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## Photogalvanic effect due to free carriers in noncentrosymmetric crystals

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An analysis is made of the photogalvanic effect in semiconductors and metals in the case when the frequency of light is insufficient for impurity-band and band-band transitions. It is shown that the photocurrent appears because of the asymmetry of the scattering of electrons (holes) by impurities, phonons, and electrons (holes) in the field of a light wave, and that the magnitude of this photocurrent is proportional to the coefficient of absorption of light. The order of magnitude of the photocurrent normalized to the absorption coefficient is the same as that for band-band optical transitions.

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### 1. INTRODUCTION

The photogalvanic effect is the appearance of a static photocurrent in a homogeneous noncentrosymmetric crystal under the action of homogeneous illumination; it has been observed in several experiments.<sup>[1-3]</sup> The microscopic theory of the effect is proposed in Refs. 4-6. However, this theory is limited to the case of impurity-band<sup>[5]</sup> and band-band<sup>[6]</sup> optical transitions.

The microscopic mechanism of the photogalvanic effect in noncentrosymmetric semiconductors is discussed by Genkin and Mednis<sup>[7,8]</sup> in the case when the photon energy is insufficient for band-band optical transitions. Genkin and Mednis allow for virtual optical transitions of an electron to other bands of a semiconductor, which results in the asymmetry of the renormalization of the electron dispersion law in the case of elliptically polarized light. However, this asymmetry does not give rise to a static photocurrent. The photocurrent  $J$  can be found by integration with respect to the quasimomentum  $k$ :

$$j = \int \nabla_k \epsilon_k / k dk. \quad (1)$$

Illumination alters both the dispersion law of elec-

trons  $\epsilon_k$  and their distribution function  $f_k$ . The change in the function  $f_k$  due to illumination is ignored by Genkin and Mednis.<sup>[7,8]</sup> This change is due to intraband electron scattering processes. In the principal approximation, we find that  $f_k$  remains the Boltzmann distribution function even if allowance is made for scattering but this distribution function is now coupled to an asymmetric dispersion law. In this approximation, the photocurrent (1) vanishes since the total derivative in respect of the quasimomentum  $k$  occurs in the integral (1). The formal mechanism responsible for the vanishing of the photocurrent<sup>[7,8]</sup> is discussed in the present paper.

We shall be concerned with the photogalvanic effect due to free carriers in noncentrosymmetric semiconductors and metals.

We shall obtain an exact expression for the tensor of the photogalvanic effect (photogalvanic tensor)  $\beta_{in}$  using the Keldysh diagram technique<sup>[9]</sup> (analog of the Kubo formula) and consider various mechanisms of electron scattering by impurities and phonons and the electron-electron scattering in metals in the presence of a light wave. The scattering asymmetry<sup>[5]</sup> in noncentrosymmetric crystals is responsible for the appearance of a

current. The use of the diagram technique makes it possible to demonstrate clearly the contributions of various scattering mechanisms to the photogalvanic effect.

## 2. GENERAL RELATIONSHIPS

The photocurrent  $\mathbf{j}$  is a quadratic function of the field intensity of a light wave:

$$j_i = \beta_{ijn} E_{i\omega} E_{n\omega}^* \quad (2)$$

Since the photocurrent is real, it follows that  $\beta_{ijn}^* = \beta_{inl}$ , i.e., the part symmetric in respect of the indices  $ln$  is real and the antisymmetric part is imaginary:

$$j_i = \beta_{ijn} E_i E_n^* + i\beta_{il}^a [E \times E^*]_i, \quad (3)$$

$$\beta_{ijn}^a = 1/2(\beta_{ijn} + \beta_{inl}), \quad \beta_{il}^a = -1/2i\beta_{ilab} \epsilon_{abl}.$$

The sign of the current  $\mathbf{j}$  changes as a result of spatial reflections but the value of  $E_i E_n^*$  does not change so that the tensor  $\beta_{ijn}$  differs from zero only for noncentrosymmetric crystals, as pointed out by Genkin and Mednis.<sup>[7,8]</sup>

Time inversion alters the sign of the current and the value of  $E_i E_n^*$  becomes  $E_i^* E_n$ , i.e., the tensor  $\beta_{ijn}^*$  changes its sign as a result of time inversion but there is no change of sign in the case of  $\beta_{ijl}^a$ . Time inversion also alters the sign of the dissipative constants,<sup>1)</sup> so that  $\beta_{ijn}^s$  becomes an odd function of the dissipative constants, and  $\beta_{ijl}^a$  becomes an even function. The mechanism of the photogalvanic effect contributing to the antisymmetric part of the tensor  $\beta_{ijn}$  was discussed earlier by the author.<sup>[10]</sup> The present method for calculating the tensor  $\beta_{ijn}$  is based on the exact expression for the nonlinear response (2). Instead of the standard Kubo formula, we shall obtain an exact expression for the photogalvanic tensor  $\beta_{ijn}$  using the Keldysh diagram technique,<sup>[9]</sup> which reveals effectively the characteristic indeterminacies of the 0/0 type, typical of problems of this kind.<sup>2)</sup> The static current can be described by

$$\mathbf{j} = \Omega^{-1} \text{Sp}(\hat{\rho}), \quad \langle \mathbf{x}'t' | \hat{\mathbf{j}} | \mathbf{x}t \rangle = (e/m_0) \delta(t-t') \langle \mathbf{x}' | \mathbf{p} - (e/c) \mathbf{A} | \mathbf{x} \rangle. \quad (4)$$

Here,  $\rho$  is the single-particle density matrix;  $\hat{\mathbf{j}}$  is the four-dimensional current operator;  $\Omega$  is the four-dimensional averaging volume;  $e$ ,  $m_0$ , and  $\mathbf{p}$  are the charge, mass, and momentum of an electron;  $\mathbf{A}$  is the vector potential of the electromagnetic field. In the Keldysh technique, a single-particle density matrix  $\rho(t', t)$  is identical with the Green function  $G^*(t', t)$ , so that the photogalvanic tensor  $\beta_{ijn}$  is given by<sup>3)</sup>

$$\beta_{ijn} = \frac{\delta^2 j_i}{\delta E_{i\omega} \delta E_{n\omega}^*} = \Omega^{-1} \text{Sp} \left( \hat{j}_i \frac{\delta G^+}{\delta (E_{i\omega} E_{n\omega}^*)} \right) \Big|_{E_{\omega=0}} \quad (5)$$

The expression (5) for the tensor  $\beta_{ijn}$  is valid in the  $\varphi=0$  gauge of the electromagnetic field; in this case, the invariance under time inversion ensures that the contribution of the term  $(e^2/m_0 c) \mathbf{A}$  to the current also vanishes. Moreover, we shall use the fact that the time-average Green function  $\bar{G}^*$  depends on the product  $E_{i\omega} E_{n\omega}^*$ , rather than on the separate factors  $E_{i\omega}$  and  $E_{n\omega}^*$ . We shall transform Eq. (5) employing the relationships

$$\frac{\partial G}{\partial \alpha} = -G \frac{\partial G^{-1}}{\partial \alpha} G, \quad G^{-1} = G_0^{-1} + \Sigma. \quad (6)$$

Here,  $G_0$  is the free Green function and  $\Sigma$  is the mass operator. Substituting Eq. (5) in Eq. (6), we obtain

$$\beta_{ijn} = \frac{-e}{\Omega m_0} \text{Sp} \left( p_i \left( G \frac{\delta \Sigma}{\delta (E_{i\omega} E_{n\omega}^*)} G \right)^+ \right) \Big|_{E_{\omega=0}} \quad (7)$$

In specific applications, it is convenient to write Eq. (7) in the basis of the Bloch functions of a crystal and to adopt the energy representation of the Green functions:

$$\beta_{ijn} = -\frac{(2\pi)^3 e}{m_0} \sum_{nn'} \int d\epsilon dk p_{ik}^{n'n} \left( G_{ik}^n \frac{\delta \Sigma_{ik}^{nn'}}{\delta (E_{i\omega} E_{n\omega}^*)} G_{ik}^{n'} \right) \Big|_{E_{\omega=0}} \quad (8)$$

Here,  $n$  and  $n'$  are the band numbers and it is assumed that the quantities  $G_{ik}^n$ , corresponding to  $E_{\omega}=0$ , are diagonal in respect of the band numbers. Equation (7) gives the relationship between the mass operator  $\Sigma$  and the tensor  $\beta_{ijn}$ , i.e., the graphs for the mass operator containing a photon line correspond to a fully determinate contribution to  $\beta_{ijn}$ . The simplest graphs are shown in Fig. 1. We shall have to calculate that contribution to the tensor  $\beta_{ijn}$  which is diagonal in respect of the band number. We can show that, in calculating expressions of the  $(G\Sigma G)^*$  type, we cannot substitute in Eq. (8) the free Green functions for an electron because the denominator then vanishes. It is sufficient to use the exact form of the Green functions  $G$  in the special case when the distribution function of the electron quasimomentum is the energy distribution function  $f_{\mathbf{k}} \equiv f_{\epsilon_{\mathbf{k}}}$ ; in this case, we have

$$G_{\epsilon_{\mathbf{k}}} = \begin{pmatrix} G^+, G^- \\ G^+, G^c \end{pmatrix} = -(2\pi)^{-1} i [(\epsilon - \Delta_{\epsilon_{\mathbf{k}}} - \epsilon_{\mathbf{k}})^2 + \Gamma_{\epsilon_{\mathbf{k}}}^2]^{-1} \times \begin{pmatrix} \epsilon - \Delta_{\epsilon_{\mathbf{k}}} - \epsilon_{\mathbf{k}} + i\Gamma_{\epsilon_{\mathbf{k}}}(1-2f_{\epsilon_{\mathbf{k}}}), & 2i\Gamma_{\epsilon_{\mathbf{k}}}(1-f_{\epsilon_{\mathbf{k}}}) \\ -2i\Gamma_{\epsilon_{\mathbf{k}}} f_{\epsilon_{\mathbf{k}}}, & -(\epsilon - \Delta_{\epsilon_{\mathbf{k}}} - \epsilon_{\mathbf{k}} - i\Gamma_{\epsilon_{\mathbf{k}}}(1-2f_{\epsilon_{\mathbf{k}}})) \end{pmatrix}. \quad (9)$$

Here,  $\Delta_{\epsilon_{\mathbf{k}}}$  represents the renormalization of the dispersion law and  $\Gamma_{\epsilon_{\mathbf{k}}}$  is the damping frequency. This renormalization and the dependence of  $\Gamma_{\epsilon_{\mathbf{k}}}$  on  $\epsilon$  are unimportant in the treatment given below

$$(G\Sigma G)^+ = -(2\pi)^{-1} ((\epsilon - \epsilon_{\mathbf{k}})^2 + \Gamma_{\epsilon_{\mathbf{k}}}^2)^{-2} [2\Gamma_{\epsilon_{\mathbf{k}}}^2 ((1-f_{\epsilon_{\mathbf{k}}}) \Sigma_{\epsilon_{\mathbf{k}}}^+ + f_{\epsilon_{\mathbf{k}}} \Sigma_{\epsilon_{\mathbf{k}}}^-) + ((\epsilon - \epsilon_{\mathbf{k}})^2 - \Gamma_{\epsilon_{\mathbf{k}}}^2) \Sigma_{\epsilon_{\mathbf{k}}}^+ + 2i(\epsilon - \epsilon_{\mathbf{k}}) \Gamma_{\epsilon_{\mathbf{k}}} \Sigma_{\epsilon_{\mathbf{k}}}^0]. \quad (10)$$

Here,

$$\Gamma_{\mathbf{k}} = \Gamma_{\epsilon_{\mathbf{k}}}, \quad \Sigma_{\mathbf{k}}^0 = \Sigma_{\epsilon_{\mathbf{k}}}^c - \Sigma_{\epsilon_{\mathbf{k}}}^c.$$

The first two terms in Eq. (10) behave in the same way as  $\Gamma_{\mathbf{k}}^{-1}$ , whereas the second two terms are regular in the limit  $\Gamma_{\mathbf{k}}/\epsilon_{\mathbf{k}} \rightarrow 0$  and can be dropped if the first terms do not contain an additional small number. However, it is not possible to calculate the values of  $\Sigma^{\pm}$  from the perturbation theory because there is a sequence of graphs in Fig. 2 which are of the same order of magnitude. We can show that the inclusion of these graphs reduces (to within  $\Gamma_{\mathbf{k}}/\epsilon_{\mathbf{k}}$ ) to the substitution  $\Sigma_{\epsilon_{\mathbf{k}}}^c \rightarrow \Sigma_{\epsilon_{\mathbf{k}}}^n$  in Eq. (10); here,  $\Sigma_{\epsilon_{\mathbf{k}}}^n$  does not contain external enveloping dashed lines. The first two terms in Eq. (10) then acquire a factor  $\Gamma_{\mathbf{k}}/\Gamma_{\mathbf{k}}^i$ , where  $\Gamma_{\mathbf{k}}^i$  is the characteristic



FIG. 1. Simplest graphs for the mass operator contributing to the photogalvanic effect. The wavy line represents photons and the dashed line phonons.

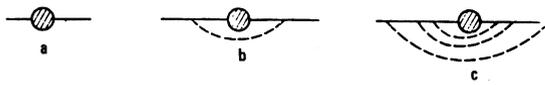


FIG. 2. Graphs of the same order in the perturbation theory series for  $\Sigma$ .

isotropization frequency. For example, in the case of an isotropic dispersion law and scattering by impurities, we have

$$\Gamma_k = \int W_{kk'} \delta(\epsilon_k - \epsilon_{k'}) dk',$$

$$\Gamma_k^i = \int \left(1 - \frac{kk'}{k^2}\right) W_{kk'} \delta(\epsilon_k - \epsilon_{k'}) dk'. \quad (11)$$

Finally, the diagonal contribution to the photogalvanic tensor  $\beta_{ilm}$  becomes

$$\beta_{ilm} = \frac{-e}{2(2\pi)^4} \int \frac{dk \nabla_{k+l} \epsilon_k}{\Gamma_k^i} \frac{\delta}{\delta(E_{l\omega} E_{n\omega}^*)} \left( (1-f_e) \Sigma_{ek}^{+n} + f_e \Sigma_{ek}^{-n} \right) \Big|_{E_{\omega=0}}. \quad (12)$$

Equation (12) represents, in fact, the solution of the transport equation for the asymmetric correction to the distribution function and the quantity

$$\left( (1-f_e) \Sigma_{ek}^{+n} + f_e \Sigma_{ek}^{-n} \right) \Big|_{E_{\omega=0}}$$

is the collision integral.

In the case when the number of quasiparticles is small, i.e., for  $f_e \ll 1$ , or  $(1-f_e) \ll 1$ , the Keldysh rules for calculating the mass operators simplify and effectively reduce to the Cutkosky rules for calculating the imaginary part of the mass operator in the field theory.<sup>[12]</sup> It is then sufficient to make a unitary cut of the graph (Fig. 1); the cut Green functions are replaced with  $G^*(G^-)$  in calculating  $\Sigma^*(\Sigma^-)$  and, to the left of the cut, all the Green functions are taken to be  $\tilde{G}^c(G^c)$ , whereas, to the right, they are  $G^c(\tilde{G}^c)$ . We can easily see that a unitary cut of the graph determines unambiguously the distribution of the indices 1 and 2 between the graph vertices. The distribution of the indices 1 and 2 which do not correspond to the cut then gives rise to a contribution proportional to some power of the parameter  $f_e$  or  $(1-f_e)$ . Equations (8) and (10) allow us to obtain any corrections to the transport equation approximation.

### 3. SCATTERING BY IMPURITIES IN NONCENTROSYMMETRIC SEMICONDUCTORS

Equations (8), (10), and (12) reduce the calculation of the tensor  $\beta_{ilm}$  to determination of the mass operators  $\Sigma_{ek}^{+n}$ . Graphs of lower order in the mass operator are given in Fig. 3. The intraband contributions to  $\Sigma_b$  are symmetric functions of  $k$  (vertex function  $\partial \epsilon_k / \partial k$ ) and do not give rise to a photocurrent. The interband contributions to  $\Sigma_b$  are odd functions of  $k$  for a noncentrosymmetric crystal and may contribute to the photocurrent. This is the effect considered by Genkin and Mednis.<sup>[7,8]</sup> However, the total contribution made to  $\beta_{ilm}$  by the graphs in Fig. 3 cancels out. The physical reason for this cancellation is explained in the Introduction. The cancellation of the contributions of  $\Sigma_b$  to the photocurrent can formally be demonstrated by writing down

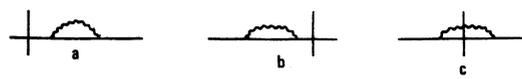


FIG. 3. Feynman graphs contributing to the asymmetry of renormalization of the dispersion law.

all the contributions to  $\Sigma_b$  and applying the sum rule which follows from the commutation relationship  $[x_i, p_j] = i\delta_{ij}$ . It should be noted that a fairly rigorous analysis has to be applied to the diagonal (in respect of the band number) contribution to the current made by the graphs in Figs. 3a and 3b; in this case, the last term in Eq. (10) makes a contribution and this is equivalent to the inclusion of the intraband scattering processes.

Since all interband processes (for example, those represented by Fig. 1b) reduce in fact to renormalization of the electron dispersion law if the energy is insufficient for real interband transitions, they make no contribution to the photocurrent. Therefore, we shall only discuss intraband processes.

The quantities  $\Sigma_{ek}^{+n}$  are calculated in different ways at different frequencies  $\omega$ . If  $\omega \gg \Gamma$  ( $\Gamma$  is the characteristic collision frequency), the graphs of  $\Sigma$  are of the kind shown in Fig. 4. The collision integral calculated for these graphs and the cuts included represents the balance of probabilities of electron scattering by an impurity accompanied by the emission and absorption of a photon. The graphs in Figs. 4a and 4e are symmetric and make no contribution to the current. The expression for the tensor  $\beta_{ilm}$  in the  $\omega \gg \Gamma$  case is

$$\beta_{ilm}(\omega) = \frac{ie^2 N}{8\pi^2 \omega^3} \int dk dk' dk'' (\Gamma_k^i)^{-1} \frac{\partial \epsilon}{\partial k_i} \times \left\{ \left[ \left( \frac{\partial \epsilon}{\partial k_i} \left( \frac{\partial \epsilon}{\partial k_{i'}} - \frac{\partial \epsilon}{\partial k_{i''}} \right) - \frac{\partial \epsilon}{\partial k_{i'}} \frac{\partial \epsilon}{\partial k_{i''}} \right) (k_{i'} - k_{i''}) \right] \times \sum_{l=1}^3 \delta(\epsilon_{k'} - l\omega - \epsilon_k) l P(\epsilon_{k'} - \epsilon_k)^{-1} (\epsilon_k - \epsilon_{k''} - i\delta)^{-1} \right. \\ \left. - [k' \leftrightarrow k''] \right\} \text{Im}(V_{k,k'} V_{k,k''} V_{k',k''}). \quad (13)$$

Here,  $V_{k,k'}$  is the matrix element of the impurity potential between the Bloch wave functions and  $N$  is the impurity concentration. The pole contribution in Eq. (13) gives rise to the part of the tensor  $\beta_{ilm}$  which is symmetric in respect of the indices  $lm$  and the principal value gives the antisymmetric part.

If  $\omega \ll \Gamma$ , additional graphs, similar to those shown in

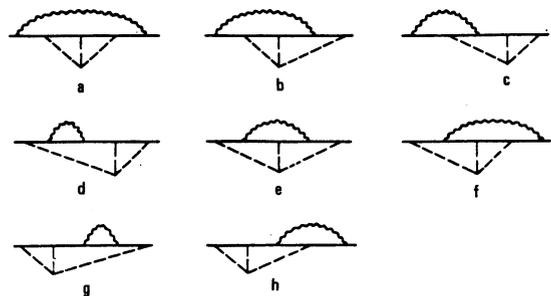


FIG. 4. Feynman graphs for the mass operator giving rise to asymmetry of the electron scattering by impurities in an electromagnetic wave field. Unitary cuts contributing to  $\beta_{ilm}$  in the  $\omega \gg \Gamma$  case are shown.

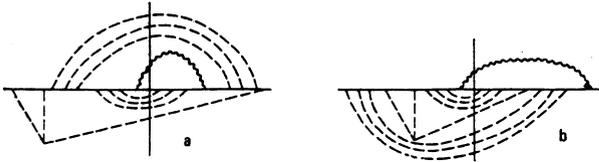


FIG. 5. Corrections to the graphs in Figs. 4g and 4h due to the scattering processes important in the  $\omega \ll 1$  case.

Fig. 2, become important. These graphs "clothe" the photon vertices and their role in the  $\omega \ll \Gamma$  case reduces to the replacement of  $\Gamma_{\mathbf{k}}$  with  $\Gamma_{\mathbf{k}}^i$  and  $\Gamma_{\mathbf{k}}^s$  in the denominators [ $\Gamma_{\mathbf{k}}^a$  is the anisotropization frequency, i.e.,  $(\Gamma_{\mathbf{k}}^a)^{-1}$  is the damping time of the second moment of the distribution function]. Typical graphs associated with those in Figs. 4g and 4h are shown in Fig. 5. The result obtained in the  $\omega \ll \Gamma$  case is equivalent to the solution of the transport equation in the  $\mathbf{A} = 0$  gauge without allowance for the dependence of the collision integral on the electromagnetic field:

$$\frac{\partial f_{\mathbf{k}}}{\partial t} + e\mathbf{E} \frac{\partial f_{\mathbf{k}}}{\partial \mathbf{k}} = \int W_{\mathbf{k}\mathbf{k}'}^s \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) (f_{\mathbf{k}'} - f_{\mathbf{k}}) d\mathbf{k}' + \int W_{\mathbf{k}\mathbf{k}'}^{as} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) f_{\mathbf{k}'} d\mathbf{k}'. \quad (14)$$

Here,  $W_{\mathbf{k}\mathbf{k}'}^{s(as)}$  is the symmetric (asymmetric) probability of scattering by impurities.<sup>[5]</sup>

The expression for the tensor  $\beta_{ijn}$  for  $\omega \ll \Gamma$  is [(A)  $\equiv d\mathbf{A}/d\varepsilon_{\mathbf{k}}$ ]

$$\beta_{ijn}(\omega) = \frac{e^2 N}{(2\pi)^4} \int \frac{d\mathbf{k} d\mathbf{k}' d\mathbf{k}''}{\Gamma_{\mathbf{k}}^i \Gamma_{\mathbf{k}'}^s} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}''}) \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}''}) \times \left\{ \frac{\partial \varepsilon}{\partial \mathbf{k}_n} \left[ \frac{\partial \varepsilon}{\partial \mathbf{k}_i} \frac{\partial \varepsilon}{\partial \mathbf{k}_j} (f_{\mathbf{k}}' (\Gamma_{\mathbf{k}}^i)^{-1})' - \left( \frac{\partial \varepsilon}{\partial \mathbf{k}_i} \frac{\partial \varepsilon}{\partial \mathbf{k}_j} ((\Gamma_{\mathbf{k}}^i)^{-1})' - \frac{\partial^2 \varepsilon}{\partial \mathbf{k}_i \partial \mathbf{k}_j} (\Gamma_{\mathbf{k}}^i)^{-1} \right) f_{\mathbf{k}}' \right] + l \leftrightarrow n \right\} \text{Im}(V_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}''} V_{\mathbf{k}''\mathbf{k}}). \quad (15)$$

We shall now calculate Eqs. (13) and (15) for the photogalvanic tensor  $\beta_{ijn}$  in the case of a nondegenerate semiconductor, i.e., we shall assume that the electron dispersion law is quadratic:  $\varepsilon_{\mathbf{k}} = \mathbf{k}^2/2m$ . We shall only consider neutral impurities (the case of charged impurities will be discussed separately later). The matrix element of the impurity potential  $V_{\mathbf{k}\mathbf{k}'}$  can be represented by the sum of matrix elements of a symmetric short-range potential and an asymmetric long-range potential<sup>[5]</sup> ( $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ ):

$$V_{\mathbf{q}} = \frac{2\pi b}{m} + \frac{4\pi iedq}{\varepsilon_0 q^2} - \frac{4\pi ie}{15} \frac{Q_{abc} q_a q_b q_c}{\varepsilon_0 q^2}. \quad (16)$$

Here,  $b$  is the characteristic length of scattering by impurities;  $d$  is the dipole moment of an impurity;  $Q_{abc}$  is the octupole moment of an impurity<sup>[13]</sup>;  $\varepsilon_0$  is the static permittivity. In the case of ferroelectric semiconductors, the photogalvanic effect is due to the second term in Eq. (16), whereas, in the case of nonferroelectric noncentrosymmetric semiconductors, the same effect is due to the last (third) term.

Simple expressions for the tensor  $\beta_{ijn}$  of Eqs. (13) and (15) are obtained in three specific frequency intervals:  $\omega \gg T$ ,  $T \gg \omega \gg \Gamma$ ,  $\omega \ll \Gamma$ . The expressions for the photogalvanic tensor  $\beta_{ijn}$  are normalized to the absorp-

tion coefficient  $\kappa$  because the maximum current observed experimentally is governed by the depth of penetration of light into a crystal, i.e., by the value of  $\kappa$ . The results of the calculations are given below:

$$\beta_{ijn} = \frac{n_{\omega} e c e^2 m}{\hbar \Gamma_i \hbar^2 k_T} b \kappa \gamma_{ijn}, \quad (17)$$

a) in the interval  $\omega \gg T$ ,

$$\gamma_{ijn}^a = \frac{\pi}{30} \frac{T}{\omega} (6c_i \delta_{in} + 11(c_i \delta_{in} + c_n \delta_{ii})) + \frac{16\pi}{5} k_T k_0 b^2 q_{ijn},$$

$$\gamma_{ii}^a = 4(\pi^2 - 1) e_{ijn} c_n, \quad (17a)$$

$$\kappa = \frac{4\pi^2 e^2 \Gamma_i k_0 n \hbar}{n_{\omega} \hbar c \omega k_T m \omega};$$

b) in the interval  $T \gg \omega \gg \Gamma$ ,

$$\gamma_{ijn}^b = \frac{\omega}{5T} \ln\left(\frac{T}{\omega}\right) (c_i \delta_{in} + c_n \delta_{ii} + c_i \delta_{in}) - 274 \frac{m \omega b^2}{\hbar} q_{ijn},$$

$$\gamma_{ii}^b = 16(\pi^2 + 4) \frac{\omega^2}{T^2} e_{ijn} c_n, \quad (17b)$$

$$\kappa = \pi^{-1/2} \left(\frac{T}{\omega}\right)^{3/2} \kappa(\omega \gg T);$$

c) in the interval  $\omega \ll \Gamma$ ,

$$\gamma_{ijn}^c = -(40\pi)^{-1} (4c_i \delta_{in} + 9(c_i \delta_{in} + c_n \delta_{ii})) - \frac{31}{15\pi} \frac{m T b^2}{\hbar^2} q_{ijn},$$

$$\gamma_{ii}^c \approx \frac{\omega}{\Gamma_i} e_{ijn}, \quad (17c)$$

$$\kappa = \frac{8}{3} (2\pi)^{1/2} \frac{e^2 n}{m c \Gamma_i n_{\omega}}.$$

Here,  $\Gamma_i = 4\pi b^2 N k_T \bar{n}/m$ ,  $k_T = (mT)^{1/2}$ ,  $k_0 = (m\omega)^{1/2}$ ;  $n$  is the electron density;  $n_{\omega}$  is the refractive index;  $\mathbf{d} = \xi e b \mathbf{c}$ ;  $\mathbf{c}$  is a unit vector along the polar axis of the crystal;  $Q_{abc} = \xi_Q e b^3 q_{abc}$ , where  $q_{abc}$  is a "unit" tensor of third rank;  $\xi$  is the characteristic asymmetry parameter.

#### 4. SCATTERING BY PHONONS AND PHOTOGALVANIC EFFECT IN NONCENTROSYMMETRIC CRYSTALS

Scattering by phonons in a noncentrosymmetric crystal in the presence of an electromagnetic wave is asymmetric and gives rise to a photocurrent. Characteristic graphs for the mass operator are given in Fig. 6. In all, there are 24 different graphs or impurities (this follows from Fig. 4). As pointed out earlier,<sup>[6]</sup> allowance for an anharmonic two-phonon vertex is essential to reveal the asymmetry of the electron-phonon scattering.

We shall now estimate the contributions made to the tensor  $\beta_{ijn}$  of the graphs in Fig. 6 for the scattering of electrons by acoustic and optical phonons. One-phonon vertex functions are<sup>[6]</sup>

$$(\Gamma_{\mathbf{q}}^i)_{ac} = i\sigma q_i + \frac{4\pi e}{\varepsilon \cdot q^2 a^2} d_{ijn}^ac q_j q_n,$$

$$(\Gamma_{\mathbf{q}}^i)_{opt} = \frac{4\pi e}{\varepsilon \cdot q^2 a^2} (iQ q_i + a_{ijn}^{opt} q_j q_n). \quad (18)$$

Here,  $\mathbf{q}$  is the phonon momentum;  $\sigma$  is the deformation potential;  $d_{ijn}$  is the piezoelectric tensor;  $\varepsilon_{\infty}$  is the permittivity;  $Q$  is the effective charge of an optical mode;  $a$  is the lattice constant. A two-phonon vertex function will be assumed to be symmetric (this does not affect the basic nature of the estimates):

$$(\Gamma_{\mathbf{q}}^i)_{ac} = \sigma' q^2 \delta_{ij}, \quad (\Gamma_{\mathbf{q}}^i)_{opt} = (\delta'/a^2) \delta_{ij}.$$

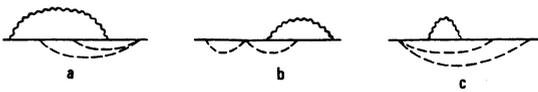


FIG. 6. Characteristic graphs for the mass operator of an electron describing the electron-phonon scattering in an electromagnetic wave field.

Here,  $\sigma$  and  $\delta'$  are nonlinear "deformation" potentials. The tensor  $\beta_{ijn}$  can be calculated using Eqs. (13) and (15); in this case, the quantity  $\text{Im}(V_q V_{q'} V_{q''})$  transforms to

$$\frac{a^6(2N_q+1)(2N_{q''}+1)}{4M\Omega_q\Omega_{q''}} \text{Im}(\Gamma_q \Gamma_{q'} \Gamma_{q''}).$$

Here,  $\Omega_q$  is the phonon frequency;  $M$  is the mass of a unit cell of a crystal;  $N_q$  is the phonon distribution function. Since at low temperatures the photocurrent decreases exponentially with temperature, we shall only consider the range of  $T$  much higher than the Debye temperature  $\Theta$ , i.e., we shall assume that  $N_q = (T/Q_q) \gg 1$ .

The angular integrals in Eqs. (13) and (15) are quite cumbersome, so we shall confine ourselves to an order-of-magnitude estimate of the photogalvanic tensor. The results of the estimates are:

a) in the frequency interval  $\omega \gg T$ ,

$$\begin{aligned} \gamma_{ac}^s &\approx \frac{T}{Mc_s^2} \frac{\sigma'}{\sigma} \frac{d}{ea} \frac{T}{\omega}, \quad \gamma_{ac}^a \approx \gamma_{ac}^s, \\ \gamma_{ac}^s &\approx \frac{\sigma^2 e^2}{\hbar^2 \omega^2 c} \frac{T}{Mc_s^2} \frac{na^2 k_0}{n\omega}, \\ \Gamma_{ac} &\approx \sigma \frac{aa^3 m k_T}{\hbar^2} \frac{T}{Mc_s^2}, \\ \gamma_{opt}^s &\approx \frac{T}{Ma^2 \Omega_0^2} \frac{\delta' a Q d' k_T}{Q^2 e^2 k_T a} \frac{a}{k_0}, \quad \gamma_{opt}^a \approx \frac{k_T}{k_0} \gamma_{opt}^s, \\ \gamma_{opt}^s &\approx \frac{e^4 Q^2 n}{amch^2 \omega^3} \frac{T}{Ma^2 \Omega_0^2} \frac{k_0}{n_a}, \\ \Gamma_{opt} &\approx \frac{e^2 Q^2 m}{a k_T \hbar^2} \frac{T}{Ma^2 \Omega_0^2}; \end{aligned} \quad (19a)$$

b) in the interval  $T \gg \omega \gg \Gamma$ ,

$$\begin{aligned} \gamma_{ac}^s &\approx \left(\frac{\omega}{T}\right)^2 \ln\left(\frac{T}{\omega}\right) \gamma_{ac}^s(\omega \gg T), \quad \gamma_{ac}^a \approx \left(\frac{\omega}{T}\right)^3 \gamma_{ac}^s(\omega \gg T), \\ \gamma_{ac}^s &\approx \left(\frac{T}{\omega}\right)^{3/2} \gamma_{ac}^s(\omega \gg T), \\ \gamma_{opt}^s &\approx \frac{\omega}{T} \ln\left(\frac{T}{\omega}\right) \gamma_{opt}^s(\omega \gg T), \quad \gamma_{opt}^a \approx \left(\frac{\omega}{T}\right)^2 \gamma_{opt}^s(\omega \gg T), \\ \gamma_{opt}^s &\approx \left(\frac{T}{\omega}\right)^{1/2} \gamma_{opt}^s(\omega \gg T); \end{aligned} \quad (19b)$$

c) in the interval  $\omega \ll \Gamma$ ,

$$\begin{aligned} \gamma_{ac}^s &\approx \frac{\omega}{T} \gamma_{ac}^s(\omega \gg T), \quad \gamma_{ac}^a \approx \left(\frac{\omega}{T}\right)^2 \gamma_{ac}^s(\omega \gg T), \\ \gamma_{ac}^s &\approx \frac{e^2 n}{mc \Gamma_{ac} n_a}, \\ \gamma_{opt}^s &\approx \gamma_{opt}^s(\omega \gg T), \quad \gamma_{opt}^a \approx \left(\frac{\omega}{T}\right)^2 \gamma_{opt}^s(\omega \gg T), \\ \gamma_{opt}^s &\approx \frac{e^2 n}{mc \Gamma_{opt} n_a}. \end{aligned} \quad (19c)$$

Here,  $c_s$  is the velocity of sound;  $\Omega_0$  is the optical phonon frequency;  $\gamma_{ijn}$  is given by the system (17).

## 5. PHOTOGALVANIC EFFECT IN METALS

The photogalvanic effect in noncentrosymmetric metals should be considered at fairly high frequencies  $\omega$  because low-frequency light does not penetrate a metal. We shall confine our attention to the frequency interval  $\varepsilon_F \gg \omega \gg T$ , where  $\varepsilon_F$  is the Fermi energy of the investigated metal.

The process of absorption of light in a metal as a result of scattering of electrons by impurities in the field of an electromagnetic wave is described by the graphs in Fig. 4, whereas the photogalvanic tensor is given by Eq. (13) because, in this case, the transport equation is linear in the electron distribution function  $f_k$ .

The matrix element of the impurity potential  $V_{k,k'}$  in the case when the momenta  $k$  and  $k'$  lie on the Fermi surface can be expanded in terms of the Legendre polynomials. We shall only retain the lowest polynomials contributing to the photogalvanic effect, i.e., the zeroth and third-order harmonics:

$$\begin{aligned} V_{k,k'} &= 2\pi b/m_F + \xi e^2 b^2 (q_{abc} n_a n_b n_c - \\ &- q_{abc} n'_a n'_b n'_c + \bar{q}_{abc} n_a n_b n_c - \bar{q}_{abc} n'_a n'_b n'_c), \\ n_a &= k_a/k_F, \quad n'_a = k'_a/k_F. \end{aligned} \quad (20)$$

Here,  $b$  is the characteristic length in the case of scattering by the potential  $V_{k,k'}$ ;  $\xi$  is the characteristic asymmetry parameter;  $q_{abc}$  and  $\bar{q}_{abc}$  are the dimensionless third-rank tensors specifying the angular asymmetry;  $m_F$  is the mass on the Fermi surface:

$$m_F = k_F/v_F, \quad v_F = \partial\varepsilon/\partial k_F.$$

Substituting Eq. (20) in Eq. (13), we obtain the following estimate of the photogalvanic tensor:

$$\begin{aligned} \beta_{imp} &\approx \xi \frac{e^2 k_F}{\hbar \Gamma} \frac{e^2 k_F}{\hbar \omega} k_F b \kappa b, \\ \kappa &\approx \frac{e^2 N b^2}{\hbar c} \left(\frac{\varepsilon_F}{\hbar \omega}\right)^2 \frac{k_F}{n_a}, \\ \Gamma &\approx N b^2 k_F / m_F. \end{aligned} \quad (21)$$

We shall calculate the contribution of electron-phonon scattering to the photogalvanic effect by expanding the electron-phonon vertex functions in terms of the spherical functions on the Fermi surface:

$$\begin{aligned} \Gamma_{kk'}^i &= ik_F (\sigma n_i - \sigma' n'_i) + (e/a^2) (d_{ijn} n_i n_j \\ &+ d_{ijn}' n'_i n'_j + \bar{d}_{ijn} n_i n_j n_k), \quad \bar{d}_{ijn} = \bar{d}_{ijn}', \\ \Gamma_{kk'}^{ij} &= (\sigma''/a^2) \delta_{ij}. \end{aligned} \quad (22)$$

The expansion (22) of the electron-phonon vertex functions is of the same form for acoustic and optical phonons since the characteristic momentum carried by phonons in the  $\omega \gg \Theta$ , case is of the order of  $k_F$ . The photogalvanic tensor  $\beta_{ijn}$  can be estimated from Eqs. (13) and (22), in accordance with the graphs in Fig. 6:

$$\begin{aligned} \beta_{phon} &\approx \xi \frac{ec}{\hbar \Gamma} \frac{\sigma''}{\sigma} \frac{edk_F^2}{\hbar \omega} \frac{\hbar k_F^2}{M\Theta} \frac{T}{\Theta} \frac{\kappa}{k} n_a, \\ \kappa &\approx \frac{e^2}{\hbar c} \left(\frac{\sigma}{\omega}\right)^2 \frac{T}{\Theta} \frac{\hbar k_F^2}{M\Theta} (k_F a), \frac{k_F}{n_a}, \\ \Gamma &\approx \sigma \frac{\sigma}{\Theta} \frac{T}{\Theta} \frac{m_F}{M} (k_F a)^2. \end{aligned} \quad (23)$$

If  $\omega \gg \Theta$ , the electron-electron scattering in metals contributes considerably to the photogalvanic effect.<sup>[14]</sup>

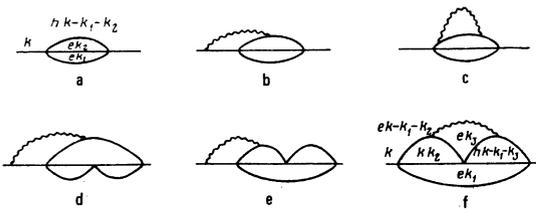


FIG. 7. Characteristic graphs for the mass operator of an electron describing the electron—electron scattering process.

Characteristic graphs for the mass operator, contributing to this effect, are given in Figs. 7d–7f. The electron—electron (hole) vertex function, considered allowing for the asymmetry on the Fermi surface, is

$$V_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} = e^2 b (1 + \xi (f_{abc} n_{1a} n_{1b} n_{1c} + \dots + \bar{f}_{abc} n_{1a} n_{1b} n_{1c})). \quad (24)$$

The damping  $\Gamma$ , absorption coefficient  $\kappa$ , and photogalvanic tensor  $\beta$  can easily be calculated from the graphs in Fig. 7. It should be pointed out that only the umklapp processes contribute to the effect because the momentum-conserving processes cannot produce an electric current in the electron system. The contribution of the umklapp processes to  $\Sigma_{ek}$  is due to a certain domain of integration with respect to the angular variables representing the momenta  $k_1$ ,  $k_2$ , and  $k_3$ . The domain of integration with respect to the moduli of the momenta  $k$ ,  $k_1$ ,  $k_2$ , and  $k_3$  is limited by the Fermi surface<sup>[14]</sup>:  $|\mathbf{k} - \mathbf{k}_F| \lesssim \omega / v_F$ . The singular  $\delta$  functions resulting from the calculation of the mass operators in Fig. 7 are obtained by integration over the angles. This analysis is sufficient to obtain estimates on the basis of the graphs in Fig. 7:

$$\begin{aligned} \beta_{e1} &\approx \frac{ec}{\hbar\Gamma} \frac{e^2 b m_F}{\hbar^2} \kappa b, \\ \kappa &\approx \frac{e^2}{\hbar c} \left( \frac{e^2 b^2 k_F m}{\hbar^2} \right)^2 k_F, \\ \Gamma &\approx \frac{e^4 b^4 m_F^3 \omega^2}{\hbar^3}. \end{aligned} \quad (25)$$

We shall conclude by noting that the “efficiencies” of the various photogalvanic effect mechanisms, i.e., the photocurrent divided by the absorption coefficient for a given scattering mechanism, are all of the same order of magnitude and are identical with the photocurrents calculated for the interband transitions.<sup>[5, 6]</sup> The main contribution to the photocurrent is due to the mechan-

ism with the maximum absorption coefficient. The conditions for observing the photocurrent in semiconductors and metals are more stringent than those for insulators because the resistance of a measuring instrument should not greatly exceed the resistance of a crystal.

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<sup>1)</sup>The dissipative constants are understood to be the quantities containing an odd number of pole contributions in calculations based on the perturbation theory.

<sup>2)</sup>The theory of nonlinear optical effects does not usually give rise to indeterminacies of the 0/0 type but these indeterminacies are familiar in the theories of various dissipative effects (see, for example, Ref. 11).

<sup>3)</sup>A similar expression can also be obtained using the causal Green function.

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