Influence of the photogalvanic effect on phase transitions in ferroelectrics

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A new mechanism of the effect of light on ferroelectric phase transitions is proposed. It is based on the renormalization, by the photogalvanic effect, of the coefficients in the expansion of the free energy of a ferroelectric in powers of the polarization.

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1. In 1974 Glass and his colleagues discovered a new physical effect in the ferroelectrics $LiNbO_3$ and $LiTaO_3$[1,2]: in the Soviet literature this is known as the photogalvanic effect.[3-6] Subsequently, this effect has been investigated in $BaTiO_3$[7] and in other ferroelectrics. The essence of the effect is the generation of a static photocurrent which is entirely due to the symmetry of the crystal and in the simplest case it is due to the presence of a polar axis. The photogalvanic effect is basically different from a wide range of photoferroelectric phenomena associated with the photoinduced changes in the spontaneous polarization **P** of a crystal.[8] The photovoltages due to a change in **P** have only a finite lifetime, which is governed either by the conductivity of the crystal or by the rate of deposition of charges from air[9]; they give rise only to a transient current.

We shall report a continuation of the intensive investigations of the mechanisms of the photogalvanic effect[3-6] and of its influence on the macroscopic properties of ferroelectrics.[1,2] We shall demonstrate the possibility of a considerable influence of this effect on ferroelectric phase transitions.

2. In the case of ferroelectrics characterized by a single polar vector—the spontaneous polarization **P**—the expression for the photogalvanic current near the phase transition point is

$$\mathbf{j}_{pg}=[\alpha\mathbf{P}+\beta\mathbf{e}(\mathbf{Pe})]I+O(\mathbf{P}^3). \tag{1}$$

Here, **e** is the polarization vector of light; I is the intensity of light; $\alpha(\omega)$ and $\beta(\omega)$ are the photogalvanic constants governed by the microscopic mechanism of the effect. According to Eq. (1), the direction and magnitude of $\mathbf{j}_{pg}$ may be controlled by the frequency and polarization of the incident light.[1]

In the case of isolated crystals the effect of light gives rise to an equilibrium in which the transfer of charge by the photogalvanic effect is compensated by the ordinary ohmic current: $\mathbf{j}_{pg}+\hat{\sigma}\mathbf{E}=0$.

Thus, a small group of nonequilibrium photoelectrons, which contribute to $\mathbf{j}_{pg}$, produces a blocking field

$$\mathbf{E}=-\hat{\sigma}^{-1}\mathbf{j}_{pg}\propto\mathbf{P}. \tag{2}$$

According to the experimental data[1,7] and the theoretical results,[3,4] far from the phase transition point this field may reach considerable values of $\sim 10^4-10^5$ V/cm. In the case of low-conductivity crystals the tensor $\hat{\sigma}$ should include also the photoconductivity. If, for simplicity, we shall assume that $\hat{\sigma}$ is a scalar, we can then write down $\sigma=\sigma_0+fI$. The dependence of the blocking field on the illumination intensity thus saturates for $I>\sigma_0 f^{-1}$.

The existence of a field associated with the photogalvanic effect gives rise to an additional contribution to the free energy of a ferroelectric δF, where $d\delta F=\mathbf{E}d\mathbf{P}$, which—in accordance with Eqs. (1) and (2)—is in the form of an expansion in powers of P^2:

$$\delta F=-\frac{I}{(\sigma_0+fI)}\frac{1}{2}(\alpha+\beta\cos^2\theta)P^2+O(P^4). \tag{3}$$

Renormalization of the coefficients of the expansion of F, given by Eq. (3), describes completely the influence of the photogalvanic effect on a phase transition. For example, in accordance with the standard thermodynamic theory of ferroelectric transitions,[8,9] Eq. (3) gives the shift of the Curie point:

$$\delta T_c=\frac{CI}{2\pi(\sigma_0+fI)}(\alpha+\beta\cos^2\theta); \tag{4}$$

here, C is the Curie–Weiss constant. Similarly,[8] we can use Eq. (3) to describe other photoferroelectric effects such as the change in the sponteneous polarization, thermal hysteresis, specific heat discontinuity, etc. The strong dependence of (3) on the characteristics of light thus provides additional opportunities for controlling the ferroelectric properties of crystals.

3. We shall now estimate the coefficients in the expansion of δF. Assuming that in Eq. (3) we have $\beta\lesssim\alpha$, we find that under saturation conditions

$$\delta F^{(2)}\approx\alpha P^2/2f. \tag{5}$$

The quantity α/f, which—according to Eqs. (1) and (2)—is the coefficient of proportionality between the field **E** and the polarization **P**, can be deduced from the experimental results[1,7] as follows:

$$\alpha/f\approx(10^{-3}-10^{-4}).$$

For typical parameters of a crystal, this estimate is in agreement with the results of a theoretical analysis of the photogalvanic effect,[3,4] which predicts

$$\alpha/f\propto v_0\tau_{ph}/\mu P_0\tau. \tag{6}$$

Here, v_0 is the velocity of electrons photoexcited to the conduction band; τ is the lifetime and τ_{ph} is the time between collisions with phonons; μ is the mobility; $P_0 = ea^{-2}$; a is the size of a unit cell.

The other terms in the expansion (3) can be estimated as follows[4]

$$\delta F^{(4)} \sim \frac{P^2}{P_0^2} \delta F^{(2)}.$$

We shall now estimate the shift of the Curie point. Substituting in Eq. (4) the value of $C = 10^{-5}$ °K (which is a typical value of the Curie–Weiss constant), we obtain

$$\delta T_c \gtrsim 2\,^\circ\mathrm{K}.$$

The sign of the shift is governed by the direction of $\mathbf{j}_{pg}$. In most experiments we have $\mathbf{j}_{pg} \uparrow\downarrow \mathbf{P}$, i.e., it agrees with the direction of the current associated with the photoexcitation of electrons.[3,4] Under these conditions illumination of a crystal lowers the ferroelectric transition temperature.

The estimates obtained indicate that the contribution of the photogalvanic effect to the free energy may be considerable, together with the corrections $\delta\bar{F}$ due to the filling of trapping levels by photoelectrons.[8] In this connection we must mention that the photogalvanic effect is in no way related to the presence of impurity levels; it exists and can have a large value even in pure crystals.[6]

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1) This is supported directly by the experimental evidence.[6]

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Characteristics of the antiferromagnetic resonance spectrum of $RbMnCl_3$

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An investigation was made of the low-frequency branch of antiferromagnetic resonance (AFMR) in $RbMnCl_3$ single crystals ($T_N = 94.6$ °K) with hexagonal structure at room temperature. The measurements were carried out in the frequency range $\nu = 16$–75 GHz applying magnetic fields up to 45 kOe at temperatures of $T = 1.2$–4.2 °K. Three resonance absorption lines, $\Delta H = 100$–300 Oe wide, were observed; the dependences of the positions of these lines on the angle between the static magnetic field H and the binary axis, on the one hand, and the basal plane, on the other (angles φ and θ), were found to be described by an empirical formula (6), given below. The value $H = 6.6 \pm 0.2$ kOe was in agreement with the spin-flopping field obtained from the static measurements [A.N. Bazhan, N.V. Fedoseeva, and S. V. Petrov. Abstracts of Papers presented at the Nineteenth All-Union Conf. on Physics of Low Temperatures, September, 1976, Institute of Solid State and Semiconductors, Academy of Sciences of the Belorussian SSR, Minsk, p. 599]; $H_\Delta = [(14 \pm 1)/T]^{1/2}$ kOe was the gap due to the hyperfine interaction. The AFMR spectrum of a hexagonal antiferromagnet was calculated. This spectrum did not agree with the experimental dependence $\nu(H)$ for $RbMnCl_3$.

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X-ray structure investigations[1,2] of rubidium trichloromanganate, carried out at room temperature, have shown that $RbMnCl_3$ has the barium titanate structure (space group D_{6h}^4) with the lattice parameters $a = 7.11 \pm 0.01$ Å and $c = 17.65 \pm 0.01$ Å. The Mn^{2+} ions occupy inequivalent positions: one-third of them are located in the octahedra of chlorine ions, connected by vertices to other octahedra, and the other two-thirds are at octahedra joined by faces. Neutron-diffraction investigations, carried out by Melamud *et al.*[2] in a wide temperature range from 4.2 to 300 °K, demonstrate that the magnetic and chemical unit cells are identical and that the magnetic structure is a set of ferromagnetic layers of Mn atoms, which are antiferromagnetically coupled. The Néel temperature of $RbMnCl_3$ is 94.6 °K.[3] According to Turov,[4] antiferromagnets with the $6_z^- 2_d^+$ structure cannot exhibit weak ferromagnetism of the kind associated with second-order invar-