle = f|b_0\rangle + g|a_0\rangle ,\qquad |a\rangle = f|a_0\rangle - g|b_0\rangle , \tag{18}$$

where

$$f = \rho(1+\rho^2)^{-1/2},\quad g = -(1+\rho^2)^{-1/2} ,\qquad \rho \equiv (E_h+E_g)/C . \tag{19}$$

From (9) and (19) it can easily be shown that

$$\rho^2+1 = 2(E_g/C)\rho,\quad \rho^2-1 = 2(E_h/C)\rho ,$$

$$f^2-g^2 = E_h/E_g,\qquad 2fg = -C/E_g , \tag{20}$$

$$f^2+g^2 = 1 .$$

It then follows that

$$\langle a|\xi|a\rangle = (C/E_g)\langle a_0|\xi|b_0\rangle ,$$

$$\langle b|\xi|b\rangle = -\langle a|\xi|a\rangle = -(C/E_h)\langle a|\xi|b\rangle , \tag{21}$$

$$\langle a|\xi|b\rangle = (E_h/E_g)\langle a_0|\xi|b_0\rangle ,$$

and (14) becomes

$$\chi^{(2)}_{123} = -(3e/E_g)\chi^{(1)}\langle b|\xi|b\rangle . \tag{22}$$

Here $e = -4.8\times10^{-10}$ esu is the electron charge, and E_g is in absolute units.

We note that the sign of $\chi^{(2)}_{123}$ is determined by the sign of $\langle b|\xi|b\rangle$, which represents the charge transfer in the covalent bond. The sign of the ionicity gap C is irrelevant and may arbitrarily be chosen positive for convenience. With ξ defined as in Fig. 1 it is clear on physical grounds that $\langle b|\xi|b\rangle \geq 0$, since the electron must be polarized by $V_a(\xi)$ toward the atom with the greater positive charge on its core. Therefore $\chi^{(2)}_{123} > 0$ in agreement with experiment.[10–12] From (12) and (21)

$$\bar{\xi} \equiv \langle b|\xi|b\rangle = 0.38\,\tau\left(\frac{a}{a_0}\right)^{1/2}\frac{C}{E_h}\left(\frac{E_g a_0}{e^2}\right)^{1/2}(\chi^{(1)})^{1/2} , \tag{23}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius and $\tau = a\sqrt{3}/4$ is the interatomic distance (bond length). It should be noted that PV did not use (23) but instead invoked a rough estimate $\bar{\xi} \sim (C/E_g)\tau$. Finally from (22) and (23)

$$\chi^{(2)}_{123} = 0.49\,\frac{a_0^2}{|e|}\left(\frac{a}{a_0}\right)^{3/2}\frac{C}{E_h}\left(\frac{e^2}{a_0E_g}\right)^{1/2}(\chi^{(1)})^{3/2} . \tag{24}$$

Using the tables of $\chi^{(1)}$, C, E_h, and E_g given by PV, and the numerical values $a_0^2/|e| = 5.83\times10^{-8}$ esu, $e^2/a_0 = 27.1$ eV, values of $\bar{\xi}/\tau$ and $\chi^{(2)}_{123}$ have been calculated and tabulated in Table I for all the zinc-blende crystals for which data on $\chi^{(2)}_{123}$ are available.

The calculated values of $\chi^{(2)}_{123}$ are in better agreement with experiment than those obtained by PV, and in some cases are within experimental uncertainty. The theory contains no adjustable parameters. The agreement obtained further establishes the physical significance of the gap parameters C, E_h, and E_g in the Phillips dielectric theory. The

TABLE I. Calculated $\chi^{(2)}$ according to (24) for zinc-blende crystals. Values of $\chi^{(1)}$, C, E_h, and E_g from Ref. 1. For information on the experimental uncertainties in the measured $\chi^{(2)}$ the indicated references should be consulted. $\bar{\xi}/\tau$ is the calculated charge transfer according to (23), $(\bar{\xi}/\tau)_{\rm mo}$ is a molecular orbital calculation using (25), and τ is the bond length. For more data on $\chi^{(2)} = 2d$, where d is the second-harmonic coefficient, see Ref. a.

Crystal	a/a_0	$\chi^{(1)}$	C (eV)	E_h (eV)	E_g (eV)	$\chi^{(2)}$ (10^{-8} esu)	$\chi^{(2)}$ (obs) (10^{-8} esu)	Ref.	$\bar{\xi}/\tau$	$(\bar{\xi}/\tau)_{\rm mo}$
GaAs	10.68	0.79	2.90	4.3	5.20	108	90	b	0.33	0.11
GaSb	11.56	1.07	2.10	3.5	4.13	193	300	b	0.31	0.085
InAs	11.41	0.90	2.74	3.7	4.58	171	200	b	0.37	0.14
InSb	12.24	1.17	2.11	3.1	3.74	286	330	c	0.36	0.11
GaP	10.30	0.65	3.28	4.7	5.75	75	52	b	0.32	0.13
ZnS	10.22	0.33	6.20	4.8	7.85	43	17	d	0.49	0.24
ZnSe	10.71	0.39	5.57	4.3	7.02	63	22	d	0.51	0.21
ZnTe	11.51	0.50	4.48	3.6	5.34	112	73	d	0.50	0.19
CdTe	12.25	0.49	4.40	3.1	5.40	134	80	e	0.59	0.21

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values calculated for $\bar{\xi}/\tau$ are quite reasonable, and tend to support the obvious interpretation that the states $|b\rangle$, $|a\rangle$ in the model refer to the bonding and antibonding orbitals in the molecular orbital picture of a covalent bond. However, it is not essential that a macroscopic theory agree in detail with any microscopic model of the covalent bond. Flytzanis and Ducuing[13] have carried out a microscopic calculation of $\chi_{123}^{(2)}$ using bond orbitals of the form

$$\Psi_b = \lambda \Psi_{\mathrm{III}} + \Psi_{\mathrm{V}} , \tag{25}$$

where Ψ_{III}, Ψ_{V} are analytic sp^3 hybridized orbitals centered on their respective atoms. For Ψ_{III}, Ψ_{V} they used analytic wave functions of the form

$$\Psi(r,\ \theta) = (16\pi)^{-1/2}(1 + 3\cos\theta) \times [(2\mu)\,!\,]^{-1/2}(2\zeta)^{\mu+1/2}\, r^{\mu-1} e^{-\zeta r} , \tag{26}$$

where μ, ζ are parameters determined by the prescriptions of Slater[14] for the ions III^-, V^+. Coulson, Redei, and Stocker[15] have given a molecular orbital description of tetrahedrally coordinated covalent crystals using (25) and (26), and they find that appropriate values for λ are $\lambda = 0.68$ (III-V crystals) and $\lambda = 0.49$ (II-VI crystals). The values labeled $(\bar{\xi}/\tau)_{\mathrm{mo}}$ in Table I have been calculated from (25). They are on the average only 37% of the value of $\bar{\xi}/\tau$ in the macroscopic theory. This should not be considered a discrepancy between the theories, since Flytzanis and Ducuing[13] obtain agreement with experiment comparable with that obtained here. They find that α for the covalent bond is nearly isotropic.

Recently Levine[16] has described a classical macroscopic model based on the Phillips dielectric theory in which all (linear and nonlinear) polarization is ascribed to the rigid displacement of a phenomenological bond charge q. Unlike the quantum model of PV, the Levine model assumes that the linear susceptibility of the bond is isotropic. Levine's result, which is in excellent agreement with experiment, can be written

$$\chi_{123}^{(2)} = 0.49 \frac{a_0^2}{|e|} \frac{a}{a_0} \frac{C}{E_g} \frac{e^2}{a_0 E_g} \frac{e}{q} (\chi^{(1)})^2 . \tag{27}$$

For the bond charge Levine assumes

$$q/e = 2/\epsilon + 0.6(E_h/E_g)^2 \approx 0.5 , \tag{28}$$

where $\epsilon = 1 + 4\pi\chi^{(1)}$ is the dielectric constant (at optical frequencies). Comparison of (27) with (24) shows that the PV and Levine models are not equivalent.

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