NONLINEAR MAGNETO-OPTICS OF ELECTRONS AND HOLES IN SEMICONDUCTORS AND SEMIMETALS

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Nonlinear behavior of conduction and valence electrons in semiconductors and semimetals due to nonparabolic or warped energy bands exhibits resonance behavior in magnetic fields which increases the nonlinear excitation by many orders of magnitude for intraband and interband transitions. Higher harmonics generated by the electrons in warped parabolic energy surfaces are linear in electric field at high powers of incoming radiation.

Among the various mechanisms proposed for nonlinear excitation of electron plasmas in solids, that due to nonparabolic bands[1] has proved to be most promising. This has been recently demonstrated experimentally by Patel, Slusher, and Fleury,[2] and explained theoretically by Wolff and Pearson.[3] The present paper extends this work to include additional magnetically induced nonlinearity and to predict a large enhancement due to resonance at high magnetic fields.[1] Resonant nonlinearity due to interband transitions in low gap semiconductors and semimetals and that of carriers moving on warped energy surfaces are also treated. The two existing sources which are best suited to demonstrate these resonant magneto-optical nonlinearities are the 10.6-μ and the 337-μ radiation of the CO_2 and cyanide lasers, respectively.

To illustrate the basic phenomena we shall simplify the calculations by not considering explicitly the terms due to the filling of the bands up to the Fermi energy.[4] Then for carriers near the edge of a nonparabolic band the energy expanded to fourth order in momentum is given by

$$\mathcal{E} \approx p^2/2m^* - p^4/4m^{*2}\mathcal{E}_g \tag{1}$$

and

$$\vec{v} = \nabla_p \mathcal{E} = (1 - p^2/m^*\mathcal{E}_g)\vec{p}/m^*, \tag{2}$$

where m^* is the mass at band edge and $\vec{v}$ is the velocity. The quadratic term in Eq. (2) is the principal source of nonlinearity without a magnetic field. In the presence of magnetic field, the equation of motion

$$\dot{\vec{p}} = -e\sum_j \vec{E}\exp(i\omega_j t) - (1 - p^2/m^*\mathcal{E}_g)\vec{p}\times\vec{\omega}_c \tag{3}$$

gives an additional source of nonlinearity proportional to the magnetic field. $\sum_j \vec{E}_j \exp(i\omega_j t)$ refers to multifrequency terms and their complex conjugates, and $\omega_c = e\vec{H}/m^*c$ is the cyclotron frequency. For the magnetic field along the z direction and transverse polarization of incoming radiation, the result for the velocity of the third harmonic is

$$\vec{v}_3 = \frac{3e^3\omega}{m^{*2}\mathcal{E}_g}(E_x^2 + E_y^2)\frac{i(3\omega^2 + \omega_c^2)\vec{E} - 4\omega\vec{E}\times\vec{\omega}_c}{(\omega^2 - \omega_c^2)^2(9\omega^2 - \omega_c^2)}. \tag{4}$$

The current will exhibit resonance at the cyclotron frequency ω_c and at $\frac{1}{3}\omega_c$. For circularly polarized light $E_x = \pm iE_y$, no harmonic generation would occur. If the magnetic field is tuned to the laser frequency (for $\lambda = 10.6\ \mu$, $H \approx 3\times 10^5$ Oe, and for $\lambda = 337\ \mu$, $H \approx 10^4$ Oe), the intensity of the third harmonic would be enhanced by a factor of $j_3(H)/j_3(0) = (\omega\tau)^2$ which is of the order of 10^4 and 10^2, respectively, for $\tau \approx 10^{-12}$ sec in InSb at low temperatures. In an analogous manner we obtain for mixed frequencies, $\omega_3 = 2\omega_1 + \omega_2$,

$$\vec{v}_3 = \frac{e^3\omega_3}{m^{*2}\mathcal{E}_g}\left\{(E_{1x}^2 + E_{1y}^2)\frac{i(\omega_2\omega_3 + \omega_c^2)\vec{E}_2 - (\omega_2 + \omega_3)\vec{E}_2\times\vec{\omega}_c}{(\omega_1^2 - \omega_c^2)(\omega_2^2 - \omega_c^2)(\omega_3^2 - \omega_c^2)} + [(\omega_1\omega_2 - \omega_c^2)\vec{E}_1\cdot\vec{E}_2 - i(\omega_1 - \omega_2)\vec{E}_1\times\vec{E}_2\cdot\vec{\omega}_c]\right.$$
$$\left.\times\frac{i(\omega_1\omega_3 + \omega_c^2)\vec{E}_1 - (\omega_1 + \omega_3)\vec{E}_1\times\vec{\omega}_c}{(\omega_1^2 - \omega_c^2)^2(\omega_2^2 - \omega_c^2)(\omega_3^2 - \omega_c^2)}\right\}. \tag{5}$$

The most important features of this result are the resonance denominators of the two nonlinear contributions obtained from Eqs. (2) and (3). In addition the magnetic field can be used to achieve phase matching in the parametric mixing of the frequencies $\vec{\beta}_3=2\vec{\beta}_1+\vec{\beta}_2$, where the $\vec{\beta}$'s are the propagation vectors which depend on magnetic field, i.e.,

$$\beta_j^{\mathrm{F}}=\eta_e[1-\omega_p^2/\omega_j(\omega_j\pm\omega_c)]^{\frac{1}{2}},$$

$$\beta_j^{\mathrm{V}}=\eta_e[1-\omega_p^2(\omega_j^2-\omega_p^2)/\omega_j^2(\omega_j^2-\omega_p^2-\omega_c^2)]^{\frac{1}{2}}$$

and where β_j^{F} and β_j^{V} are the phase constants for Faraday and Voigt configurations, η_e the index of refraction, and ω_p the plasma frequency. In a parametric device in which the sample dimension is comparable with the wavelength, the phase matching is not critical. In a cavity arrangement, the tuning of modes by the magnetic field occurs and external tuning of cavities may be required to produce oscillations. In this case, either by solving Maxwell's equations or by using depolarizing effect of the magnetoplasma, one can show that in the denominators of Eq. (5) for the Voigt configuration ω_c^2 is replaced by $\omega_c^2+\omega_p^2$. Thus the magnetoplasma resonance allows enhanced excitation at modest fields. With existing fields of the order of 100 to 150 kOe, the amplitude will increase quadratically with field for low electron densities $j_3(H)/j_3(0)\approx 1+3\omega_c^2/\omega^2$ up to a value of 2.3 and $\sim(3\omega_c^2+\omega_p^2)/\omega^2$ for larger electron densities.

Nonlinear properties of electrons in nonparabolic bands can also be demonstrated in excitations between two bands. Using the semiclassical treatment for bound oscillators, the equation of motion for electrons in the nondegenerate valence band has the form[5]

$$d\vec{p}/dt+m\omega_{\alpha\beta}^2\vec{r}-m\vec{v}\times\vec{\omega}_c=\textstyle\sum_j e\vec{E}\exp(i\omega_j t), \quad (6)$$

where $\omega_{\alpha\beta}$ denotes the frequency corresponding to the transition energy between states α and β in the valence and conduction band, respectively. Assuming two simple nonparabolic bands and using the dispersion relation given in Eq. (2), it can be transformed into

$$\ddot{\vec{p}}+(1-p^2/m^*\mathcal{E}_g)(\vec{p}\omega_{\alpha\beta}^2-\dot{\vec{p}}\times\vec{\omega}_c)$$
$$+2(\vec{p}\cdot\dot{\vec{p}})\vec{p}\times\vec{\omega}_c/m^*\mathcal{E}_g=+e\textstyle\sum_j i\omega_j\vec{E}_j\exp(i\omega_j t). \quad (7)$$

This model applies well to bismuth or PbTe; in InSb additional complications arise because of the degeneracy of the valence band. The solution of this equation for the velocity oscillating with frequency 3ω (third harmonic) is of the form

$$\vec{v}_3=\frac{9e^3\omega^3}{m^*\mathcal{E}_g}\frac{(E_x^2+E_y^2)\{[(\omega^2-\omega_{\alpha\beta}^2)(9\omega^2-\omega_{\alpha\beta}^2)+3\omega^2\omega_c^2]\vec{E}-4\omega(3\omega^2-\omega_{\alpha\beta}^2)\vec{E}\times\vec{\omega}_c\}}{[(\omega^2-\omega_{\alpha\beta}^2)^2-\omega^2\omega_c^2]^2[(9\omega^2-\omega_{\alpha\beta}^2)^2-9\omega^2\omega_c^2]}. \quad (8)$$

When this is integrated over momentum along the z direction, resonant terms of the form $(\omega_n-\omega)^{-3/2}(3\omega-\omega_n)^{-1/2}$ occur, where for the two-band nonparabolic model, neglecting spin, $\hbar\omega_n=[\mathcal{E}_g^2+4\mathcal{E}_g\hbar\omega_c(n+\frac{1}{2})]^{1/2}$. Similar types of singularities occur for mixing of frequencies for which the nonlinearity can be enhanced when 3ω is replaced by $2\omega_1\pm\omega_2$. The materials suitable would be the ternary alloys of $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$[6] and others where the energy gap is tailored to maximize these effects.

It can be seen that the magneto-optical resonances for interband transitions occur at lower magnetic fields because of the presence of energy gap, and they can be readily realized with the use of existing laboratory facilities.

Warped energy surfaces of valence electrons in germanium, silicon, and the III-V compounds can also be used as a source of nonlinearity. The onset of nonlinearity in p-type germanium has been indicated.[7] Also, heavy-hole cyclotron-resonance harmonics have been observed at microwaves.[8] Hence, there should be considerable third-harmonic generation at 112 μ with a focussed cyanide-laser beam. For heavy holes the energy-momentum relation of the center section $p_z=0$ in [100] directions can be well approximated by

$$\mathcal{E}=p^2/2m+4\alpha p_x^2p_y^2/p^2, \quad (9)$$

where $1/2m=(1/2m_0)[A-(B^2+\frac{1}{4}C^2)^{1/2}]-\alpha$, and $\alpha=C^2/[16m_0(B^2+\frac{1}{4}C^2)^{1/2}]$ in the standard notation. α is a measure of the warping, which in this case has four-fold symmetry. Hence, the velocity-momentum relation is of the form

$$v_x=p_x(1/m+8\alpha p_y^4/p^4), \quad (10)$$

and symmetrically for v_y. Thus the velocity depends linearly on the absolute value of momentum but is anisotropic in $\vec{k}$ space. Now the equation of motion $dp/dt = eEe^{i\omega t}$ for circularly polarized incoming waves can be solved to give $p = (P/i)e^{i\omega t} + p_0$, where $P = eE/\omega$. The initial value p_0 is determined by the Fermi level and the orientation in k space, and the final results are to be averaged over the whole Fermi surface. This can be done exactly in our case; we will, however, do it for two limiting cases.

First we assume that $P/p_0 \ll 1$, i.e., the perturbation is small compared with the equilibrium values. The components of momentum can be substituted into Eq. (10) and everything expanded in powers of P/p_0. We obtain the velocity, i.e., the response function as a power series in P with the amplitudes of linear response at the frequency ω and nonlinear ones at 3ω, $5\omega, \cdots$ proportional to P, P^3, $P^5, \cdots$, respectively. This field dependence is in agreement with general quantum mechanical[9] and classical results based on the Boltzmann equation, which use expansions in powers of the perturbation. However, after integrating over the Fermi surface, the amplitudes of higher harmonics average to 0 (we have checked it for the third). Thus, in this approximation of small perturbation the considered medium is essentially linear.

We can compute the velocity components in the opposite limiting case $P/p_0 \gg 1$. This condition is fairly easy to achieve with existing laser sources. Then in the first approximation we can neglect the initial conditions, and the final result is

$$\begin{Bmatrix} v_x \\ v_y \end{Bmatrix} = \left(\frac{1}{m} + \alpha\right) P \begin{Bmatrix} \sin\omega t \\ -\cos\omega t \end{Bmatrix} + \frac{3}{2}\alpha P \begin{Bmatrix} \sin 3\omega t \\ \cos 3\omega t \end{Bmatrix} + \frac{1}{2}\alpha P \begin{Bmatrix} \sin 5\omega t \\ -\cos 5\omega t \end{Bmatrix}, \quad (11)$$

i.e., the response contains also higher harmonics because of the warping of the energy surfaces. The surprising feature is that the higher harmonic generation occurs here in first order in the electric field. In our estimation there is no contradiction between this result and the general statements cited before, since they all use the expansion in powers of the perturbation, whereas our case is so simple that we can solve it exactly. Another well-known case in which the expansion in powers of the electric field is not strictly observed is the phenomenon of saturation. Our treatment assumes the validity of the effective mass approximation (EMA) so that the electric field amplitude should satisfy $p_0 \ll P < p_{\rm max}$, where $p_{\rm max}$ denotes the values of momentum for which EMA still holds. It should also be mentioned that the response of the light holes will partly cancel the nonlinear response of the heavy holes, but because of the difference in the density of states, the net nonlinear current will occur.

A very similar result is obtained in the presence of a magnetic field with linearly polarized incoming radiation.

In graphite, the strong warping and threefold symmetry of hole energetic surfaces should allow for two-photon mixing. Again, the amplitude of all higher harmonics is of the first order in electric field with the multiples of the third harmonic absent.

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[1]B. Lax, A. L. McWhorter, and J. G. Mavroides, in Quantum Electronics, Proceedings of the Third International Congress, Paris, 1964, edited by P. Grivet and M. Bloembergen (Columbia University Press, New York, 1964), Vol. II, pp. 1521-1526.

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

[3]P. A. Wolff and G. A. Pearson, Phys. Rev. Letters 17, 1015 (1966).

[4]Wolff and Pearson derive their expressions with a term $(1+1.6\mathcal{E}_{\rm F}/\mathcal{E}_g)^{-5/2}$ corresponding to the mass correction of the electrons at the Fermi level. Our results can be multiplied by this value, but in addition the cyclotron frequencies should be corrected, i.e., $\omega_c = eH/m_0{}^*c(1+4\mathcal{E}_{\rm F}/\mathcal{E}_g)^{-1/2}$ or, more appropriately, $\omega_c = \omega_{c0}(1+4\hbar\omega_{c0}/\mathcal{E}_g)^{-1/2}$, where $\omega_{c0} = eH/m_0{}^*c$ since $\mathcal{E}_{\rm F} \approx 10^{-3}$ eV and $\hbar\omega_{c0} \approx 0.02$ eV for $N = 10^{17}/{\rm cm}^3$ and $H = 150$ kOe.

[5]J. Kolodziejczak, B. Lax, and Y. Nishina, Phys. Rev. 128, 2655 (1962); W. Zawadzki, Q. H. F. Vrehen, and B. Lax, Phys. Rev. 148, 849 (1966). The selection rules for interband transitions are determined mainly by spin, so that the Landau spacing is replaced by the effective spin splitting.

[6]J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Letters 16, 26 (1966).

[7]K. J. Button, private communication.

[8]R. N. Dexter, H. J. Zeiger, and B. Lax, Phys. Rev. 104, 637 (1956).

[9]M. Lax, Phys. Rev. 109, 1921 (1958).