

Nonlinear Optical Effects of Conduction Electrons in Semiconductors

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The Boltzmann transport equation for conduction electrons in solids is solved to third order in the applied optical fields, including nonlinearities due to the nonparabolicity of the conduction band and the momentum-dependent relaxation times. It is shown that the nonlinearity calculated from the hot-electron approximation fails to include changes described in terms of the higher-order derivatives of the distribution function. The nonlinearity arising from the momentum dependence of the relaxation times is of little importance in III-V compounds because of the predominance of the nonparabolicity effect. The relaxation-time effect should be observable in degenerate *n*-type Si and Ge samples where it exceeds the bound-electron nonlinearity, and in metals where it is expected to be larger than the nonlinearity of the electron plasma by a factor of 10^3 - 10^4 .

THE nonlinear optical effects of conduction electrons in semiconductors have been the subject of several recent publications. It has been proposed that the observed optical mixing¹ arises from the momentum dependence of the effective electron mass² (due to the nonparabolicity of the conduction band), and from the momentum dependence of the relaxation times^{3,4} of the conduction electrons. In this paper, the Boltzmann equation for the conduction electrons is solved to third order in the applied optical fields, including both nonparabolicity and relaxation-time effects. It is shown that our approach reproduces the result of Wolff and Pearson² for the nonparabolicity effect, but the hot-electron approach^{3,4} is found to be deficient in that it fails to include changes described in terms of the higher-order derivatives of the distribution function. It is concluded that the nonparabolicity effect is dominant in the experiments of Ref. 1, but the effect of momentum-dependent relaxation times should be observable in metals, and in degenerate *n*-type silicon and germanium samples.

In the momentum space, the Boltzmann transport equation for the conduction electrons is

$$\frac{\partial f(\mathbf{p}, t)}{\partial t} + e\mathbf{E} \cdot \frac{\partial f(\mathbf{p}, t)}{\partial \mathbf{p}} = 2\pi \int_0^\pi S(p, \varphi) [f(\mathbf{p}', t) - f(\mathbf{p}, t)] \sin \varphi d\varphi, \quad (1)$$

where $f(\mathbf{p}, t)$ is the distribution function, $\mathbf{E} = \mathbf{E}_a \cos \omega_a t + \mathbf{E}_b \cos \omega_b t$ is the electric field amplitude of the incident optical beam having two collinear frequency components at ω_a and ω_b , and the term $\mathbf{p} \times \mathbf{B}$ has been neglected.² It is explicitly assumed here that the scattering prob-

ability $S(p, \varphi)$ depends only on the scattering angle φ between the momentum vectors before and after the scattering. (*Note added in proof.* The authors wish to thank Professor N. Bloembergen for calling to their attention the fact that the present description is valid only when the ratio of the duration of a collision to the period of the optical field is small. It can be shown that the relaxation-time nonlinearity to be described below decreases to zero as this ratio increases.) Under this assumption, Eq. (1) may be solved by iteration to yield a solution of the form

$$f(\mathbf{p}, t) = f_0 + f_1^{(1)} + f_2^{(2)} + f_3^{(3)} + \dots, \quad (2)$$

where f_0 is the equilibrium distribution, and $f^{(l)}$ indicates the solution to first order in the applied field, etc. Substituting Eq. (2) and equating terms in Eq. (1) with the same power in the applied field, one obtains the following expression for $f^{(3)}(\omega_3)$, the third-order change in the distribution function at $\omega_3 = 2\omega_a \pm \omega_b$:

$$f^{(3)}(\omega_3) = [\chi_{31}(p)P_1(\cos\theta) + \chi_{33}(p)P_3(\cos\theta)]e^{i\omega_3 t} + c.c., \quad (3)$$

$$\begin{aligned} \chi_{31}(p) = & i\frac{2}{5}e^3 E_a^2 E_b p g_{13} \left\{ \left(1 + \frac{4}{5}\alpha\right) \right. \\ & \times [\beta(f_0'' + \frac{2}{5}p^2 f_0''') + \beta'(f_0' + \frac{4}{5}p^2 f_0'') + \frac{2}{5}\beta'' p^2 f_0'] \\ & \left. + (8/25)\alpha' p^2 (\beta f_0'' + \beta' f_0') \right\}, \quad (4) \end{aligned}$$

$$\begin{aligned} \chi_{33}(p) = & i\frac{2}{5}e^3 E_a^2 E_b p^3 g_{33} [\alpha' (\beta f_0'' + \beta' f_0') \\ & + \alpha (\beta f_0''' + 2\beta' f_0'' + \beta'' f_0')]. \quad (5) \end{aligned}$$

Here the primes indicate derivatives with respect to p^2 , θ is the angle between \mathbf{E} and \mathbf{p} , $P_l(\cos\theta)$ is the Legendre polynomial of order l and

$$1/\tau_l(p) = 2\pi \int_0^\pi S(p, \varphi) [1 - P_l(\cos\varphi)] \sin \varphi d\varphi$$

is the corresponding momentum relaxation time which assumes different dependence on the carrier momentum for different scattering mechanisms;

$$\begin{aligned} g_{ln} = & (1/\tau_l + i\omega_n)^{-1}; \quad \omega_2 = \omega_a - \omega_b; \quad \alpha = i\omega_2(1/\tau_1 + i\omega_2)^{-1}; \\ \beta = & (g_{1a} + g_{1b})/\omega_2 + g_{1a}/2\omega_a. \end{aligned}$$

¹ C. K. N. Patel, R. E. Slusher, and P. A. Fleury, Phys. Rev. Letters **17**, 1011 (1966).

² P. A. Wolff and G. A. Pearson, Phys. Rev. Letters **17**, 1015 (1966).

³ P. Kaw, Phys. Rev. Letters **21**, 539 (1968).

⁴ B. S. Krishnamurthy and V. V. Paranjape, Phys. Rev. **181**, 1153 (1969). The authors are indebted to Professor Krishnamurthy and Professor Paranjape for making available a copy of their paper prior to publication.

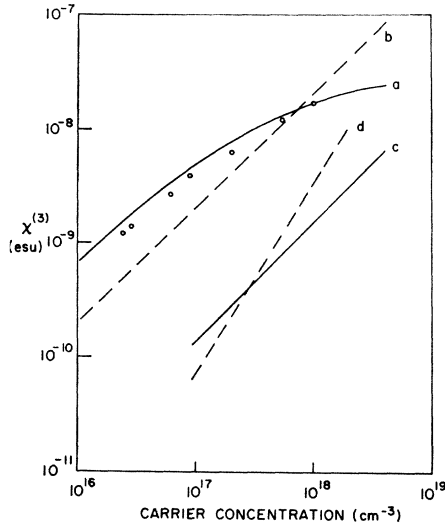


FIG. 1. Plot of nonlinear susceptibility constant of InAs at room temperature. The curves correspond respectively to the nonlinearity due to (a) nonparabolicity effect for a degenerate distribution, (b) nonparabolicity effect for a nondegenerate distribution, and the relaxation-time effect with $n = -3$ for (c) a degenerate distribution, and (d) nondegenerate distribution. The dots represent experimental data reproduced from Ref. 1 and adjusted to fit the nonlinearity due to the nonparabolicity effect at $N = 10^{18} \text{ cm}^{-3}$. $\chi^{(3)}(\omega_3) = ij^{(3)}(\omega_3)/3\omega_3 E_a^2 E_b$.

The third-order current induced at ω_3 is given by

$$j^{(3)}(\omega_3) = (2e/\hbar^3) \iiint I(p) p \cos\theta f^{(3)}(\omega_3) d\mathbf{p}, \quad (6)$$

where $I(p) = 1/m^*(p)$ is the inverse of the effective mass of the conduction electron with momentum p . Since the term proportional to $P_3(\cos\theta)$ does not contribute to the nonlinear current in Eq. (6), the final expression for this nonlinear current does not contain $\chi_{33}(p)$. Substitution of Eq. (4) then gives, after integration by parts,

$$j^{(3)}(\omega_3) = i \frac{5}{36\pi^2} \left(\frac{e^4}{\hbar^3} \right) E_a^2 E_b \left\{ \int_0^\infty I(p) \times \left[\left(1 + \frac{4}{5}\alpha \right) (g_{13}' + \frac{2}{5}p^2 g_{13}'') + (8/25)p^2 \alpha' g_{13}' \right] \times p^3 \beta f_0' d(p^2) + \int_0^\infty \left[\left(1 + \frac{4}{5}\alpha \right) g_{13} (I' + \frac{2}{5}p^2 I'') + (8/25)p^2 I' (\alpha' g_{13} + (2\alpha + \frac{5}{2}) g_{13}') \right] p^3 \beta f_0' d(p^2) \right\}. \quad (7)$$

Equation (7) represents the central result of our analysis. It includes both nonparabolicity and relaxation-time effects, as well as effects resulting from the coupling between these two types of nonlinearities. These coupling terms must be considered when both types of nonlinearities are of comparable importance. Thus, when the nonparabolicity effect alone is present,² substitution of $I(p) = 1/m^*(1 + 2p^2/m^*E_g)^{1/2}$ in

Eq. (7) gives

$$j^{(3)}(\omega_3) = i \frac{3}{8} N E_a^2 E_b (e^4/\omega_a^2 \omega_b m^* E_g) \frac{(1 + 8E_F/5E_g)}{(1 + 4E_F/E_g)^{5/2}}, \quad (8)$$

for a degenerate distribution and

$$j^{(3)}(\omega_3) = i \frac{3}{8} N E_a^2 E_b (e^4/\omega_a^2 \omega_b m^* E_g) (1 + 6kT/E_g)^{-7/2} \quad (9)$$

for a nondegenerate (Maxwell-Boltzmann) distribution. Here N is the carrier density in the conduction band; m^* is the effective mass at the band edge; $E_F = (\hbar^2/4m^*)(3\pi^2 N)^{2/3}$ is the Fermi energy for the degenerate distribution; and T is the lattice temperature. As expected, Eq. (8) is identical to Eq. (9) of Ref. 2.

When the effect associated with the momentum-dependent relaxation times alone is present, Eq. (7) reduces to

$$j^{(3)}(\omega_3) = -i(5/24) N E_a^2 E_b (e^4/m^{*3}) \times \langle \beta [(1 + \frac{4}{5}\alpha) (g_{13}' + \frac{2}{5}p^2 g_{13}'') + (8/25)p^2 \alpha' g_{13}'] \rangle_F \quad (10)$$

for a degenerate distribution. Here $\langle \rangle_F$ indicates that the quantities inside the bracket is to be evaluated at the Fermi momentum $p_F = (2m^*E_F)^{1/2}$. To facilitate comparison with the results of Refs. 3 and 4, one writes $1/\tau = ap^n$, where n is an integer. To second order in $(\omega\tau)^{-1} \ll 1$, Eq. (10) then becomes

$$j^{(3)}(\omega_3) = \frac{3}{80} N E_a^2 E_b \left(\frac{e^4}{m^* E_F \omega_a^2 \omega_b} \right) \times n \left[\frac{1}{2} (n+3) \frac{1}{\omega_3 \tau_1} + \frac{i}{(\omega_3 \tau_1)^2} \left((2n+3) - 2(n+3) \frac{\omega_a}{\omega_2} \right) + i(2/9)(2n+3) \frac{1}{\omega_2 \omega_3 \tau_1 \tau_2} \right]. \quad (11)$$

For a nondegenerate distribution, the corresponding expression is given by

$$j^{(3)}(\omega_3) = \frac{1}{40} N E_a^2 E_b \left(\frac{e^4}{m^* k T \omega_a^2 \omega_b} \right) \times n \left[\frac{1}{2} (n+3) \left\langle \frac{1}{\omega_3 \tau_1} \right\rangle + i \left((2n+3) - 2(n+3) \frac{\omega_a}{\omega_2} \right) \times \left\langle \frac{1}{\omega_3^2 \tau_1^2} \right\rangle + i(2/9)(2n+3) \left\langle \frac{1}{\omega_2 \omega_3 \tau_1 \tau_2} \right\rangle \right], \quad (12)$$

where $\langle \rangle$ indicates averaging over the carrier distribution. Equations (11) and (12) differ from the results in Refs. 3 and 4 in the dependence on n as well as in the frequency dependence. These differences result from the failure of the hot-electron approximation to include changes associated with the higher-order derivatives of the distribution function, as may be

demonstrated by noting that these incorrect results can be reproduced from Eqs. (3) and (6) if terms therein proportional to f_0'' and f_0''' and higher-order derivatives of other functions are ignored.

Examination of Eqs. (11) and (12) shows that for acoustic scattering ($n=1$) the term first order in $(\omega\tau)^{-1}$ exists and adds in quadrature to the nonlinearity arising from the nonparabolicity of the conduction band. For scattering by ionized impurities ($n=-3$), this term vanishes, leaving only contributions second order in $(\omega\tau)^{-1}$. For intervalley scattering and scattering by optical modes,⁵ the scattering probability is essentially independent of the carrier momentum ($n=0$) so that the corresponding nonlinearity vanishes entirely.

We have compared the numerical values calculated from Eqs. (8), (9), (11), and (12) with the measured values for the various semiconductor samples reported to date.^{1,6} Since the results for InSb and GaAs were qualitatively similar to those for InAs, it suffices to discuss only InAs in the following.

Figure 1 shows the calculated nonlinear susceptibility constant due to nonparabolicity and relaxation time effects in InAs for various carrier concentrations. At room temperature, the mobility of the electrons in InAs is limited by both ionized impurity scattering and scattering by optical modes,⁷ with scattering by optical modes being the dominant mechanism. In order to establish an upper bound for the relaxation-time effect, it is assumed that $\tau_1 \approx \tau_2$ and that both are due to ionized impurity scattering only.⁸ The experimental results of Ref. 1, adjusted to fit the nonlinearity due to the nonparabolicity effect at $N=10^{18}$ cm⁻³, are shown for comparison. At room temperature where the experi-

mental results reproduced in Fig. 1 were taken, the electron distribution in InAs becomes degenerate at $N > 2 \times 10^{16}$ cm⁻³. It is seen that the experimental results are in good agreement with the calculated values for the degenerate nonparabolicity effect, as is expected for the carrier concentrations which were investigated. Figure 1 also shows that the relaxation-time nonlinearity calculated with $n=-3$ may be above the estimated bound electron nonlinearity, but is still below the nonlinearity due to the nonparabolicity effect by about an order of magnitude.

In Si and Ge, the nonlinearity due to the nonparabolicity of the conduction band is expected to be negligible.⁹ Assuming that the dominant scattering mechanism in Si and Ge is ionized impurities,^{10,11} and using Eq. (11) to compute the relaxation-time nonlinearity, it is found that the bound electron nonlinearity^{6,12} is larger than the relaxation-time effect for carrier concentrations below about 10^{17} cm⁻³ in both Si and Ge. For carrier concentrations above 10^{18} cm⁻³, the relaxation-time nonlinearity is expected to be at least an order of magnitude larger than the bound electron nonlinearity and should therefore be observable in degenerate n -type Si and Ge samples.

In metals the nonlinearity arising from density fluctuations of the electrons² is lower than the relaxation-time nonlinearity by a factor of the order of $(\omega_p/qv_F)^2(\omega_3\tau)^{-1}$, where q is the propagation vector of the light wave. This factor is of the order of 10^3 - 10^4 at room temperature for light waves in the infrared and visible range. Therefore, by studying the harmonic wave reflected from metal surfaces¹³ it should be possible to observe the nonlinear relaxation time effect in metals. Experiments are currently underway to study these effects.

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⁸ We note that the values for the relaxation-time effects are meant to be representative only, as some scattering mechanisms, such as ionized impurity scattering, are not intrinsic properties of the material. Therefore, the computed values for the relaxation-time nonlinearity could vary widely from sample to sample depending, for example, upon the extent of compensation.

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