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THE RELATION BETWEEN SHIFT AND BALLISTIC CURRENTS IN THE THEORY OF PHOTOGALVANIC EFFECT

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For phototransitions between nondegenerate bands the shift contribution to current, related to the density matrix elements that are nondiagonal regarding the numbers of bands, is compared with the contributions of common nature, conforming to asymmetry of carrier velocity distribution. It is shown that the shift recombination contribution to current, directed along the polar axis can prevail on the absorption edge of ferroelectric crystals. The shift and ballistic phonon contributions in piezoelectrics are comparable in magnitude and can partially compensate for each other. The character of the compensation depends on the type of optical transition and on the form of electron-phonon interaction.

Generation of direct current $\vec{j}$ under the action of light due to the absence of the crystal symmetry center is known as a photogalvanic effect (PGE). The PGE is defined by the phenomenological relation

$$j_i = \beta_{inl} e_n e_l^* J \tag{1}$$

where $\vec{e}$ is the unit vector of light wave polarization, J is intensity.[1] The tensor β_{inl} is called photogalvanic.

At present time, the PGE has been discovered and investigated in a number of types of crystals without symmetry centers: pyroelectric, piezoelectric, gyrotropic.[1–3] A lot of papers have been devoted to the theory of the effect. When determining the current one usually starts from the formula

$$\vec{j} = e \sum_{s,k} f_{sk} \vec{V}_{sk} \tag{2}$$

where f_{sk} and $\vec{V}_{sk}$ are the distribution function and the carrier velocity in the band s, respectively. According to (2) the current is related to the distribution asymmetry of quasi-momenta of particles, $f_{sk} \neq f_{s-k}$. It is called ballistic current. Different PGE mechanisms related to (2) are in conformity with different reasons of asymmetry arising in optical transitions of either this or that type (impurity-band, band-band, etc.). The authors reviewed these types of mechanisms in Ref. 1.

Starting from 1979 some attempts have been undertaken to include to the PGE theory the contribution to the current, related to the density matrix ρ elements that are nondiagonal regarding the numbers of bands.[4–6]

$$\vec{j}^{\,\mathrm{sh}} = \frac{e}{m} \sum_{\substack{s \neq s' \\ k,k'}} \vec{P}_{sks'k'} \rho_{s'k'sk}, \tag{3}$$

$\vec{P}_{sks'k'}$ is the matrix element of the momenta operator. It should be mentioned that the contribution (3) was sometimes met with before in consideration of photogalvanic effects,[7] but it was small as compared with (2) regarding the parameter a/l where a—the lattice period, l—the carrier path length. Papers 4–6 did not lead to real results. In them a number of contribution, which give substantial compensation have not been taken into account. The physical sense and the essential regard for nondiagonal summands remained unrevealed. In References 5 and 6 there are explicit mistakes which lead to unreasonable results.

The answers to the general questions on the nondiagonal contribution to the current were presented in Reference 8. This paper constructed the PGE theory based on successive regard for (3). Free of limitations general formulae were derived, that expressed $\vec{j}^{sh}$ in terms of the distribution functions f_{sk} and the carrier shifts in coordinate space for quantum transitions. The shifts $\vec{R}_{sks'k'}$ observed for transitions of $s'k' \to sk$ type are expressed in terms of phases of matrix elements of the transitions and have independent physical sense. The current $\vec{j}^{sh}$ is known as shift current. It is independent of the carrier free path length and is nonzero on symmetrical (though nonequilibrium) distribution functions, $f_{sk} = f_{s-k}$.

General considerations on comparative magnitude of the shift and ballistic currents have been presented in Reference 9. It has been pointed out, in particular, that $\vec{j}^{sh}$ needs not to be regarded in calculation of the part of the current in formula (1), that is proportional to the degree of circular polarization $i[\vec{e} \times \vec{e}^*]$ (circular PGE[1]). As for the part of the current connected with the symmetrized product $e_n e_l^* + e_n^* e_l$ (linear PGE[1]) the situations where j^{sh} is comparable with j^b are possible here. First of all, this can be referred to the case of interband transitions.† Anomalous smallness of the ballistic contribution to the current with respect to the parameter a/l is a distinguishing feature of the above case. It is just this smallness that makes impossible to consider the shift current as a small contribution.

The possibility of existence of currents j^b and j^{sh}, that are comparable in magnitude, but different in the physical sense, raised the problem of their separation. First it seemed that direct separation is possible in a classical strong magnetic field that turn $\vec{j}^b$ and does not act upon $\vec{j}^{sh}$. This separation, however, proved to be impossible.[9] The attempts to obtain accurate calculation of j^b and j^{sh} for well studied semiconductor crystals such as GaAs also appeared to be hardly realizable.[10] Thus, the problem on the relation between j^b and j^{sh} in interband transitions still remains unsolved.

In the present paper we analyze the role of the shift and ballistic contributions for simplest models of band structure in pyro- and piezoelectrics relying on the general formulae from papers.[8,11] Without loss of generality we take the light polarization as linear one, $\vec{e} = \vec{e}^*$.

Let us consider the direct optical transition between the nondegenerate valence band and the conductivity band. As it is shown in Reference 8, the intraband transitions are insignificant on the absorption edge, $ka \ll 1$, and the current $\vec{j}^{sh}$ is connected with the shifts in interband transitions. The final expressions for $\vec{j}^{sh}$ are presented in the same paper.

† It should be expected that $j^b \gg j^{sh}$ in impurity-band transitions.

Unlike $\vec{j}^{sh}$ the current $\vec{j}^{b}$ requires that the interaction between electrons and holes either with phonons[11] or between theselves[12] must be taken into account. Three different contributions arise in this case: $\vec{j}^{b} = \vec{j}_1 + \vec{j}_2 + \vec{j}_c$. Asymmetry of the electron-photon interaction is taken into account in calculation of the phonon contribution $\vec{j}_1$, while Hamiltonians of electron-phonon and hole-phonon interactions $\hat{v}^{e,h}$ are considered to be invariant to spatial inversion.[11] When calculating $\vec{j}_2$ only the asymmetry $\hat{v}^{e,h}$ is taken into account.[11] Finally, when calculating $\vec{j}_c$ symmetrical Coulomb interaction and asymmetry of photon interaction are taken into consideration.[12] Only $\vec{j}_i$ is expressed in terms of the same characteristics as $\vec{j}^{sh}$. Just these currents must be compared. The contributions $\vec{j}_2$ and $\vec{j}_c$ contain independent parameters, they can be more or less than j_1.

The phonon PGE mechanisms are considered in Reference 11. But the calculations and the evaluations presented there are not enough to compare j_1 and j^{sh}. The point is that independence of j_1 of the carrier free path lengths is of an implicit character. It turns out that tedious formulae for $\vec{j}_1$ can be essentially reduced under minimum simplifying assumptions by expressing explicitly transport times of electrons and holes $\tau_{e,h}$ in terms of electron-phonon interaction.

When determining $\vec{j}_1$ the expression for asymmetrical (i.e. odd in $\vec{k}$) part of electron and hole photogeneration rates $I_k^{e,as}$, $I_k^{h,as}$ is taken as assumption. As shown in Reference 11,

$$I_k^{e,as} = \frac{J}{2\hbar c}\sum_{s=\pm 1}\int Jm[(\vec{e}\vec{D}_k)(\vec{e}\vec{D}_{k'})^* v^e_{\vec{k}-\vec{k}'} v^h_{\vec{k}'-\vec{k}}](2N_{\vec{k}-\vec{k}'} + S + 1)Q_s^e(\vec{k},\vec{k}')\frac{d^3k'}{(2\pi)^3} \quad (4)$$

$$Q_s^e = \mathcal{P}\Bigg\{\delta(\hbar\omega - \varepsilon_k^e - \varepsilon_k^h - s\hbar\Omega)\left[\frac{\delta(\hbar\omega - \varepsilon_{k'}^e - \varepsilon_{k'}^h)}{\varepsilon_{k'}^h - \varepsilon_k^h + s\hbar\Omega} + \frac{\delta(\hbar\omega - \varepsilon_k^e - \varepsilon_k^h)}{\varepsilon_{k'}^e - \varepsilon_k^e - s\hbar\Omega}\right]$$

$$+ \delta(\hbar\omega - \varepsilon_k^e - \varepsilon_k^h)\Bigg[\delta(\hbar\omega - \varepsilon_{k'}^e - \varepsilon_{k'}^h)\left(\frac{1}{\varepsilon_k^e - \varepsilon_{k'}^e - s\hbar\Omega} + \frac{1}{\varepsilon_k^h - \varepsilon_{k'}^h - s\hbar\Omega}\right)$$

$$+ \frac{\delta(\varepsilon_k^e - \varepsilon_{k'}^e - s\hbar\Omega) - \delta(\varepsilon_k^h - \varepsilon_{k'}^h - s\hbar\Omega)}{\varepsilon_k^e - \varepsilon_{k'}^e + \varepsilon_k^h - \varepsilon_{k'}^h}\Bigg]\Bigg\}.$$

Here ω is light frequency; N_k and Ω_k are occupation numbers and phonon frequency, respectively; $\varepsilon_k^{e,h}$ are electron and hole energies; $\vec{D}_k = \frac{ie}{m\omega}\langle ck|\vec{P}|vk\rangle$ is matrix element of the dipole operator; $v^{e,h}_{\vec{k}-\vec{k}'} = \langle\vec{k}|\hat{v}^{e,h}|\vec{k}'\rangle$ are matrix elements of electron-phonon and hole-phonon interactions; symbol $\mathcal{P}$ in (4) denotes the principal integral value.

In subsequent calculations we assume that the energies counted from bands edges essentially surpass $T, \hbar\Omega$. On one band, this enables to use τ-approximation when calculating on the other hand, to simplify (4). As can be seen, for parabolic laws of dispersion of electrons and holes with effective masses $m_{e,h}$

$$\sum_s (2N + S + 1)Q_s^e = -\frac{2m_e}{\mu}(2N + 1)\frac{d}{d\varepsilon_0}[\delta(\varepsilon - \varepsilon_0)\delta(\varepsilon' - \varepsilon_0)] \quad (5)$$

where $\mu = m_e m_h/(m_e + m_h)$ is reduced mass; $\varepsilon = k^2\hbar^2/2\mu$ is effective energy; $\varepsilon_0 = k_0^2\hbar^2/2\mu = \hbar\omega - E_g$; E_g is the forbidden band.

The current $\vec{j}_1$ is calculated according to the standard plan.[1] The elementary contribution associated with photo-excitation is equal to

$$\vec{j}_1^e = \frac{e}{\hbar}\int I_k^{e,\mathrm{as}} \tau_k^e \vec{\nabla}_k \varepsilon_k^e \, d^3k \tag{6}$$

$$(\tau_k^e)^{-1} = \frac{\pi}{\hbar}\int (2N_{\vec{k}-\vec{k}'}+1)\,|v^2_{\vec{k}-\vec{k}'}|^2\,\delta(\varepsilon_k^e-\varepsilon_{k'}^e)\,|\vec{h}-\vec{h}'|^2\frac{d^3k'}{(2\pi)^3}; \qquad \vec{h}=\vec{k}/k.$$

After calculations have been done we obtain for $\vec{j}_1 = \vec{j}_1^e + \vec{j}_1^h$

$$\vec{j}_1 = e\frac{\alpha J}{\hbar\omega}\vec{l}^* \tag{7}$$

$$\vec{l}^* = -\frac{4\mu}{\langle |eD_k|^2\rangle}\frac{d}{d\varepsilon_0}\varepsilon_0\{\langle (2N+1)\vec{h}Jm[(\vec{e}\vec{D}_k)(\vec{e}\vec{D}_{k'})^* V^e_{\vec{k}-\vec{k}'}V^h_{\vec{k}'-\vec{k}}]\rangle\cdot$$

$$[(m_e\langle (2N+1)\,|V^e_{\vec{k}-\vec{k}'}|^2\,|\vec{h}-\vec{h}'|^2\rangle)^{-1}+(m_h\langle (2N+1)\,|V^h_{\vec{k}-\vec{k}'}|^2\,|\vec{h}-\vec{h}'|^2\rangle)^{-1}]\}$$

where α is the light absorption coefficient. The angular brackets in (7) denote averaging in the directions $\vec{h}$ and $\vec{h}'$; all the values are taken at $k = k_0(\varepsilon = \varepsilon_0)$. It can be seen from (7) that the effective path length l^* depends on the relationship between the kinetic parameters only. Polarization dependence of the current is defined by the expression in braces because the dependences on $\vec{e}$ α and $\langle|\vec{e}\vec{D}_k|^2\rangle$ are identical. Note, that expression (7) may describe the ballistic contribution to the current even in case of impurity character of the main scattering mechanism. For this, one should place $N=0$ and by $v^{e,h}_{\vec{k}-\vec{k}'}$ mean corresponding matrix elements of the impurity potential.

At small momenta, $ka \ll 1$, for $\vec{D}_k$ the expansion

$$D_i(k) = D_i^*(-k) = ea(f_i + ig_{il}k_la + h_{inl}k_nk_la^2) \tag{8}$$

is true, where the dimensionless real quantities f, g, h are characteristics of the crystal. $f \neq 0$, and the last addend in (8) is inessential when dipole transition on the absorption edge is allowed by the crystal symmetry. Two of the last addends are responsible for j_1 if such transition is forbidden.

Let us first consider the dipole-allowed transitions. When the interaction with the phonons is connected with long-range forces then $v^e_{\vec{k}-\vec{k}'} = v^h_{\vec{k}-\vec{k}'} \equiv v_{\vec{k}-\vec{k}'} = v^*_{\vec{k}'-\vec{k}}$. As can be easily seen, in this case dependence of j_1 on electron-phonon interaction parameters completely vanishes, and (taking into account[8] for j^{sh}) the ionization contributions

$$j_{1i}^{\mathrm{ex}} = -j_i^{\mathrm{sh,ex}} = 3ea\frac{\alpha_{11}J}{\hbar\omega}\frac{g_{ni}e_n(\vec{f}\vec{e})}{3f^2+k_0^2a^2(g_{ne}c_n)^2}; \qquad \vec{c}=\frac{\vec{f}}{f}; \tag{9}$$

α_{11} is the value of at $\vec{e} \parallel \vec{c}$. Thus, the ionization contributions to the current are completely compensated for. In pyroelectric crystals the contributions to j_1, j^{sh} connected with recombination are other than zero, as well. And the ballistic recombination contribution j_1^r is small in comparison with (9) by the parameter T/ε_0, where T is the crystal temperature.[1] As for the shift contribution to the current, here $j^{\mathrm{sh},r} \gg j^{\mathrm{sh,ex}}$.[8] Thus, the shift contribution to $\vec{j}$, caused by recom-

bination dominates at the absorption edge in pyroelectric crystals. If one neglects anisotropy g_{nl} according to Reference 8, then

$$\vec{j}^{\,\mathrm{sh},r} = ea\frac{\alpha J}{\hbar\omega}\frac{fg\vec{c}}{f^2 + 3g^2k_T^2a^2/2} \tag{10}$$

$k_T = \hbar^{-1}(2\mu T)^{1/2}$ is the thermal momentum. The current is directed along the $\vec{c}$ vector that can be identified with a polar axis in pyroelectrics. The polarization dependence of $\vec{j}^{\,\mathrm{sh},r}$ is the same as of the absorption coefficient α. Note that the Coulomb contribution j_c, that we have not taken into account, may complete with the current (10) $j^{\mathrm{sh}} > j_c$ if the carrier free path length $l \ll \hbar\bar{\varepsilon}/\mu e^2$, where $\bar{\varepsilon}$ is dielectric constant. This condition can be really fulfilled in ferroelectrics, where usually $\bar{\varepsilon} \gg 1$.

It should be mentioned that the relationship $j^{\mathrm{sh},r} \gg j^{\mathrm{sh,ex}}$ is typical of shift PGE in pyroelectrics. There is no connection between it and the type of optical transition and the character of electron-phonon interaction. If (as usually) the ionization contribution $j^{\mathrm{sh,ex}}$ has no essential smallness in comparison with the ballistic contribution j^{b}, then at $\varepsilon_0 \gg T$ the shift PGE predominates at the absorption edge in pyroelectrics. Therefore, below we will be interested in nonpyroelectric piezoelectrics where there are no recombination contributions Reference 1. In piezoelectrics the compensation of $\vec{j}_1$ and $\vec{j}^{\,\mathrm{sh}}$ with long-range forces and dipole-allowed transitions means that j_2 and $\vec{j}_c$ should be taken into account. Note that the vector $\vec{c}$ is not identified with the polar axis in this case.

When the electron-phonon interaction is connected with short-range forces then at small momenta one may think that (see Reference 11 and 13)

$$(2N_q + 1)\,|v_q^{e,h}|^2 = \mathrm{const}; \qquad v_q^e/v_q^h = -\sigma_e/\sigma_h \tag{11}$$

where $\sigma_{e,h} > 0$ are energetic parameters. Expression (11) can be referred both to acoustic and optical phonons. In the first case $\sigma_{e,h}$ are usual constants of the deformation potential. The expression for $\vec{j}_1$ has the form

$$\vec{j}_1 = -\vec{j}^{\,\mathrm{sh}}\frac{(m_e\sigma_e\sigma_h^{-1} + m_h\sigma_h\sigma_e^{-1})}{m_e + m_h} \tag{12}$$

$\vec{j}^{\,\mathrm{sh}}$ is set by (9). The currents compensation takes place at $\sigma_{e,h} \sim m_{e,h}^{-1}$. Approximation of this kind is often used in consideration of the deformation interaction.

Let us finally investigate the relation between j^{sh} and j_1 in dipole-forbidden transitions, i.e. at $f = 0$ in formula (8). The situation is such, for instance, in cubic crystals of T and T_d classes. Neglecting the anisotropy effects one may believe that $g_{il} = g\delta_{il}$, then the absence of central symmetry of the crystal is characterized by tensor h_{inl} in (8). Both for longitudinal optical and acoustic phonons $(2N_q + 1)\,|v_q|^2 \sim q^{-2}$ in case of long-range electron-phonon interaction.

In this connection

$$j_{1i} = ea\frac{\alpha J}{\hbar\omega}g^{-1}h_{\mathrm{inl}}e_n e_l = -\frac{1}{2}j_i^{\mathrm{sh}}. \tag{13}$$

In this case there is no full compensation of ionization contributions.

As can be easily seen from (7), the current $\vec{j}_1$ is expressed in terms of the trace of tensor h_{ill} if the interaction with phonons is associated with short-range forces. This value is zero in piezoelectrics. Therefore, the change of the mechanism of electron-phonon interaction with increasing ε_0 can lead to doubling of the value $(j^{sh}+j_1)\alpha^{-1}$.

Finally we dwell upon PGE pecularities observed in transitions between electron (hole) bands. Additional differentiation $df(\varepsilon_0)/d\varepsilon_0 \simeq -f(\varepsilon_0)\varepsilon_0 T^{-1}$ appears in this case when $j_{1,2}$ is being calculated. Therefore, roughly speaking, $j^b/j^{sh} \sim \varepsilon_0 T^{-1} \gg 1$ here.

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