Photogalvanic effect in the field of a strong electromagnetic wave

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A theory is constructed of the photogalvanic effect in crystals without symmetry centers at high radiation intensities. The interaction with the light is taken into account with the aid of a canonical transformation [V. M. Galitskiĭ *et al.*, Sov. Phys. JETP **30**, 117 (1970)], to new quasiparticles α and β with asymmetric dispersion law $\varepsilon_k \neq \varepsilon_{-k}$. The relaxation processes (collisions with phonons or impurities, spontaneous emission) are described by the kinetic equations for the new particles. The distribution functions, which are in equilibrium in the new representation, are not in equilibrium for the electrons and holes. Because of the asymmetry of the dispersion law, the constant current does not vanish for equilibrium distributions of the particles α and β, and exists also in the vacuum state of the new field. The photo-induced currents do not depend on the relaxation parameters of the crystal and realize its transition into a nonequilibrium and nondissipative current state. The energy balance of the crystal in the regime of nondissipative currents is investigated.

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INTRODUCTION

Belinicher, Malinovskiĭ, and the author[1] initiated a theoretical study of a new effect in solid state physics—the photogalvanic effect (PGE). The gist of the new phenomenon is that in crystals without a symmetry center practically any disequilibrium of the electron-hole subsystem leads to ordered motion of the carriers—to an electric current.

The most important class of crystals with the PGE are ferroelectrics, in which the light-induced currents produce fields up to 10^4–10^5 V/cm and exert a substantial effect on the physics of the ferroelectric phenomena.

The PGE due to asymmetry of elementary electronic processes (scattering by impurities or phonons, photoionization) was investigated in Refs. 1–3 in the relaxation-time approximation for the kinetic equation at low light intensities.

The present paper deals with the case of large light intensities, when the characteristic frequency of the transition between the bands $\lambda \equiv \mathbf{E} \cdot \mathbf{D}_{cv}$ ($\mathbf{D}_{cv}$ is the matrix element of the transition) exceeds the reciprocal times Γ of the relaxation processes (interactions with phonons or impurities, spontaneous emission, and others). These intensities are easily attained in laser pulses.

The PGE in the region of strong light fields is of particular interest. Since the light-induced transitions prevail over the relaxation transitions, the photogalvanic current in the field of a circularly polarized wave turns out to be independent of the relaxation parameters and thus realizes a nonequilibrium and nondissipative current state of the crystal. One can speak conditionally of a phase transition in a ferroelectric at high light intensities.

The simplest PGE models are obtained if relaxation is completely neglected (§1), when the problem of interband transitions in the RF field reduces to a two-level system and is solved exactly with arbitrary initial conditions. The dynamic PGE model obtained in this manner describes the current state of the crystal at times $t < \Gamma^{-1}$. A similar model was constructed for impurity-band transitions. The collisions at longer times, generally speaking, causse the electrons (holes) to leave the resonance region and decrease the PGE. A consistent theory of the effect should be based on a rigorous allowance for the slow mixing processes in **k**-space. An appropriate technique was developed by Galitskiĭ, Goreslavskiĭ, and Elesin.[4] According to them, the resonant part of the interaction with the RF field is included in the zeroth-approximation Hamiltonian H_0, i.e., it is taken into account exactly. The Hamiltonian H_0 is reduced with the aid of a unitary transformation to a time-independent form and is diagonalized by a u, v transformation. The introduced quasiparticles are superpositions of an electron and a hole in the field of the light wave and have in our problem an asymmetric dispersion law

$$\varepsilon_{\mathbf{k}} \neq \varepsilon_{-\mathbf{k}}.$$

The photogalvanic current is expressed in terms of the density matrix of the new particles (§2). In the first-order approximation in Γ/λ, it is diagonal and satisfies the standard kinetic equations.[4,5] The solutions of these equations, which are in equilibrium in the new representation, are non-equilibrium for the electrons and holes. We emphasize that, owing to the asymmetry of $\varepsilon_{\mathbf{k}}$, the constant current does not vanish on the distribution functions of the quasiparticles, which depend on the energy $\varepsilon_{\mathbf{k}}$, and exist also in the vacuum state of the new field.

In §3 are obtained expressions for the photogalvanic current; these expressions correspond to the cases $\Gamma_{ef} \gg \gamma$ and $\Gamma_{ef} \ll \gamma$, where γ^{-1} is the radiative-recombination time and Γ_{ef} is the frequency of the electron-phonon collisions. These relations do not contain the dissipative parameters of the crystal. In the limit $\gamma \gg \Gamma_{ef}$ the expression for the current coincides with the one obtained in the dynamic model. In the same section is considered also the case of linear polarization of the pump wave,

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corresponding to a symmetrical law of dispersion of ε_k. In this situation the PGE is due to the asymmetry of the relaxation processes and appears in the next higher order of perturbation theory in Γ/λ, when account is taken of the off-diagonal elements of the density matrix. The current due to the electron-impurity interaction is calculated.

In §4 is considered the energy balance of the crystal in the regime of nondissipative photogalvanic currents.

In §5 are estimated the values of the currents and the possible experimental consequences of the considered effect are indicated.

A system of units with $\hbar = c = 1$ is used throughout.

§1. DYNAMIC MODELS OF PHOTOGALVANIC EFFECT

We consider the interband transition induced by an RF field

$$\mathbf{E} = \mathbf{E}_0 e^{-i\omega t} + \text{c.c.}$$

The frequency ω is taken close to the width Δ of the forbidden band. By virtue of the momentum conservation law, in the absence of collisions each of the states of the valence band is bound with one state in the conduction band. Therefore the probability amplitudes of finding an electron in the upper and lower bands, a_k and b_k, satisfy the equations of a two-level system.[6] Assuming that $a_k = 0$ and $b_k = 0$ at $t = 0$, we have

$$a_k = -i\frac{\lambda_k}{\varepsilon_k}\exp(i\zeta_k t)\sin\varepsilon_k t, \quad b_k = \exp(-i\zeta_k t)\left(\cos\varepsilon_k t + i\frac{\zeta_k}{\varepsilon_k}\sin\varepsilon_k t\right). \tag{1.1}$$

Here $\zeta_k = \frac{1}{2}(E_k^c - E_k^v - \omega)$ is the detuning away from resonance,

$$\lambda_k = i\frac{e}{m\omega}\langle c, \mathbf{k}|\hat{\mathbf{P}}\mathbf{E}_0|v, \mathbf{k}\rangle \tag{1.2}$$

is the matrix element of the transition between the Bloch wave functions

$$\varepsilon_k = (\zeta_k^2 + |\lambda_k|^2)^{1/2}. \tag{1.3}$$

The starting point for the understanding of the origin of the photogalvanic current is the asymmetry of the parameter λ_k:

$$|\lambda_k| \neq |\lambda_{-k}|.$$

In fact, the only general symmetry relation for the momentum matrix element, which follows from the symmetry properties of the Bloch wave functions $\psi_k = \psi_{-k}^*$, is

$$\langle v, \mathbf{k}|\hat{P}|c, \mathbf{k}\rangle = -\langle v, -\mathbf{k}|\hat{P}|c, -\mathbf{k}\rangle^*. \tag{1.4}$$

For complex $\mathbf{E}_0$, i.e., for circularly polarized light, λ_k has therefore an asymmetrical part[7,8]

$$|\lambda_k|^2 = |\lambda_k|_s^2 + |\lambda_k|_{as}^2, \quad |\lambda_k|_s^2 = |\lambda_{-k}|_{as}^2. \tag{1.5}$$

In ferroelectrics characterized by a single polar vector $\mathbf{c}$, the following expansion[1)] is valid at small values of the momentum (see also Ref. 2)

$$\lambda_k = \mathbf{E}_0(\alpha\mathbf{c} + i\beta\mathbf{k}).$$

Here

$$|\lambda_k|_s^2 = \alpha^2|\mathbf{cE}|^2, \quad |\lambda_k|_{as}^2 = \alpha\beta\mathbf{kS}, \quad \mathbf{S} = i[\mathbf{c}\times[\mathbf{E}\times\mathbf{E}^*]]. \tag{1.6}$$

The asymmetry of λ_k means that the rates of the interband transitions for the states $\mathbf{k}$ and $-\mathbf{k}$, just as the numbers of the electrons in these states, are different, i.e., a current is produced. Assuming for simplicity quadratic dispersion laws for the electron and the hole, and assuming the masses of the holes to be equal:

$$E_k^c = -E_k^v = \Delta/2 + \varepsilon_k^0, \quad \varepsilon_k^0 = k^2/2m, \tag{1.7}$$

we obtain from (1.1) for the photogalvanic current

$$\mathbf{j} = \frac{e}{(2\pi)^3}\int\frac{|\lambda_k|^2}{\varepsilon_k^2}\frac{\partial\varepsilon_k^0}{\partial\mathbf{k}}d\mathbf{k}. \tag{1.8}$$

The integral (1.8) can be easily calculated, and is determined by the resonant energy region $\zeta_k \sim \lambda_k$. Taking (1.6) into account, we obtain at small values of $\mathbf{k}_0$

$$\mathbf{j} = \frac{1}{12\pi}ek_0^3\frac{\beta}{|\mathbf{cE}_0|}\mathbf{S}, \tag{1.9}$$

$\mathbf{k}_0$ is determined from the resonance condition $\zeta_{k_0} = 0$. A characteristic feature of expressions (1.8) and (1.9) is the square-root dependence of the current on the light intensity, $j \propto I^{1/2}$. When averaged over the light polarizations, j vanishes.

We can consider analogously the PGE due to photoionization of deep impurity levels in the forbidden band. The Schrödinger equation for the amplitudes a_0 and a_k of finding the electron on a discrete level of an asymmetrical potential and in a continuous spectrum can be solved by the Wigner-Weisskopf method.[9,10] The solution describes the exponential decrease of the amplitude a_0 in the time $t \sim \lambda^{-1}$ and the asymmetric distribution of the free electrons. In the considered situation, the PGE becomes possible also when the light is linearly polarized. This is connected with the need for using for the asymmetrical potential exact wave functions containing diverging or converging waves.[6] In the case of circular polarization of the light, the distortion of the Bloch functions by the impurity potential is immaterial and the expression for the photogalvanic current takes the simple form

$$\mathbf{j} = eN_0 v_{k_0}\frac{\langle\mathbf{n}|\lambda_{k_0}|^2\rangle}{\langle|\lambda_{k_0}|^2\rangle}, \tag{1.10}$$

where N_0 is the impurity concentration, $v_{k_0} = d\varepsilon_{k_0}^0/d\mathbf{k}_0$ is the velocity of the resonant electrons, and $n = \mathbf{k}/k$; the averaging is over the equal-energy surface $\varepsilon_k^0 = \varepsilon_{k_0}^0$. Formula (1.10) describes the total ionization of the impurity with asymmetrical distribution of the emitted electrons. The value of the photogalvanic current, as seen from (1.10), undergoes saturation. At low values of $\mathbf{k}_0$, using the representation (1.6), we get

$$\mathbf{j} = \frac{1}{3}eN_0 v_{k_0}\frac{\beta k_0}{\alpha}\frac{\mathbf{S}}{|\mathbf{cE}_0|^2}. \tag{1.11}$$

We note that the expressions (1.8) and (1.10) for the photogalvanic currents reverse sign upon time reversal, i.e., they agree with the general invariance properties of the initial equations of motion.

The relations obtained for the photogalvanic currents neglect completely the slow relaxation processes, and thus describe only crystal current states that are asymptotic for the times $\lambda^{-1} < t < \Gamma^{-1}$. That this description is unsatisfactory can be seen even from the fact that the photogalvanic currents depend on the initial conditions. Thus, the initial conditions $a_k = 1$ and $b_k = 0$ (all

electrons are in the upper band) lead to reversal of the sign in (1.8). In the sections that follow we shall use a more rigorous approach based on a consistent allowance for the small parameter Γ/λ of the theory. We confine ourselves hereafter to interband transitions.

§2. CANONICAL TRANSFORMATION

Following the authors of Ref. 4, we include the resonant part of the interaction with the RF field in the zeroth-approximation Hamiltonian

$$H_0=\sum_{\mathbf{k}}\{(\Delta/2+\varepsilon_{\mathbf{k}}^0)(a_{\mathbf{k}}^+a_{\mathbf{k}}+b_{\mathbf{k}}^+b_{\mathbf{k}})+\lambda_{\mathbf{k}}a_{\mathbf{k}}^+b_{-\mathbf{k}}^+e^{-i\omega t}+\lambda_{\mathbf{k}}^*b_{-\mathbf{k}}a_{\mathbf{k}}e^{i\omega t}\}, \quad (2.1)$$

where $a_{\mathbf{k}}^+$ and $b_{\mathbf{k}}^+$ are the electron and hole creation operators. We use next the unitary transformation[4]

$$U(t)=\exp\Big\{-\frac{i\omega t}{2}\sum_{\mathbf{k}}(a_{\mathbf{k}}^+a_{\mathbf{k}}+b_{\mathbf{k}}^+b_{\mathbf{k}})\Big\}$$

to change over to a representation in which H_0 does not depend on the time[2]:

$$H_0=\sum_{\mathbf{k}}\zeta_{\mathbf{k}}(a_{\mathbf{k}}^+a_{\mathbf{k}}+b_{-\mathbf{k}}^+b_{-\mathbf{k}})+|\lambda_{\mathbf{k}}|(a_{\mathbf{k}}^+b_{-\mathbf{k}}^++b_{-\mathbf{k}}a_{\mathbf{k}})$$

and diagonalize it with a u, v transformation

$$a_{\mathbf{k}}=u_{\mathbf{k}}\alpha_{\mathbf{k}}+v_{-\mathbf{k}}\beta_{-\mathbf{k}}^+, \quad b_{-\mathbf{k}}=u_{\mathbf{k}}\beta_{-\mathbf{k}}-v_{-\mathbf{k}}\alpha_{\mathbf{k}}^+, \quad (2.2)$$

$$u_{\mathbf{k}}^2, v_{-\mathbf{k}}^2=1/2(1\pm\zeta_{\mathbf{k}}/\varepsilon_{\mathbf{k}}), \quad u_{\mathbf{k}}v_{-\mathbf{k}}=|\lambda_{\mathbf{k}}|/2\varepsilon_{\mathbf{k}}.$$

We ultimately get

$$H_0=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}(\alpha_{\mathbf{k}}^+\alpha_{\mathbf{k}}+\beta_{-\mathbf{k}}^+\beta_{-\mathbf{k}}). \quad (2.3)$$

The operators $\alpha_{\mathbf{k}}^+$ and $\beta_{-\mathbf{k}}^+$ are the operators for the creation of new quasiparticles α and β that are superpositions of an electron and a hole. They satisfy the usual anticommutation rules. The quasiparticle energy, equal to $\varepsilon_{\mathbf{k}}^{\alpha}=\varepsilon_{-\mathbf{k}}^{\beta}\equiv\varepsilon_{\mathbf{k}}=(\zeta_{\mathbf{k}}^2+|\lambda_{\mathbf{k}}|^2)^{1/2}$, is not an even function of the momentum. We note that in crystals without a symmetry center the energy gap $|\lambda_{\mathbf{k}}|$, as seen from (1.5) exists at all directions of the momentum $\mathbf{k}$.

We now find the time-invariant part of the current operator $e(\hat{\mathbf{P}}-e\hat{\mathbf{A}})/m$ in the new representation:

$$\hat{\mathbf{j}}=-e\sum_{\mathbf{k}}\frac{\partial\varepsilon_{\mathbf{k}}^0}{\partial\mathbf{k}}\Big\{\frac{\zeta_{\mathbf{k}}}{\varepsilon_{\mathbf{k}}}(1-\hat{n}_{\mathbf{k}}^{\alpha}-\hat{n}_{-\mathbf{k}}^{\beta})+\frac{|\lambda_{\mathbf{k}}|}{\varepsilon_{\mathbf{k}}}(\alpha_{\mathbf{k}}^+\beta_{-\mathbf{k}}^++\beta_{-\mathbf{k}}\alpha_{\mathbf{k}})\Big\}. \quad (2.4)$$

the photogalvanic current is thus expressed in terms of the single-particle density matrix of the new quasiparticles. It satisfies the usual evolution equation with a Hamiltonian that describes the collisions of the α and β particles with phonons, impurities, etc. The Hamiltonians of the interaction with the phonons or photons are given in the new representation in Refs. 4 and 5. We present only the Hamiltonian of the interaction with the impurities, which we shall need later. We start with the expression[11]

$$H_{imp}=\sum_{\mathbf{k}\mathbf{k}'}(a_{\mathbf{k}}^+a_{\mathbf{k}'}g_{\mathbf{k}\mathbf{k}'}^c+b_{-\mathbf{k}}b_{-\mathbf{k}'}^+g_{\mathbf{k}\mathbf{k}'}^v)c_{\mathbf{k}-\mathbf{k}'}, \quad (2.5)$$

where $g_{\mathbf{k}\mathbf{k}'}^{c,v}=(g_{\mathbf{k}'\mathbf{k}}^{c,v})$ are the matrix elements of the impurity potential between the Bloch wave functions in the upper and lower bands, $c_{\mathbf{k}}$ is the Fourier component of the impurity distribution function, and $\overline{c_{\mathbf{k}}c_{\mathbf{k}'}}^*=N_0\delta_{\mathbf{k}\mathbf{k}'}$. The averaging is over the ensemble of the impurities, in the new representation, H_{imp} takes the form

$$H_{imp}=\sum_{\mathbf{n}_1\mathbf{n}_2}G_{\mathbf{n}_1\mathbf{n}_2}\alpha_{\mathbf{n}_1}^+\alpha_{\mathbf{n}_2}c_{\mathbf{k}_1-\mathbf{k}_2}, \quad G_{\mathbf{n}_1\mathbf{n}_2}=G_{\mathbf{n}_2\mathbf{n}_1}^*, \quad (2.6)$$

$$G_{\mathbf{k}_1\mathbf{k}_2}^{11}=u_{\mathbf{k}_1}u_{\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^c+v_{-\mathbf{k}_1}v_{-\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^v, \quad G_{\mathbf{k}_1\mathbf{k}_2}^{22}=u_{\mathbf{k}_1}u_{\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^v+v_{-\mathbf{k}_1}v_{-\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^c,$$

$$G_{\mathbf{k}_1\mathbf{k}_2}^{12}=(G_{\mathbf{k}_2\mathbf{k}_1}^{21})^*=u_{\mathbf{k}_1}v_{-\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^c-v_{-\mathbf{k}_1}u_{\mathbf{k}_2}g_{\mathbf{k}_1\mathbf{k}_2}^v.$$

To abbreviate the notation, we have used the symbols $\mathbf{n}\equiv(i,\mathbf{k})$; $i=1,2$; $\alpha_{\mathbf{k}}^1=\alpha_{\mathbf{k}}$; $\alpha_{\mathbf{k}}^2=\beta_{-\mathbf{k}}^+$. The Hamiltonian (2.6) describes the elastic scattering and the mutual conversion of the particles α and β.

In the first approximation in Γ/λ, the density matrix is diagonal and satisfies the standard kinetic equations for the distribution functions of the new quasiparticles $n_{\mathbf{k}}^{\alpha}$ and $n_{-\mathbf{k}}^{\beta}$. The off-diagonal elements can be expressed in the next order in Γ/λ in terms of the solution of the kinetic equations.[5]

§3. PHOTOGALVANIC TERMS

Before we proceed to determine the stationary values of the photogalvanic currents, we obtain the value of $\mathbf{j}$ that sets in at short times $t\ll\Gamma^{-1}$ when the RF field is turned on sufficiently slowly, adiabatically. If the turning-on time $t_0>\lambda^{-1}$, then, as indicated in Ref. 4, the distributions $n_{\mathbf{k}}^{\alpha}$ and $n_{-\mathbf{k}}^{\beta}$ take the form of steps

$$n_{\mathbf{k}}^{\alpha}=n_{-\mathbf{k}}^{\beta}=\begin{cases}1, & \zeta_{\mathbf{k}}<0,\\ 0, & \zeta_{\mathbf{k}}>0.\end{cases} \quad (3.1)$$

In this case we have according to (2.4)

$$\mathbf{j}=-e\sum_{\mathbf{k}}\frac{|\zeta_{\mathbf{k}}|}{\varepsilon_{\mathbf{k}}}\frac{\partial\varepsilon_{\mathbf{k}}^0}{\partial\mathbf{k}}. \quad (3.2)$$

At small values of $\mathbf{k}_0$, using (1.6), we easily obtain

$$\mathbf{j}=\frac{1}{6\pi^2}ek_0^3\frac{\beta}{|c\mathbf{E}_0|}\mathbf{S}. \quad (3.3)$$

It is interesting to note that this quantity is smaller by a factor $\pi/2$ than the current (1.9) obtained when the RF field is turned on instantaneously.

We proceed to study the stationary currents. We consider first the simplest case when the fastest relaxation process is radiative recombination, $\gamma\gg\Gamma$. In this case, as shown in Refs. 4 and 5, the solution of the kinetic equation is

$$n_{\mathbf{k}}^c=n_{-\mathbf{k}}^v\equiv n_{\mathbf{k}}=v_{-\mathbf{k}}^2, \quad (3.4)$$

i.e., it takes the form of step that is smeared out by an amount equal to the interaction. We note that according to (2.2) this solution describes the electron and hole distribution localized near the resonance region:

$$n_{\mathbf{k}}^c=n_{-\mathbf{k}}^v=\frac{1}{2}\frac{|\lambda_{\mathbf{k}}|^2}{\zeta_{\mathbf{k}}^2+|\lambda_{\mathbf{k}}|^2},$$

and has a lucid physical meaning. Substituting (3.4) in (2.2) we obtain for the current an expression that coincides identically with (1.8). Thus, the photogalvanic current is described in the limit $\Gamma\ll\gamma$ by a dynamic model. This result is, of course, a direct consequence of the verticality of the transitions, i.e., the absence of redistribution over the spectrum.

The situation $\gamma>\Gamma$ can be realized in pure crystals at sufficiently low temperatures $T\ll\Theta$ (Θ is the Debye temperature), when the collisions with the phonons are strongly suppressed[12]:

$$\Gamma_{ef}\approx\Gamma_0+T(T/\Theta)^4, \quad \Gamma_0\ll\Theta.$$

We consider now the most typical case of weak radiative recombination, $\Gamma_{ef} \gg \gamma$. If $|\lambda_{k_0}| < \Omega_k$, where Ω_k is the phonon frequency, then the energy gap does not prevent the creation and annihilation of α and β pairs (in other words, the indirect electron and hole production processes are the effective ones). In this case we can neglect completely the recombination, and assume that the particles α and β have a Fermi distribution and a chemical potential $\mu = 0$ (Ref. 4):

$$n_k = (\exp[\varepsilon_k/T]+1)^{-1}. \tag{3.5}$$

The phonons are assumed to be in thermodynamic equilibrium. We must thus calculate the current with the energy functions of the new quasiparticles. As seen from (2.2), the current does not vanish and can be rewritten in the form

$$j = \frac{1}{2} e \sum_k \varepsilon_k^{-1} \operatorname{th} \frac{\varepsilon_k}{2T} \nabla_k |\lambda_k|^2. \tag{3.6}$$

We emphasize that the equilibrium distribution (3.5) for the particles α and β is, of course in disequilibrium for the electrons and holes.

A characteristic feature of the considered situation is the decrease of the photogalvanic current as a result of the smearing of the resonant character of the effect, owing to the departure of the electrons from the region of the interaction with the RF field. We turn first to the case $T \ll |\lambda|$, which corresponds to a vacuum of the particles α and β, $n_k = 0$. The distribution of the electrons and holes takes in this case the form of a smeared step with limiting momentum $\mathbf{k}_0$:

$$n_k^c = n_{-k}^v = \frac{1}{2}\left(1 - \frac{\zeta_k}{\varepsilon_k}\right).$$

This result is physically obvious; it corresponds to filling, at $T = 0$, of the bottom of the band by electrons on account of the phonon emission. The vacuum current

$$j_{vac} = \frac{1}{2} e \sum_k \varepsilon_k^{-1} \nabla_k |\lambda_k|^2$$

can be roughly estimated at

$$j_{vac} \sim e\alpha\beta \frac{k_0^3}{\varepsilon_{k_0}} \ln \left| \frac{\varepsilon_{k_0}}{\lambda_{k_0}} \right| S. \tag{3.7}$$

At high temperatures $T \gg \lambda$ there appears another cause of the smallness of the PGE. In the region $\varepsilon_k \ll T$ we have $n_k^c = n_{-k}^v \approx 1/2$, and the effect is therefore additionally cancelled within the limits of each band. The corresponding estimate for the current yields

$$j_T \sim e\alpha\beta \frac{k_0^3}{\varepsilon_{k_0}} \ln \left| \frac{\varepsilon_{k_0}}{T} \right| S. \tag{3.8}$$

It is assumed that $\varepsilon_{k_0} \gg T$.

We call attention to the fact that even though the effect becomes weaker, it still has a resonant character. In fact, let the allowed bands be narrow, $\Delta\varepsilon \ll \Delta$, and let the detuning from resonance be large, $\omega \gg |\omega - \Delta| \gg \Delta\varepsilon$. In this case, as follows from (3.6), the PGE decreases rapidly like $(\Delta\varepsilon/\omega - \Delta)^2 \ll 1$. We note also that calculations of λ_k in the tight-binding approximations show that the sign of the photogalvanic current can depend on the frequency of the light.

In superstrong fields, $\lambda \gg \Omega$, when the production of the α and β pairs becomes forbidden, an equilibrium concentration of the particles sets in because of radiative recombination. In this case n_k retains a Fermi distribution with a chemical potential $\mu \approx \frac{1}{3}\varepsilon_{k_0}$ (Ref. 13). The current j reverses sign in this case, and its value is given by (3.7).

So far we have regarded photogalvanic currents due to circular polarization of the wave, when the source of the asymmetry is the Hamiltonian H_0. In the case of linear polarization H_0 is invariant to spatial reflections and the PGE can be due only to the asymmetry of the relaxation terms. To calculate the current it is necessary to go outside the scope of the kinetic equation and calculate the off-diagonal elements of the density matrix. We note that this procedure makes it possible to establish a connection with the description of the PGE at low light intensities.[1,2]

We now calculate the photogalvanic current due to scattering by asymmetric impurities. Just as in Ref. 1, we assume that the impurity has a short-range potential with scattering light R as well as a long-range dipole potential. The impurities are assumed randomly distributed by all equally oriented along the c axis. For simplicity we confine ourselves to the first term of expansion (1.5) for λ_k. Expressing in standard fashion (see, e.g., Ref. 5) the off-diagonal element of the density matrix in terms of the solution of the kinetic equation n_k, we have for the contribution due to the impurities

$$\langle \alpha_n^+ \alpha_{n'} \rangle = \frac{N_0}{2\varepsilon_k} \sum G_{n'n_1} G_{n_1 n} \left[\frac{n_n - n_{n_1}}{\varepsilon_n - \varepsilon_{n_1} + i\delta} + \frac{n_{n'} - n_{n_1}}{\varepsilon_{n_1} - \varepsilon_{n'} + i\delta} \right], \tag{3.9}$$

$$\varepsilon_{1k} = \varepsilon_k, \quad \varepsilon_{2k} = -\varepsilon_k, \quad n_{1k} = n_k, \quad n_{2k} = 1 - n_k.$$

Using next (2.2) and (2.6), we obtain for the photogalvanic current

$$j = 4\pi N_0 e \sum_{kk_1} \varepsilon_k^{-1} \frac{\partial \varepsilon_k^v}{\partial k} u_k u_{k_1} v_{-k} v_{-k_1} \delta(\varepsilon_k - \varepsilon_{k_1}) \operatorname{Im}(g_{kk_1}^c g_{k_1 k}^v)(n_k - n_{k_1}). \tag{3.10}$$

It is seen that to obtain a nonzero current it is necessary, first, to take into account the difference between n_k and n_{ε_k}. We assume that the principal current in the kinetic equation is the one responsible for the radiative recombination, so that $n_k = v_{-k}^2$. Second, we must take into account the difference between the matrix elements[3] g_{kk_1} and $g_{kk_1}^v$. In the free-electron approximation we have[1]

$$\operatorname{Im}(g_{kk_1}^c g_{k_1 k}^v) = 8\pi^2 \frac{edR}{m^*} \frac{(\mathbf{k} - \mathbf{k}_1, \mathbf{c})}{(\mathbf{k} - \mathbf{k}_1)^2}, \tag{3.11}$$

where d/e is the effective displacement of the dipole. Substituting (3.11) in (3.10) we obtain after simple calculations

$$j = {}^1/_3 e^2 N_0 |\lambda_{k_0}| m^* dR c.$$

Just as before in (1.9), $j \propto I^{1/2}$, where I is the light intensity. We note that allowance for the succeeding terms of the expansion of λ_k would lead to a dependence of j on the polarization of the light.

The electron-impurity interaction considered above is the simplest example of relaxation-process asymmetry that leads in the nonequilibrium situation to a photogalvanic current. Other sources of the asymmetry can be electron-phonon[2] and electron-hole[3] interactions.

§4. ENERGY BALANCE

Regardless of the concrete microscopic mechanisms, the PGE must satisfy general requirements that result from the energy conservation law.

We denote by $\tilde{Q}$ and $\bar{Q}$ the energy fluxes in the crystal corresponding to the high and low frequencies. Obviously, $\bar{Q}=\mathbf{E}(\mathbf{j}+\sigma_0\mathbf{E})$, where σ_0 is the static conductivity. The stationary value of the internal field $\mathbf{E}$ is determined by the boundary conditions and can range from $\mathbf{E}=0$ (ideal conductivity of the surroundings) to $\mathbf{E}=-\mathbf{j}/\sigma_0$ (insulated crystal). In our regime the crystal operates like a current generator, i.e., $\bar{Q}<0$, with $\bar{Q}_{min}=-j^2/4\sigma_0$ reached at $\mathbf{E}=-\mathbf{j}/2\sigma_0$. From the obvious requirement $\tilde{Q}+\bar{Q}>0$ we get[4)]

$$\tilde{Q}>j^2/4\sigma_0. \tag{4.1}$$

It is of interest to note that at low light intensities, when j is determined by the phenomenological relation $j=f\varkappa I$ (f is the Glass coefficient[14] and $\varkappa$ is the absorption coefficient), we get from (4.1) a lower bound of the photoconductivity

$$4\sigma_0>fj, \tag{4.2}$$

which is significant, for example, when polaron models of the PGE are considered.

Let us examine how the condition (4.1) is satisfied in the region of a strong RF field. We investigate first the case $\gamma>\Gamma$. The absorption $\tilde{Q}$ and the conductivity σ_0 can be estimated in the following manner. The electrons in the conduction band are concentrated near $\mathbf{k}=\mathbf{k}_0$ in an energy interval $\delta\varepsilon_{k_0}{}^0\sim|\lambda|$. Their total number is therefore $n_0\sim k_0{}^2|\lambda|dk_0/d\varepsilon_{k_0}$ and accordingly

$$\tilde{Q}\sim m\gamma\omega|\lambda|k_0,\quad \sigma_0\sim e^2k_0|\lambda|\gamma^{-1}. \tag{4.3}$$

We note that the estimate of $\tilde{Q}$ agrees, apart from a numerical factor, with the results of the exact calculations.[4,5] Using (4.3), we find that satisfaction of (4.1) is equivalent to the inequality

$$\omega|\lambda|_e{}^2>\varepsilon_{k_0}{}^0|\lambda|_{ei}{}^2, \tag{4.4}$$

which is obviously always valid.

We turn now to the case $\Gamma>\gamma$, which is of greatest interest. As shown in Refs. 4 and 5, the absorption of the RF wave decreases abruptly and in the limit as $\gamma\to0$ we have $\tilde{Q}=0$ (saturation effect). At the same time, according to (3.6)–(3.8) we have nonzero photogalvanic currents and, generally speaking, a nonzero conductivity σ_0. The resultant contradiction with (4.1) is eliminated in the following manner. In Ref. 5 the value of Q was determined under the assumption of no LF dissipation, i.e., with Fermi distribution functions for the particles α and β. Physically, however, it is obvious that the maintenance of the energy release in a static field $\mathbf{E}$ via injection of electrons into the conduction band calls for additional energy consumption and must lead to the appearance of light absorption, denoting by $\bar{S}_k=\bar{S}_k\{n_k,n_{k'}\}$ the collision term in the kinetic equation for n_k, we have

$$\bar{Q}=\int\varepsilon_k\bar{S}_k\,d\mathbf{k}. \tag{4.5}$$

A similar relation holds for $\tilde{Q}$ (Ref. 5):

$$\tilde{Q}=\omega\int\tilde{S}_k d\mathbf{k}, \tag{4.6}$$

with $\bar{S}_k\sim\tilde{S}_k$. For Fermi distribution functions $\bar{S}_k\tilde{S}_k=0$. According to (4.5) and (4.6) we have the estimate

$$\tilde{Q}/\bar{Q}\leqslant\frac{\varepsilon_{k0}}{\omega}\ll1,$$

which agrees with (4.1). We emphasize that in the limit when $\gamma=0$ the energy dissipation is due exclusively to the finite dimensions of the sample. In an unbounded crystal the PGE is nondissipative, i.e., $\tilde{Q}=\bar{Q}=0$

§5. DISCUSSION

We estimate first the magnitude of the PGE. The maximum value of the current is given by (1.8) and (1.9). Putting $|\lambda_{k_0}|\sim10^{13}$ sec^{-1} ($I\approx10^7$ W/cm^2), $k_0\sim10^7$ cm^{-1}, and $\gamma\approx10^{10}$ sec^{-1}, we get

$$j\sim10^{14}\ \text{CGSE}.$$

For the maximum value of the internal field we have from (1.9) and (4.3)

$$E_{max}\sim\gamma k_0/e.$$

This expression is of the same order as that obtained in Ref. 1 at low light intensities. We note that the maximal values of $\mathbf{j}$ and $\mathbf{E}$ do not depend on the electron mass m^*.

So far, in view of the smallness of the wave vector $\mathbf{q}$, we assumed the optical field to be spatially homogeneous. It must be borne in mind, however, that the crystals are as a rule optically anisotropic. Therefore the waves with circular polarization are not natural oscillations of this field.[15] These natural oscillations are linearly polarized waves, while in a uniaxial crystal they are the ordinary and extraordinary waves. This leads, as can be easily seen, to spatial oscillations of the photogalvanic current (to domain formation) with a period $l\approx2\pi/q\Delta n$, where $\Delta n=n_0-n_e$ is the value of the birefringence (see also Ref. 8), and hinders the direct observation of the photogalvanic currents in bulky samples.

The spatial inhomogeneity of the photogalvanic currents leads, however, to an important effect—to the appearance of a new mechanism of nonlinear interaction of the ordinary and extraordinary waves. In fact, if an ordinary and extraordinary wave exist with vectors $\mathbf{q}_1$ and $\mathbf{q}_2$, then the separation of the charges and the linear electro-optical effect lead to formation of a spatial refractive-index grating $\Delta n(\mathbf{r})$ that leads to a redistribution of the light intensity. This interaction mechanism is already included in the phenomenology of the effect, $\mathbf{j}\propto\mathbf{S}$, and exists at all light intensities.

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[1)]It is realized, for example in the case of transitions between S bands of a crystal if the crystallographic field of the ferroelectric is taken into account.

[2)]We have included the phase of λ_k in the definition of the operators a_k and b_k. Generally speaking, this renormalizes the vertices of the electron-phonon interaction.

[3)]Or take into account the next term of the expansion in (1.5).

[4)]The inequality (4.1) can be regarded as a restriction on the efficiency η of the crystal in the current-source regime, $\eta_{max}<1$.

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Hyper-Raman scattering in an $LiNbO_3$ crystal

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It was found that the hyper-Raman scattering of light can be observed even in noncentrosymmetric crystals if the exciting radiation travels along a direction for which which was no phase matching. A multichannel photoelectric recording system was used in an investigation of the hyper-Raman spectra of crystalline $LiNbO_3$ in various scattering geometries. The time taken to record spectra in the 0–900 cm^{-1} range did not exceed 12 min. The E vibrations dominated the spectra in the investigated geometries. Estimates were obtained of the scattering cross section and nonlinear susceptibility in the hyper-Raman scattering in $LiNbO_3$.

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INTRODUCTION

1. The hyper-Raman scattering (HRS) of light is a three-photon process in which a system interacts with two photons of frequency ν_0 and emits one photon at a frequency $2\nu_0 \pm \nu_{ph}$ (ν_{ph} is the frequency of an optical phonon). The HRS is a quadratic term in the expansion of the polarization P of a medium as a series in powers of the field intensity E of the exciting wave:

$$P=\alpha E+{}^1/_2\beta E^2+\ldots \qquad (1)$$

The hyperpolarizability β is much less than the polarizability α. Therefore, the HRS can only be observed in sufficiently strong fields. The activity of vibrations in the HRS is governed by a rank-four hyperpolarizability tensor and it may be found that vibrations which do not participate in the spontaneous Raman scattering or in infrared absorption can take part in the HRS.[1,2] The HRS spectra have been recorded for gases, liquids, and solids.[3,4]

Although the HRS was discovered over 10 years ago,[5] it has been observed in just four noncentrosymmetric solids: fused quartz,[5] crystals of NH_4Cl,[6] diamond,[7] and CsI (Ref. 8). It is difficult to observe the HRS in noncentrosymmetric crystals because of the possible generation of the second harmonic of the exciting radiation ν_0 which may then give rise to the spontaneous Raman scattering in the same part of the spectrum as the HRS. We shall use the example of a nonlinear $LiNbO_3$ crystal to show that, if the exciting radiation travels along a direction for which there is no second-harmonic phase matching, the HRS can also be easily observed in a noncentrosymmetric crystal.

Crystals of $LiNbO_3$ have lower damage thresholds than those of the materials investigated earlier.[5-8] Therefore, we restricted the density of the exciting radiation to $\lesssim 10^8$ W/cm^2. Use was made of a multichannel photoelectric recording system by means of which we were able to obtain weak HRS spectra of $LiNbO_3$ at a relatively low exciting radiation density. The scattering cross sections and nonlinear susceptibility in the HRS process were determined for this crystal.

DESCRIPTION OF EXPERIMENTS

We used the apparatus shown schematically in Fig. 1. The HRS spectra of an $LiNbO_3$ crystal were excited by the $\lambda = 1064$ nm line of a pulsed YAG laser 1 ($I_0 \approx 2\times 10^4$ W, $\tau_p \sim 10^{-8}$ sec, divergence $\sim 10^{-3}$ rad, pulse repetition frequency 25 Hz). The spontaneous Raman scattering spectra of the crystal were excited under similar con-

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