Nonlinear Optical Susceptibilities of Covalent Crystals

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The dielectric theory of electronegativity differences is used to calculate second- and third-order nonlinear susceptibilities of covalent crystals. With no adjustable parameters excellent agreement is obtained for $\chi^{(2)}$ when allowance is made for Coulombic correlations. The experimental values $\chi^{(3)}$ appear to be in error.

SEVERAL phenomenological and empirical models have been proposed to describe the contributions of bound valence electrons to the second- and third-order nonlinear optical susceptibilities $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$.[1] In homopolar crystals like Si and Ge, one has by inversion symmetry $\chi^{(2)} = 0$. Thus the nonlinear susceptibilities represent direct measures of charge-transfer polarizabilities, and for this reason calculations of $\chi^{(2)}$ and $\chi^{(3)}$ are thought to be quite difficult.[1] Here we show that the dielectric theory of electronegativity differences[2] can be utilized to calculate $\chi_{\xi\xi\xi}^{(2)}$ and $\chi_{\xi\xi\xi\xi}^{(3)}$ in an elementary manner. The theory contains *no* adjustable parameters.

The central idea of the dielectric model is that in sp^3-bonded crystals of the diamond, zinc-blende, and wurtzite types it is a good approximation to use one energy gap E_g to describe excitations from bonding states $|b\rangle$ to antibonding states $\langle a|$. One decomposes E_g into a homopolar part E_h and a heteropolar part C according to the relation

$$E_g^2 = E_h^2 + C^2. \tag{1}$$

Values of E_h and C have been tabulated for 68 crystals of the diamond, zinc-blende, wurtzite, and NaCl types.[3]

With the assumption of a single energy gap, one can show[1] that at zero frequency

$$\chi_{\xi\xi\xi}^{(2)} = -\frac{3e}{2E_g}\chi_{\xi\xi}^{(1)}\frac{\langle\xi\overset{\leftrightarrow}{\xi}\xi\rangle}{\langle\xi^2\rangle}, \tag{2}$$

where $\chi_{\xi\xi}^{(1)}$ is the static linear susceptibility and

$$\chi_{\xi\xi\xi\xi}^{(3)} = \frac{2e^2}{E_g^2}\chi_{\xi\xi}^{(1)}\frac{\langle\xi\overset{\leftrightarrow}{\xi}^2\xi\rangle - 2\langle\xi^2\rangle^2}{\langle\xi^2\rangle}. \tag{3}$$

In (2) and (3), the dipole matrix elements are denoted by

$$\langle\xi^2\rangle = |\langle b|\xi|a\rangle|^2, \tag{4}$$

$$\langle\xi\overset{\leftrightarrow}{\xi}\xi\rangle = |\langle b|\xi|a\rangle|^2(\langle a|\xi|a\rangle - \langle b|\xi|b\rangle), \tag{5}$$

and

$$\langle\xi\overset{\leftrightarrow}{\xi}^2\xi\rangle = |\langle b|\xi|a\rangle|^2(\langle a|\xi|a\rangle - \langle b|\xi|b\rangle)^2. \tag{6}$$

A characteristic feature of the two-band, two-center model, which we shall verify below, is that with the origin of coordinates chosen halfway between the two centers we have

$$\langle a|\xi|a\rangle = -\langle b|\xi|b\rangle. \tag{7}$$

Inserting (7) in (5) and (6), we find that (2) and (3) simplify to

$$\chi_{\xi\xi\xi}^{(2)} = (3e/E_g)\chi_{\xi\xi}^{(1)}\langle b|\xi|b\rangle \tag{8}$$

and

$$\chi_{\xi\xi\xi\xi}^{(3)} = \frac{8e^2}{E_g^2}\chi_{\xi\xi}^{(1)}|\langle b|\xi|b\rangle|^2 - \frac{2(\chi_{\xi\xi}^{(1)})^2}{E_g N}, \tag{9}$$

where N is the number of valence electrons per unit volume. Within the two-band model, a general relation exists between $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ when N is approximated by $N(\text{Ge})$:

$$\chi^{(1)}\chi^{(3)} = 2(\tfrac{2}{3}\chi^{(2)})^2 - 7.5(\chi^{(1)})^3 \times 10^{-12}/E_g \text{ esu}, \tag{10}$$

where E_g is in eV. Because $\chi^{(1)} \sim 1$ and $\chi^{(2)} \lesssim 10^{-6}$ esu, the relation (10) predicts that $\chi^{(3)} \sim 10^{-12}$ esu. The experimental values[4] for $\chi^{(3)}$ for Si and Ge differ by a factor of 20 and are of order 10^{-10} esu. We suggest that further experimental work is needed before detailed comparison between theory and experiment is warranted for $\chi^{(3)}$.

Experimental values for $\chi^{(2)}$ are much better established. To calculate $\langle b|\xi|b\rangle$, we note that the model Hamiltonian[5] associated with the dielectric two-band model may be transformed to

$$H_2 \sim \frac{1}{2}\begin{pmatrix} -E_h & C \\ C & E_h \end{pmatrix}. \tag{11}$$

The basis states for the homopolar case, i.e., $C = 0$, are

$$|b_0\rangle = (1/\sqrt{2})(|A\rangle + |B\rangle) \tag{12}$$

and

$$|a_0\rangle = (1/\sqrt{2})(|A\rangle - |B\rangle), \tag{13}$$

where $|A\rangle$ and $|B\rangle$ denote hybridized orthogonalized sp^3 orbitals centered on atoms A and B, respectively. Diagonalizing (11), one obtains

$$|b\rangle = a_1|b_0\rangle + a_2|a_0\rangle = c_1|A\rangle + c_2|B\rangle \tag{14}$$

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[1] See S. S. Jha and N. Bloembergen, Phys. Rev. **171**, 891 (1968), and references cited therein. Equations (2) and (3) were first derived by F. N. H. Robinson, Bell System Tech. J. **46**, 913 (1967).

[2] J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968).

[3] J. A. Van Vechten, Phys. Rev. **182**, 889 (1969).

[4] J. J. Wynne and G. D. Boyd, Appl. Phys. Letters **12**, 191 (1968).

[5] J. C. Phillips, Phys. Rev. **168**, 905 (1968).

TABLE I. Parameters appropriate to the zinc-blende and wurtzite crystals listed as obtained in Ref. 3 and $\chi^{(2)}$ as calculated by Eqs. (8) and (16). For reasons discussed in the text the theory (random-phase approximation) overestimates $\chi^{(2)}$ in the more ionic crystals. Better agreement with experiment is obtained by multiplying the theoretical values of $\chi^{(2)}$ by the correction factor f_c^2. Observed values of $|\chi^{(2)}|$ are reported in the last column. In Ref. 10 it is shown that for wurtzite crystals, the sign of $\chi_{311}^{(2)}$ should be opposite to that of $\chi_{333}^{(2)}$.[a]

Zinc-blende crystals

Crystal	$\chi^{(1)}$	C (eV)	τ (a_0)	E_g (eV)	f_c	$\chi^{(2)}$ (10^{-8} esu)	$f_c\chi^{(2)}$ (10^{-8} esu)	$f_c^2\chi^{(2)}$ (10^{-8} esu)	$\|\chi^{(2)}\|$ (obs) (10^{-8} esu)
GaAs	0.79	2.90	4.63	5.20	0.690	256	177	122	180±60,[b] 170±40[e,d] 160±30,[e] 90±30[f]
GaSb	1.07	2.10	5.00	4.13	0.739	429	318	235	310,[g] 250[f]
InAs	0.90	2.74	4.94	4.58	0.643	380	244	157	200±60[b], 240,[f] 230±50[d]
InSb	1.17	2.11	5.30	3.74	0.679	611	415	282	330±70[d]
GaP	0.65	3.28	4.46	5.75	0.676	186	126	85	50±10,[f,h] 30±10,[e] 40±10[f]
InP	0.68	3.34	4.80	5.16	0.579	269	156	106	
AlAs	0.74	2.69	4.60	5.14	0.792	227	180	142	
AlSb	0.73	3.05	5.02	4.66	0.574	337	193	111	
BN	0.28	7.71	2.96	15.2	0.744	18.1	13.4	10.0	
SiC	0.45	3.85	3.56	9.12	0.823	49.0	40.6	33.4	
ZnS	0.33	6.20	4.43	7.85	0.377	114	42.8	16.1	15±4,[b] 17±5[e]
ZnSe	0.39	5.57	4.64	7.02	0.374	134	50.0	18.7	37±14,[b] 22±10[e]
ZnTe	0.50	4.48	4.98	5.34	0.454	257	117	53	44±16,[b] 73±22,[e] 66±30[d]
CdTe	0.49	4.40	5.30	5.40	0.235	257	83.7	27	80±30[b]
CuCl	0.22	8.27	4.42	9.57	0.254	56.2	14.7	3.7	2[i]
CuI	0.36	5.50	4.95	6.60	0.308	146	45.0	13.8	
AgI	0.39	5.65	5.30	6.44	0.230	184	42.3	9.7	

Wurzite crystals

Crystal	$\chi_{av}^{(1)}$	C (eV)	τ (a_0)	E_g (eV)	f_c	$\chi_{333}^{(2)}$ (10^{-8} esu)	$f_c^2\chi_{333}^{(2)}$ (10^{-8} esu)	$f_c^2\chi_{333}^{(2)}$ (10^{-8} esu)	$f_c^2\chi_{311}^{(2)}$ (10^{-8} esu)	$\|\chi_{333}^{(2)}\|$ (obs) (10^{-8} esu)	$\|\chi_{311}^{(2)}\|$ (obs) (10^{-8} esu)
BeO	0.16	14.1	3.12	18.2	0.398	13.8	5.5	2.2	−0.9		
CuBr	0.27	6.90	4.70	8.04	0.265	88	23.5	6.2	−2.6		
AlN	0.31	7.21	3.58	10.9	0.551	43	23.9	13.2	−5.4		
GaN	0.37	6.32	3.67	9.92	0.593	58	34	20.4	−8.3		
ZnO	0.24	9.30	3.74	11.9	0.384	38	14.9	5.7	−2.3	4.3±0.1[e]	1.3[e]
CdS	0.33	5.86	4.78	7.08	0.315	120	38	11.9	−4.9	21 ±,[b] 19±4[j]	12.6±3.0,[b] 9.6±2.0[j]
CdSe	0.38	5.50	4.97	6.58	0.301	158	47	14.3	−5.9	26 ±,[b] 54±2[e]	13.6±3.0[b]
ZnS	0.33	6.20	4.43	7.85	0.377	114	43	16.1	−6.6	17.8±6.0,[b] 9.2±3.0[e]	9.0±3.0[b]

[a] We are grateful to S. K. Kurtz for supplying us with these references to experimental data. See also R. Bechmann and S. K. Kurtz, in *Landbolt Börnstein: Numerical Data and Functional Relationships, Group III: Crystal and Solid State Physics*, edited by K. H. and A. M. Hellwege (Springer-Verlag, Berlin, 1970), Vol. 1. In Ref. h it is shown that the sign of $\chi^{(2)}$ in GaP is consistent with our model (change centered nearer the atom of larger valence in state $|b\rangle$), and this result is confirmed for GaAs, GaSb, and InSb in Ref. f.
[b] C. K. N. Patel, Phys. Rev. Letters 16, 613 (1966).
[c] R. C. Miller, Appl. Phys. Letters 5, 17 (1964).
[d] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Letters 15, 415 (1965).
[e] R. A. Soref and H. W. Moos, J. Appl. Phys. 35, 2152 (1964).
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and

$$|a\rangle = c_2|A\rangle - c_1|B\rangle, \qquad (15)$$

where (a_1, a_2) is the ground-state eigenvector of H_2. Let $\tau = \frac{1}{4}\sqrt{3}a$ denote the nearest-neighbor separation, and place the origin of coordinates midway between the two atoms in the unit cell. Then from (14) and (15) one establishes (7) and also

$$\langle b|\xi|b\rangle = 11\tau(c_1^2 - c_2^2)/8$$
$$= 11\tau C/8E_g. \qquad (16)$$

As discussed below, the factor 11/8, which arises from summing $\langle \xi\xi\xi \rangle$ over bonds, is uncertain to about 10% because the contributions of different bonds are not additive for higher-order tensors. More significant is the functional dependence of (16) on C and E_h. Reading off the values of C and E_h for each zinc-blende or wurtzite crystal from Ref. 3, we obtain the theoretical values for $\chi^{(2)}$ shown in Table I.

Figure 1 is a plot of $\chi^{(2)}$(theory)/$\chi^{(2)}$(expt.) against the fraction of covalent character defined by

$$f_c = (E_h/E_g)^2. \qquad (17)$$

Clearly, (16) gives good results for f_c near unity, but for smaller values of f_c (more ionic binding) the formula (16) overestimates $\chi^{(2)}$. Very good agreement with experiment is obtained if (16) is multiplied by f_c^2, as seen both from Table I and Fig. 1.

There are two possible reasons why $\chi^{(2)}$ should be multiplied by f_c^2. First note that (16) assumes that the bond dipole moment arises from charge transfer between $|A\rangle$ and $|B\rangle$. Molecular calculations[6] based on linear combinations of atomic orbitals indicate that in covalent systems charge transfer accounts for only a small fraction (say, $\frac{1}{4}$) of the bond dipole moment. The

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[6] J. A. Pople and G. A. Segal, J. Chem. Phys. 43, S136 (1965); 44, 3289 (1966).

larger part arises from s-p hybridization. However, when the valence orbitals exhibit tetrahedral sp^3 symmetry, hybridization should not make the dominant contribution to dipole moments.

A second mechanism involves vertex corrections associated with excited-state interactions between electrons and holes. Consider the extreme ionic limit in which $c_1 = 1$ and $c_2 = 0$. Then (14) and (15) imply that the electron and hole are centered on sublattices B and A, respectively. But if the hole is localized on $|A\rangle$ and the electron is bound to it (excitonic state), then the electron remains centered on $|A\rangle$, and $\langle a|\xi|a\rangle - \langle b|\xi|b\rangle = 0$.

In tetrahedrally coordinated crystals the fraction of oscillator strength associated with bound excitons is small. Several workers[7,8] have found, however, that in III-V and especially II-VI crystals there may be a large enhancement of the observed peak in the band spectrum of $\epsilon_2(\omega)$ assigned to Λ transitions above the predicted one-electron value. Cohen has speculated[7] that this enhancement of one-electron oscillator strength of scattering states may be associated with Coulombic vertex corrections. Because of uncertainties in the Kramers-Kronig transforms of reflectivity data (which may be unreliable at high energies), this disagreement between theory and experiment for $\chi^{(2)}(\omega)$ could not be regarded as conclusive evidence for large vertex corrections. Combined with the present results for $\chi^{(2)}$, however, it appears that the $\chi^{(1)}(\omega)$ discrepancy does represent a many-body effect arising from Coulombic correlations. These enhance the first large peak in $\chi^{(1)}(\omega)$, and reduce $\langle\xi\rangle^2/\langle\xi^2\rangle$ in $\chi^{(2)}$ or $\langle\xi^2\rangle/\langle\xi^2\rangle$ in $\chi^{(3)}$. A simple phenomenological model which incorporates these effects is given elsewhere.[9]

We conclude with some remarks about wurtzite crystals, which are of special interest because of their birefringent properties. In this case the third-order tensor $\chi_{ijk}{}^{(2)}$ contains three independent components: $\chi_{113}{}^{(2)}$, $\chi_{311}{}^{(2)}$, and $\chi_{333}{}^{(2)}$. To compute these, one must average $\langle\xi\xi\xi\rangle$ over the four tetrahedral bonds (00τ),

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[7] M. L. Cohen, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968), p. 490.
[8] D. J. Stukel *et al.*, Phys. Rev. **179**, 740 (1969).
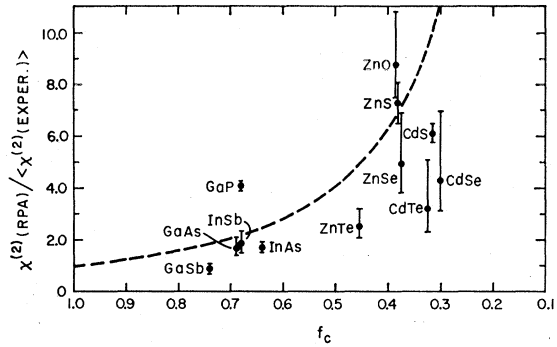[9] B. Levine, Phys. Rev. Letters **22**, 787 (1969).

FIG. 1. Ratios of $\chi^{(2)}$ calculated in random-phase approximation, Eqs. (8) and (16), and the average of experimental values versus fraction of covalent character f_c. The error bars represent one standard deviation of the reported values, or, if only one value is available, the experimentalist's estimate of his error (see Table I). Shown by dashed curve is $f_c{}^{-2}$, the proposed correction factor for the overestimates of higher-order dipole moments inherent in the random-phase approximation (RPA). *Note added in proof.* The point for GaSb is misplotted. See Table I for correct values.

$(\frac{1}{2}\sqrt{3}\tau, 0, -\frac{1}{2}\tau)$, and $(-\frac{1}{4}\sqrt{3}\tau, \pm\frac{3}{4}\tau, -\frac{1}{2}\tau)$. When this is done, one finds that

$$\chi_{\xi\xi\xi}{}^{(2)}(\text{zinc blende}) = \chi_{333}{}^{(2)}(\text{wurtzite}) \qquad (18)$$

and

$$\chi_{113}{}^{(2)}(\text{wurtzite}) = \chi_{311}{}^{(2)}(\text{wurtzite})$$
$$= -(9/22)\chi_{\xi\xi\xi}{}^{(2)}. \qquad (19)$$

In ZnS one finds that (17) and (18) are both well satisfied (see Table I). The factor 1.00 in Eq. (17) and the factor $-9/22$ in Eq. (18) differ from the factors 1.15 and $-\frac{1}{2}$ derived by Robinson[10] from the symmetry properties of isolated AB_4 tetrahedra. Our model treats A and B symmetrically, but makes an assumption of additivity of bond polarizabilities which is itself not exact. The difference between the two factors is a measure of the errors inherent in the different separability assumptions; these errors are of order 10%.

ACKNOWLEDGMENTS

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[10] F. N. H. Robinson, Phys. Letters **26A**, 435 (1968).