THIRD-ORDER OPTICAL SUSCEPTIBILITIES IN IV-IV AND III-V SEMICONDUCTORS

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The third-order susceptibility for optical frequencies between the lattice resonances and the electronic transitions is calculated from first principles for Si, Ge, Sn, InSb, InAs, InP, GaSb, GaAs, GaP and AlSb. A correlation is found to exist between the normalized third-order susceptibility ansitropy and the heteropolarity of the bonds in these semiconductors.

The third-order susceptibility $\chi^{(3)}$ relates the third harmonic polarisation $P^{(3)}$ in a crystal to the applied macroscopic electric field. For cubic crystals with the diamond or zinc-blende structure the fourth-rank tensor $\chi^{(3)}$ has two independent components [1], $\chi^{(3)}_{1111}$ and $\chi^{(3)}_{1122}$, and shows a directional anisotropy in contrast to the linear susceptibility $\chi^{(1)}$ which behaves as a scalar. For electric fields directed either along the ⟨100⟩- or the ⟨111⟩-crystal directions the macroscopic third-order induced polarisation is $P^{(3)}_{100} = \chi^{(3)}_{1111}E^3$ and $P^{(3)}_{111} = \frac{1}{3}(\chi^{(3)}_{1111} + 6\chi^{(3)}_{1122})E^3$ respectively, while the linear polarisation is given by $P^{(1)} = \chi^{(1)}E$.

Recently $\chi^{(3)}$ has been measured experimentally [2] for frequencies below the onset of the electronic transitions but above the lattice resonances. Only the valence electrons forming tetrahedral bonds between adjacent atoms contribute to the dielectric properties in this frequency range [3,4] and the linear and nonlinear susceptibilities can be satisfactorily accounted for in terms of the corresponding bond polarizabilities. Denoting by α_{ij} and γ_{ijk} the linear and third-order bond polarizabilities we obtain

$$\chi^{(1)} = \tfrac{16}{3}(f/a^3)(\alpha_{zz} + 2\alpha_{xx}) \tag{1}$$

$$\chi^{(3)}_{1111} = \tfrac{16}{9}(f^4/a^3)(\gamma_{zzzz} + 4\gamma_{xxxx} + 12\gamma_{xxzz}) \tag{2a}$$

$$\chi^{(3)}_{1122} = \tfrac{16}{9}(f^4/a^3)(\gamma_{zzzz} + 2\gamma_{xxxx}) \tag{2b}$$

where a is the lattice constant and f is the effective field factor, $E_{\mathrm{eff}} = fE$, assumed constant over the bond; the z-axis is taken along the bond. We introduce also the normalized third-order susceptibility anisotropy $\sigma = (3\chi^{(3)}_{1122} - \chi^{(3)}_{1111})/\chi^{(3)}_{1111}$.

For the calculation of the bond polarizabilities both $\psi^{(1)}$ and $\psi^{(2)}$, the first and second order perturbed parts of the bond ground state wave function are needed. These were calculated by the variational perturbation procedure [5]; appropriate polynomial forms were chosen for F_1 and F_2, defined respectively by $\psi^{(1)} = F_1\psi^{(0)}$ and $\psi^{(2)} = F_2\psi^{(0)}$ and the parameters were determined by minimizing two functionals. The different choices of F_1 were given in ref. 4 while for F_2 a 9-parameter form was used. The molecular orbitals of Coulson et al. [6] were used as unperturbed wave functions $\psi^{(0)}$. The effective field factor was determined from eq. (1) as in ref. 4.

The results of the calculation for $\chi^{(3)}_{1111}$ and $\rho = \chi^{(3)}_{1122}/\chi^{(3)}_{1111}$ are given in table 1. Only the values with a 5-parameter choice for F_1 are represented. The effective field factor has intermediate values, between the full Lorentz correction $(\epsilon_\infty + 2)/3$ and unity [4] but since it occurs in the fourth power in eqs. (2) it contributes substantially to the magnitude of $\chi^{(3)}$.

The agreement both in magnitude and sign between our calculated values for $\chi^{(3)}$ with the variational procedure and the experimental [2] ones for Si, Ge and GaAS is good. For the other compounds no experimental values exist.

In table 1 we give also the values of σ; the agreement is satisfactory for Ge and Si but the calculation fails to reproduce the negative sign of σ for GaAs. This quantity is very sensitive to the ground state wave function and should actually vanish for spherical bonds. Our calculation shows further that σ has lower values for the more heteropolar semiconductors than for the less heteropolar or the homopolar ones. It would be interesting to study this polarity-dependent behaviour of σ in connection with the relation which was found [7] to exist between $\chi^{(3)}$ and the Franz-Keldysh effect. Recent calculations [8,9]

Table 1

Values of the third-order optical susceptibility component $\chi^{(3)}_{1111}$, ratio $\rho = \chi^{(3)}_{1122}/\chi^{(3)}_{1111}$ and anisotropy $\sigma = (3\chi^{(3)}_{1122} - \chi^{(3)}_{1111})/\chi^{(3)}_{1111}$.

Semic.	Calculated				Experimental		
	f	$10^{12}\chi^{(3)}_{1111}$ e.s.u.	ρ	σ	$10^{12}\chi^{(3)}_{1111}$ e.s.u.	ρ	σ
Si	1.86	17.5	0.71	1.13	24 ± 12[2]	0.48	0.44
Ge	2.32	120	0.80	1.40	400 ± 200[2]	0.61	0.83
Sn	2.94	410	0.86	1.58			
InSb	1.93	151	0.52	0.56			
InAs	1.40	62	0.48	0.44			
InP	1.23	30	0.50	0.50			
GaSb	1.91	74	0.66	0.98			
GaAs	1.54	24	0.50	0.50	48 ± 24[2]	0.25	-0.25
GaP	1.25	10	0.49	0.47			
AlSb	1.29	9	0.58	0.74			

show that only some few critical points in the joint density of states contribute mostly to $\chi^{(3)}$.

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