RESONANCE MIXING OF LASER FREQUENCIES IN A SEMICONDUCTOR

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Laser frequency mixing is considered for semiconductors with a narrow forbidden band. It is shown that near the threshold for two-photon production of a real electron-hole pair, the frequency mixing probability grows as $|\ln\Delta|^2$ when there is degeneracy of the conduction electrons, and as $|\Delta|^{-1}$ if the transitions take place between Landau levels in a magnetic field (Δ is the energy above threshold).

THE power of laser beams is sufficient for the observation of optical nonlinearity of solids. Patel et al.[1] have observed mixing of the frequencies (MF) $\omega_1 = 1.77 \times 10^{14}$ s^{-1} and $\omega_2 = 1.95 \times 10^{14}$ s^{-1} of a CO_2 laser in the processes $(2\omega_1 \to \omega_2,\ 2\omega_1 - \omega_2)$ and $(2\omega_2 \to \omega_1,\ 2\omega_2 - \omega_1)$, i.e., absorption of two photons from one beam with subsequent stimulated emission of a photon of another beam and a photon carrying the remainder of the energy. The initial and final states of the crystal coincide, so that the processes are coherent. The experiments in[1] were carried out on crystals of InAs, InSb, GaAs, and PbTe. A strong dependence of output power at the frequency $2\omega_1 - \omega_2$ on the concentration of conduction electrons was noted. Wolff and Pearson[2] carried out a theoretical treatment, ascribing the principal role in the nonlinearity to the conduction electrons, and the nonlinearity itself was explained by a nonparabolic dispersion law in the conduction band. The emission of the electron was treated in[2] as the radiation of a classical charged particle moving under the influence of an alternating field, and the specifics of the semiconductor enter via the dispersion law.

The classical treatment is appropriate if the energy of the quantum is small compared to the energy of the interband transitions. If this condition is not fulfilled, it is impossible to express the magnitude of the nonlinearity solely in terms of the dispersion law of the conduction band.

The substances investigated in[1] differ strongly with respect to the width of the forbidden band: $\epsilon_g > 1$ eV for GaAs, $\epsilon_g = 0.19$ eV for PbTe,[3] and $\epsilon_g \sim 0.2$ to 0.3 eV for InSb and InAs. The energy of the quanta is $\hbar\omega_1 = 0.117$ eV and $\hbar\omega_2 = 0.129$ eV. It follows from this that in PbTe, InSb, and InAs the nonlinearity must be treated by quantum methods with account taken of the specific band structure.

Calculation of the probability of MF in the general case requires knowledge of the wave functions far from the band extrema. However, the favorable relation of the parameters—the closeness of the widths of the forbidden bands in PbTe, InSb, and InAs and twice the energy of the quanta obtainable from the CO_2 laser—allows us to pose the problem of the peculiarities of the probability of MF at the threshold for two-photon creation of a real electron-hole pair. In this, the form and magnitude of the peculiarity is determined by integration in the matrix element over the momentum of the virtual pair near the extrema of the conduction and valence bands, i.e., in that region of the Brillouin zone that is well known in many semiconductors.

As is known, the Hamiltonian of the electron-photon interaction in the nonrelativistic case is the sum of two terms, one of which is linear in the vector potential of the photon and the other quadratic. The process of interest to us is of fourth order in the electron-photon interaction and is manifested as the scattering of light by light. There are three forms of diagrams that give a contribution to the matrix element of the process M:

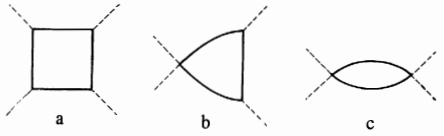

FIG. 1

Of importance to us are those diagrams which, by breaking two electron lines, can be divided into a diagram pertaining to two-photon creation of a real pair and one belonging to its two-photon annihilation. Since the term that is quadratic in the vector potential in the interaction Hamiltonian depends weakly on the coordinates due to the smallness of the photon wave vector, its contribution to the probability of pair creation is negligibly small, and so diagrams of the type b and c in Fig. 1 should be eliminated.

We assume that the two photons are identical; hence for a given direction of going around the electron loop there are in all three different diagrams of type a. Of these, two diagrams, which involve transposition of the final photons, give a contribution to the probability of MF of interest to us:

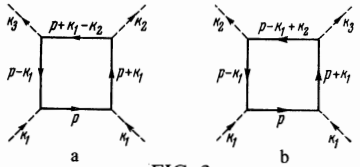

FIG. 2

Since we shall consider only these two diagrams and ignore the remaining diagrams of fourth-order perturbation theory, the expressions obtained below are only those parts of the general gauge-invariant expressions which are important near resonance. This explains the absence of gauge-invariance in our final results.

The probability per unit time w of creating a photon with frequency $\omega_3 = 2\omega_1 - \omega_2$ and a given polarization

is expressed in terms of the matrix element M in customary fashion[4]:

$$w=\frac{2\pi}{\hbar}\int\frac{d^3\mathbf{k}_3}{(2\pi)^3}\frac{|M|^2}{2\hbar\omega_3}\delta(2\hbar\omega_1-\hbar\omega_2-c_0k_3\hbar)[(2\pi)^3\delta(2\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3)]^2, \tag{1}$$

where c_0 is the velocity of light in the crystal. We shall assume the sample size to be sufficiently small and neglect the nonparallelism of the laser rays and the dispersion of light in the semiconductor. Then, integrating over $\mathbf{k}_3$ as in[5], we obtain

$$w=\frac{L^2S}{2c_0\hbar^3\omega_3}|M|^2. \tag{2}$$

Here L is the length of the crystal in the direction of light propagation, and S is the cross section of the region in which MF takes place.

CONCENTRATION DEPENDENCE OF THE PROBABILITY OF FREQUENCY MIXING

We shall carry out the calculation for the example of a semiconductor with the band structure of PbTe. As pointed out in[3], in PbTe the band extrema are located on the edge of the Brillouin zone on the [111] axes, and the bands are described by an equation that differs from the Dirac equation by the anisotropy of the effective masses. Aronov and Pikus[3] show that a coordinate transformation can bring the equation for each minimum to the Dirac form with replacement of the velocity of light by $s=(\epsilon_g/2m)^{1/2}$, where $m=(m_{\parallel}m_{\perp}^2)^{1/2}$ is the mass of the density of states, which enters in the equation as the electron mass; $m_{\parallel}$ and $m_{\perp}$ are the principal values of the effective mass tensor. The total matrix element is the sum of four matrix elements for different minima. The term in the total matrix element which corresponds to a given diagram and given minimum is obtained from the expression pertaining to this same diagram in quantum electrodynamics,[4] after the following operations: 1) deletion everywhere of the photon momentum compared to the electron momentum; 2) replacement everywhere of the velocity of light by s and the mass by m; 3) replacement of the scalar products of the vector potentials by their combination with the inverse effective mass tensor m_{ij}^{-1} for a given minimum according to the rule $\mathbf{A}\cdot\mathbf{B}\to A_i(m/m_{ij})B_j$; 4) if the conduction band is filled with electrons up to the Fermi level ϵ_F, integration over the modulus of momentum is carried out between the limits (p_F,∞), where $p_F=[2m\epsilon_F(1+\epsilon_F/\epsilon_g)]^{1/2}$.

These rules are easily obtained with the aid of the results of[3] after writing out the expression for the S-matrix. We give the part of the matrix element that corresponds to diagram a of Fig. 2:

$$M_a=e^4\sqrt{4\pi}\int\limits_{|p|>p_F}\frac{d^4p}{(2\pi)^4}$$
$$\times\,\mathrm{Sp}\{\hat{A}G(p)\hat{A}G(p-k_1)\hat{e}G(p+k_1-k_2)\hat{B}G(p+k_1)\}. \tag{3}$$

Here we take $s=\hbar=1$ and use the notation of[4]; **A** and **B** are the vector potentials of the laser fields, **e** is the polarization vector of the emitted photon. Calculation of the trace is facilitated if it is taken into account that **A**, **B**, and **e** do not have temporal components and the spatial components of the 4-momentum of the photon are eliminated. To simplify the angular functions, we take the polarizations of all photons to be identical and linear. In view of the fact that[4]

$$G(p)=\frac{\hat{p}+m}{p^2-m^2+i\delta},\quad \delta\to+0, \tag{4}$$

the necessary traces, summed over the minima, can be obtained from the general expression

$$\sum_{\alpha=1}^{4}\mathrm{Sp}\{\hat{n}(\hat{p}+m)\hat{n}(\hat{p}_1+m)\hat{n}(\hat{p}_2+m)\hat{n}(\hat{p}_3+m)\}$$
$$=16/9\,\Phi(\theta)\{m^4+m^2(pp_2+p_1p_3)-(m^2+2/3\,\mathbf{p}^2)(pp_1+p_1p_2+p_2p_3+p_3p)+3[(pp_1)(p_2p_3)+(p_1p_2)(pp_3)-(pp_2)(p_1p_3)]+8/3m^2\mathbf{p}^2+8/5\mathbf{p}^4\}, \tag{5}$$

where **n** is the unit polarization vector; p, p_1, p_2, p_3 are 4-vectors with spatial component **p** and different temporal components. The scalar product of the 4-vectors a and b is written in the form

$$ab\equiv(ab)=a_0b_0-\mathbf{ab}. \tag{A}$$

The function $\Phi(\theta)$ determines the dependence of the matrix element on the direction of **n** relative to the crystal axes:

$$\Phi(\theta)=\left(\frac{2m}{m_{\perp}}+\frac{m}{m_{\parallel}}\right)^2+8\left(\frac{m}{m_{\perp}}-\frac{m}{m_{\parallel}}\right)^2\left(1-\sum_{i=1}^{3}\cos^4\theta_i\right), \tag{6}$$

where the θ_i are the angles between **n** and the fourfold axes. In calculating Eq. (5), an average over the directions of **p** was made to bring out the angular dependence explicitly.

From (3) and (4) it is seen that the integral in (3) diverges logarithmically at the upper limit. This indicates the inadequacy of the two-band approximation for calculating the probability of MF. We are interested, however, in the case when the integral diverges at the lower limit of integration over the modulus of **p**. This occurs at $2\hbar\omega_1=\epsilon_g+\epsilon_F$ (ϵ_F is the Fermi energy), i.e., at the threshold of creation of a real electron-hole pair. Writing out an expression for M_b analogous to (3), using (5), and calculating the part of M logarithmically diverging at the lower limit with the assumption $\epsilon_F<\epsilon_g$, which is almost always true, we obtain the final expression

$$w=\left(\frac{5}{27}\right)^2\frac{L^2S}{\pi^3}\frac{e^2}{mc_0}\left(\frac{\varepsilon_g}{\hbar\omega_2}\right)^2\left(\frac{\varepsilon_g}{\hbar\omega_2}\right)^3\left(\frac{eE_1}{\hbar\omega_1}\right)^4\left(\frac{eE_2}{\hbar\omega_2}\right)^2$$
$$\times\Phi^2(\theta)\left(\frac{\varepsilon_F}{\varepsilon_g}\right)^3\left|\ln\frac{\varepsilon_g+\varepsilon_F-2\hbar\omega_1}{\varepsilon_g}\right|^2, \tag{7}$$

where E_1 and E_2 are the amplitudes of the laser fields at frequencies ω_1 and ω_2. In the calculations, we take $2\hbar\omega_1=\epsilon_g$ everywhere except in the logarithm. The logarithm is real for positive values of the argument, and for negative values it acquires the addition of $i\pi$; hence at the threshold w goes to infinity as $\ln^2|x|$ and undergoes a finite jump. The magnitude of the singularity of (7) compared to the smooth part of w is given, in order of magnitude, by the last two factors in (7). Since the inequality $\epsilon_F<\epsilon_g$ holds up to concentrations of $\sim10^{18}$, the singularity of (7) should be considered weak. The concentration dependence, according to our calculation, is not monotonic, thus differing from[1,2]. The angular dependence of (7) and (6) shows that near threshold the maximum and minimum of w are attained at polarizations respectively along the three- and fourfold axes. Since usually $m_{\parallel}>m_{\perp}$, the maximum and minimum values of w can differ by not more than 49/9

= 5.4 times. For PbTe, where $m_{\parallel}/m_{\perp} \approx 11$, they differ by a factor of 4.

DEPENDENCE OF THE PROBABILITY OF FREQUENCY MIXING IN A MAGNETIC FIELD

We shall carry out the calculation for a model semiconductor in which the conduction and valence bands are isotropic and are described by the Dirac equation

$$(\hat{p} - e\hat{A}_H + m)\psi = 0; \quad \hat{a} = a_0\gamma^0 - \mathbf{a}\boldsymbol{\gamma} \quad (\hbar = s = 1). \tag{8}$$

We represent the matrix γ^μ in the form

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \boldsymbol{\gamma} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$
$$\sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{9}$$

The magnetic field H = cH′/s (c is the velocity of light) is directed along the z axis, and its vector potential $\mathbf{A}_H$ = (0, H′x, 0). Solving the squared Dirac equation, we find the four orthonormal solutions:

$$\psi_{pn\mu\pm}(x, y, z) = \psi_{pn\mu\pm}(\xi)\frac{\exp(ip_y y + ip_z z)}{\Omega^{1/2}} \quad (\mu = \pm 1). \tag{10}$$

Here Ω is a two-dimensional volume (y, z), $\xi = (eH')^{1/2}(x - p_y/eH')$,

$$\psi_{pn\mu\pm}(\xi) = \frac{(\hat{p} - e\hat{A}_H + m)\,v^{(n)}(\xi)\,B_\mu}{[2(p_0^2 \pm p_0 m)]^{1/2}}; \quad B_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad B_{-1} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \tag{11}$$

$v^{(n)}(\xi)$ is the n-th normalized function of the harmonic oscillator, $p_0 = [m^2 + p_z^2 + eH'(2n - \mu + 1)]^{1/2}$, and we use the convention that the sign before p_0 in $\hat{p}$ coincides with the subscript + or − of the wave function, so that later in calculations of the matrix elements it must always be remembered to which wave function the operator $\hat{p}$ belongs. Using (10) and (11) we write the Green function in mixed variables

$$G_{ik}(x, x', p_y, p_z, \omega) = \sum_{n\mu}\left[\frac{\overset{i}{\psi}_{pn\mu+}(\xi)\overline{\overset{k}{\psi}}_{pn\mu+}(\xi')}{\omega - p_0 + i\delta} + \frac{\overset{i}{\psi}_{pn\mu-}(\xi)\overline{\overset{k}{\psi}}_{pn\mu-}(\xi')}{\omega + p_0 - i\delta}\right]; \tag{12}$$

here, as usual, $\bar{\psi} = \psi^*\gamma^0$. Equation (12) was obtained assuming the absence of conduction electrons. Since the energy of the electron is independent of p_y and we neglect the momentum of the photon, it follows that in calculating the S-matrix we can at once complete the integration over p_y taking into account that the region of integration is eH′ (region of integration over x). The rules for writing down the contribution to the matrix element M from diagrams of the types a and b in Fig. 2 are changed as follows: the indices x, x′, x″, x‴ are assigned to the four vertices of the diagram; in place of the functions G(p) are substituted G(x, x′, p_z, ω) ≡ G(x, x′, 0, p_z, ω) (see Eq. (12)); the integration goes over x, x′, x″, x‴, ω, and p_z; all expressions are multiplied by eH′/2π. Diagram a, for example, gives the following contribution to the matrix element:

$$M_a = e^2\sqrt{4\pi}\frac{eH'}{2\pi}\int\frac{d\omega}{2\pi}\int\frac{dp_z}{2\pi}\int dx\,dx'\,dx''\,dx'''\,\mathrm{Sp}\{\hat{A}G(x, x', p_z, \omega)$$
$$\times\hat{A}G(x', x'', p_z, \omega - \omega_1)\hat{e}G(x'', x''', p_z, \omega + \omega_1 - \omega_2)\hat{B}G(x''', x, p_z, \omega + \omega_1)\}. \tag{13}$$

In contrast to the preceding section, finding the trace now requires cumbersome calculations and leads in the general case to cumbersome results. From (13) and (12) it is seen that it is necessary, first of all, to have a convenient expression for the matrix element:

$$\int_{-\infty}^{\infty}\bar{\psi}_\nu(\xi)\hat{A}\psi_{\nu'}(\xi)\,dx = \int_{-\infty}^{\infty}\varphi_\nu(x)[(\hat{p} - e\hat{A}_H + m)\hat{A}(\hat{p} - e\hat{A}_H + m)]\varphi_{\nu'}(x)\,dx, \tag{14}$$

where ν and ν' symbolize all quantum numbers, the definition of $\varphi_\nu(x)$ is obvious, and as already indicated the sign of p_0 in $\hat{p}$ is the same as the index + or − of the closest function. The operator within the square brackets is matricized in the vectors B_μ, so that only the left upper matrix (2 × 2) is important in it.

We limit ourselves to the calculation of the singularity in the probability of MF when $2\hbar\omega_1$ is close to the energy of an allowed real transition between two Landau levels. As in the preceding section, the singularity is obtained upon integration of the resonant energy denominator near $p_z = 0$; hence, we may neglect p_z in the remaining places. Assuming that the light propagates along the magnetic field ($A_z = 0$), we introduce the notation $2A^+ = A_x + iA_y$ and $2A^- = A_x - iA_y$. The operators acting on the oscillator functions in (14) we shall write in terms of the creation operator a^+ and annihilation operator a with nonzero matrix elements $a^+_{nn-1} = a_{n-1,n} = (2n)^{1/2}$. Then the operator in brackets in (14) becomes

$$i\sqrt{eH'}\left\{\begin{pmatrix} \varepsilon + m & 0 \\ 0 & \varepsilon' + m \end{pmatrix}A^- a - \begin{pmatrix} \varepsilon' + m & 0 \\ 0 & \varepsilon + m \end{pmatrix}A^+ a^+\right\}, \tag{15}$$

where ϵ is p_0 taken with the proper sign, ϵ pertains to the left and ϵ' to the right function. The operator (15) is diagonal in μ, so that contributions to (13) from states with $\mu = \pm 1$ are additive.

We choose the polarization of the rays to be the same and circular, so that A^+ appears for absorption of a photon, and A^- for emission. In expressions of the type (13) it is convenient to divide the products of the vector potentials and G into factors $\hat{A} + G$, $G\hat{B}^-$, G, $\hat{A} + G\hat{B}^-$ (for $\mu = 1$) or $\hat{B} - G$, $G\hat{A}^+$, G, $\hat{B} - G\hat{A}^+$ (for $\mu = -1$) and to transform, with the aid of (15), from the x-representation to the n-representation. The nonzero matrix elements ($\mu = 1$) are

$$(\hat{A}^+G)_{n+1,n} = -\frac{i\sqrt{2eH'(n+1)}\,A^+}{\omega^2 - p_{0n}^2 + i\delta}, \quad (G\hat{B}^-)_{n,n+1} = \frac{i\sqrt{2eH'(n+1)}\,B^-}{\omega^2 - p_{0n}^2 + i\delta},$$

$$G_{nn} = \frac{\omega - m}{2neH'(\omega^2 - p_{0n}^2 + i\delta)}, \quad (\hat{A}^+G\hat{B}^-)_{nn} = \frac{2neH'(\omega + m)}{\omega^2 - p_{0,n-1}^2 + i\delta}. \tag{16}$$

Here $p_{0n} = (m^2 + p_z^2 + 2neH')^{1/2}$. We shall not write out the matrix elements for $\mu = -1$. Using (16) and analogous relations for $\mu = -1$, we write the integral in (13) in the form

$$\int\frac{d\omega}{2\pi}\int\frac{dp_z}{2\pi}\sum_n 4eH'n[\omega^2 - \omega_1^2 - m^2]A^+A^+B^-e^-$$
$$\times\{(\omega^2 - p_{0n}^2)[(\omega - \omega_1)^2 - p_{0,n-1}^2][(\omega + \omega_1 - \omega_2)^2 - p_{0n}^2]$$
$$\times[(\omega + \omega_1)^2 - p_{0,n+1}^2]\}^{-1}. \tag{17}$$

The imaginary additions in the denominators are implicit. The corresponding integral for M_b differs from (17) by the replacement of $\omega_1 - \omega_2$ in the third denominator for $\omega_2 - \omega_1$.

A singularity in w appears at $2\omega_1 = p_{0,n-1} + p_{0,n+1}$ ($p_z = 0$). To determine it, it is necessary to deduct ω in

the left pole of the second denominator of (17) and calculate the integral over p_z, keeping in mind that the principal contribution is given by the integration of the last denominator close to $p_z = 0$. We present the final expression:

$$w = \frac{L^2 S}{128\pi} \frac{e^2}{mc_0} \left(\frac{\varepsilon_g}{\hbar\omega_2}\right)^2 \left(\frac{\varepsilon_g}{\hbar\omega_3}\right)^3 \left(\frac{eE_1}{\hbar\omega_1}\right)^4 \left(\frac{eE_2}{\hbar\omega_2}\right)^2 \left(\frac{\hbar\omega_0}{\varepsilon_g}\right)^4 \frac{n^2\varepsilon_g}{|2\hbar\omega_1 - \varepsilon_{n-1} - \varepsilon_{n+1}|}, \quad (18)$$

where $\omega_0 = eH/mc$ is the cyclotron frequency, $\epsilon_n = [(\epsilon_g^2/4) + n\hbar\omega_0\epsilon_g]^{1/2}$, and everywhere, except in the resonant denominator, $2\hbar\omega_1 = \epsilon_g$. Although the fourth power of the ratio $\hbar\omega_0/\epsilon_g$ enters in (18) (ϵ_g for PbTe, measured in Oersteds, $\sim 10^6$), this factor can be effectively compensated near resonance, since smearing of the resonance occurs only as a result of electron collisions and equals $\hbar/\tau \ll \epsilon_g$, where τ is the mean free path time.

We know of experimental data on MF in a magnetic field. Van Tran et al.[6] observed a tripling of frequency in a magnetic field in InSb. Since frequency tripling is a process analogous to MF, we may be confident that the resonant dependence observed in[6] ought to be just as clearly manifested in MF also.

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