

Nonlinear Optical Susceptibilities in Group-IV and III-V Semiconductors*

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The contribution of the valence electrons to the nonlinear optical susceptibilities may be estimated on the basis of simple tetrahedral bonding orbitals. The coefficient for second-harmonic generation in III-V compounds is in satisfactory agreement with the theoretical estimate. The same model contributes to the third-order nonlinearity, which describes scattering processes between four light waves. Again reasonable agreement is obtained with data for combination frequency generation in Si and Ge. The much larger effects in *n*-type InAs and InSb are due to conduction electrons. Their contribution has been calculated exactly under the assumption of Kane's theory for the band structure. The contribution of the valence electrons is, however, not negligible.

I. INTRODUCTION

THE second-harmonic generation, described by a nonlinear susceptibility $\chi_{123}^{(2)}(2\omega)$, has been studied experimentally¹ at different wavelengths in various III-V compounds. Patel, Slusher, and Fleury² have measured the next-order nonlinearity $\chi_{1111}^{(3)}(\omega_1, \omega_1, -\omega_2)$ in *n*-type InAs, InSb, and GaAs by using the 10.6 μ ($\hbar\omega_a = 0.118$ eV) and 9.6 μ ($\hbar\omega_b = 0.13$ eV) radiation from a CO₂ laser. This effect is particularly large in semiconductors with carriers in a conduction band having appreciable nonparabolicity. Recently, Wynne and Boyd³ have observed similar optical difference frequency mixing, described by the nonlinear susceptibility $\chi_{1111}^{(3)}(\omega_1, \omega_1, -\omega_2)$ or $\chi_{1122}^{(3)}(\omega_1, \omega_1, -\omega_2)$, due to bound electrons in Ge and Si.

With varying degree of success, several phenomenological and empirical models⁴ have been considered to find the order of magnitude of the second-order nonlinear susceptibility due to bound electrons in a solid. In the electric-dipole approximation, the conduction electrons do not contribute to the second-harmonic generation because of the time-reversal symmetry. In order to explain the order of magnitude of the third-order nonlinearity at the combination frequency $2\omega_a - \omega_b$ and their variations with carrier concentration *n*, Wolff and Pearson⁵ (WP) have calculated the low-frequency limit of these nonlinearities by considering the effective one-band Hamiltonian which describes electrons in the conduction band. However, the one-band calculation can be correct only for photon energies

much smaller than the energy gaps between the conduction and other bands. In particular, the photon energies must be smaller than the energy gap between the conduction and valence bands. For photon energies of the order of the band gap E_G , the result of one-band calculations must be modified in two different ways: The nature of variation of the susceptibility with the carrier concentration *n* is different, and the electrons in valence bands are expected to make appreciable contribution to the third-order susceptibility. For example, since the band gap E_G ($\cong 0.22$ eV at 80°K) for InSb is, in fact, smaller than $2\hbar\omega_a$, the result should be quite different than that predicted by the WP calculation. Thus, in general, one must write

$$\chi^{(3)} = \chi^{(3)b} + \chi^{(3)n}, \quad (1.1)$$

where $\chi^{(3)b}$ is the part of the third-order susceptibility which is independent of *n* and $\chi^{(3)n}$ is the part of the susceptibility due to carriers in the conduction band.

In order to obtain reliable results for $\chi^{(3)n}$, we consider two representative III-V compounds: InSb with the bandgap comparable to $2\hbar\omega_a$ and InAs with the bandgap larger than $2\hbar\omega_a$. We use the band structure for the conduction and valence bands given by Kane⁶ for InSb. Since for low-carrier concentrations the contribution to $\chi^{(3)n}$ comes only from the region of the Brillouin zone close to $\mathbf{k}=0$, we assume that the spin-orbit splitting is large enough to neglect the effect of the split-off band and consider only three doubly degenerate bands, i.e., the conduction band, the heavy-mass band and the light-mass band. Except for the difference in the energy gap E_G , we assume that the band structure of InAs is described by the same model.

The calculation of the bound-electron contribution to the linear dielectric constant is quite difficult, and similarly calculations of $\chi^{(3)b}$ and $\chi^{(2)}$ are much more difficult, because they depend on the detailed band structure throughout the Brillouin zone.

A fairly good approximation for the average contribution of all bound electrons may be obtained by considering the tetrahedral molecular bonding orbitals of

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¹ R. K. Chang, J. Ducuing, and N. Bloembergen, *Phys. Rev. Letters* **15**, 415 (1965); R. C. Miller, *Appl. Phys. Letters* **5**, 17 (1964); C. K. N. Patel, *Phys. Rev. Letters* **16**, 613 (1966); D. A. Kleinman, *Phys. Rev.* **126**, 1977 (1962).

² C. K. N. Patel, R. E. Slusher, and P. A. Fleury, *Phys. Rev. Letters* **17**, 1011 (1966).

³ J. J. Wynne and G. D. Boyd, *Appl. Phys. Letters* **12**, 191 (1968).

⁴ See N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965); C. G. B. Garrett and F. N. H. Robinson, *J. Quantum Electron.* **QE-2**, 328 (1966).

⁵ P. A. Wolff and G. A. Pearson, *Phys. Rev. Letters* **17**, 1015 (1966).

⁶ E. O. Kane, *J. Phys. Chem. Solids* **1**, 249 (1957).

the form $\frac{1}{2}\Phi_{ns} + \frac{1}{2}\sqrt{3}\Phi_{np}$ centered at each atomic site, with the p orbital pointing in the crystallographic $[111]$ directions. In the low-frequency approximation, i.e., for optical frequencies small compared to the bandgap, we calculate $\chi_{\xi\xi\xi}^{(2)}$ and $\chi_{\xi\xi\xi\xi}^{(3)b}$ for Ge, Si, InSb, InAs, GaSb, and GaAs, where ξ is the coordinate in the bond direction. This is done by using the standard time-independent perturbation theory with the approximation where we replace all energy denominators by a common average energy, chosen here to be the bandgap $\hbar\omega_G$. In Si and Ge the contributions of orbitals on neighboring atoms to $\chi^{(2)}$ exactly cancel, in agreement with the existence of a center of inversion symmetry. The same orbitals are used to calculate $\chi^{(3)b}$.

In Sec. II, we examine general expressions for $\chi^{(3)b}$ and $\chi^{(3)n}$. In Sec. III, we briefly describe the model of the band structure used in calculating $\chi^{(3)n}$. We find that the result obtained by WP is quite good for InAs, which has a larger bandgap ($E_G = 0.35$ eV) than that in InSb. However, our result differs considerably for the case of InSb.

In Sec. IV, we calculate the low-frequency limit of $\chi_{\xi\xi\xi}^{(2)}$ and $\chi_{\xi\xi\xi\xi}^{(3)b}$ due to valence electrons, on the basis of simple tetrahedral banding orbitals for the ground-state wave function. Numerical results for $\chi_{\xi\xi\xi}^{(2)}$ are in reasonable agreement with experimental values of the second harmonic created by 10.6μ radiation in GaAs, InSb, and InAs. The degree of ionicity, or the effective charge at each lattice site, plays a sensitive role in these numerical results. The result is less satisfactory for GaSb, presumably because of rather large ionic character of this compound. Our results for $\chi_{\xi\xi\xi\xi}^{(3)}$ for Ge and Si are also in good agreement with the observations of Wynne and Boyd.³ When these same calculations are made for InAs and InSb, it appears that $\chi_{1111}^{(3)b}$ is by no means negligible in InSb. The nonlinearity is enhanced above the low-frequency limit because of dispersion associated with two photon-absorption processes.

II. THIRD-ORDER SUSCEPTIBILITY χ^3

Various authors⁷⁻⁹ have derived general expressions for the third-order current density induced in a medium. In the electric-dipole approximation for the electromagnetic field, the component of the current density induced at the frequency $\omega_1 + \omega_2 + \omega_3$, due to fundamental fields at frequencies ω_1 , ω_2 , and ω_3 , can be written as

$$J_\mu^{(3)}(\omega_1 + \omega_2 + \omega_3) = -i(\omega_1 + \omega_2 + \omega_3)\chi_{\mu\alpha\beta\gamma}^{(3)}(\omega_1, \omega_2, \omega_3) \times \mathcal{E}_\alpha(\omega_1)\mathcal{E}_\beta(\omega_2)\mathcal{E}_\gamma(\omega_3) + \text{terms obtained by distinct permutations of the electric-field amplitudes at different frequencies.} \quad (2.1)$$

⁷ J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962); J. F. Ward, Rev. Mod. Phys. **37**, 1 (1965); V. M. Fain and E. G. Yashchin, Zh. Eksperim.

In writing Eq. (2.1), we have followed the convention to expand¹⁰ the electric field and the current density, respectively, as

$$\mathbf{E}(t) = \sum_{\omega} \mathbf{E}(\omega)e^{-i\omega t} \quad (2.2)$$

and

$$\mathbf{J}(t) = \sum_{\omega} \mathbf{J}(\omega)e^{-i\omega t}, \quad (2.3)$$

where

$$\mathbf{E}(-\omega) = \mathbf{E}^*(\omega), \quad (2.4)$$

$$\mathbf{J}(-\omega) = \mathbf{J}^*(\omega). \quad (2.5)$$

Let the unperturbed Bloch states for the electrons in the solid be represented by $|\mathbf{r}\mathbf{k}\rangle$ with energy $E_{r\mathbf{k}}$, where r is the band index. Then $\chi_{\mu\alpha\beta\gamma}^{(3)}(\omega_1, \omega_2, \omega_3)$ is given by¹¹

$$\chi_{\mu\alpha\beta\gamma}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{e^4}{m^4\omega_1\omega_2\omega_3(\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \times \sum_{\mathbf{k}} \sum_{r,s,t,u} \sum_P \frac{1}{6} P(\alpha\omega_1, \beta\omega_2, \gamma\omega_3) \times p_{rs}^\alpha(\mathbf{k})p_{st}^\beta(\mathbf{k})p_{tu}^\gamma(\mathbf{k})p_{ur}^\mu(\mathbf{k}) \times R(r\mathbf{k}, s\mathbf{k}, t\mathbf{k}, u\mathbf{k}, \omega_1, \omega_2, \omega_3), \quad (2.6)$$

where

$$R(a, b, c, d, \omega_1, \omega_2, \omega_3) = \frac{N(a, b, c, \omega_1, \omega_2) - N(b, c, d, \omega_2, \omega_3)}{E_a - E_d - \hbar\omega_{123}}, \quad (2.7)$$

$$N(a, b, c, \omega_1, \omega_2) = \frac{M(a, b, \omega_1) - M(b, c, \omega_2)}{E_a - E_c - \hbar\omega_{12}}, \quad (2.8)$$

$$M(a, b, \omega_1) = \frac{f_0(E_a) - f_0(E_b)}{E_a - E_b - \hbar\omega_1}, \quad (2.9)$$

$$p_{rs}^\alpha(\mathbf{k}) = \langle r\mathbf{k} | p_\alpha | s\mathbf{k} \rangle, \quad (2.10)$$

$$\hbar\omega_{ij} = \hbar\omega_i + \hbar\omega_j, \quad (2.11)$$

$$\hbar\omega_{ijl} = \hbar\omega_i + \hbar\omega_j + \hbar\omega_l, \quad (2.12)$$

and where V is the volume of the solid, $-e$ and m are, respectively, the mass and the charge of the electrons, and the symbol \sum_P represents the summation over permutations $P(\alpha\omega_1, \beta\omega_2, \gamma\omega_3)$. In Eq. (2.9), $f_0(E_{r\mathbf{k}})$ is the Fermi distribution function for the electrons which at low temperatures can be assumed to be either one or zero.

i Teor. Fiz. **46**, 695 (1964) [English transl.: Soviet Phys.—JETP **19**, 474 (1964)]; S. Kielich, Acta Phys. Polon. **29**, 875 (1966).

⁸ P. N. Butcher and T. P. McLean, Proc. Phys. Soc. (London) **81**, 219 (1963).

⁹ S. S. Jha and C. S. Warke, Nuovo Cimento **53B**, 120 (1968).

¹⁰ This expansion differs by a factor of $\frac{1}{3}$ from that used by P. D. Maker and R. W. Terhune, Phys. Rev. **137**, 801 (1965) and also by WP. Thus $\chi^{(3)}$ defined here is larger by a factor of 4 from that defined in Refs. 2, 3, and 5.

¹¹ The damping due to electron collisions can be taken into account by changing the resonant frequency $\omega_{ab} = \hbar^{-1}(E_a - E_b)$ of the states to $\omega_{ab} - i\omega_c$ in Eqs. (2.7)–(2.9), where $\omega_c/2\pi$ is the collision frequency of the electrons. This is nearly equivalent to the replacement of ω_λ by $\omega_\lambda + i\omega_c$ for computational purposes.

Let us confine ourselves to the experimental situation where all the fundamental fields are polarized in the same direction which is in the direction of a crystallo-

graphic axis. In this case, it is enough to consider the component $\chi_{1111}^{(3)}(\omega_1, \omega_2, \omega_3)$ of the general tensor defined in Eq. (2.6). This may be written as

$$\chi_{1111}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{e^4}{m^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \sum_{\mathbf{k}} \sum_{r,s,t,u} f_0(E_{r\mathbf{k}}) Q_{1111}(r,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}), \quad (2.13)$$

where

$$Q_{1111}(r,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}) = \frac{1}{6} \sum_P P(\omega_1, \omega_2, \omega_3) p_{rs}^x(\mathbf{k}) p_{st}^x(\mathbf{k}) p_{tu}^x(\mathbf{k}) p_{ur}^x(\mathbf{k}) \\ \times \left[\frac{[2E_{ru}(\mathbf{k}) - \hbar\omega_{12}]}{[E_{rs}(\mathbf{k}) - \hbar\omega_1][E_{rt}(\mathbf{k}) - \hbar\omega_{12}][E_{ru}(\mathbf{k}) - \hbar\omega_{123}][E_{ru}(\mathbf{k}) + \hbar\omega_3]} + (\omega_\lambda \rightarrow -\omega_\lambda) \right], \quad (2.14)$$

with

$$E_{ij}(\mathbf{k}) = E_i(\mathbf{k}) - E_j(\mathbf{k}). \quad (2.15)$$

If c denotes the conduction band of an n -type semiconductor, the expressions for $\chi^{(3)n}$ and $\chi^{(3)b}$ are given, respectively, by

$$\chi_{1111}^{(3)n}(\omega_1, \omega_2, \omega_3) = \frac{e^4}{m^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \\ \times \sum_{\mathbf{k}} \sum_{s,t,u} f_0(E_{c\mathbf{k}}) Q_{1111}(c,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}), \quad (2.16)$$

$$\chi_{1111}^{(3)b}(\omega_1, \omega_2, \omega_3) = \frac{e^4}{m^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \\ \times \sum_{\mathbf{k}} \sum_{s,t,u} \sum_{r \neq c} f_0(E_{r\mathbf{k}}) Q_{1111}(r,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}). \quad (2.17)$$

From Eqs. (2.6)–(2.9), it is clear that $\chi_{\mu\alpha\beta\gamma}^{(3)}$ is identically zero, if all the bands are completely full. If we consider only the conduction and completely full valence bands and ignore all other higher empty bands in the solid, it allows us to write

$$\chi_{1111}^{(3)b}(\omega_1, \omega_2, \omega_3) = - \frac{e^4}{m^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \\ \times \sum_{\mathbf{k}} \sum_{s,t,u} Q_{1111}(c,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}). \quad (2.18)$$

The right-hand side of Eq. (2.18) is opposite in sign and equal in magnitude to the conduction-electron contribution $\chi^{(3)N}$, if the conduction band were completely filled with N electrons representing the total number of states in the band.

By using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, Butcher and McLean⁸ have shown that in the zero frequency limit

$$\sum_{s,t,u} Q_{\alpha\beta\gamma\delta}(r,s,t,u, \omega_1, \omega_2, \omega_3, \mathbf{k}) \Big|_{\omega_1=\omega_2=\omega_3=0} \\ = \frac{1}{3!} \frac{m^4}{\hbar^4} \frac{\partial^4 E_{r\mathbf{k}}}{\partial k_\alpha \partial k_\beta \partial k_\gamma \partial k_\delta}, \quad (2.19)$$

so that

$$\chi_{1111}^{(3)n}(\omega_1, \omega_2, \omega_3) \Big|_{\omega_1=\omega_2=\omega_3=0} = \frac{e^2}{6\hbar^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \\ \times \sum_{\mathbf{k}} f_0(E_{c\mathbf{k}}) \frac{\partial^4 E_{c\mathbf{k}}}{\partial k_x^4} \quad (2.20)$$

and

$$\chi_{1111}^{(3)b}(\omega_1, \omega_2, \omega_3) \Big|_{\omega_1=\omega_2=\omega_3=0} = \frac{e^4}{6\hbar^4 \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1}{V} \\ \times \sum_{\mathbf{k}} \sum_{r \neq c} f_0(E_{r\mathbf{k}}) \frac{\partial^4 E_{r\mathbf{k}}}{\partial k_x^4}. \quad (2.21)$$

These results may be understood by noting that for a single electron the left-hand side is proportional to $\partial^4 E_{r\mathbf{k}} / \partial A_x^4$ as would result from a $\mathbf{p} \cdot \mathbf{A}$ perturbation calculation by an electromagnetic potential \mathbf{A} .

Because of the periodicity of the Bloch energy $E_{r\mathbf{k}}$, the quantity $\omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3) \chi_{1111}^{(3)b}$ will vanish in the zero-frequency limit. It is therefore not possible to obtain the low-frequency contribution to $\chi_{1111}^{(3)b}$ from the simple expression (2.21). One has to return to the general expressions (2.14) and (2.18).

The calculation of WP corresponds to the calculation of $\chi_{1111}^{(3)n}$ from Eq. (2.20), with the actual values for the frequencies, where they have used the band energy for the conduction electrons as given by Kane⁶ in the limit where spin-orbit splitting is assumed to be large. Since this band model is not accurate near the zone boundary, the result obtained by WP does not go to zero when the conduction band is completely full. Even for low carrier concentrations, their result is, however, not valid at optical frequencies, and one has to consider the general expressions (2.14) and (2.16) to calculate $\chi_{1111}^{(3)n}$. This calculation is described in Sec. III.

III. BAND-STRUCTURE CALCULATION OF $\chi^{(3)n}$ IN InSb AND InAs

Kane⁶ has calculated the band structure of InSb, where he has treated the conduction and valence band

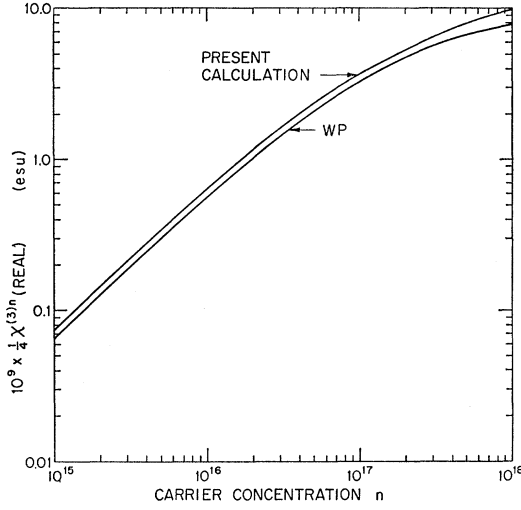


FIG. 1. Variation of the real part of $\frac{1}{4}\chi_{1111}^{(3)n} \equiv \frac{1}{4}\chi^{(3)n}$ for InAs with the carrier concentration n . In our model with spherical bands $\chi_{1122}^{(3)n} \cong \frac{1}{3}\chi_{1111}^{(3)n}$.

interactions exactly. If we ignore all other bands except the conduction and valence bands, in the limit where the spin-orbit splitting Δ is large, Kane's solutions for the doubly degenerate conduction band and three doubly degenerate valence bands may be written as

$$E_{c\mathbf{k}} = \hbar^2 k^2 / 2m + \frac{1}{2}E_G + \frac{1}{2}E_G \sec \Theta_{\mathbf{k}}, \quad (3.1)$$

$$E_{V1\mathbf{k}} = \hbar^2 k^2 / 2m, \quad (3.2)$$

$$E_{V2\mathbf{k}} = \hbar^2 k^2 / 2m + \frac{1}{2}E_G - \frac{1}{2}E_G \sec \Theta_{\mathbf{k}}, \quad (3.3)$$

$$E_{V3\mathbf{k}} = -\Delta + \frac{\hbar^2 k^2}{2m} \frac{E_G^2 \tan^2 \Theta_{\mathbf{k}}}{8(E_G + \Delta)}, \quad (3.4)$$

where

$$\tan \Theta_{\mathbf{k}} = [\sqrt{(8/3)}] Pk / E_G \quad (3.5)$$

and

$$imP/\hbar = \langle S | p_z | Z \rangle = \langle S | p_x | X \rangle = \langle S | p_y | Y \rangle. \quad (3.6)$$

In Eqs. (3.1)–(3.6), E_G is the bandgap, $|S\rangle$ is the appropriate s -state atomic wave function for the conduction band at $\mathbf{k}=0$, and $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ are the degenerate p -state atomic functions for the valence band at $\mathbf{k}=0$. In our numerical calculation, we would ignore the split-off band given by Eq. (3.4). If one writes the Bloch wave functions as

$$\Phi_{u,\mathbf{k}} = (1/N) \Psi_u(\mathbf{k}, \mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (3.7)$$

the cell-periodic functions $\Psi_u(\mathbf{k}, \mathbf{r})$ for the doubly degenerate bands C , V_1 , and V_2 , with \mathbf{k} in the z direction, are given by

$$\Psi_{c\alpha}(k_z) = \cos \frac{1}{2} \Theta_{\mathbf{k}} |iS\downarrow\rangle + \left(\frac{1}{3}\right)^{1/2} \sin \frac{1}{2} \Theta_{\mathbf{k}} |(X-iY)/2^{1/2}\uparrow\rangle + \left(\frac{2}{3}\right)^{1/2} \sin \frac{1}{2} \Theta_{\mathbf{k}} |Z\downarrow\rangle, \quad (3.8)$$

$$\Psi_{c\beta}(k_z) = \cos \frac{1}{2} \Theta_{\mathbf{k}} |iS\uparrow\rangle + \left(\frac{1}{3}\right)^{1/2} \sin \frac{1}{2} \Theta_{\mathbf{k}} |-(X+iY)/2^{1/2}\downarrow\rangle + \left(\frac{2}{3}\right)^{1/2} \sin \frac{1}{2} \Theta_{\mathbf{k}} |Z\uparrow\rangle, \quad (3.9)$$

$$\Psi_{V1\alpha}(k_z) = |(X+iY)/\sqrt{2}\uparrow\rangle, \quad (3.10)$$

$$\Psi_{V1\beta}(k_z) = |(X-iY)/\sqrt{2}\downarrow\rangle, \quad (3.11)$$

$$\Psi_{V2\alpha}(k_z) = -\sin \frac{1}{2} \Theta_{\mathbf{k}} |iS\downarrow\rangle + \left(\frac{1}{3}\right)^{1/2} \cos \frac{1}{2} \Theta_{\mathbf{k}} |(X-iY)/2^{1/2}\uparrow\rangle + \left(\frac{2}{3}\right)^{1/2} \cos \frac{1}{2} \Theta_{\mathbf{k}} |Z\downarrow\rangle, \quad (3.12)$$

$$\Psi_{V2\beta}(k_z) = -\sin \frac{1}{2} \Theta_{\mathbf{k}} |iS\uparrow\rangle + \left(\frac{1}{3}\right)^{1/2} \cos \frac{1}{2} \Theta_{\mathbf{k}} |-(X+iY)/2^{1/2}\downarrow\rangle + \left(\frac{2}{3}\right)^{1/2} \cos \Theta_{\mathbf{k}} |Z\uparrow\rangle, \quad (3.13)$$

where the symbol \uparrow means the spin-up wave function and \downarrow means the spin-down wave function for the electron.

In order to find the nonlinear susceptibility, one needs to know the momentum matrix elements $p_{rs}^\alpha(\mathbf{k})$ for any general \mathbf{k} vector. If θ and φ are the usual polar angles of the \mathbf{k} vector referred to the crystal symmetry axes x , y , and z , in terms of the wave functions with $\mathbf{k} = k_z \hat{z}$ one finds

$$p_{rs}^\alpha(\mathbf{k}) = \langle r, \mathbf{k} | p_\alpha | s, \mathbf{k} \rangle = \langle r, \mathbf{k} = k_z \hat{z} | p_\beta R_{\beta\alpha}(\theta, \varphi) | s, \mathbf{k} = k_z \hat{z} \rangle, \quad (3.14)$$

where $R(\theta, \varphi)$ is the rotation matrix given by

$$R(\theta, \varphi) = \begin{bmatrix} \cos \theta \cos \varphi & \cos \theta \sin \varphi & -\sin \theta \\ -\sin \varphi & \cos \varphi & 0 \\ \sin \theta \cos \varphi & \sin \theta \sin \varphi & \cos \theta \end{bmatrix}. \quad (3.15)$$

With the known values of the band gap E_G , the frequencies ω_1 , ω_2 , and ω_3 , the collision parameter $\hbar\omega_c$, the momentum matrix element parameter P as defined in Eq. (3.6), and the density n of the electrons in the conduction band, it is now straightforward to calculate $\chi_{1111}^{(3)n}$ as defined in Eq. (2.16). We choose P^2 to be 0.44 atomic units^{6,12} corresponding to $(4m/3\hbar^2)P^2 = 17$ eV;

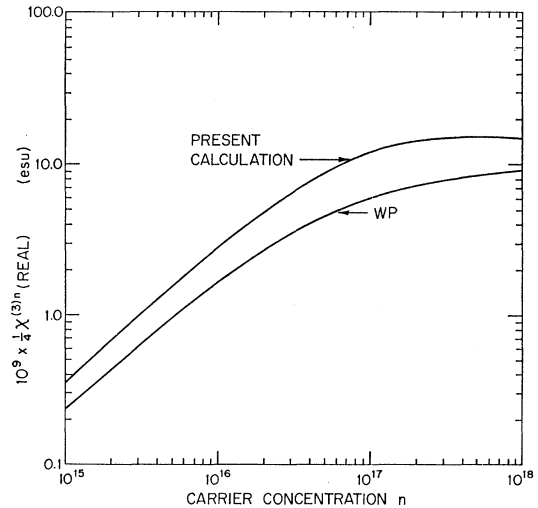


FIG. 2. Variation of the real part of $\frac{1}{4}\chi_{1111}^{(3)n} \equiv \frac{1}{4}\chi^{(3)n}$ with the carrier concentration n for InSb.

¹² H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).

$\hbar\omega_1 = \hbar\omega_2 = 0.118$ eV, $\hbar\omega_3 = -0.13$ eV, and $\hbar\omega_c$ to be 0.04 eV corresponding to the collision time $\tau_c = 10^{-13}$ sec. With $E_G = 0.35$ eV for InAs and $E_G = 0.22$ eV for InSb, we have obtained the real and imaginary parts of $\chi_{1111}^{(3)n}$ as a function of n .

The real parts of $\frac{1}{4}\chi_{1111}^{(3)n}$ for InAs and InSb are plotted, respectively, in Figs. 1 and 2. For comparison we have also plotted in these figures the low-frequency results as obtained from the WP calculation. As pointed out earlier, the WP result can be derived directly from Eqs. (2.20), (3.1), and (3.5) to find, in our notation,

$$\chi_{1111}^{(2)n}(\omega_1, \omega_2, \omega_3) \Big|_{\omega_1 = \omega_2 = \omega_3 \rightarrow 0} = \chi_{(WP)}^{(3)n} = \frac{e^4 n}{m^{*2} E_G \omega_1 \omega_2 \omega_3 (\omega_1 + \omega_2 + \omega_3)} \frac{1 + 8E_F/5E_G}{(1 + 4E_F/E_G)^{5/2}}, \quad (3.16)$$

where

$$\frac{m}{m^*} = \frac{2 |\hat{p}_{CV}^x(\mathbf{k}=0)|^2}{m E_G} = \frac{4P^2 m}{3\hbar^2 E_G} \quad (3.17)$$

and

$$E_F = (\hbar^2/2m^*)(3\pi^2 n)^{2/3}. \quad (3.18)$$

As expected, we find a considerable difference in our results for InSb from that of the WP result. The imaginary parts of $\chi_{1111}^{(3)n}$ for InAs and InSb are plotted in Fig. 3. If the correct band structure were known up to the zone boundary, we could have extended our calculation to the full conduction band, i.e., find $\chi_{1111}^{(3)n}$ for $n = N$, where N is the total number of states in the conduction band. In that case we could have obtained both the real and imaginary parts of $\chi_{1111}^{(3)b}$ which are equal in magnitude but opposite in sign from the real and imaginary parts of $\chi_{1111}^{(3)n}$ ($n = N$). A correct extrapolation of our curves to $n = N$ ($\approx 3 \times 10^{22}$ cm $^{-3}$) is not possible.

IV. BONDING ORBITAL CALCULATION OF $\chi^{(2)}$ AND $\chi^{(3)b}$

In the electric-dipole approximation, one defines the polarization \mathbf{P} induced in a medium in terms of linear and higher-order susceptibilities by the relation

$$P_i = \chi_{ij}^{(1)} \mathcal{E}_j + \chi_{ijk}^{(2)} \mathcal{E}_j \mathcal{E}_k + \chi_{ijkl}^{(3)} \mathcal{E}_j \mathcal{E}_k \mathcal{E}_l + \dots, \quad (4.1)$$

where \mathcal{E} is the electric-field vector and where repeated indices imply summations over those indices. For a static electric field (zero-frequency limit), the total energy W of the system in presence of the field is given by

$$W = -\frac{1}{2} \chi_{ij} \mathcal{E}_i \mathcal{E}_j - \frac{1}{3} \chi_{ijk}^{(2)} \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k - \frac{1}{4} \chi_{ijkl}^{(3)} \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k \mathcal{E}_l, \quad (4.2)$$

where susceptibility tensors of all orders are symmetric under exchange of any two indices. Thus the knowledge of the total energy W as a power-series expansion in the electric field \mathcal{E} allows us to find the static limit of the susceptibility of order r from the relation

$$\chi_{\alpha_1 \alpha_2 \dots \alpha_{r+1}}^{(r)}(0) = -\frac{1}{r!} \frac{\partial^{r+1} W}{\partial \mathcal{E}_{\alpha_1} \partial \mathcal{E}_{\alpha_2} \dots \partial \mathcal{E}_{\alpha_{r+1}}} \Big|_{\mathcal{E} \rightarrow 0}. \quad (4.3)$$

Since the plane wave part of the wave functions for electrons in a solid does not contribute to $\chi^{(2)}$ and $\chi^{(3)b}$, it is enough to consider the average property¹³ of valence electrons in any single unit cell. Let us assume that there are N independent unit cells per unit volume. If the Hamiltonian for each unit cell is written as

$$\mathcal{H} = \mathcal{H}_0 + e\mathbf{x} \cdot \mathcal{E}, \quad (4.4)$$

the total energy in the ground state is given by (standard perturbation theory¹⁴)

$$W = NE_0, \quad (4.5)$$

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + E_0^{(3)} + E_0^{(4)} + \dots, \quad (4.6)$$

$$\mathcal{H}_0 |m\rangle = E_m^{(0)} |m\rangle, \quad (4.7)$$

$$E_0^{(1)} = e \mathcal{E}_i \langle 0 | x_i | 0 \rangle \equiv e \mathcal{E}_i \bar{x}_i, \quad (4.8)$$

$$E_0^{(2)} = -e^2 \mathcal{E}_i \mathcal{E}_j \sum_s' \left[\frac{\langle 0 | x_i | s \rangle \langle s | x_j | 0 \rangle}{E_s^{(0)} - E_0^{(0)}} \right], \quad (4.9)$$

$$E_0^{(3)} = e^3 \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k \sum_s' \sum_t' \left[\frac{\langle 0 | x_i | s \rangle \langle s | x_j - \bar{x}_j | t \rangle \langle t | x_k | 0 \rangle}{(E_s^{(0)} - E_0^{(0)})(E_t^{(0)} - E_0^{(0)})} \right], \quad (4.10)$$

$$E_0^{(4)} = -e^4 \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k \mathcal{E}_l \sum_s' \sum_t' \sum_u' \left[\frac{\langle 0 | x_i | s \rangle \langle s | x_j - \bar{x}_j | t \rangle \langle t | x_k - \bar{x}_k | u \rangle \langle u | x_l | 0 \rangle}{(E_s^{(0)} - E_0^{(0)})(E_t^{(0)} - E_0^{(0)})(E_u^{(0)} - E_0^{(0)})} \right] - e^2 E_0^{(2)} \mathcal{E}_k \mathcal{E}_l \sum_u' \left[\frac{\langle 0 | x_k | u \rangle \langle u | x_l | 0 \rangle}{(E_u^{(0)} - E_0^{(0)})^2} \right]. \quad (4.11)$$

¹³ G. Leman and J. Friedel, J. Appl. Phys. **33S**, 281 (1962).

¹⁴ See, e.g., A. Dalgarno, in *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. 1, p. 171.

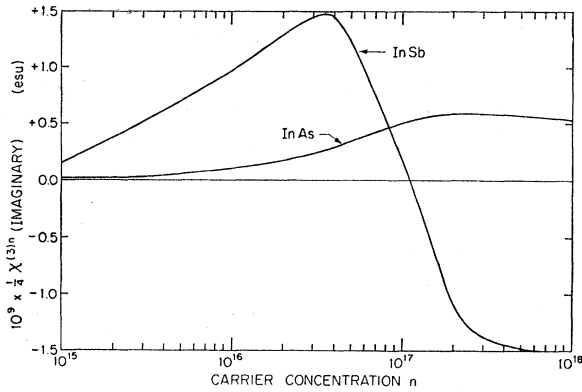


FIG. 3. Variation of the imaginary parts of $\frac{1}{4}\chi_{111}^{(3)n} \equiv \frac{1}{4}\chi^{(3)n}$ for InAs and InSb. The value of $\chi_{111}^{(3)n}$ (imaginary) for $n=N$, where N is the total number of states in the conduction band, gives the magnitude (opposite in sign) of the imaginary part of $\chi_{111}^{(3)b}$.

If the expectation value \bar{x}_i is zero in the ground state, which is true for our calculation, and if we can replace all energy denominators by some average energy denominator $\hbar\omega_0$, from Eqs. (4.3) and (4.5)–(4.10) we obtain

$$\chi_{ij}^{(1)}(0) = (2e^2N/\hbar\omega_0)\langle x_i x_j \rangle, \quad (4.12)$$

$$\chi_{ijk}^{(2)}(0) = -(3e^3N/\hbar^2\omega_0^2)\langle x_i x_j x_k \rangle, \quad (4.13)$$

and

$$\chi_{ijkl}^{(3)}(0) = (4e^4N/\hbar^3\omega_0^3)[\langle x_i x_j x_k x_l \rangle - 2\langle x_i x_j \rangle \langle x_k x_l \rangle], \quad (4.14)$$

where $\langle \dots \rangle$ means ground-state average. The factor 2 in the second term in Eq. (4.14) comes from changing the restricted summations over the intermediate states in the first term of Eq. (4.11) to unrestricted summations. Before we proceed further, note that it is not necessary to assume \bar{x}_i to be zero. If $\bar{x}_i \neq 0$, we may redefine the displacement operators in Eqs. (4.12)–(4.14) by changing x_i to \tilde{x}_i , where

$$\tilde{x}_i = x_i - \bar{x}_i. \quad (4.15)$$

Using Eq. (4.12) to eliminate N from Eqs. (4.13) and (4.14) and replacing x_i by \tilde{x}_i , we then obtain

$$\chi_{ijk}^{(2)}(0) = -(3X_{\alpha\alpha}^{(1)}e/2\hbar\omega_0\langle \tilde{x}_\alpha^2 \rangle)\langle \tilde{x}_i \tilde{x}_j \tilde{x}_k \rangle \quad (4.16)$$

and

$$\chi_{ijkl}^{(3)}(0) = (2X_{\alpha\alpha}^{(1)}e^2/\hbar^2\omega_0^2\langle \tilde{x}_\alpha^2 \rangle) \times [\langle \tilde{x}_i \tilde{x}_j \tilde{x}_k \tilde{x}_l \rangle - 2\langle \tilde{x}_i \tilde{x}_j \rangle \langle \tilde{x}_k \tilde{x}_l \rangle]. \quad (4.17)$$

These results are expected to be valid also for low frequencies, i.e., for optical frequencies small compared to the band gap, if we replace the linear static susceptibility in Eqs. (4.16) and (4.17) either by

$$\chi_{ij}^{(1)}(0) \rightarrow \chi_{ij}^{(1)}(\omega) = [2e^2N\omega_0/\hbar(\omega_0^2 - \omega^2)]\langle \tilde{x}_i \tilde{x}_j \rangle \quad (4.18)$$

or, as suggested by Robinson,¹⁵ by its observed low-

frequency value. In the calculation to be described below we use the observed values for optical susceptibility $\chi_{\alpha\alpha}^{(1)}$ in Eqs. (4.16) and (4.17) and will assume further that $\hbar\omega_0$ may be approximated by the minimum band gap between the valence and the conduction band.

From the expressions derived for the low-frequency limit of the susceptibilities, it is clear that these can be obtained by finding various moments of the charge distribution in the ground state. The ground-state wave function of a bound electron in group IV and III-V compounds may be described by sp^3 tetrahedral bonding orbitals centered at atomic sites and pointing in the crystallographic $\{111\}$ directions. The wave functions for each of the four bonds in III-V compounds may be written as

$$\Psi_{\text{III-V}} = (\lambda\Psi_{\text{III}} + \Psi_{\text{V}})(1 + \lambda^2)^{-1/2}, \quad (4.19)$$

$$\Psi_{\text{III}} = \frac{1}{2}\Phi_{n_s} + \frac{1}{2}\sqrt{3}\Phi_{n_{p\xi}}, \quad (4.20)$$

$$\Psi_{\text{V}} = \frac{1}{2}\Phi_{m_s} - \frac{1}{2}\sqrt{3}\Phi_{m_{p\xi}}, \quad (4.21)$$

where $(1 - \lambda^2)(1 + \lambda^2)^{-1}$ gives the ionic character of the bond which is related to the effective charge at each lattice site, Φ_{n_s} , $\Phi_{n_{p\xi}}$, etc., are hydrogenlike orthogonal atomic wave functions for the electrons outside the closed shells and ξ is the coordinate in the bond direction. If we neglect the overlap of orbitals at different sites, for a single bond the expectation value of ξ^q , $q=1, 2, 3, 4$, etc., may be obtained from the relation

$$\langle \xi^q \rangle_{\text{orb}} \approx \frac{\lambda^2}{1 + \lambda^2} \langle \Psi_{\text{III}} | \xi^q | \Psi_{\text{III}} \rangle + \frac{1}{1 + \lambda^2} \langle \Psi_{\text{V}} | \xi^q | \Psi_{\text{V}} \rangle. \quad (4.22)$$

For ξ in the $[111]$ direction from the group-III to the group-V atom, the contribution due to all four bonds¹⁶ can be written as

$$\langle \xi^q \rangle = B_q \langle \xi^q \rangle_{\text{orb}}, \quad (4.23)$$

where $B_1=0$, $B_2=\frac{4}{9}$, $B_3=8/9$, and $B_4=28/27$. For the odd moments, two terms in Eq. (4.22) have opposite

¹⁶ When the electric-field vector \mathbf{E} is parallel to one of the bonds in the $[111]$ direction, there are components of this field in the directions parallel (say ξ') and in the directions perpendicular (say, η') to the axis of the other three bonds. Thus, for these three bonding orbitals one must calculate both $\langle \xi'^q \rangle_{\text{orb}}$ and $\langle \eta'^q \rangle_{\text{orb}}$ to find the expectation values $\langle (\mathbf{x} \cdot \mathbf{E})^q \rangle_{\text{orb}}$. Similarly, in order to find $\langle (\mathbf{x} \cdot \mathbf{E})^4 \rangle$, one has to consider $\langle \xi'^4 \rangle$, $\langle \xi'^2 \eta'^2 \rangle$, and $\langle \eta'^4 \rangle$. The contributions due to terms proportional to $\langle \xi'^q \eta'^q \rangle$ for $q=3$ and $\langle \xi'^2 \eta'^2 \rangle$ and $\langle \eta'^4 \rangle$ for $q=4$ are ignored for the following reasons. If one takes into account of these contributions to calculate $\chi_{\xi\xi\xi}^{(2)}$ and $\chi_{\xi\xi\xi\xi}^{(3)}$, he must necessarily consider the effect of the off-diagonal matrix elements of the perturbation between different degenerate orbitals, which are of the same form and order. Thus in a complete calculation one has to use a degenerate perturbation theory instead of the nondegenerate perturbation theory used here. To be consistent, only charge displacements along the directions of the unperturbed bonds should be retained in the present calculation.

After this paper had been submitted for publication, Dr. J. Ducuing informed us that a similar bonding-orbital approach has been used by C. Flytzanis and J. Ducuing, Phys. Letters **26A**, 315 (1968) to calculate $\chi_{\xi\xi\xi}^{(2)}$ in III-V compounds.

¹⁵ F. N. H. Robinson, Bell System Tech. J. **46**, 913 (1967).

signs. For example, for $q=3$,

$$\langle \xi^3 \rangle_{\text{orb}} = \frac{1}{2}\sqrt{3} \left[\frac{\lambda^2}{1+\lambda^2} \langle ms | \xi^3 | np_\xi \rangle - \frac{1}{1+\lambda^2} \langle ms | \xi^3 | mp_\xi \rangle \right]. \quad (4.24)$$

Thus the value of λ plays a sensitive role in the numerical results for $\chi_{\xi\xi\xi}^{(2)}$. Depending on the value of λ , $\chi_{\xi\xi\xi}^{(2)}$ can be either positive or negative. However, we have consistently followed the approach of Gill and Bloembergen¹⁷ to find the values of λ from the modified Szigetti formula, i.e., the Szigetti formula without the local-field correction factor.

The wave functions for valence electrons in semiconductors like Ge and Si are of the same form as that given by Eqs. (4.19)–(4.21), except that in these materials $\lambda=1$ and both Ψ_{III} and Ψ_{V} are replaced by Ψ_{IV} with total quantum numbers $n=m=4$ for Ge and $n=m=3$ for Si. The contributions to $\langle \xi^3 \rangle$ of orbitals on neighboring atoms exactly cancel in these cases. This is consistent with the fact that $\chi_{ijk}^{(2)}$ vanishes identically for solids with inversion symmetry.

Since $\langle \xi \rangle = 0$ in our case, to calculate the contribution of valence electrons we use the formula

$$\chi_{\xi\xi\xi}^{(2)} = \frac{-3\chi_{\xi\xi}^{(1)}e}{2\hbar\omega_G \langle \xi^2 \rangle} \langle \xi^3 \rangle \quad (4.25)$$

and

$$\chi_{\xi\xi\xi}^{(3)b} = \frac{2\chi_{\xi\xi}^{(1)}e^2}{\hbar^2\omega_G^2 \langle \xi^2 \rangle} [\langle \xi^4 \rangle - 2\langle \xi^2 \rangle^2], \quad (4.26)$$

where $\hbar\omega_G$ corresponds to the minimum energy gap in these solids. Note that no Lorentz-type local-field correction factors^{15–17} are applied in this calculation. This correction factor would probably lie between one and two. A similar uncertainty exists in the choice of the common energy denominator. By taking for the latter the lowest possible value, equal to the energy gap, we have at least a partial cancellation of these important, but uncertain corrections.

We list our results¹⁸ for $\chi_{\xi\xi\xi}^{(2)}(2\omega)$ for InSb, InAs, GaSb, and GaAs in Table I, together with the experi-

TABLE I. $\chi_{\xi\xi\xi}^{(2)}(2\omega)$.

Semi-conductors	$\chi_{\xi\xi}^{(1)}$ (esu)	$\hbar\omega_G$ (eV) (Minimum gap)	λ	$\chi_{\xi\xi\xi}^{(2)}$ (10^{-6} esu) (Theor.)	$ \chi_{\xi\xi\xi}^{(2)} $ (10^{-6} esu) (Expt.) ^a
InSb	1.27	0.22	0.4	– 6.0	3.1
InAs	1.04	0.35	0.2	– 3.5	2.4
GaSb	1.11	0.8	0.4	– 18.0	3.1
GaAs	0.91	1.4	0.4	– 1.0	2.0

^a References 1, 4, and 15.

¹⁷ D. Gill and N. Bloembergen, Phys. Rev. **129**, 2398 (1963).

¹⁸ In the coordinate system defined by the crystallographic axes, only nonvanishing components of $\chi_{ijk}^{(2)}$ for these compounds

TABLE II. $\chi_{\xi\xi\xi}^{(3)}(\omega_1, \omega_1, -\omega_2)$.

Semi-conductors	$\chi_{\xi\xi}^{(1)}$	$\hbar\omega_G$ (eV) (Minimum gap)	λ	$\chi_{\xi\xi\xi}^{(3)}$ (10^{-10} esu) (Theor.)	$ \chi_{\xi\xi\xi}^{(3)} $ (10^{-10} esu) (Expt.) ^a
Ge	1.19	0.6	1.0	– 3.5	$6.0 \pm 50\%$
Si	0.86	1.1	1.0	– 0.25	$0.32 \pm 50\%$
InSb	1.27	0.22	0.4	– 50.0	...
InAs	1.04	0.35	0.2	– 6.0	...
GaSb	1.11	0.8	0.4	– 80.0	...
GaAs	0.91	1.4	0.4	– 0.5	...

^a Reference 3.

mental results. Except for GaSb, our numerical results are in reasonable agreement with the experimental values. As mentioned earlier, numerical values are sensitive to the choice of λ . For example, for GaAs $\chi_{\xi\xi\xi}^{(2)}$ changes from -1×10^{-6} for $\lambda=0.4$ to 2.5×10^{-6} for $\lambda=0.69$. However, because of various approximations involved in our calculation and because of the lack of knowledge of the sign of the experimental values of $\chi_{\xi\xi\xi}^{(2)}$, it is not worthwhile to vary λ to fit the experimental results.

In Table II, we tabulate¹⁹ our results for $\chi_{\xi\xi\xi}^{(3)b}$ for Ge, Si, InSb, InAs, GaSb, and GaAs, together with the experimental results of Wynne and Boyd for Ge and Si. The agreement of our results for Ge and Si with the experimental observation is quite good. Since the fourth moment $\langle \xi^4 \rangle$ is not very sensitive to the value of λ , we think that except for GaSb our numerical results for other III-V compounds are close to actual values. Thus the bound-electron contribution to $\chi^{(3)}$ is equal to the contribution of 3×10^{15} to 3×10^{16} electrons/cm³ in the conduction band.

V. DISCUSSION AND CONCLUSION

Although the agreement between the simple model to describe the valence electrons and the observed magnitude of the optical nonlinearities is gratifying, it should be emphasized that the simplification introduced in the calculation does not account for many details. There appears to be little doubt that these details are contained in the complete theoretical expression, but this expression cannot be evaluated because the exact wave functions throughout the bands are not known.

The simplified expressions, Eqs. (4.16) and (4.17), do not give the correct frequency dependence at higher frequencies. The experimental data in the near infrared and the visible region²⁰ demonstrate that the frequency

are $\chi_{123}^{(2)}$, $\chi_{132}^{(2)}$, $\chi_{231}^{(2)}$, $\chi_{213}^{(2)}$, $\chi_{312}^{(2)}$, $\chi_{321}^{(2)}$, which are all equal. $\chi_{\xi\xi\xi}^{(2)}$ is $\pm \frac{1}{3}\sqrt{3}\chi_{123}$.

¹⁹ In the low-frequency limit, two independent components of $\chi_{ijkl}^{(3)}$ are $\chi_{1111}^{(3)} = \chi_{2222}^{(3)} = \chi_{3333}^{(3)}$ and

$$\begin{aligned} \chi_{1122}^{(3)} &= \chi_{1212}^{(3)} = \chi_{1221}^{(3)} = \chi_{1133}^{(3)} = \chi_{1313}^{(3)} = \chi_{1331}^{(3)} = \chi_{2233}^{(3)} \\ &= \chi_{2323}^{(3)} = \chi_{2332}^{(3)} = \chi_{2211}^{(3)} = \chi_{2121}^{(3)} = \chi_{2112}^{(3)} = \chi_{3311}^{(3)} \\ &= \chi_{3131}^{(3)} = \chi_{3113}^{(3)} = \chi_{3322}^{(3)} = \chi_{3232}^{(3)} = \chi_{3223}^{(3)}. \end{aligned}$$

For spherical bands, $\chi_{1122}^{(3)} = \frac{1}{3}\chi_{1111}^{(3)}$. In general,

$$\chi_{\xi\xi\xi}^{(3)} = \frac{1}{3}(\chi_{1111}^{(3)} + 6\chi_{1122}^{(3)}).$$

²⁰ R. K. Chang, J. Ducuing, and N. Bloembergen (Ref. 1).

dependences of $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$ is not identical to that of $\chi_{ij}^{(1)}$, as suggested by Eqs. (4.16) and (4.17). In the strongly absorbing regions of the spectrum, the simple closure approximation is clearly inadequate. The detailed nonlinear dispersion at high frequencies requires the consideration of critical points in the joint densities of states.²⁰

Another feature which is not adequately represented by the *s-p* tetrahedral orbitals is the tensorial character of $\chi^{(3)}$. Our model is isotropic and predicts $\chi_{1122}^{(3)} = \frac{1}{3}\chi_{1111}^{(3)}$. The experimental ratio for Si is 0.48, and for Ge 0.61 instead of $\frac{1}{3}$. This probably is connected with the anisotropic band structure of these materials. One could, of course, introduce an anisotropy in the energy denominators, or $(\hbar\omega_G)^2$, in an *ad hoc* manner. This procedure begs the question, which can only be resolved by taking more realistic and accurate wave functions. The spherical approximation may, however, be reasonable in several III-V compounds. It would be very desirable to obtain data on the anisotropy of $\chi^{(3)b}$ in InSb. The experimental difficulty is to separate this contribution from $\chi^{(3)n}$, since the actual carrier concentration of the sample exposed to an intense 10.6 μ laser beam is in doubt. Two photon-absorption processes could perhaps be eliminated by efficient cooling of the sample. At any rate, the data of Patel *et al.*² should be reanalyzed with due regard for $\chi^{(3)b}$.

Another interesting experimental check would be afforded by the determination of the sign of $\chi_{\xi\xi\xi}^{(2)}$. Our calculations show that this quantity should be negative for all III-V compounds in the low-frequency approximation. When the fundamental field is applied in a [111] direction, the second-harmonic polarization should point from a group-III layer with [111] normal to the nearest neighboring group-V layer, at the time that the fundamental field reaches its maximum value. When the fundamental field passes through zero, the second-harmonic polarization should point in the opposite direction. The relative sign of $\chi^{(2)}$ can be

determined by second-harmonic interference experiments.²¹

The limitations of the model are also apparent in the case of GaSb, where the predicted magnitude of $\chi_{\xi\xi\xi}^{(2)}$ is definitely too large. As the material becomes more ionic in nature, the simple assumption about the bonding orbital becomes less accurate. Hybridization with other atomic orbitals and nonorthogonality of the wave functions centered at adjacent lattice sites becomes increasingly important.

The order of magnitude of the valence electrons to the optical nonlinearities can be estimated correctly on the basis of a simple LCAO (linear combination of atomic orbitals) model of cohesive bonding. The second-harmonic generation in III-V compounds is entirely due to noncanceling contributions of bonding orbitals of group-III and group-V atoms, respectively. The same model also describes correctly the next higher nonlinearity $\chi^{(3)}(2\omega_1 - \omega_2)$, responsible for the generation of combination frequencies in Si and Ge. Details of the nonlinear dispersion at frequencies larger than the band gap and exact values of the nonlinearity and its anisotropy cannot be obtained from this model. Exact calculations of the nonlinear index for bound electrons cannot be carried through, because detailed wave functions throughout the valence band are not known. However, the contribution of conduction electrons in nonparabolic bands to $\chi^{(3)}(2\omega_1 - \omega_2)$ can be calculated accurately. It is the dominant contribution in InSb, if the concentration of carriers is larger than 10^{16} cm⁻³.

ACKNOWLEDGMENTS

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²¹ R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Letters **15**, 6 (1965); J. Simon and N. Bloembergen, Phys. Rev. **171**, 1104 (1968).