

Theory of field-even current in ferroelectrics

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A theory of the field-even current in a ferroelectric is proposed. The mechanism of the current is related to the asymmetric scattering of the carriers by charged centers that (in the presence of spontaneous polarization) cause a local asymmetry of the polarization charge. The current is expressed in terms of the coefficients of the Taylor expansion of free energy in the polarization. This makes it possible to predict its unique critical behavior in phase transitions, a behavior that differs substantially from that of the order parameter. The theory explains the main experimental peculiarities of the field-even current, which was first observed recently in ferroelectrics. It is shown also that the proposed asymmetric-scattering mechanism can determine the photovoltaic current observed in ferroelectrics in many experiments. A new effect is possible in the paraelectric phase, namely, absolute negative conductivity that leads to spontaneous formation of a stationary domain structure.

1. INTRODUCTION

A field-even current

$$j_i = \sigma_{ikm} E_k E_m \quad (1)$$

determined by a third-rank tensor can exist in crystals without inversion centers along with the ohmic current. The field-even current was first considered theoretically in Ref. 1, where its connection was noted with asymmetric carrier scattering which does not occur in the first Born approximation, but appears in higher orders. In succeeding theoretical papers^{2,3} the mechanism of the field-even current in semiconductors was attributed to asymmetric scattering by phonons or by impurity centers having specified odd multipole (dipole or octupole) moments.

The field-even current was investigated experimentally in the piezoelectrics GaAs and InP (Ref. 4). Recently, however, it was observed also in a crystal of another class—in the semiconducting ferroelectric SbSI at a temperature close to the phase transition.⁵ This current was observed in a single-domain sample and was directed along the polar axis z perpendicular to the applied field:

$$j_z = \sigma_{zzx} E_x^2. \quad (2)$$

It vanished when the crystal was converted into the paraelectric phase, reversing sign on reversal of the spontaneous polarization, and did not appear in a polydomain sample. It was experimentally established that this current is due to carrier scattering by charged centers making up the injected space charge captured by the traps. The current j_z is not produced in the absence of such a charge. These experimental features, and also the large magnitude of the effect ($j_z/j_x \approx 6\%$, $j_x = \sigma_{xx} E_x$) could not be explained on the basis of the theory¹⁻³ developed for piezoelectrics.

We propose here a theory of a field-even current in a ferroelectric. The onset of this current, just as in Refs. 1–3, is attributed to asymmetric scattering of carriers, but another asymmetry mechanism is considered (see also the brief communication in Ref. 6). It is proposed that the role of asymmetric scatterers is assumed by charged centers present in the ferroelectric. Since the polarization $P(E)$ is nonlinear, their Coulomb field produces a polarization charge

$\rho = -\text{div } P$ near the centers. In the presence of spontaneous polarization P_0 , the charge density acquires an additional term of opposite sign on the right and left of the point charge center, and it is this which determines the symmetry of the scattering potential.

These concepts permit a natural explanation of the main features of the even current that appears in the experiment. Thus, in the model given, the injected charges bound on the traps are precisely the asymmetric scatterers that determine the current. On the other hand the sign and existence of their asymmetry are due to the polarization P_0 , as was indeed observed.

In this paper we calculate the antisymmetric part of the scattering probability and the field-even current j_z . The result agrees in order of magnitude with experiment and in a ferroelectric it exceeds substantially the current considered earlier in Refs. 1–3.

The current j_z is expressed in terms of familiar phenomenological parameters of a ferroelectric—the coefficients α , β , and γ of the expansion of the free energy in terms of the polarization. This makes it possible to track its unique critical behavior in first- and second-order phase transitions. One prediction of the theory is that near the singular point T_1 where the coefficient β vanishes there can exist a temperature at which the current j_z increases with decrease of temperature like

$$j_z/j_x \propto (T_1 - T)^{1/2},$$

notwithstanding the decrease of the order parameter

$$P_0 \propto (T_1 - T)^{-1/2}.$$

The same dependence on the pressure should appear when the crystal is compressed. The different critical behavior of the current j_z and of the order parameter P_0 is a specific feature of this mechanism and is connected with the fact that the current j_z is proportional, in addition to P_0 , also to the coefficient β that characterizes the nonlinearity of the $P(E)$ dependence.

It is also shown that asymmetric scattering of photoexcited electrons by the centers in question may possibly determine the photovoltaic current in ferroelectrics, the nature of which is not clear even now. In addition, this scattering can

lead to a new effect in the paraelectric phase—to a domain electrical instability due to absolute negative conductivity. Here $P_0 = 0$ and the role of the priming asymmetry is played by the polarization due to the fluctuations of the field E_z .

Note that charged centers in ferroelectrics were studied earlier in investigations of their contribution to the polarizability and heat capacity of the crystal.⁷ Similar centers were considered also in the calculation of the photovoltaic current in Ref. 8 where, however, unjustified simplifying assumptions were made and were strongly reflected in the results.

2. SCATTERING ASYMMETRY

The field-even current scattered by asymmetric centers will be expressed in terms of the antisymmetric part $W_{k,k'}^{AS}$ of the carrier transition probability from a state with wave vector k to a state with k' :

$$W_{k,k'}^{AS} = -W_{-k,-k'}^{AS}. \quad (3)$$

This quantity arises in second-order perturbation theory and is proportional to the product of the scattering amplitude in first order and the pole contribution to the amplitude in second order^{9,10}

$$W_{k,k'}^{AS} = \frac{1}{(2\pi)^4 \hbar} \text{Im} \int V_{k,k'} V_{k',k''} V_{k'',k} \delta(\mathcal{E}_k - \mathcal{E}_{k'}) \delta(\mathcal{E}_k - \mathcal{E}_{k''}) dk''. \quad (4)$$

Here $\mathcal{E}_k = \hbar^2 k^2 / 2m$ is the energy of the scattered particle with effective mass m ; $V_{k,k'}$ is the matrix element of the potential of the center between the Bloch functions.

Let us calculate the probability $W_{k,k'}^{AS}$ for the center of interest to us, which is a point charge e_0 located in a single-domain ferroelectric with spontaneous polarization P_0 at a temperature close to the phase-transition point. The asymmetric potential of such a center is determined by the polarization charge resulting from the nonlinear dependence of the polarization on the field.

The distribution of the polarization P and of the potential of the center are described by the equation of state of the ferroelectric and by the Poisson equation:

$$-\frac{\partial \Phi}{\partial z} = -\alpha P + \beta P^3 + \gamma P^5 - \kappa \nabla^2 P, \quad (5)$$

$$e_{\perp} \left(\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} \right) + \frac{\partial^2 \Phi}{\partial z^2} = 4\pi \frac{\partial P}{\partial z} + \frac{\Phi}{R^2} - 4\pi e_0 \delta(r). \quad (6)$$

Here α, β , and γ are the known Landau–Ginzburg–Devonshire expansion coefficients, $\kappa \nabla^2 P$ is the gradient term, and z is the polar axis. We assume the crystal to be uniaxial, so that the vector \mathbf{P} is parallel to the z axis as a result of the strong anisotropy ($\epsilon_{xx} = \epsilon_{yy} = \epsilon_{\perp} \ll \epsilon_{zz} = \epsilon_{\parallel}$). Account is taken in Eq. (6) of the Debye screening ($R^2 = 4\pi T / e^2 n$, n is the carrier density, and T is the crystal temperature in energy units), since it will be shown that the integral (4) diverges as $R \rightarrow \infty$. The boundary condition for Eqs. (5) and (6) is the requirement that $P = P_0$ hold far from the center.

We solve Eqs. (5) and (6) by starting with the case of a second-order phase transition. Here we have $\beta > 0$,

$$P_0 = (\alpha/\beta)^{1/2}, \quad \epsilon_{\parallel} = 2\pi/\alpha$$

and the term γP^5 is immaterial. Linearizing (5) and (6) in terms of the small deviation of P from P_0 and taking the Fourier transform we obtain the symmetric part $V_{k,k'}^S$ of the matrix element of the potential $V_{k,k'} = e\varphi_{k',k''}$:

$$\begin{aligned} V_{k',k''}^S &= 4\pi e_0 e (\kappa k^2 + 2\alpha) / \Phi_k, \\ \Phi_k &= 4\pi k_z^2 + (\kappa k^2 + 2\alpha) (\epsilon_{\perp} k_{\perp}^2 + k_z^2 + R^{-2}), \\ \mathbf{k} &= \mathbf{k}' - \mathbf{k}'', \quad k_{\perp}^2 = k_x^2 + k_y^2, \end{aligned} \quad (7)$$

where e is the carrier charge. The antisymmetric part $V_{k',k}^{AS'}$ appears when the linear term βP^3 in second order is expanded in terms of the parameter $(P - P_0)/P_0$:

$$V_{k',k}^{AS} = 4\pi i \frac{k_x}{\Phi_k} \kappa V_0, \quad V_0 = \frac{3}{8\pi^{1/2}} \frac{e e_0^2 \beta P_0 \ln(\epsilon_{\parallel}/\epsilon_{\perp})}{(\epsilon_{\perp} \kappa^3)^{1/2}}. \quad (8)$$

Equation (8) is valid with logarithmic accuracy for $\kappa k^2 \ll 1$. An estimate shows that this inequality, and also the condition $V_{kk'}^{AS} \ll V_{kk'}^S$ for applicability of the linearization are satisfied at thermal values of k , which are the ones essential for further calculations.

The spatial distributions of the potentials V^S and V^{AS} , which follow from Eqs. (7) and (8), are shown in Fig. 1. At the very largest distances from the center $z \gg \kappa^{1/2}/\alpha$ the antisymmetric part V^{AS} is the dipole potential in a medium with anisotropic dielectric constant $\epsilon_{\perp}, \epsilon_{\parallel}$: $V^{AS} \propto z^{-2}$ ($x = y = 0$). For $\kappa^{1/2} \ll z \ll \kappa^{1/2}/\alpha$ the gradient term predominates in (5) and V^{AS} decreases with distance more slowly:

$$V^{AS} = \frac{V_0}{4} \left(\frac{\kappa}{\pi \epsilon_{\perp}} \right)^{1/2} \frac{1}{z}, \quad x = y = 0. \quad (9)$$

The symmetric potential V^S is close to a Coulomb one, but spatial dispersion is significant at short distances.

We proceed to calculate the probability $W_{k,k'}^{AS}$ of scattering by the considered static potential $V = V^S + V^{AS}$. If the asymmetry is weak ($V^{AS} \ll V^S$) the main contribution to the integral (4) is made by terms proportional to ($q^2 \ll \alpha/\kappa$, $q_z^2 \ll \alpha^2/\kappa$). Substituting (7) and (8), we obtain after simple transformation

$$W_{k,k'}^{AS} = \frac{4}{\pi} \frac{m k e^2 e_0^2}{\hbar^3} \kappa V_0 \delta(\mathcal{E}_k - \mathcal{E}_{k'}) W_{k,k'}, \quad (10)$$

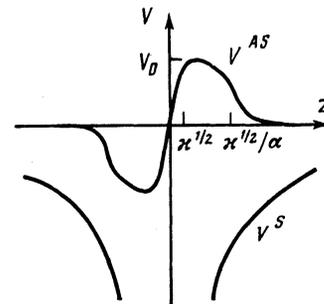


FIG. 1. Schematic distributions of symmetric $V^S(z)$ and antisymmetric $V^{AS}(z)$ parts of potential for $x = y = 0$, produced in a single domain ferroelectric by a point charge.

where

$$\begin{aligned} & \bar{W}_{\mathbf{k}, \mathbf{k}'} \\ &= \int \frac{q_z (\kappa q'^2 + 2\alpha) (q''^2 - q^2) + q_z' (\kappa q^2 + 2\alpha) (q''^2 - q'^2)}{\Phi_q \Phi_{q'} \Phi_{q''}} d\Omega'', \\ & \mathbf{q} = \mathbf{k} - \mathbf{k}', \quad \mathbf{q}' = \mathbf{k}'' - \mathbf{k}, \quad \mathbf{q}'' = \mathbf{k}' - \mathbf{k}'', \quad k = k' = k'', \end{aligned} \quad (11)$$

with the integration carried out over the angles of the vector \mathbf{k}'' . Here and below we neglect the inessential anisotropy of the effective mass and of other crystal parameters compared with the strong anisotropy of the dielectric constant.

If the change of the particle momentum by scattering is small enough ($q^2 \ll \alpha/\kappa$, $q_z^2 \ll \alpha^2/\kappa$), the main contribution to the integral (11) is made by the region

$$\varepsilon_{\perp} R^{-2} \ll q'^2 = q''^2 \ll \alpha/\kappa, \quad q_z^2 = q_z''^2 \sim \alpha q'^2.$$

We then have

$$W_{\mathbf{k}, \mathbf{k}'}^{AS} = \frac{1}{2i} V_q^{AS} \frac{e^2 e_0^2 m}{\hbar^3} \delta(\mathcal{E}_{\mathbf{k}} - \mathcal{E}_{\mathbf{k}'}) W, \quad (12)$$

$$W = \frac{1}{4k_{\perp}} \frac{\kappa \ln(\alpha R^2/\kappa)}{(2\pi^3 \alpha \varepsilon_{\perp}^3)^{1/2}}. \quad (13)$$

If α^2/κ , $\kappa q^4 \ll q_z^2 \ll \kappa k_{\perp}^4$ in (11), the region where $q^2 = q'^2 \sim q_z/\kappa^{1/2}$, $q_z' \sim q_z'' \sim q_z$ is significant, and we obtain in place of (13)

$$W = \frac{1}{4k_{\perp}} \left(\frac{4\kappa^3}{\pi^3 \varepsilon_{\perp}^5 q_z^2} \right)^{1/2}. \quad (14)$$

For $\kappa q^4 \gg q_z^2 \gg \alpha^2/\kappa$ there exists in (11) a region with $q^2 \sim q'^2 \sim q^2$ and $q_z' = q_z'' \gg q_z$. In this case

$$W = -\frac{1}{q k_{\perp}} \left(\frac{\kappa}{\pi \varepsilon_{\perp}^3} \right)^{1/2}. \quad (15)$$

In the last of the possible limiting cases, $q_z^2 \gg \kappa k_{\perp}^4$, we have

$$W = \frac{32(k_x k_x' + k_y k_y')}{q_z^2} \left(\frac{\kappa^3}{\pi^3 \varepsilon_{\perp}} \right)^{1/2}, \quad (16)$$

and the main contribution to the integral (11) is made by the regions near $q'_z = 0$ and $q''_z = 0$.

The scattering probability in a ferroelectric with a second-order phase transition is thus determined by Eqs. (12)–(16). Note that they are valid for $R^2 \gg \kappa/\alpha$ and $k_{\perp}^2 \gg \alpha/\kappa$. The last condition is violated only for a negligible fraction of thermal carriers that are incident on the scatterers at small angles to the z axis.

We consider now the case of a first-order phase transition. Here, putting $\beta < 0$ in (5), we obtain the familiar expression

$$P_q^2 = -\frac{\beta}{2\gamma} \left[1 + \left(1 + \frac{4\alpha\gamma}{\beta^2} \right)^{1/2} \right]. \quad (17)$$

Acting as in the preceding case, we show easily that the distribution of the center potential and the scattering probability are described by Eqs. (7)–(16), with the substitutions

$$\alpha \rightarrow 2\alpha - \beta P_0^2, \quad 3\beta P_0 \rightarrow 10\gamma P_0^3 + 3\beta P_0, \quad (18)$$

where P_0 is given by Eq. (17).

3. FIELD-EVEN CURRENT

We calculate the field-even current (2) assuming that the field E is applied to a uniaxial crystal perpendicular to the polar z axis (to be specific, along the x axis). We use for this purpose the Boltzmann kinetic equation

$$-eE_x \frac{1}{\hbar} \frac{\partial f_{\mathbf{k}}}{\partial k_x} = \hat{I} f_{\mathbf{k}}, \quad \hat{I} = \hat{I}^S + \hat{I}^{AS}, \quad (19)$$

confining ourselves to the simplest model in which the symmetric part \hat{I}^S of the collision integral is characterized by a single relaxation time¹ τ :

$$\hat{I}^S f_{\mathbf{k}} = -(f_{\mathbf{k}} - f_{\mathbf{k}}^0)/\tau. \quad (20)$$

Here $f_{\mathbf{k}}^0$ is the carrier equilibrium distribution function. The antisymmetric part \hat{I}^{AS} is

$$\hat{I}^{AS} f_{\mathbf{k}} = N \int (W_{\mathbf{k}', \mathbf{k}}^{AS} f_{\mathbf{k}'} - W_{\mathbf{k}, \mathbf{k}'}^{AS} f_{\mathbf{k}}) d\mathbf{k}', \quad (21)$$

where N is the density of the asymmetric scatterers. Note that a kinetic theory of a field-even current was proposed for a more complicated model in Ref. 2.

Equations (19)–(21) yield for current j_z

$$j_z = \frac{e\hbar\tau}{m} \int k_z \hat{I}^{AS} f_{\mathbf{k}} d\mathbf{k}. \quad (22)$$

One can neglect in the calculation of the distribution function $f_{\mathbf{k}}$ the antisymmetric part of the collision integral in the weak-asymmetry ($\hat{I}^{AS} \ll \hat{I}^S$) approximation. Expanding $f_{\mathbf{k}}$ in powers of E_x we obtain from (19) and (20)

$$f_{\mathbf{k}} = f_{\mathbf{k}}^0 + \frac{\tau e E_x \hbar k_x}{mT} f_{\mathbf{k}}^0 + \left(\frac{\tau e E_x}{mT} \right)^2 (\hbar^2 k_x^2 - mT) f_{\mathbf{k}}^0. \quad (23)$$

With this expression substituted in (22), a nonzero contribution comes only from the term proportional to $E_x^2 k_x^2$, since the integral (21) is equal to zero if $f_{\mathbf{k}}$ depends on the modulus of k . As a result we get from (21)–(23)

$$j_z = e \left(\frac{eE_x}{T} \right)^2 \left(\frac{\tau\hbar}{m} \right)^3 N \int k_x' k_x^2 f_{\mathbf{k}}^0 W_{\mathbf{k}, \mathbf{k}'}^{AS} d\mathbf{k} d\mathbf{k}'. \quad (24)$$

We now determine the field-even current for the scatterers of interest to us. Substituting (10) and (11) in (24) we find after integration that for a second-order phase transition the current is given by

$$\frac{j_z}{j_x} = -\frac{\mu E_x}{v} \tau \Omega, \quad \Omega = \frac{1}{2} \left(\frac{ee_0}{\hbar v} \right)^2 N \kappa^2 k (30\kappa k^2 + \alpha) \frac{V_0}{\hbar}. \quad (25)$$

Here $j_x = e\mu n E$, n and $\mu = e\tau/m$ are the carrier density and mobility, and $v(2T/m)^{1/2}$ and $k = mv/\hbar$ are their thermal velocity and the wave vector, V_0 is given by Eq. (8). Note that the condition $\hat{I}^{AS} \ll \hat{I}^S$ used for the solution of the kinetic equation reduces to the requirement $\Omega\tau \ll 1$. The results are only qualitatively correct if the asymmetry parameter satisfies $\Omega\tau \sim 1$.

The minus sign in (25) means that the current j_z is directed counter to the spontaneous-polarization vector \mathbf{P}_0 . Its direction is independent of the signs of the charge e_0 of the centers or e of the carriers, since $j_z \propto e^6 e_0^4$. The result can be generalized to include a first-order transition by using Eqs. (17) and (18).

Let us estimate the field-even current j_z for SbSI, using the typical parameters $N \sim 10^{19} \text{ cm}^{-3}$, $\mu \sim 50 \text{ cm}^2/\text{V}\cdot\text{s}$, $\beta \sim 10^{-12}$ and $\gamma \sim 10^{-22}$ cgs units, $\alpha_0 \sim 3 \cdot 10^{-5} \text{ K}^{-1}$, $\kappa \sim 10^{-15} \text{ cm}^2$ (see Ref. 11). The ratio j_z/j_x can be reached here in fields $E_x \sim 10^3 \text{ V/cm}$, in good agreement with experiment.⁵ In ferroelectrics with stronger nonlinearity ($\beta \sim 10^{-9}$ cgs) the field-even current can be much larger.

The scattering-asymmetry mechanism substantially exceeds those considered earlier. In particular, an estimate of the current j_z for centers with specified dipole moment d of atomic order yields

$$\Omega = \frac{1}{\hbar} \frac{N}{T^2} \left(\frac{edk}{\epsilon} \right)^3, \quad (26)$$

making the result several orders of magnitude smaller than Eq. (25). The reason is that the potential V^{AS} of interest to us, in contrast to the dipole potential, decreases weakly over distances on the order of the de Broglie wavelength $\Lambda \sim k^{-1}$ of the thermal carriers, which are the ones that make the main contribution to the scattering. Note also that the previously considered asymmetry mechanisms are much weaker in ferroelectrics than in ordinary semiconductors, owing to the large ϵ and small τ , and cannot account for the large field-even currents and for the photovoltaic currents in these materials.

4. CRITICAL BEHAVIOR OF THE CURRENT IN PHASE TRANSITIONS

The temperature dependence of the current j_z in the phase-transition region can be obtained from Eq. (25) through the usual linear expansion of the coefficient α near the Curie point T_c :

$$\alpha = \alpha_0(T_c - T). \quad (27)$$

In a second-order phase transition the current vanishes like

$$\frac{j_z}{j_x} \propto (T_c - T)^{1/2} \ln \frac{\epsilon_{\perp} \alpha_0 (T_c - T)}{2\pi}. \quad (28)$$

It is assumed here that the values of N and τ vary little in the temperature interval we are considering.

For lower temperatures (for $\alpha \gg 30\kappa k^2$ we have

$$\frac{j_z}{j_x} \propto (T_c - T)^{1/2} \ln \frac{\epsilon_{\perp} \alpha_0 (T_c - T)}{2\pi}. \quad (29)$$

In the case of a first-order phase transition the current j_z should, in accordance with (25), (27), (17), and (18), appear discontinuously at the transition point.

It is of interest to consider also the behavior of the current j_z when the crystal is compressed, since the sign of the coefficient β of SbSI is reversed when the pressure p is changed.¹¹ It is remarkable that experiments on precisely this ferroelectric¹² confirmed the tricritical point, described by Landau, on a p - T diagram in which both coefficients α and β vanish simultaneously, and phase transitions of first and second order go over smoothly into each other (see Fig. 2). Near this point (T_3, p_3), the equations obtained for a first-order transition are valid, and both coefficients α and β can be linearized with respect to p and T . In this case

$$P_0 = (\alpha/\gamma)^{1/4}, \quad j_z/j_x \propto \alpha^{3/4} \ln(\epsilon_{\parallel}/\epsilon_{\perp}). \quad (30)$$

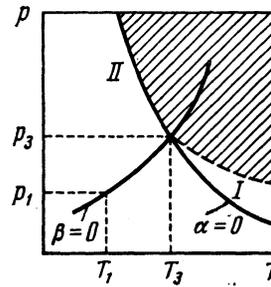


FIG. 2. Schematic p - T diagram of ferroelectric. The paraelectric phase region is hatched. The solid lines correspond to the conditions $\alpha = 0$ and $\beta = 0$. Section II corresponds to second-order phase transitions, and dashed line I to first-order.

The critical behavior of these quantities in response to variations of T or p are determined by the substitution

$$\alpha \sim \begin{cases} T_3 - T, & p = p_3, \\ p_3 - p, & T = T_3. \end{cases}$$

We consider now the behavior of the current j_z near a point (T_1, p_1) belonging to the line $\beta = 0$ in the region of the ferroelectric phase and not too close to the tricritical point (see Fig. 2). In this case one can neglect the dependence of α on T and p and linearize² β :

$$\beta = \begin{cases} \beta_p(p - p_1), & T = T_1, \\ \beta_T(T_1 - T), & p = p_1. \end{cases}$$

Using (26), (17), and (18) we find that Eqs. (30) remain valid in the region very close to the point (T_1, p_1), i.e., for $\beta^2 \ll \alpha\gamma$, and consequently P_0 and j_z are constant. Outside this region (at $\beta^2 \gg \alpha\gamma$) we obtain for $p = p_1$

$$P_0 = \left(\frac{\beta}{\gamma} \right)^{1/4} \propto [\beta_T(T - T_1)]^{1/4}, \quad (31)$$

$$\frac{j_z}{j_x} \propto \beta^{3/4} \propto [\beta_T(T - T_1)]^{3/4}, \quad \beta_T(T - T_1) > 0,$$

$$P_0 = \left(\frac{\alpha}{\beta} \right)^{1/4} \propto [\beta_T(T_1 - T)]^{-1/4},$$

$$\frac{j_z}{j_x} \propto \beta^{3/4} \propto [\beta_T(T_1 - T)]^{-3/4}, \quad \beta_T(T - T_1) < 0. \quad (32)$$

A similar dependence on the pressure occurs at $T = T_1$.

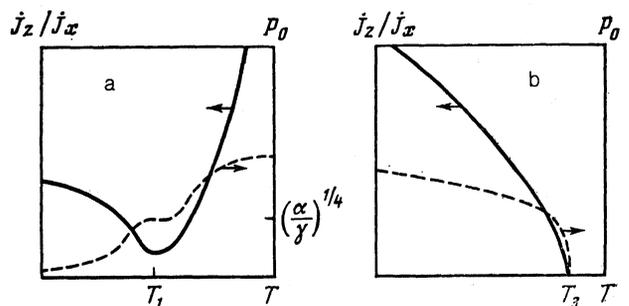


FIG. 3. Schematic temperature dependences of the current j_z (solid line) and spontaneous polarization P_0 (dashed line) near: a—the point T_1 corresponding to the condition $\beta(T_1) = 0$, $T_1 < T_3$, $p = p_1$, and b—tricritical point (T_3, p_3).

Thus, in accordance with (32), the ratio j_z/j_x increases as the temperature is lowered (or as the pressure is raised), notwithstanding the decrease of the order parameter P_0 . The temperature dependence of the current j_z , which follows from Eqs. (30) and (32), is shown in Fig. 3.

This unusual behavior of the current in a phase transition is a characteristic feature of the present mechanism. It has not yet been investigated experimentally, but it was noted in Ref. 5 that the current j_z vanishes upon transition to the paraelectric phase.

5. CONCLUSION

Let us consider briefly certain other effects connected with this scattering mechanism. One of them is the photovoltaic current j_{PV} due to the asymmetry of the elementary electronic processes and produced when noncentrosymmetric crystals are illuminated in the absence of an electric field.¹³⁻¹⁵ The nature of this current in ferroelectrics still remains unclear, despite numerous investigations. If it is assumed that the current j_{PV} is the result of asymmetric scattering of photoexcited electrons aligned in momentum along the centers considered above, one can get the estimate

$$j_{PV} \sim eV \frac{\tilde{\kappa} I \tau}{\hbar \omega} \left(\frac{k_0}{k} \right)^2 \tau \Omega,$$

where I is the intensity of the light, ω its frequency, $\tilde{\kappa}$ is the absorption coefficient, and k_0 is the wave vector of the photoexcited electrons. For SbSI, the Glass constant $G = j_{PV}/\tilde{\kappa}I$, which characterizes the current, we obtain $G \sim 10^{-8} - 10^{-7} \text{ A} \cdot \text{cm}/\text{W}$, with good agreement with experiment¹¹ and substantially higher than the value obtained for previously considered mechanisms.¹⁵

In the paraelectric phase we have $P_0 = 0$ and the currents described above are impossible. In the presence of a weak field, however, a polarization $P_0' = E_z/\alpha$ is produced, and an asymmetric potential $V^{AS} \propto P_z'$ appears at the charged centers. The photoelectron scattering by this potential produces a current directed counter to the field E_z , and can serve as the mechanism of the absolute negative photoconductivity¹ considered phenomenologically earlier in Ref. 17. Such a conductivity leads to formation of a stationary domain structure. A similar effect is possible also in the absence of irradiation in the presence of a field E_z (see Ref. 6). In the latter case the current is given by

$$j_z = -\sigma_{zzzz} E_z^2 E_z$$

and leads to effects similar to the many-valued Sasaki effect.¹⁸ A detailed investigation of the negative conductivity in the paraphase is of independent interest and is outside the scope of the present paper.

Note that this mechanism of the field-even current and of the photovoltaic current is universal for ferroelectrics, since its existence does not call for any special assumptions, other than the presence of charge centers, which always exist in real crystals. On the other hand, this mechanism produces an effect larger than those previously considered. It is therefore natural to assume that it also determines the currents observed in numerous experiments on ferroelectrics. A check on this assumption may be an experimental investigation of the critical behavior in phase transitions (see Sec. 4), which should coincide for photovoltaic and field-even currents.

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¹ The relaxation time τ can be determined by symmetric scatterers present in the crystal alongside the asymmetric centers.

² For SbSI we have $\beta_p > 0$ and $\beta_r > 0$, although in the general case the signs of these coefficients are arbitrary.

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