Anomalous photovoltaic effect in systems with electron and phonon order parameters

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A theory is developed of the anomalous photovoltaic effect due to the contributions of the off-diagonal density-matrix elements. It is shown that the presence of electron and phonon anomalous mean values leads automatically to a stationary current that is quadratic in the field and is independent of intraband relaxation processes.

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1. We propose here a theory of a new mechanism of the anomalous photovoltaic effect that is essentially connected with a phase transition in a system. It is known that a ferroelectric phase transition of the displacement type can be attributed to the presence of a strong interband electron-phonon coupling. Below the transition point there appear in the system two types of anomalous mean values (phonon and electron order parameters) that describe respectively the restructuring of the phonon and electron subsystems.[1] We shall show that spontaneous breaking of the dynamic symmetry of the electron subsystem leads automatically to the appearance of a homogeneous and stationary current, i.e., to the anomalous photovoltaic effect, if the frequency of the external electromagnetic field $\Omega > E_g$, where E_g is the band gap. It is important that the value of the current is determined entirely by the same parameters as the phase transition. This current is determined by the interband density-matrix elements and does not depend on intraband relaxation processes. This last circumstance distinguishes in principle this anomalous photovoltaic mechanism from the traditional ones (Ref. 2).[1)]

In Sec. 2 we consider a two-band model that contains all the essential features of the phenomenon. Section 3 is devoted to a multiband generalization of the problem, to a discussion of the results, and to an estimate of the magnitude of the effect. The estimated parameter values are close to the experimental ones.

2. The two-band model is described by the Hamiltonian

$$H=H_e+H_{ph}+H_{eph}+H_f, \tag{1}$$

where H_e corresponds to electrons in bands $\alpha = 1$ and 2 with energies $\varepsilon_{\alpha p}$, H_{ph} corresponds to optical phonons of frequency ω_0, and H_{eph} to interband electron-phonon interaction:

$$H_{eph}=\sum_{\mathbf{p},\mathbf{q}} \Gamma_{12}(\mathbf{nc})\,(\omega_0/2N)^{1/2}(b_{\mathbf{q}}+b_{-\mathbf{q}}^{+})\,(a_{1\mathbf{p}}^{+}a_{2\mathbf{p}-\mathbf{q}}+\text{c.c.}), \tag{2}$$

with Γ_{12} a constant, $\mathbf{c}$ the phonon polarization vector, and $\mathbf{n}=\mathbf{p}/|\mathbf{p}|$. The interaction (2) presupposes an active polar (transverse) optical oscillation, so that a polar axis appears spontaneously in the system below the transition point (spontaneous polarization). The angular dependence of $\Gamma_{12}(\mathbf{n}\cdot\mathbf{c})$ corresponds to interaction of the dipole moment in the cell, due to the transverse optical oscillations, with the dipole moment of the electron subsystem.[1] In this case $\Gamma_{12} \propto r_{12}$. It is convenient to assume that Γ_{12} is real, and it is this which determines the choice of the phase shifts in (4).

Finally, H_f corresponds to dipole interaction with an external electromagnetic field of frequency Ω:

$$H_f=\sum_{\mathbf{p},\alpha,\beta}\lambda_{\alpha\beta}(\mathbf{p})\,a_{\alpha\mathbf{p}}^{+}a_{\beta\mathbf{p}}(e^{i\Omega t}+e^{-i\Omega t}). \tag{3}$$

The quantities $\lambda_{\alpha\beta}$ are determined by the wave field E and by the velocity-operator matrix elements:

$$\lambda_{\alpha\beta}=eEv_{\alpha\beta}(\mathbf{ne})/2\Omega, \quad \lambda_{12}\equiv i\lambda_0(\mathbf{ne})=-\lambda_{21}, \tag{4}$$

where $\mathbf{e}$ is the field-polarization vector and $\mathbf{v}_{\alpha\beta}\equiv\mathbf{n}v_{\alpha\beta}$.

The field frequency satisfies the inequality $\delta\equiv(\Omega-E_g)/\Omega \ll 1$, so that the dependence of λ_0 on the modulus of p can be neglected. In addition, we assume below that $\lambda_0\tau \ll 1$ (weak fields, τ is the interband-recombination time), and the system can therefore be assumed to be in weak disequilibrium and the usual temperature technique can be used.

In the absence of a field ($H_f = 0$), the phonon subsystem is unstable if the coupling constant Γ_{12} satisfies the threshold inequality

$$\Delta_0=\frac{4\Gamma_{12}^2}{N}\sum_{\mathbf{p}}\frac{(\mathbf{nc})^2}{\varepsilon_{1\mathbf{p}}-\varepsilon_{2\mathbf{p}}}-1=\frac{4\Gamma_{12}^2}{E}-1>0 \tag{5}$$

and undergoes a phase transition at $T = T_c$. Below T_c there appears an order parameter

$$\Phi=\Phi_0\mathbf{c}, \quad \Phi_0=\Gamma_{12}(\omega_0/2N)^{1/2}\langle b_0+b_0^{+}\rangle,$$

that describes the displacement of the sublattices along the (spontaneous) direction $\mathbf{c}$ and satisfies the equation

$$\Phi_0=-\frac{2T}{N}\sum_{\mathbf{p},\omega_n}\Gamma_{12}^2(\mathbf{nc})\,[G_{12}(\mathbf{p},\omega_n)+G_{21}(\mathbf{p},\omega_n)]. \tag{6}$$

The anomalous Green's functions $G_{\alpha\beta}$ are themselves dependent on Φ_0, so that (6) is actually a self-consistency equation. A closed system of equations for $G_{\alpha\beta}$ can be formulated and solved (see Ref. 1), but what will matter subsequently is the following: the appearance of Φ_0 leads automatically to nonzero anomalous electronic mean values and introduces in the diagonal functions $G_{\alpha\alpha}$ corrections proportional to even powers of Φ_0.

In an external field the situation changes. Relation (6) remains unchanged—the operators b_q and b_q^{+} commute

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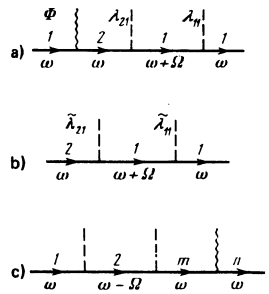

FIG. 1.

with H_f, but the equations for $G_{\alpha\beta}$ acquire new terms that are linear in Φ_0 and are due to the additional polarization of the system. The determination of $G_{\alpha\beta}$ is greatly simplified by the presence of the two small parameters $(\Phi_0/\bar{E})^2 \approx \Delta_0 \ll 1$ and $\lambda/\Omega \ll 1$, so that the exact functions can be expanded in the free electronic functions $G^0_{\alpha\alpha}$. Typical corrections due to the field are shown in Fig. 1(a), where the frequency arguments and the band indices of the free G^0 functions are explicitly indicated. It is easy to verify that at $\Omega > E_g$, i.e., in the presence of real transitions,

$$\mathrm{Im}\sum_{\omega}\delta G_{\alpha\beta}\neq 0.$$

In accordance with the general formula[4] for the current in the system

$$\mathbf{j}(\omega=0)=-e\frac{T}{N}\mathrm{Im}\sum_{\substack{\mathbf{p},\omega_n\\ \alpha,\beta}} G_{\alpha\beta}(\mathbf{p},\omega_n)v_{\beta\alpha} \tag{7}$$

this leads to the appearance of a nonzero homogeneous stationary current. It is obvious also that $j \propto E^2$ and vanishes with the field.

We have used above as the basis the wave functions of the high-temperature symmetrical phase. For a concrete analysis of the current, however, it is more convenient to go over to a wavefunction basis for the sublattices displaced as a result of this transition. To this end we diagonalize the effective Hamiltonian

$$H_{eff}=\sum_{\alpha,\mathbf{p}}\varepsilon_{\alpha\mathbf{p}}a_{\alpha\mathbf{p}}^{+}a_{\alpha\mathbf{p}}+\Phi_0\sum_{\mathbf{p}}(\mathbf{nc})\,(a_{1\mathbf{p}}^{+}a_{2\mathbf{p}}+a_{2\mathbf{p}}^{+}a_{1\mathbf{p}})\equiv\sum_{\alpha\mathbf{p}}E_{\alpha\mathbf{p}}A_{\alpha\mathbf{p}}^{+}A_{\alpha\mathbf{p}}, \tag{8}$$

so that the new states $A_{1,2\mathbf{p}}$ are a mixture of the old ones (let, for simplicity, $\varepsilon_{1\mathbf{p}}=-\varepsilon_{2\mathbf{p}}$):

$$\begin{aligned} &a_{1,2\mathbf{p}}=u_{\mathbf{p}}A_{1\mathbf{p}}\pm v_{\mathbf{p}}A_{2\mathbf{p}}, \quad E_{1,2\mathbf{p}}=\pm[\varepsilon_{1\mathbf{p}}^2+\Phi_0^2(\mathbf{nc})^2]^{1/2},\\ &u_{\mathbf{p}}^2,v_{\mathbf{p}}^2=1/2[1\pm\varepsilon_{1\mathbf{p}}/E_{1\mathbf{p}}], \quad u_{\mathbf{p}}v_{\mathbf{p}}=-\Phi_0(\mathbf{nc})/2E_{1\mathbf{p}}. \end{aligned} \tag{9}$$

The remaining terms in H_{eph} with $\mathbf{k}\neq 0$ introduce in (7) only small corrections, proportional to $T/\bar{E} \ll 1$, and will be omitted below.

The transformation (8) leads to a renormalization of the vertices $\lambda_{\alpha\beta}$ in H_f and of the matrix elements of the velocity $v_{\alpha\beta}$:

$$\tilde{\lambda}_{\alpha\beta}=\frac{e\bar{E}\tilde{v}_{\alpha\beta}}{2\Omega}=\begin{pmatrix}\lambda_{11}; & \lambda_{12}+u_{\mathbf{p}}v_{\mathbf{p}}(\lambda_{11}-\lambda_{22})\\ \lambda_{21}+u_{\mathbf{p}}v_{\mathbf{p}}(\lambda_{11}-\lambda_{22}); & \lambda_{22}\end{pmatrix}. \tag{10}$$

In the new basis, the contribution to the current is made by the diagrams shown in Fig. 1(b). It is seen that in the new basis the current is pure interband and should be connected with the change, in the external field, of the off-diagonal elements of the density matrix. Using (7), (9), and (10) and making the necessary transformations we have

$$\mathbf{j}=\frac{e^3E^2\Phi_0}{\Omega^2}\mathrm{Im}\int\frac{d\mathbf{p}\,(\mathbf{nc})\,(\mathbf{ne})^2\mathbf{n}v_{12}(v_{11}-v_{22})^2}{(\varepsilon_{1\mathbf{p}}-\varepsilon_{2\mathbf{p}})^2(\varepsilon_{1\mathbf{p}}-\varepsilon_{2\mathbf{p}}-\Omega-i0)}. \tag{11}$$

The interband current (11) has a specific dependence on the experimental geometry when the angle θ between $\mathbf{c}\parallel z$ and $\mathbf{e}$ is varied, the x axis lies in the plane of $\mathbf{c}$ and $\mathbf{e}$,

$$j_z=\mathrm{const}(2\cos^2\theta+1), \quad j_x=\mathrm{const}\cdot\sin 2\theta, \quad j_y=0. \tag{12}$$

The longitudinal current oscillates about the value $\bar{j}_z=2$ const without vanishing, while $j_{z\max}=3j_{z\min}$. The transverse component oscillates about zero.

For the important case of congruent parabolic bands, the expression for the current becomes $(eE\approx\lambda_0 m^{1/2}\Omega^{1/2})$

$$\mathbf{j}=-\frac{e|v_{12}|(m\Omega)^{1/2}}{2\pi}\left(\frac{\Phi_0}{\Omega}\right)\left(\frac{\lambda_0}{\Omega}\right)^2\delta^{1/2}[2(\mathbf{ce})\mathbf{e}+\mathbf{c}]. \tag{13}$$

We note that the squared interband velocity $v^2_{\alpha\alpha}$ contained in (11) can be connected with the two-band character of the problem. Indeed, the presence of additional bands with allowed transitions leads to the diagrams of Fig. 1(c), which do not contain intraband velocities. The model, however, can be easily generalized to a system with an arbitrary number of bands.

3. The multiband generalization includes two essential aspects. First, a change in the transition dynamics: the active branch mixes now the states from all (symmetry-allowed) bands, which leads to a more complicated renormalization of the spectra. Second, the external field also causes virtual transitions between all the bands. Just as before, we assume that real transitions proceed between two bands (1 and 2) and that the resonance condition $\delta \gg 1$ is satisfied.

The system is described by a Hamiltonian similar to (1)–(3) with vertices $\Gamma_{nm}=\Gamma_{mn}$ and λ_{nm}, where the subscripts run through all the band numbers ($\Gamma_{nn}=0$). In the absence of a field, $H_f=0$, the instability and the structural transition are connected with a threshold inequality similar to (5):

$$\Delta_0=\frac{4}{N}\sum_{\mathbf{p},c,v}\frac{\Gamma_{cv}^2(\mathbf{nc})^2}{\varepsilon_c-\varepsilon_v}\equiv 4\left(\frac{\overline{\Gamma^2}}{\bar{E}}\right)-1>0, \tag{14}$$

where the entire assembly of bands is broken up into empty (c) and filled (v), so that

$$\sum_n=\sum_c+\sum_v.$$

It can be shown that the transition temperature $T_c \approx \Delta_0\bar{E}$ and consequently inclusion of many bands reduces to an effective renormalization of the coupling constant Γ_{12} and of the characteristic energy $\bar{E}$.

The order parameter Φ_0 appears at temperatures below T_c; the self-consistency equation (6) takes the form

$$\Phi_0=-\frac{2T}{N}\sum_{\substack{n,m\\ \mathbf{p},\omega_n}}(\mathbf{nc})\Gamma_{nm}G_{mn}(\mathbf{p},\omega_n). \tag{15}$$

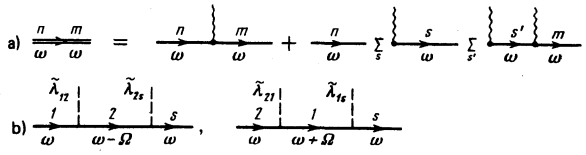

FIG. 2.

The interband functions G_{nm} at $T=0$ are shown in Fig. 2(a), where the wavy lines correspond to $\Phi_{nm}\equiv\Gamma_{nm}\Phi_0$. The temperature dependence of Φ_0 is similar to that in the two-band model[1]: At $T\neq 0$ there appear diagrams with phonon insets that decrease Φ_0, so that $\Phi_0=0$ at $T\geqslant T_c$.

In the diagonalization of H_{eff} we neglect the renormalization of the bands, i.e., the difference between E_n and ε_n in (9); this does not affect the expressions of interest to us, which are linear in Φ_0. In this approximation, the relations between the old and new states take the form

$$a_{np}=A_{np}-\sum_{s\neq n}\varphi_{ns}A_{sp},\quad \varphi_{ns}=\frac{\Phi_{ns}(\mathbf{ne})}{\varepsilon_n-\varepsilon_s}\equiv\frac{\Gamma_0 r_{ns}(\mathbf{ne})}{\varepsilon_n-\varepsilon_s}.$$

These transformations lead to new vertices:

$$\tilde\lambda_{nm}=\lambda_{nm}+\sum_{s\neq n}\varphi_{ns}\lambda_{sm}-\sum_{s\neq m}\lambda_{ns}\varphi_{sm} \tag{16}$$

and to similar equations for the transformation of the velocities.

As already noted, real transitions proceed only between bands 1 and 2, therefore the Green's function that contributes to the current must contain a resonance vertex $\tilde\lambda_{12}$ or $\tilde\lambda_{21}$ [Fig. 2(b)]. After summation over the frequencies and obvious transformations, the expression for the current becomes

$$\mathbf{j}=\mathbf{j}_{12}-\mathbf{j}_{21},$$

$$\mathbf{j}_{\alpha\beta}=-\frac{e^3E^2}{4\Omega^2}\operatorname{Im}\sum_{p,s}\frac{\tilde v_{12}(\mathbf{ne})^2\mathbf{n}}{\varepsilon_{1p}-\varepsilon_{2p}-\Omega-i0}\left(\frac{\tilde v_{\beta s}\tilde v_{s\alpha}}{\varepsilon_{sp}-\varepsilon_{\alpha p}}-\frac{\tilde v_{\beta s}\tilde v_{s\alpha}}{\varepsilon_{\beta p}-\varepsilon_{sp}}\right). \tag{17}$$

Substituting in (17) the renormalized vertices and velocities (16), we need retain only the terms linear in Φ_0. It must be noted that the equation for the current contains in fact a double summation over the intermediate bands: in (17) directly and in (16) in the calculation of the $\tilde v_{nm}$ vertices. The first summation entails no difficulty and can be carried out, for example, in analogy with Ref. 3. It is impossible, however, to calculate $\tilde v_{12}$ without assuming symmetry of the bands. Expression (16) for $\tilde v_{12}$ can be rewritten in the form

$$\tilde v_{12}=v_{12}-(\mathbf{ne})w,$$

$$w=\frac{\Phi_{12}(v_{11}-v_{22})}{\varepsilon_1-\varepsilon_2}-\Gamma_0\sum_{s\neq 1,2}\left(\frac{v_{1s}v_{s2}}{(\varepsilon_1-\varepsilon_s)^2}-\frac{v_{1s}v_{s2}}{(\varepsilon_s-\varepsilon_2)^2}\right). \tag{18}$$

If the initial (high-temperature) phase has an inversion center, then the bands can be classified by parity, and dipole transitions are allowed between bands of different symmetry. In this case the sum in (18) is zero and relation (17) takes the form

$$\mathbf{j}\propto-\frac{e|v_{12}|}{4\pi}(m\Omega)^{3/2}\left(\frac{\Phi_{12}}{\Omega}\right)\left(\frac{\lambda_0}{\Omega}\right)^2\delta[2(\mathbf{ce})\mathbf{e}+\mathbf{c}]. \tag{19}$$

If, however, there is no inversion center at $T>T_c$, transitions between all bands can be allowed and the principal terms in (18) are the ones without intraband velocities (we recall that $\delta\ll 1$, and the contribution to the current is made by momenta $p^*\propto\delta^{1/2}$). Since the series in (18) convergence rapidly enough ($\propto\varepsilon_n^{-2}$), we can confine ourselves to the first terms, after which we obtain for the current ($\overline{\Phi}\equiv\Phi_0\overline{\Gamma}$)

$$\mathbf{j}\propto-\frac{e|v_{12}|}{\pi}(m\Omega)^{3/2}\left(\frac{\overline{\Phi}}{\overline{E}}\right)\left(\frac{\lambda_0}{\Omega}\right)^2\delta^{3/2}[2(\mathbf{ce})\mathbf{e}+\mathbf{c}]. \tag{20}$$

In conclusion, let us estimate the resultant current. The traditional expression for j is

$$j=K\alpha(\Omega)S, \tag{21}$$

where $\alpha(\Omega)$ is the absorption coefficient, S is the field-energy flux, and K is the Glass constant, which is the main characteristic of the anomalous photovolatic effect. It is clear from (19) and (20) that K is proportional to $\Phi_0(T)$, and can therefore be estimated at

$$K\approx\frac{e|v_{12}|}{\Omega^2}\left(\frac{\Phi}{\overline{E}}\right)\delta^n\approx 10^{-9}-10^{-10}A\cdot\text{cm/W}, \tag{22}$$

where n is equal to $\frac{1}{2}$ and 0 for cases (19) and (29), respectively (it is recognized that $\alpha\propto\delta^{1/2}$). The estimate (22) agrees with the experimental data[2] at typical values of the parameters $E_g\approx\overline{E}\approx\Omega\approx 10^{15}$ sec^{-1}, $|v_{12}|\sim 10^8$ cm/sec, and $\delta\approx 10^{-1}-10^{-2}$. According to Ref. 1 we have far from the transition $\Phi/\overline{E}\sim(T_c/E)^{1/2}\sim 10^{-2}-10^{-3}$.

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[1)] It is shown in Ref. 3 that the appearance of a current quadratic in the field is possible in principle if the matrix elements are suitably asymmetric. The parameters of this asymmetry, which determine the value of the current, cannot be obtained in Ref. 3 and must be specified independently.

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