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Parameters Determining the Bulk Photovoltaic Effect in Crystals with Various Band Structures

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A microscopic theory of the bulk photogalvanic effect, based on the interband theory of phase transitions in ferroelectrics is proposed. Parameters of the phase transition and the electron spectra are related to the current by directly taking into account the electron subsystem. The current is shown to be proportional to the imaginary part of the abnormal interband Green functions in the presence of lighting with the frequency exceeding the energy gap. Extreme cases of weak and strong fields are investigated. A connexion with the phase transition into the state with the spontaneous current is traced.

§1. Introduction

The bulk photovoltaic (photogalvanic) effect (BPGE), i.e. appearance of a constant current in homogeneous anisotropic media in the presence of an external electromagnetic field has been intensively investigated (the review and references see ref. 1). All the proposed models of BPGE in ferroelectrics are based on the indirect connection between polar axis and the anisotropy of microscopic parameters, *e.g.* potentials of impurities, vertices of the electron-light interaction etc.

The present article deals with the interband (vibronic) model of ferroelectrics which immediately includes both electron and phonon subsystems. It enables to explain BPGE in perfect crystals without any additional assumptions. The influence of band parameters on the BPGE efficiency is shown.

§2. The Hamiltonian

The total Hamiltonian of our system may be written as

$$H=\sum_{\alpha p}\varepsilon_{\alpha p}a_{\alpha p}^{+}a_{\alpha p}+\sum_{q}\omega_0 b_q^{+}b_q + H_{\rm eph}+H_{\rm f}, \qquad (1)$$

where $\varepsilon_{\alpha p}$'s are electron energies in bands $\alpha=1,2$ and ω_0 is the transverse optical phonon frequency. $H_{\rm eph}$ and $H_{\rm f}$ describe the electron-phonon coupling and the interaction with an external field:

$$H_{\rm eph}=\sum_{qp\sigma}\Gamma\sqrt{\frac{\omega_0}{2N}}(b_q+b_{-q}^{+})\times(a_{1p+q}^{+}a_{2p}+a_{2p+q}^{+}a_{1p}),$$

$$H_{\rm f}=\sum_{p}\lambda_p(a_{1p}^{+}a_{2p}e^{-i\omega_L t}+a_{2p}^{+}a_{1p}e^{i\omega_L t}). \qquad (2)$$

Here $\lambda=\boldsymbol{A}\boldsymbol{v}_{\alpha\beta}/2\equiv\lambda_0(\boldsymbol{ne}), \boldsymbol{E}=-\partial\boldsymbol{A}/\partial t, \boldsymbol{v}_{\alpha\beta}$ is the interband matrix element of the velocity, $\boldsymbol{n}$ and $\boldsymbol{e}$ denote unit vectors along the momentum $\boldsymbol{p}$ and the field $\boldsymbol{E}$ respectively.

In the absence of the field ($H_{\rm f}=0$) the electron-phonon interaction causes a lattice instability if $4\Gamma^2/\bar{E}>1$,[2,3] $\bar{E}$ being some average effective gap.

Below the phase transition, $T<T_c$, appears the order parameter $\phi\ll\bar{E}$ which is proportional to the sublattice shift and connected with the abnormal Green functions $G_{\alpha\beta}=\langle Ta_{\alpha}^{+}a_{\beta}\rangle$.[4]

In the case of BPGE it is important to take into account that $\boldsymbol{\phi}$ is a vector directed along the polar axis coinciding with the polarization of phonons: $\boldsymbol{\phi}=\phi\boldsymbol{c}$ and the coupling constant Γ depends on all the vectors $\boldsymbol{n}$, $\boldsymbol{c}$, $\boldsymbol{q}$; in the model discussed in ref. 4, $\Gamma=\Gamma_0(\boldsymbol{nc})$.

We obtain explicit formulae in two extreme cases. In a weak field, $\lambda\tau\ll 1$, where τ denotes the interband relaxation time, the perturbation theory is valid. If $\lambda\tau\gg 1$ the external field must be treated exactly in terms of new quasiparticles. We suppose the frequency of lighting $\omega_{\rm L}$ only slightly exceeds the energy gap $E_{\rm g}$ so that $\delta\equiv(\omega_{\rm L}-E_{\rm g})/\omega_{\rm L}\ll 1$. It should be mentioned at last that $\lambda/\bar{E}\ll 1$ in all real cases.

§3. The BPGE Current in a Weak Field

The constant current $j=\delta p(\varrho v)$ in the presence of lighting is related with $G_{\alpha\beta}$ proportional to the density matrix $\varrho_{\alpha\beta}$:

$$j(\omega=0)=-eIm\int dp\,d\omega v_{12}[G_{12}(p\omega)+G_{21}(p\omega)]. \quad (3)$$

The real part describes some additional polarization, it does not vanish if $\omega_L<E_g$ and may be related to the so-called optical detection.

The physical meaning of complicated expressions for $G_{\alpha\beta}$ becomes clear if we exclude the order parameter using the $u-v$ transformation

$$a_{1p}=u_p\alpha_{1p}+v_p\alpha_{2p};\quad a_{2p}=u_p\alpha_{2p}-v_p\alpha_{1p};$$
$$u_p^2, v_p^2=\frac{1}{2}[1\pm\varepsilon_{1p}/D], D=\sqrt{\varepsilon_{1p}^2+\phi^2}, \quad (4)$$

diagonalizing the effective Hamiltonian

$$H_{\text{eff}}=\sum_{\alpha p}\varepsilon_{\alpha p}a_{\alpha p}^+a_{\alpha p}+\phi\sum_p(a_{1p}^+a_{2p}+a_{2p}^+a_{1p}). \quad (5)$$

In our new representation

$$j=-eIm[\iint dp\,d\omega\, v_{12}(g_{12}+g_{21})+ +\iint dp\,d\omega\, v_{12}[g_{11}+g_{22}]]\equiv j_{\text{inter}}+j_{\text{intra}}, \quad (6)$$

where $g_{\alpha\beta}=\langle T\alpha_\alpha^+\alpha_\beta\rangle$. Here we study only the proper interband current j_{inter} while j_{intra} connected with $g_{\alpha\alpha}$ is some part of processes studied earlier by supposing a phenomenological anisotropy of the electron-light vertex λ.[1)]

Evaluating the first non-vanishing diagram for $g_{\alpha\beta}$ proportional to ϕ and λ^2 we obtain for $\Gamma=\Gamma_0(\boldsymbol{nc})$ and isotropic bands:

$$j=\frac{e^3v_{12}^3}{8\pi\omega_L^2}\phi E^2[2(\boldsymbol{ce})\boldsymbol{e}+\boldsymbol{c}]Y, \quad (7)$$

$$Y=4\pi Im\int dp(n_{1p}-n_{2p})(\varepsilon_{1p}-\varepsilon_{2p}-\omega_L-i0)^{-1}$$

Thus the scalar function Y includes the distribution functions and depends on the band structure. For important cases

a) $E_g(p)=E_g+p^2/m$; b) $E_g(p)=2(E_g^2/4+b^2p^2)^{1/2}$

we have respectively

$$\text{a) } Y=\left(\frac{m}{\omega_L}\right)^{3/2}\sqrt{\frac{\omega_L-E_g}{\omega_L}};\ \text{b) } Y=\frac{\sqrt{\omega_L^2-E_g^2}}{4\omega_L b^3}. \quad (8)$$

The BPGE current may also be rewritten as

$$j=K\alpha(\omega_L)S,\ K=(ev_{12}/\omega_L^2)(\phi/\bar{E}), \quad (9)$$

where α is the extinction coefficient and S denotes the intensity of lighting. Assuming $\omega_L\simeq E_g\simeq 10^{15}/S^{-1}$, $v_{12}\simeq 10^8$ cm/s and $\phi/\bar{E}\simeq(T_c/\bar{E})^{1/2}\simeq 10^{-2}\div 10^{-3}$, we obtain $K\simeq 10^{-9}\div 10^{-10}$ A·cm/W in agreement with the experimental data.[1)]

§4. The Influence of Impurities

Impurities (including non-polar ones), *e.g.* acceptors near the valence band, give an additional contribution to BPGE if they also interact with the other (conductivity) band via electron-phonon coupling:

$$H_{\text{imp}}=\sum_n\varepsilon_n' A_n^+A_n + \sum_{nq}\Gamma_n(b_q+b_{-q}^+)(A_n^+a_{1q}+A_na_{1q}^+), \quad (10)$$

where the sum over n includes all impurities with energies ε_n'. We have the following symbolic equations for full Green functions:

$$G_{12}=G_1^0\phi G_{22}+G_1^0\phi G_{2'2};\ G_{2'2}=G_{2'}^0\phi G_{12} \quad (11)$$

where $2'$ denotes acceptor levels and the order parameter ϕ includes both interband and band-impurities transitions so that it does not contain the relatively small concentration of impurities N'. Thus the BPGE does not vanish if $\omega_L\lesssim E_g$ when $j\simeq N'S\varrho(E_g-\omega_L)$ and ϱ denotes the energy distribution of impurities.

§5. Strong Field

In the case $\lambda\tau\gg 1$, the field must be exactly taken into account. The total Hamiltonian without H_{eph} may be diagonalized by means of two transformations as in ref. 5. In our new representation energies of quasiparticles are $E_{1,2p}=\pm\sqrt{\lambda_p^2+\zeta_p^2}$, $2\zeta_p=E_g(p)-\omega_L$, bare phonon frequencies do not change and the term H_f vanishes. However, the electron-phonon interaction has now a complicated nonstationary form

$$H_{\text{eph}}=\sum_{\alpha\beta,pq,\pm}\gamma_{\alpha\beta}^{\pm}\sqrt{\frac{\omega_0}{2N}}(b_q+b_{-q}^+)\times A_{\alpha p}^+A_{\beta p+q}e^{\pm i\omega_L t},$$

$$\gamma^+=\Gamma\begin{vmatrix}-u_pv_{p+q} & u_pu_{p+q}\\ -v_pv_{p+q} & v_pu_{p+q}\end{vmatrix};\ u_p^2, v_p^2=\frac{1}{2}[1\pm\zeta_p/E_{1p}], \quad (12)$$

where $\gamma^-(u,v)=\gamma^+(v,u)$.

It was shown in ref. 5 for the Hamiltonian without electron-phonon coupling that new quasiparticles A_p have usual thermal equilibrium distribution. It holds in the presence of our interband interaction too, since the bare phonon frequency $\omega_0 \ll \omega_L$, E_g so that real interband transitions due to these phonons are impossible and the equilibrium is not disturbed. Thus we can develop the perturbation technique for H_{eph} with the Green functions $g_{\alpha\beta}(t, t') = \langle TA_\alpha^+ A_\beta \rangle$ depending on t and t' separately, so that

$$g_{12}(\omega, \omega-\omega_L) = g_1^0 \sum_{\omega', \pm} \phi(\omega')(\gamma_{12}^{\pm} g_{22} + \gamma_{11}^{\pm} g_{12}) \tag{13}$$

and the energy conservation law is valid in each vertex. Besides the equation of motion

$$\phi(\omega) = \sqrt{\frac{\omega_0}{2}} \langle b_q + b_{-q}^+ \rangle = -\frac{2\omega_0^2 \Gamma^2}{N(\omega^2+\omega_0^2)} \sum_{p\omega'} (F_{12}+F_{21}),$$

$$F_{12}(\omega', \omega'-\omega_L-\omega) = u_p^2 g_{21} - v_p^2 g_{12} + u_p v_p (g_{22}-g_{11}), \tag{14}$$

where the arguments of $g_{\alpha\beta}$ are the same as in F_{12}, and F_{21} differs from F_{12}. By replacement $1 \rightleftarrows 2$, $\omega_L \rightleftarrows -\omega_L$, we obtain the similar equation

$$j(\omega) = -eIm \sum_{p\omega} (F_{12}+F_{21}).$$

For real values $\lambda_p \ll E_g$ final expressions for the current are similar to those in a weak field. For example, omitting higher powers of ϕ and $v_p^2 \ll 1$ we obtain $j \backsim (\lambda/\omega_L)^2 (\phi/\omega_L)(m\omega_L\hbar)^{3/2}$ in the case of initially parabolic bands. However, now there is no simple connexion between the BPGE current and the extinction coefficient $\alpha(\omega_L)$: it is known[5)] that $\alpha \to 0$ if $\lambda\tau \gg 1$ and the interband recombination time τ is much less than the intraband relaxation time.

§6. Concluding Remarks

Within the framework of the proposed model the intraband interaction of electrons with longitudinal optical phonons may also be taken into account. In such a case the expression (7) for the current holds while the parameters ϕ, m_{eff} and T_c increase as the intraband interaction becomes stronger and reach their maxima in the limit of small polaron conductivity. Moreover the interaction with longitudinal phonons leads to some renormalization of both electron-phonon and electron-photon vertices Γ and λ. It can be shown that such a renormalization enhances the value of the BPGE current, too.

The appearance of the BPGE current may also be treated as the phase transition in the presence of an external field into state with the spontaneous current. From this point of view the BPGE current resembles the phase transition into the superdiamagnetic state discussed recently.[6)] The order parameter in ref. 6 is pure imaginary one while in our case if $\omega_L > E_g$ both the solution of equations for $G_{\alpha\beta}$ and the order parameter acquire an imaginary additive. However, there is important distinction of our model: the spontaneous current without external field in ref. 6 corresponds to the ground state while our phase transition is essentially non-equilibrium one. This fact excludes the prohibition of a homogeneous current due to the Bloch theorem.

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