Thermopolarization effect in an incommensurate phase of a crystal

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An anomalous thermopolarization effect has been observed in the incommensurate phase of the ferroelectric Rb_2ZnCl_4. Specifically, the dielectric polarization induced by a temperature gradient has a nontrivial temperature dependence and does not vanish when the gradient is reduced to zero. The relationship between the anomalies in this effect and features of other physical properties of incommensurate phases is discussed.

The "thermopolarization effect" is the appearance of a dielectric polarization P proportional to a temperature gradient $\partial T/\partial x$ in a continuous medium:

$$P_i = b_{ij}\partial T/\partial x_j, \tag{1}$$

where $b_{ij} = b_{ij}^{(\mathrm{T})} + b_{ij}^{(\mathrm{K})}$; $b_{ij}^{(\mathrm{T})}$ is the thermodynamic component of the effect, and $b_{ij}^{(\mathrm{K})}$ is the kinetic component.[1,2] The first component is the result of the appearance, because of the nonuniform temperature distribution, of a strain gradient $\partial u_{kl}/\partial x_j = \alpha_{kl}\partial T/\partial x_j$ (α_{kl} is the thermal-expansion tensor). This gradient in turn induces a polarization $P_i = \gamma_{ijkl}\partial u_{kl}/\partial x_j$ (this is a flexoelectric effect). The component $b_{ij}^{(\mathrm{T})}$ in (1) is then given by

$$b_{ij}^{(\mathrm{T})} = \gamma_{ijkl}\alpha_{kl}. \tag{2}$$

Taking into account the invariants $\epsilon_{ii}^{-1}P_i^2$ and $r_{ijkl}P_i\partial u_{kl}/\partial x_j$ in the free-energy density, we easily see that we have $\gamma_{ijkl} = (\epsilon_{ii})r_{ijkl}$ and that (2) becomes

$$b_{ij}^{(\mathrm{T})} = (\epsilon_{ii})r_{ijkl}\alpha_{kl}. \tag{3}$$

Here (ϵ_{ii}) is the principal value of the dielectric tensor ϵ_{ij} along the X_i axis.

The kinetic component of the effect arises because of a phonon mechanism for the appearance of a polarization. The coefficient $b_{ij}^{(\mathrm{K})}$, like $b_{ij}^{(\mathrm{T})}$, is proportional to ϵ (Ref. 1), so we would expect the largest effect in ferroelectrics.

The effect has been observed experimentally by Kholkin *et al.*,[2] who found b_{ij} to be close in order of magnitude to the theoretical predictions in (1)–(3) (Ref. 1). Strukov *et al.*[3] have studied the effect near the ferroelectric phase transition.

In this letter we are reporting the observation of some qualitatively new aspects of the thermopolarization effect, which stem from the particular physical properties of an incommensurate phase of a ferroelectric.

We studied the crystal Rb_2ZnCl_4 (of space group *Pmcn*), which has structural phase transitions at $T_i \simeq 300$ and $T_c \simeq 190$ K. The intermediate phase is incommensurate. It is modulated along the c axis (X_3). The low-temperature phase is a polar phase, with a spontaneous polarization along the b (X_2) axis (this is an extrinsic ferroelectric, of space group $Pn2_1a$; Ref. 4).

The crystal samples were small bars with sides of $3.5\times3.2\times3.8$ mm, oriented along the a, b, and c crystallographic axes, respectively. Electrodes were applied with a silver paste to the faces perpendicular to the b axis (X_2). The polarization was measured by an electrometer method. An optical vacuum cryostat was used. A temperature gradient $\sim$40 K/cm was set up along the X_2 axis by an IR source and was monitored by two thermocouples on faces of the sample. One of these faces remained at a constant temperature, by virtue of the good thermal contact with the copper substrate. The other face, whose electrode was grounded, was subjected to a heat flux. The temperatures at the faces were regulated within 0.15 K. The measurements were carried out after the crystal had been cooled to the temperature of interest.

Figure 1 shows the temperature dependence of the polarization P_2 which arises at $\partial T/\partial x_2 = 40$ K/cm, along with the thermal polarization coefficient b_{22}. In the initial, uniform phase ($T > T_i$), the value of P_2 (and that of b_{22}) is essentially independent of T. A dependence arises only in the incommensurate phase ($T_c < T < T_i$); P_2 increases sharply toward the point of the transition to the commensurate polar phase, T_c. In the

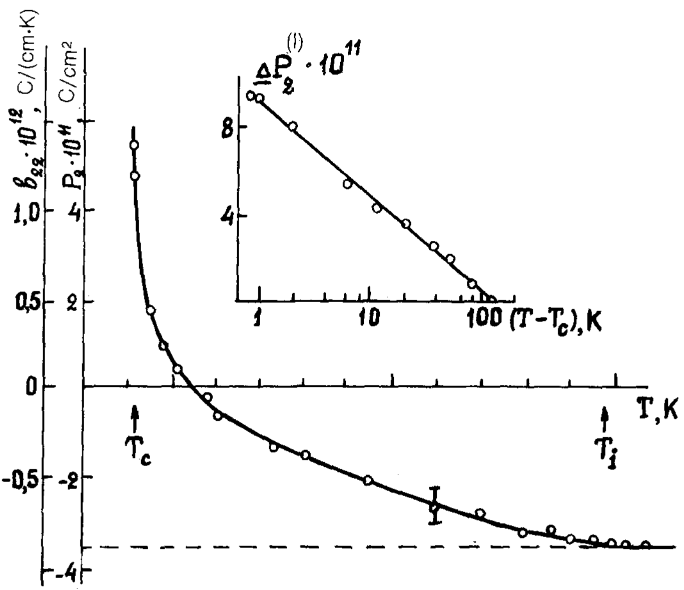

FIG. 1. Temperature dependence of the thermopolarization effect in the incommensurate phase of the Rb_2ZnCl_4 crystal. P_2—Polarization at $\partial T/\partial x_2 = 40$ K/cm; b_{22}—thermopolarization coefficient. The inset shows the increment in the polarization, $\Delta P_2^{(I)}$, in the incommensurate phase.

crystal samples studied, a change in the sign of $\partial T/\partial x_2$ was accompanied by a change in the sign of P_2, in agreement with Eq. (1). At $\partial T/\partial x_2 = 0$, a uniform change in the temperature of the sample did not give rise to P_2 (the ordinary pyroelectric effect did not occur). In other words, the observed change in P_2 is the result of the thermopolarization effect alone. The value of b_{22} is close in order of magnitude to the data of Ref. 2 and to estimates from (3). Measurements were not carried out in the polar phase ($T < T_c$), because the effect was masked there by the ordinary pyroelectric effect.

We can distinguish two new aspects of the effect, which were not present in Refs. 2 and 3. First, the additional temperature-dependent component in the effect, due to the incommensurate phase, $\Delta P_2^{(I)}$ (see the inset in Fig. 1), has the sign opposite that of the effect in the uniform phase. As a result, P_2 (b_{22}) crosses zero at $T \simeq 205$ K. The second new feature is that the dependence of P_2 on $\partial T/\partial x_2$ is a hysteresis loop, which is more obvious at temperatures close to T_c. The hysteresis has a residual P_2 (Fig. 2). A temperature gradient can thus send a crystal sample in the incommensurate phase into a state with a nonzero polarization. This new state is fairly stable; the time scale of the relaxation to the previous state is ~ 1 h. This time increases rapidly as $T \to T_c$.

Let us take a more detailed look at the results of these measurements. The thermal strain u_{ii} and $\alpha_{ii} = \partial u_{ii}/\partial T$ in the incommensurate phase should have increments $\Delta u_{ii}^{(\mathrm{I})}$ and $\Delta \alpha_{ii}^{(\mathrm{I})}$, $T < T_i$ corresponding to the amplitude of the order parameter ρ ($\rho = 0$ at $T \geqslant T_i$, and $\rho \neq 0$ at $T < T_i$): $u_{ii} = u_{ii}^0 + \Delta u_{ii}^{(\mathrm{I})}$, $\alpha_{ii} = \alpha_{ii}^0 + \Delta \alpha_{ii}^{(\mathrm{I})}$ (u_{ii}^0 and α_{ii}^0 are the values at $\rho = 0$). Since the free energy of this crystal[4] includes the invariants $c_{iijj} u_{ii} u_{jj} + a^{(i)} u_{ii} \rho^2$ ($i,j = 1,2,3$), these increments should be of the type $\Delta u_{ii}^{(\mathrm{I})} = A^{(i)} \rho^2$ and $\Delta \alpha_{ii}^{(\mathrm{I})} = A^{(i)} d\rho^2/dT$, where the constants $A^{(i)}$ are expressed in terms of the elastic moduli c_{iijj} and the constants $a^{(i)}$. The signs of $\Delta u_{ii}^{(\mathrm{I})}$ and $\Delta \alpha_{ii}^{(\mathrm{I})}$ are deter-

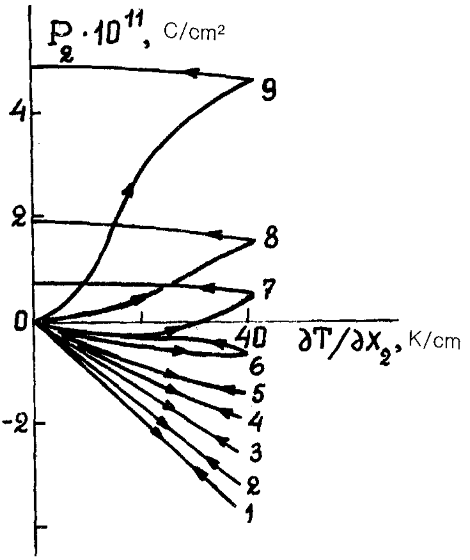

FIG. 2. The polarization P_2 versus the temperature gradient $\partial T/\partial x_2$ in the region of the incommensurate phase of the Rb_2ZnCl_4 crystal at various temperatures: 1—302 K; 2—295; 3—270; 4—245; 5—228; 6—213; 7—202; 8—197; 9—192 K.

mined by the signs of $A^{(i)}$ (or $a^{(i)}$), which are generally arbitrary ($d\rho^2/dT<0$: Ref. 4). For this particular crystal we have $\alpha_{11}^0>0$, $\Delta\alpha_{11}^{(I)}>0$, $\alpha_{22}^0>0$, $\Delta\alpha_{22}^{(I)}>0$, $\alpha_{33}^0>0$, but $\Delta\alpha_{33}^{(I)}<0$. In other words, we have $A^{(1)}<0$ and $A^{(2)}<0$, but $A^{(3)}>0$. Near T_c, the increment $\Delta\alpha_{33}^{(I)}$ increases sharply in absolute value, so $\alpha_{33}=\alpha_{33}^0+\Delta\alpha_{33}^{(I)}$ goes negative.[4] According to Eqs. (1) and (3), the quantities $P_2=(\gamma_{2211}\alpha_{11}+\gamma_{2222}\alpha_{22}+\gamma_{2233}\alpha_{33})\partial T/\partial x_2$ and $b_{22}^{(T)}=(\epsilon_{22})(r_{2211}\alpha_{11}+\mathrm{d}r_{2222}\alpha_{22}+r_{2233}\alpha_{33})$, which have a temperature dependence $\epsilon d\rho^2/dT$, should therefore change sign (as in Figs. 1 and 2) if the (negative) third term in parentheses is larger in absolute value than the sum of the first two terms. It also follows from a comparison of the values of α_{11}, α_{22}, and α_{33} in Ref. 4 that a necessary condition here is that γ_{2233} (r_{2233}) be larger than γ_{2211} (r_{2211}) and γ_{2222} (r_{2222}). Unfortunately, there are no experimental data on the constants γ_{ijkl} (or r_{ijkl}). There is the possibility, however, that the necessary conditions on these coefficients are satisfied and that the change in the sign of P_2 (or b_{22}), as for α_{33}, results from a nonlinear dependence of the thermal strain on the order parameter, which is characteristic of extrinsic ferroelectrics.

A distinctive feature of the incommensurate phase of a crystal is a set of metastable states, which result from a pinning of the incommensurate superstructure at various inhomogeneities in the crystal.[4] Each state is characterized by certain thermodynamic properties, in particular, a certain strain. A transition from one state to another can be induced by various external agents. After the agent is turned off, the crystal remains "frozen" in its new state (there is a structural memory). The hysteresis on the plot of P_2 versus $\partial T/\partial x_2$, with a residual P_2 (Fig. 2), is apparently a manifestation of this particular feature of the incommensurate phase, but in the case of a nonuniform external force. The gradient of T induces a nonuniform strain distribution, which persists after the gradient of T is "turned off," along with the polarization P_2 which arises because of the flexoelectric effect. As in the case of a uniform external agent, the effect is more obvious at temperatures close to T_c. An uncontrollable gradient of T may be a reason for the observation of a spontaneous polarization in the incommensurate phase. Such a polarization is forbidden by the symmetry of the infinite uniform crystal.

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