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Effect of Carrier Scattering on Nonlinear Optical Susceptibility due to Mobile Carriers in InSb, InAs, and GaAs

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To estimate the effect of carrier scattering on the low-frequency nonlinear optical response of mobile carriers in semiconductors, the Boltzmann transport equation is solved in a generalized relaxation-time approximation. Two cases, one in which the elastic scattering of carriers by ionized impurities dominates the transport properties and the other in which inelastic scattering by longitudinal optical phonons is the most important scattering mechanism, are considered in detail for InSb, InAs, and GaAs. We find that the inclusion of carrier scattering affects the third-order nonlinear susceptibility in two distinct ways. First, the contribution due to nonparabolicity is modified in a nontrivial fashion. This modification becomes important in the optical-frequency-mixing experiments, when the difference frequency is comparable to the "average" collision frequency. Second, an additional nonlinearity arises because of the energy dependence of carrier collision frequency. This is estimated to be unimportant in most cases for which detailed experimental data are available at present, but is shown to be quite important when the difference frequency becomes smaller. It is found that, at low temperatures, the additional nonlinearity due to energy-dependent scattering can be significant in InSb and InAs samples, with $n \approx 10^{18}$ cm^{-3}, even for the frequencies used in the presently available experimental investigations.

I. INTRODUCTION

Using the infrared radiation from a CO_2 laser, third-order optical-frequency-mixing experiments[1,2] have been performed, in recent years, to measure the magnitude of the nonlinear optical-susceptibility tensor $\chi^{(3)}_{ijkl}(\omega_a, \omega_a, -\omega_b)$ in n-type III-V semiconductors. The bound-electron contribution to $\chi^{(3)}$ is separated from that due to mobile carriers by measuring $\chi^{(3)}$ as a function of the carrier concentration n. The mobile-carrier contribution is principally attributed to two sources: the interband $\vec{k}\cdot\vec{p}$ interaction[3-5] between the conduction and valence bands which describes the nonparabolicity of the conduction band, and the energy dependence of the carrier relaxation processes.[6-9] For the case, when $2\hbar\omega_a$ and $\hbar\omega_b$ are small compared to the band gap E_g, Jha and Bloembergen[4] have shown that a one-band effective Hamiltonian[5] may be used to obtain the mobile-carrier contribution to $\chi^{(3)}$ arising from the nonparabolicity of the conduction band. It is expected that a semiclassical description of the electronic motion, employing the Boltzmann transport equation, may be used to calculate the effect of carrier scattering on the low-frequency optical response of mobile carriers in n-type semiconductors. In this approach, we represent the collision integral in a generalized relaxation-time approximation (RTA). A similar approach was used very recently, by Wang and Ressler (WR).[7] They showed that Kaw's[6] earlier calculation of the carrier-scattering contribution to $\chi^{(3)}$, based on the "hot-electron" approach, is inadequate for the purpose since it does not incorporate changes described in terms of higher-order derivatives of the distribution function. The treatment of WR is, however, valid only for elastic scattering. WR also assume that all the incident fields are polarized in the same direction. The general solutions of the Boltzmann equation, obtained in Sec. II, include the effect of elastic as well as inelastic scattering of carriers and are valid for arbitrary polarizations of the incident fields. It is observed that a simple universal RTA, which gives correct results for the linear response, may overestimate[8] the third-order nonlinearity due to energy dependence of the relaxation time if the decay of an isotropic perturbation is much slower than that of anistropic perturbations.

In general, it is very difficult to determine the energy dependence of the carrier relaxation time from either experiments or theory because of the great complexity of the problem. In limited ranges of temperature and carrier concentration one can, nevertheless, obtain reliable estimates of the energy dependence of the momentum relaxation time by analyzing the low-field-mobility data. At low temperatures ($T \lesssim 80$ °K), the elastic scattering of carriers by ionized impurities is the dominant scattering mechanism in n-type InAs and InSb with $n \gtrsim 10^{16}$ cm^{-3}. This is considered in Sec. III. Compared to InAs and InSb, the low-temperature-mobility data for GaAs can depend considerably on the sample preparation. The results obtained in this section are, therefore, somewhat less realistic for GaAs. We note that for the carrier energies involved in our discussion, the energy dependence of the momentum relaxation time τ is much slower than the $\mathcal{E}^{3/2}$ dependence usually quoted in litera-

ture.[10] WR have used the $\mathcal{E}^{3/2}$ dependence to conclude, incorrectly, that the contribution of ionized-impurity scattering to $\chi^{(3)}$ is at most of the order $(\omega\tau)^{-2}$. It is found that the contribution of order $(\omega\tau)^{-1}$ is purely imaginary and is added to the real contribution due to nonparabolicity. Energy relaxation processes become important when the difference frequency $\omega_a - \omega_b$ becomes very small.

Carrier scattering from longitudinal optical (polar) phonons, considered in Sec. IV, is the most important mechanism[10-12] of carrier scattering in III-V semiconductors at higher temperatures $T \gtrsim 300\,^{\circ}\mathrm{K}$. The collision integral for polar scattering involves a difference operator in $\mathcal{E}$. Only for carrier energy $\mathcal{E} \gg \hbar\omega_l$, the polar-phonon energy, can the collision integral be approximated to obtain an effective RTA. For nondegenerate statistics the use of RTA is strictly valid only for $T \gg \Theta_D$, the Debye temperature. By comparing the variational calculation of mobility with that using RTA, it is expected that RTA is a fairly good approximation for $T \gtrsim 2\Theta_D$. In GaAs, for $T = 2\Theta_D$ and $n = 10^{16}\ \mathrm{cm}^{-3}$, the nonlinearity due to the energy dependence of τ is found to be quite small. However, the effect of including an average energy-independent $\langle\tau\rangle$ is not small since $1/\langle\tau\rangle$ is comparable to the difference frequency $\omega_a - \omega_b$.

Finally, in Sec. V our results are summarized, and the validity of various approximations in our analysis is considered. Attention is drawn to the fact that the relative importance of the two sources of nonlinearity is a sensitive function of the difference frequency $\omega_a - \omega_b$, and depends considerably the band gap E_g, the average carrier energy $\langle\mathcal{E}\rangle$, the carrier concentration n, and the temperature T. The applicability of our results to Wynne's experimental determination[2] of the nonparabolicity of the conduction band in GaAs is also discussed.

II. SOLUTION OF THE BOLTZMANN EQUATION

The motion of conduction electrons in n-type semiconductors, under the influence of a slowly varying electric field $\vec{E}(t)$, can be described by the Boltzmann equation

$$\frac{\partial}{\partial t} f(\vec{k}, t) - \frac{e}{\hbar}\vec{E}(t)\cdot\frac{\partial}{\partial \vec{k}} f(\vec{k}, t) = \left(\frac{\partial f(\vec{k}, t)}{\partial t}\right)_{\mathrm{coll}}, \quad (2.1)$$

where the distribution function $f(\vec{k}, t)$ is the probability of occupation of a state of Bloch wave vector $\vec{k}$ at time t. The right-hand side of Eq. (2.1) represents the collision integral, i.e., the time rate of change in $f(\vec{k}, t)$ due to carrier scattering. In the long-wavelength limit for the incident electric field, the space variation of $f(\vec{k}, t)$ is neglected. It is implicitly assumed in this approach that $\vec{E}(t)$ varies negligibly during a collision. Following Jha and Bloembergen[4] we expand the incident electric field $\vec{E}(t)$

$$\vec{E}(t) = \sum_{\omega_i} \vec{E}(\omega_i) e^{-i\omega_i t}, \quad (2.2)$$

where ω_i are the incident frequencies. Since all $\vec{E}(\omega_i)$ are not necessarily in the same direction, we expand $f(\vec{k}, t)$ in terms of spherical harmonics,

$$f(\vec{k}, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} f_{lm}(\mathcal{E}, t)\, Y_{lm}(\Omega_k), \quad (2.3)$$

where $\Omega_k \equiv (\theta_k, \phi_k)$ are the spherical polar angles specifying the orientation of $\vec{k}$ with respect to a *fixed* set of axes and $\mathcal{E}$ is the carrier energy assumed to be a function of k only. In our generalized RTA, we assume that the collision integral may be written as

$$\left(\frac{\partial f(\vec{k}, t)}{\partial t}\right)_{\mathrm{coll}} = -\sum_{lm} \nu_l [f_{lm}(\mathcal{E}, t) - \delta_{l,0} f_{00}^{(0)}(\mathcal{E})] Y_{lm}(\Omega_k), \quad (2.4)$$

where ν_l's are the collision frequencies (inverse of relaxation times) whose energy dependence is governed by the details of scattering mechanisms, and

$$f^{(0)}(\mathcal{E}) = Y_{00} f_{00}^{(0)}(\mathcal{E}) \quad (2.5)$$

denotes the equilibrium distribution function. The collision frequency ν_0 characterizing the decay of an isotropic disturbance in $f^{(0)}$ is due entirely to the inelastic scattering processes. Our results indicate that it is a good approximation to assume that all ν_l are independent of the perturbation.

In the spherical tensor notation,[13] the components of a vector $\vec{A}$ are given by

$$A_{\pm} = \mp(1/\sqrt{2})(A_x \pm iA_y), \quad A_0 = A_z. \quad (2.6)$$

We use the gradient formula in terms of the Glebsch-Gordon coefficients,[13,14] to write

$$\frac{\partial}{\partial t} f_{l'm'}(\mathcal{E}, t) + \nu_{l'}(f_{l'm'} - \delta_{l',0} f_{00}^{(0)}) = \frac{e}{\hbar}\sum_{lm}\sum_{\alpha} (-1)^{\alpha} E_{-\alpha}(t)\delta_{m',m+\alpha}\left[\delta_{l',l+1}\left(\frac{l+1}{2l+3}\right)^{1/2} \times (lm1\alpha|l1\ l+1\ m')\left(\frac{\partial}{\partial k} - \frac{l}{k}\right) f_{lm}(\mathcal{E}, t) - \delta_{l',l-1}\left(\frac{l}{2l-1}\right)^{1/2} (lm1\alpha|l1\ l-1\ m')\left(\frac{\partial}{\partial k} + \frac{l+1}{k}\right) f_{lm}(\mathcal{E}, t)\right]. \quad (2.7)$$

To solve Eq. (2.7), we treat the effect of $\vec{E}(t)$ as a small perturbation and expand

$$f_{lm}(\mathcal{E}, t) = \delta_{l,0} f_{00}^{(0)} + f_{lm}^{(1)} + f_{lm}^{(2)} + f_{lm}^{(3)} + \cdots, \quad (2.8)$$

where the superscript is used to denote the order

of the quantity in the incident field. It is important to note that in treating $\vec{E}(t)$ as the incident field, we have neglected the generated fields in the force term. This is justified in the present case since, in the electric dipole approximation, the conduction electrons do not contribute to the second-order nonlinearity.

From Eqs. (2.7) and (2.8), we can write the distribution functions in the first, second, and third order, successively. It is verified that to the zeroth order in the incident field, $f_{lm}^{(0)}(\mathcal{E}, t) = \delta_{l,0}\delta_{m,0} f_{00}^{(0)}(\mathcal{E})$ is a solution of Eq. (2.7). In the first order, we obtain

$$f_{lm}^{(1)}(\mathcal{E}, t) = \left(\frac{4\pi}{3}\right)^{1/2} \delta_{l,1} \frac{e}{\hbar} \sum_{\omega_i} (-1)^m E_{-m}(\omega_i) \times e^{-i\omega_i t} g_1(\omega_i) \frac{\partial f}{\partial k} f^{(0)} , \quad (2.9)$$

where

$$g_l(\omega) \equiv (\nu_l - i\omega)^{-1}, \quad l = 0, 1, 2, \ldots . \quad (2.10)$$

When one combines this result with the general expression[15]

$$j_\alpha^{(n)}(t) = (-1)^{\alpha-1} \frac{e}{\hbar} \left(\frac{4\pi}{3}\right)^{1/2} \frac{2}{(2\pi)^3} \int dk^2 k^2 \frac{\partial \mathcal{E}}{\partial k^2} f_{1,-\alpha}^{(n)}(\mathcal{E}, t) \quad (2.11)$$

for the nth-order current density $\vec{j}^{(n)}(t)$, one obtains the familiar form of Ohm's law for the linear reponse. In the second order, we obtain

$$f_{lm}^{(2)}(\mathcal{E}, t) = \delta_{l,0} f_{00}^{(2)}(\mathcal{E}, t) + \delta_{l,2} f_{2,m}^{(2)}(\mathcal{E}, t) . \quad (2.12)$$

Equations (2.11) and (2.12) imply that the second-order current density would vanish, as expected. The third-order distribution function is given by

$$f_{lm}^{(3)}(\mathcal{E}, t) = \delta_{l,3} f_{3m}^{(3)}(\mathcal{E}, t) + \delta_{l,1} f_{1m}^{(3)}(\mathcal{E}, t) , \quad (2.13)$$

where $f_{3m}^{(3)}$ and $f_{1m}^{(3)}$ are known explicitely in terms of $\mathcal{E}$, ν_l, $f^{(0)}$ and their derivatives with respect to k. We note, however, that to calculate $\vec{j}^{(3)}(t)$ we need only $f_{1m}^{(3)}$. After substitution in Eq. (2.11), we finally obtain[16]

$$j_\mu^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3) = \frac{e^4}{\hbar^4} \frac{8}{3\pi^2} \sum_{\alpha,\beta,\gamma} E_{-\alpha}(\omega_1) E_{-\beta}(\omega_2) E_{-\gamma}(\omega_3) [\delta_{\gamma,-\mu}(1/\sqrt{3})(1\alpha 1\beta | 1100)(001\gamma | 011\gamma) X(\omega_1, \omega_2, \omega_3) + \delta_{\alpha+\beta+\gamma,-\mu}(2/\sqrt{15})(1\alpha 1\beta | 112\alpha+\beta)(2\alpha+\beta 1\gamma | 211-\mu) Y(\omega_1, \omega_2, \omega_3)] + (\text{terms obtained by taking distinct permutations of } \omega_1, \omega_2, \omega_3) , \quad (2.14)$$

with

$$X(\omega_1, \omega_2, \omega_3) = \int_0^\infty dk^2 g_1(\omega_1) f^{(0)\prime}(\epsilon) \{[k^5 g_0(\omega_1+\omega_2) \times (\mathcal{E}' g_1(\omega))']' + \tfrac{3}{2} k^3 g_0'(\omega_1+\omega_2) \mathcal{E}' g_1(\omega)\} , \quad (2.15)$$

$$Y(\omega_1, \omega_2, \omega_3) = \int_0^\infty dk^2 g_1(\omega_1) f^{(0)\prime}(\mathcal{E}) \times \{k^5 g_2(\omega_1+\omega_2) [\mathcal{E}' g_1(\omega)]'\}' , \quad (2.16)$$

where the prime denotes differentiation with respect to k^2. Equations (2.14)–(2.16) enable us to calculate the third-order current density induced by the incident electric fields with arbitrary polarizations. When all the incident fields are polarized in the x direction, we express our result in terms of the susceptibility tensor[16] component

$$\chi_{xxxx}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{4e^4}{3\pi^2\hbar^4(i\omega)} \sum_{\mathcal{P}} \frac{1}{6} \mathcal{P}(\omega_1, \omega_2, \omega_3) \int_0^\infty dk^2 g_1(\omega_1) f^{(0)\prime} [[\{k^5 [\tfrac{2}{3} g_0(\omega_1+\omega_2) + \tfrac{8}{15} g_2(\omega_1+\omega_2)][\mathcal{E}' g_1(\omega)]'\}' + k^3 g_0'(\omega_1+\omega_2) \mathcal{E}' g_1(\omega)]] , \quad (2.17)$$

where $\omega = \omega_1 + \omega_2 + \omega_3$, and $\mathcal{P}$ denotes all permutations of frequencies ω_1, ω_2, ω_3. The above expression for $\chi^{(3)}$ contains the contribution due to the nonparabolicity of the conduction band as well as that due to the energy dependence of momentum and energy relaxation times. We separate these contributions by writing

$$\chi^{(3)} = \chi^{(3)\mathrm{NP}} + \chi^{(3)\mathrm{SC}} + \chi^{(3)\mathrm{NS}} , \quad (2.18)$$

where the superscripts NP and SC specify the contributions due to the nonparabolicity and the energy-dependent scattering alone while the last term $\chi^{(3)\mathrm{NS}}$ is due to the coupling of the two sources of nonlinearity. The contributions $\chi^{(3)\mathrm{NP}}$ and $\chi^{(3)\mathrm{SC}}$ are easily obtained by collecting terms independent of ν_l' and $\mathcal{E}''$, respectively, in the square brackets in Eq. (2.17).

We should remark that in a universal, but rather crude, relaxation-time approximation, $\nu_0 = \nu_1 = \nu_2$, Eq. (2.17) reduces to our earlier result.[8] If ν_l are not all equal but are of the same order of magnitude, we find that Eq. (4) of Ref. 8, for the degenerate case, should be modified to

$$\chi^{(3)SC}_{xxxx}(\omega_1, \omega_1, -\omega_2) \simeq \frac{e^4 n}{3m^{*2}\omega_1\omega_2(2\omega_1-\omega_2)^2} \times\left(\frac{\partial\gamma_0}{\partial\mathcal{E}_k}\right)_F \frac{2\gamma_{1F}-i(\omega_1-\omega_2)}{(\nu_{0F}-i\omega_1+i\omega_2)^2}\ , \quad (2.19)$$

where the subscript F denotes values at the Fermi level. Since in most cases at low temperatures the energy relaxation processes are much less efficient than those involving momentum relaxation, we expect $\nu_0 \ll \nu_1, \nu_2$, so that the contribution of the terms retained in Eq. (2.19) may be much smaller than that calculated in Ref. 8 WR did not obtain any such terms since their treatment is valid for elastic scattering only, so that, in their analysis $\nu_0 = 0$.

Explicit expressions for other nonvanishing components of the susceptibility tensor are obtained similarly. It is interesting to note that consistent with the general symmetry considerations,[17] we obtain

$$\chi^{(3)}_{xxzz}(\omega, \omega, \omega) = \tfrac{1}{3}\chi^{(3)}_{xxxx}(\omega, \omega, \omega)\ , \quad (2.20)$$

but the relation

$$\chi^{(3)}_{xxzz}(\omega_1, \omega_2, \omega_3) = \tfrac{1}{3}\chi^{(3)}_{xxxx}(\omega_1, \omega_2, \omega_3) \quad (2.21)$$

is *not* valid in general. In some limiting cases[8] the deviation from this relation may be helpful in separating $\chi^{(3)SC}$ from $\chi^{(3)NP}$.

The energy dependence of ν_0, ν_1, and ν_2 will, in general, depend on the relative importance of the various mechanisms of carrier scattering which can be a sensitive function of the details of sample preparation. In Secs. III and IV, we will consider two relevant situations in which it is possible to explore the importance of carrier scattering in the third-order response.

III. IONIZED-IMPURITY SCATTERING (ELASTIC)

Elastic scattering of carriers by ionized impurities dominates the momentum-relaxation processes in the moderately doped n-type semiconductors InSb and InAs at temperatures below the liquid-nitrogen temperature. In the Brooks-Herring formulation[18] of the ionized-impurity scattering, one replaces each ionized impurity by a screened Coulomb potential

$$V(r) = (e/\kappa r)\, e^{-r/R}\ , \quad (3.1)$$

where κ is the dc dielectric constant and R is the screening length which is given by

$$R^2 = \left(\frac{\pi}{3n}\right)^{1/3} \frac{\hbar^2\kappa}{4e^2 m^*} \quad (3.2)$$

for a degenerate Fermi gas. Here, m^* is the average effective mass, assumed to be the same as the band-edge effective mass for our calculation. The Born approximation is used to calculate the probability $S(k, \theta_{kk'})$ of an electron of wave vector $\vec{k}$ to scatter elastically through an angle $\theta_{kk'}$ to a state of wave vector $\vec{k}'$. The collision integral can then be written as

$$\left(\frac{\partial f(\vec{k}, t)}{\partial t}\right)_{\text{imp}} = \int S(k, \theta_{kk'})\,[f(\vec{k}', t) - f(\vec{k}, t)]\, d\Omega_{k'} = -\sum_{lm} \nu_l f_{lm}(\mathcal{E}, t)\, Y_{lm}(\Omega_k)\ , \quad (3.3)$$

where we have used the expansion (2.3) and the orthogonality of spherical harmonics, with the definition

$$\nu_l = 2\pi \int_0^\pi S(k, \theta)\,[1 - P_l(\cos\theta)]\sin\theta\, d\theta\ , \quad (3.4)$$

where $P_l(\cos\theta)$ denotes the Legendre polynomial of order l. Consistent with the fact that elastic scattering does not contribute to the decay of an isotropic perturbation on $f^{(0)}(\mathcal{E})$, we observe that ν_0 vanishes while ν_1 and ν_2 are given in the Brooks-Herring formulation by

$$\nu_1(k) = \frac{2\pi N_i e^4 m^*}{\kappa^2\hbar^3 k^3}\left(\ln(1+z) - \frac{z}{1+z}\right), \quad (3.5)$$

$$\nu_2(k) = \frac{2\pi N_i e^4 m^*}{\kappa^2\hbar^3 k^3}\left[(3+6/z)\ln(1+z) - 6\right], \quad (3.6)$$

where N_i is the density of ionized impurities and

$$z = 4k^2R^2\ . \quad (3.7)$$

It is important to emphasize that only ν_1 is involved in the linear response of mobile carriers, so that, by analyzing the low-field-mobility data, we obtain the relative importance of scattering mechanisms in determining ν_1 only. One can reasonably expect that the process giving the major contribution to ν_1 also dominates in determining ν_2, since ν_1 and ν_2 both describe the decay of anisotropic perturbations in the distribution function. However, even at low temperatures, ν_0 must be nonzero for the system to be stable against isotropic perturbations in the distribution function. In the following we assume ν_0 to be energy independent since ν_0 is expected to be small compared to ν_1 and ν_2, especially in the degenerate case. Assuming only ionized-impurity scattering, Kolodziejczak[19] has explained the linear transport properties of n-type InSb at low temperatures between 2 and 100 °K. The data quoted by Hilsum and Rose Innes[10] are also in good agreement with the theoretically calculated values of mobility. For InAs also, the calculated mobility agrees very well with the experimental results for $n = 10^{16}$–10^{19} cm^{-3}. We assume $N_i = n$ in our calculations and replace m^* in Eqs. (3.5) and (3.6) by its value at the Fermi level. The values of all constants used in our calculations are given in Table I.

To discuss the relative importance of the two nonlinearities in the low-temperature measurements of Patel, Slusher, and Fluery,[1,20] we write the various contributions to $\chi^{(3)}_{xxxx}(\omega_a, \omega_a, -\omega_b)$, to the lowest

TABLE I. Numerical values of parameters used in calculations.

	InSb	InAs	GaAs	Reference
Band gap E_g (eV)	0.22	0.35	1.4	4
Band edge Effective mass (m^*/m)	0.013	0.021	0.072	
Debye temperature Θ_D (°K)	264	334	408	11
Reduced mass M (amu)	59.1	45.3	36.1	
Callen's effective charge e^*/e	0.16	0.23	0.20	11
dc dielectric constant κ	17.0	14.5	12.5	10
E_0 (V/cm)	5.15×10^2	2.17×10^3	6.1×10^3	

order in (ν_l/ω_i):

$$\chi^{(3)NP}_{xxxx}(\omega_a,\ \omega_a,\ -\omega_b)=\frac{e^4 n(1+4\mathcal{E}_F/E_g)^{-5/2}(1+8\mathcal{E}_F/5E_g)}{m^{*2}E_g\omega_a^2\omega_b\omega}$$
$$\times\left[1+\frac{10}{9}\frac{\omega_a}{\omega}\frac{(2\nu_1-\nu_0)}{(\nu_0-i\Omega)}+\frac{8}{9}\frac{\omega_a}{\omega}\frac{(2\nu_1-\nu_2)}{(\nu_2-i\Omega)}\right]_F, \quad (3.8)$$

$$\chi^{(3)SC}_{xxxx}(\omega_a,\ \omega_a,\ -\omega_b)=\frac{i}{3}\frac{e^4 n(1+4\mathcal{E}_F/E_g)^{-1/2}}{m^{*2}\mathcal{E}_F\omega_a\omega_b\omega^3}k_F^2$$
$$\times\left[(\nu_1'+\frac{2}{5}k^2\nu_1'')\left(\frac{3}{2}\frac{\omega}{\omega_a}+\frac{5}{3}\frac{2\nu_1-\nu_0}{\nu_0-i\Omega}+\frac{4}{3}\frac{2\nu_1-\nu_2}{\nu_2-i\Omega}\right)\right.$$
$$\left.-\frac{8}{15}k^2\nu_1'\nu_2'\frac{2\nu_1-i\Omega}{(\nu_2-i\Omega)^2}\right]_F, \quad (3.9)$$

$$\chi^{(3)NS}_{xxxx}(\omega_a,\ \omega_a,\ -\omega_b)=-\frac{4}{3}\frac{e^4 n(1+4\mathcal{E}_F/E_g)^{-3/2}}{m^{*2}E_g\omega_a\omega_b\omega^2}k_F^2$$
$$\times\left(\frac{4}{15}\nu_2'\frac{(2\nu_1-i\Omega)}{(\nu_2-i\Omega)^2}+i\frac{8}{15}\frac{\nu_1'}{\omega}\frac{2\nu_1-\nu_2}{\nu_2-i\Omega}\right.$$
$$\left.+i\frac{2}{3}\frac{\nu_1'}{\omega}\frac{2\nu_1-\nu_0}{\nu_0-i\Omega}+i\frac{3}{5}\frac{\nu_1'}{\omega_a}\right)_F, \quad (3.10)$$

where $\Omega=\omega_a-\omega_b$, $\omega=2\omega_a-\omega_b$, m^* is the band-edge effective mass, and $\mathcal{E}_F=\hbar^2k_F^2/2m^*$. We have assumed Kane's model[3] for the conduction band of InSb and InAs:

$$\mathcal{E}_k=\tfrac{1}{2}E_g\left[(1+2\hbar^2k^2/m^*E_g)^{1/2}-1\right]. \quad (3.11)$$

It is important to note that the difference frequency Ω is an order of magnitude smaller than ω_a and ω_b in the experiments of Patel *et al.*[1] and Wynne.[2] It can, in principle, be made arbitrarily small. Owing to this, we have not assumed Ω to be large compared to ν_1 and ν_2. When Ω becomes less than ν_1 or ν_2, ν_0 also plays an important part. In Fig. 1 we have plotted $\chi^{(3)}$ as a function of Ω, calculated with and without the inclusion of carrier scattering for InSb with $n=10^{17}$ cm^{-3} and $\nu_0=3\times10^{11}$ sec^{-1}. As expected, carrier scattering becomes more important when Ω is made smaller.

One must emphasize that there are two distinct effects of including the collision integral in our calculation. The contribution due to nonparabolicity is modified in a way which is *not* equivalent to replacing all ω_i by $\omega_i+i\nu_l$. This modification has nothing to do with the energy dependence of ν_l, but becomes important when Ω is comparable to the magnitude of ν_l. Energy dependence of ν_l introduces an additional nonlinearity expressed by $\chi^{(3)SC}$ and $\chi^{(3)NS}$ which are of the order

$$\frac{E_g}{\mathcal{E}_F}\frac{k_F^2}{\omega}\left(\frac{\partial\nu_1}{\partial k^2}\right)_F \text{ and } \frac{k_F^2}{\Omega}\left(\frac{\partial\nu_2}{\partial k^2}\right)_F,$$

respectively, compared to the nonparabolicity contribution. For $n\gtrsim10^{18}$ cm^{-3}, E_g and $\mathcal{E}_F$ are comparable in InSb and InAs, so that, $\chi^{(3)NS}$ is more important than $\chi^{(3)SC}$ even at the frequencies used by Patel *et al.*[1] For a given carrier concentration, $\mathcal{E}_F$ is nearly proportional to $1/E_g$. Thus, $\chi^{(3)SC}$ is much more important in GaAs than in InSb or InAs, if the mechanism of scattering is same in all the cases. Unfortunately, an analysis of the carrier scattering mechanisms in GaAs is much more complex than that in InSb and InAs. The major difficulty arises from the fact that impurities in GaAs seem to behave[21] quite differently than those in InSb or InAs. In Figs. 2 and 3 we plot the real and imaginary parts of $\chi^{(3)}$ versus n for InSb and InAs, with and without the inclusion of carrier collisions, for $\omega_a=1.78\times10^{14}$ sec^{-1} and $\omega_b=1.96\times10^{14}$ sec^{-1}.

For $\nu_l\ll\Omega$, the lowest-order contribution in $\chi^{(3)SC}$ is proportional to

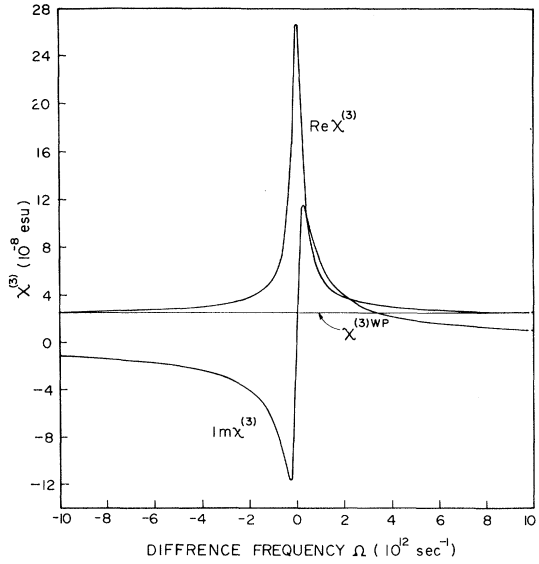

FIG. 1. Variation of real and imaginary parts of $\chi^{(3)}_{xxxx}(\omega_a,\ \omega_a,\ -\omega_b)\equiv\chi^{(3)}$ with the difference frequency Ω, for degenerate InSb with carrier concentration $n=10^{17}$ cm^{-3}, $\nu_0=3\times10^{11}$ sec^{-1}, and $\omega_a=1.78\times10^{14}$ sec^{-1}. $\chi^{(3)WP}$ denotes the values obtained by neglecting collisions.

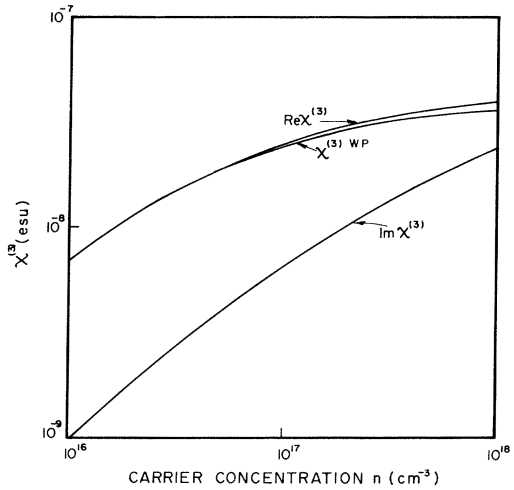

FIG. 2. Variation of real and imaginary parts of $\chi^{(3)}_{xxxx}(\omega_a, \omega_a, -\omega_b) \equiv \chi^{(3)}$ with the carrier concentration n for degenerate InSb. $\chi^{(3)WP}$ denotes the values obtained by neglecting collisions.

$$\left(\frac{\partial \nu_1}{\partial k^2} + \frac{2}{5} k^2 \frac{\partial^2 \nu_1}{\partial (k^2)^2}\right) \quad ,$$

which vanishes for $\nu_1 = a_1 k^{-3}$, as discussed by WR. We note, however, that at the energies under consideration, the logarithmic terms modify the energy dependence of ν_1 and ν_2 considerably. In fact, $\nu_l = a_l k^{-2}$ appears to be a much better approximation to the actual behavior than $\nu_l = a_l k^{-3}$. In our calculations we have considered the exact energy dependence of ν_1 and ν_2 as given by Eqs. (3.5) and (3.6). It is also interesting to note that at very high carrier energies, where $\nu_l = a_l k^{-3}$ becomes a good approximation, $\nu_2 \approx 3\nu_1$.

The importance of using correct statistics in the calculation of transport properties of semiconductors is well known. When the approximation of degenerate statistics is not valid, it is usually a good approximation to evaluate the final integrals by replacing all slowly varying functions of energy by their value at $\mathcal{E}_0$, the energy at which $\mathcal{E}^{3/2} f^{(0)\prime}$ attains a maximum value. For the nondegenerate case, $\mathcal{E}_0 = \frac{3}{2} k_B T$, where k_B is the Boltzmann constant. In this case, the relative importance of the two sources of nonlinearity is nearly independent of the carrier concentration, but depends on the temperature T of the system. For the chemical potential $\mu_0 < -2k_B T$, it is a good approximation to assume nondegenerate statistics, while degenerate statistics may be used for all positive μ_0.

IV. POLAR SCATTERING (INELASTIC)

Polar scattering of carriers by longitudinal optical phonons play an important role[11] in the transport properties of InSb, InAs, and GaAs at high temperatures, $T \gtrsim 300\,^\circ$K. Assuming that the phonon distribution is always maintained in equilibrium, we can write the collision integral, due to polar scattering of electrons with an effective mass m^*, as

$$\left(\frac{\partial f(\vec{k}, t)}{\partial t}\right)_{\text{polar}} = \frac{eE_0\hbar}{2\pi m^*} \int d^3k' \frac{1}{|\vec{k} - \vec{k}'|^2} \{\delta(\mathcal{E}' - \mathcal{E} - \hbar\omega_l)[(N+1) f(\vec{k}')(1 - f(\vec{k})) - N f(\vec{k})(1 - f(\vec{k}'))]$$
$$+ \delta(\mathcal{E}' - \mathcal{E} + \hbar\omega_l)[N f(\vec{k}')(1 - f(\vec{k})) - (N+1) f(\vec{k})(1 - f(\vec{k}'))]\} , \tag{4.1}$$

where ω_l is the longitudinal optical-phonon frequency, assumed to be independent of the phonon wave vector, N is the equilibrium phonon distribution and E_0, an equivalent electric field, [22] is given by

$$eE_0 = 4\pi m^* e^2 e^{*2} / M\hbar\omega_l V_a \ , \tag{4.2}$$

where e^* is the effective charge defined by Callen.[23] Here M denotes the reduced mass of the two ions in each unit cell and V_a is the volume of the unit cell. It should be noted that the collision integral could be linearized by omitting the factors representing the probability of final states being empty. In calculating the nonlinear response, however, the terms involving products of induced distribution functions should be neglected only when such terms are small compared to the corresponding contribution from the force term.

To simplify the collision integral we use expansions (2.3), (2.8), and

$$\frac{1}{|\vec{k} - \vec{k}'|^2} = \frac{2\pi}{kk'} \sum_{lm} Q_l\left(\frac{k^2 + k'^2}{2kk'}\right) Y_{lm}(\Omega_k)\, Y^*_{lm}(\Omega_{k'}) \ , \tag{4.3}$$

where Q_l's are the Legendre functions of the second kind. The nth ($n \geq 1$) order (in the incident field) contribution of the collision integral is then obtained as

$$\left(\frac{\partial f(\vec{k}, t)}{\partial t}\right)^{(n)}_{\text{polar}} = \frac{eE_0}{\hbar k} \sum_{lm} Y_{lm}(\Omega_k) \{[(N + 1 - f^{(0)}(\mathcal{E}))$$
$$\times Q_{l+} f^{(n)}_{lm}(\mathcal{E} + \hbar\omega_l) - (N + f^{(0)}(\mathcal{E} + \hbar\omega_l)) Q_{0+} f^{(n)}_{lm}(\mathcal{E})]$$
$$+ \theta(\mathcal{E} - \hbar\omega_l)[(N + f^{(0)}(\mathcal{E})) Q_{l-} f^{(n)}_{lm}(\mathcal{E} - \hbar\omega_l)$$
$$- (N + 1 - f^{(0)}(\mathcal{E} - \hbar\omega_l)) Q_{0-} f^{(n)}_{lm}(\mathcal{E})]\}$$
$$- \frac{eE_0}{\hbar k} \sum_{n'=1}^{n-1} \sum_{lml'm'} Y_{lm}(\Omega_k)\, Y_{l'm'}(\Omega_k)\, f^{(n')}_{lm}(\mathcal{E})$$
$$\times [Q_{l'+} f^{(n-n')}_{l'm'}(\mathcal{E} + \hbar\omega_l) - \theta(\mathcal{E} - \hbar\omega_l) Q_{l'-} f^{(n-n')}_{l'm'}(\mathcal{E} - \hbar\omega_l)] \ , \tag{4.4}$$

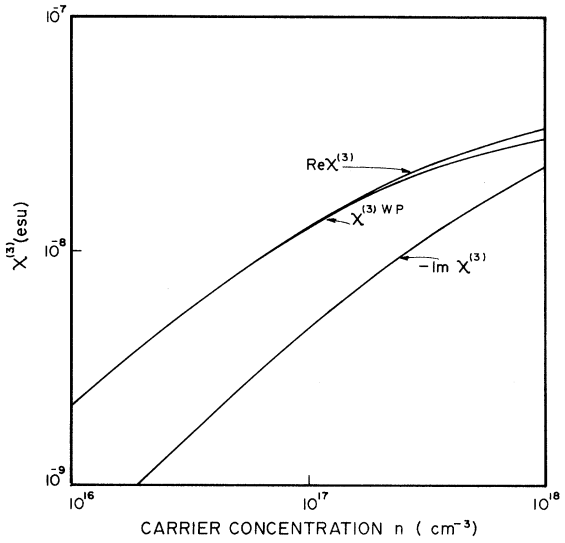

FIG. 3. Variation of real and imaginary parts of $\chi^{(3)}_{xxxx}(\omega_a, \omega_a, -\omega_b) \equiv \chi^{(3)}$ with the carrier concentration n for degenerate InAs. $\chi^{(3)WP}$ denotes the values obtained by neglecting collisions.

where $\theta(\mathcal{E}-\hbar\omega_l)$ is $+1$ for $\mathcal{E}>\hbar\omega_l$ and 0 for $\mathcal{E}<\hbar\omega_l$, and the suffixes $\pm$ denote that the quantity is evaluated at $\mathcal{E}'=\mathcal{E}\pm\hbar\omega_l$. In the zeroth order, it is easily verified that the complete collision integral (4.1) vanishes for $f(\vec{k}, t)=f^{(0)}(\mathcal{E})$, the Fermi function. It can be seen from Eq. (4.4) that the same method of solving the Boltzmann equation successively in each order can be adopted, in general, except that now we must solve a linear difference equation for each f_{lm}. In particular, Eqs. (2.12) and (2.13) are still valid.

It is interesting to note that the additional nonlinearity in the optical response, represented by the second term in Eq. (4.4), depends crucially on the statistics of the carriers. For degenerate Fermi gas, the changes induced in $f(\vec{k}, t)$ by the incident field are nonvanishing only for $\mathcal{E}$ in the interval $\mathcal{E}_F \pm k_B T$, so that products like $f^{(n)}(\mathcal{E})f^{(n')}(\mathcal{E}\pm\hbar\omega_l)$ are vanishingly small for $\hbar\omega_l \gg k_B T$. For nondegenerate statistics, the additional nonlinearity can be shown to be negligible for $T \gg \Theta_D$, the Debye temperature, but for temperatures $T \lesssim \Theta_D$ this nonlinearity may be sizable. We shall neglect this nonlinearity since we will consider only the $T \gg \Theta_D$ case.

To obtain an effective RTA we write

$$f^{(n)}_{lm}(\mathcal{E}, t) = -k\frac{\partial f^{(0)}}{\partial \mathcal{E}}\, C^{(n)}_{lm}(\mathcal{E}, t)\,, \tag{4.5}$$

where $C^{(n)}_{lm}$'s are assumed to be slowly varying functions of $\mathcal{E}$. For $\mathcal{E} \gg \hbar\omega_l$, this reduces the collision integral to the form given by Eq. (2.4), with

$$\nu_1 = \tfrac{2}{3}\nu_2 = \frac{eE_0}{(2m^*\mathcal{E})^{1/2}}\,(2N-1)\,, \tag{4.6}$$

$$\nu_0 = \frac{\hbar\omega_l}{2\mathcal{E}}\left(\ln\frac{4\mathcal{E}}{\hbar\omega_l}\right)\frac{eE_0}{(2m^*\mathcal{E})^{1/2}}\left(1+\frac{2\mathcal{E}}{C^{(n)}_{00}(\mathcal{E})}\,\frac{\partial C^{(n)}_{00}(\mathcal{E})}{\partial \mathcal{E}}\right). \tag{4.7}$$

The collision frequency ν_0 is, therefore, not independent of the isotropic perturbation on $f^{(0)}(\mathcal{E})$. One should note, however, that for $\mathcal{E} \gg \hbar\omega_l$, ν_0 is considerably smaller than ν_1 and ν_2, if $C^{(n)}_{00}(\mathcal{E})$ varies as some small power of $\mathcal{E}$. In a rough approximation, we replace ν_0 by a constant value which is assumed to be a small fraction of ν_1.

The utility of RTA for polar scattering is limited by the fact that for most materials of interest the Debye temperature Θ_D is quite large (see Table I) and RTA is valid only for $T \gg \Theta_D$. However, a comparison[24] of the linear transport properties calculated using a heuristic RTA with those obtained by using a variational principle show that RTA may be a good approximation to determine ν_1 and ν_2 even at $T = 2\Theta_D$. In GaAs, at $T = 2\Theta_D$ with $n = 10^{16}$ cm^{-3}, we find $\nu_1(\mathcal{E} = \frac{3}{2}k_B T) = 8.5\times10^{12}$ sec^{-1}, which is comparable with $\Omega = -1.8\times10^{13}$ sec^{-1}, in the experiments of Patel *et al.*[1] and Wynne.[2] In this case, with $\nu_0 = 10^{12}$ sec^{-1}, the ratios, $\chi^{(3)NP}/\chi^{(3)WP}$, $\chi^{(3)SC}/\chi^{(3)WP}$, and $\chi^{(3)NS}/\chi^{(3)WP}$ are estimated[25] to be $1.17 - i\,1.25$, $-0.16 - i\,0.14$, and $0.10 - i\,0.11$, respectively, where $\chi^{(3)WP}$ is the third-order susceptibility calculated for $\nu_l = 0$. These results show that although the additional nonlinearity introduced by the energy dependence of collision frequencies is small, the effect of including an average collision frequency is not negligible.

At lower temperatures, the collision frequency ν_1 decreases so that a considerable reduction in the effect of collisions on $\chi^{(3)NP}$ can be expected. However, a more accurate treatment of ν_0 is needed in this case since our approximation of energy independent $\nu_0 \ll \nu_1$ is difficult to justify when $\mathcal{E}$ is comparable to $\hbar\omega_l$.

V. CONCLUSION

In a generalized relaxation-time approximation, we have calculated the linear and nonlinear current density induced in a semiconductor plasma by a slowly varying electric field. The Boltzmann-equation approach used in our work assumes that the time duration of a collision is much smaller than the time that a carrier spends between two successive collisions and the time period of variation of the electric field. The relaxation time characterizing the decay of a perturbation in the distribution function $f(\vec{k}, t)$ depends on the angular dependence of the perturbation in the $\vec{k}$ space. The decay of an isotropic perturbation is governed entirely by inelastic scattering of carriers and is usually much slower than the decay of an anisotropic perturbation which is caused by elastic as well as inelastic scattering. Our method of the solution of

the Boltzmann equation is similar to, but more general than, that used by Wang and Ressler.[7] First, we have relaxed WR's condition that all fields be polarized in the same direction. This enables us to calculate all components of the third-order susceptibility tensor. Second, our treatment includes elastic as well as inelastic scattering processes, while the collision integral used by WR is valid for elastic scattering only.

There are two distinct effects of including the collision integral in our calculation. The third-order nonlinearity due to the nonparabolicity is modified in a way which is not equivalent to replacing all ω_i by $\omega_i + i\nu$ in the result obtained by neglecting collisions. This modification is important when ν_i is comparable to the difference frequency Ω.[26] The second effect is that an additional nonlinearity occurs due to the energy dependence of the carrier collision frequencies ν_i. Since ν_i's usually vary as a small power of the carrier energy, this effect is also more important when ν_i's become comparable to Ω. It is pointed out that the relative importance of this effect increases with an increase in the ratio $E_g/\mathcal{E}_0$ of the band gap E_g and the energy $\mathcal{E}_0$ of the carriers dominating the transport properties. Thus, this effect should be much more important for GaAs than for InSb or InAs, because the calculated collision frequencies in the three cases do not differ very much. As in most other properties of a semiconductor plasma, a correct consideration of statistics plays an important role in our discussion.

Any attempt to compare our results for InSb and InAs at low temperatures with the present or future experimental data must consider two limitations on our calculations. First, the one-band description used in our work is valid[4] only when frequencies $2\omega_a$ and ω_b are small compared to the band gap E_g. At the frequencies used in the available experimental[1-2] investigations, Jha and Bloembergen[4] have shown that a complete calculation of the mobile-carrier contribution to $\chi^{(3)}$ in InSb and InAs gives considerably different results than those obtained by a one-band calculation by Wolff and Pearson.[5] For very low frequencies, on the other hand, lattice contribution to the optical response must also be considered. Since the band gap in GaAs is considerably larger, the low-frequency limit is a good approximation in this case even at the infrared frequencies of a CO_2 laser. Thus, in GaAs samples, in which ionized-impurity scattering is the dominant carrier-scattering mechanism at low temperatures, it should be possible to observe the nonlinearity due to the energy dependence of ν_i's. It is important to note that since for $\nu_i \ll \omega$ the lowest-order contribution in $\chi^{(3)}$ due to energy-dependent carrier scattering is purely imaginary, its effect is much more pronounced in the phase of $\chi^{(3)}$ than in its magnitude. This may be helpful in experimentally separating the contribution due to the energy dependence of ν_i's from that due to the nonparabolicity. It is also apparent from our results that the effect of carrier scattering on $\chi^{(3)}(\omega_a, \omega_a, \omega_a)$ is less important than that on $\chi^{(3)}(\omega_a, \omega_a, -\omega_b)$. The third-harmonic generation experiments are, therefore, expected to yield a more accurate estimate of the nonparabolicity of the conduction band in GaAs.

In many practical situations, two or more scattering mechanisms, with ν_i's having different energy dependences are effective. If two mechanisms have opposite energy dependences of ν_1, their lowest-order contribution to $\chi^{(3)}$ will tend to cancel each other. Moderately doped InSb and InAs at room temperature are such examples, where the acoustic-phonon scattering ($\nu_1 \approx ak$) and the ionized-impurity scattering are both quite important.

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[14]Greek indices $\alpha, \beta, \gamma, \mu$ denote spherical tensorial components of a vector.

[15]We have made the usual approximation of replacing the $\vec{k}$-summation over the first Brillouin zone by one over the entire $\vec{k}$ space. Since most of the electrons occupy states very near the bottom of the band, this is a good

approximation.

[16]We follow the conventions of Ref. 4.

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[20]The mobility of the samples used by Patel *et al.* seems to lie within the general pattern described by the data compiled in Ref. 10. We are very grateful to Dr. C. K. N. Patel for making available some of their unpublished data.

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