Theory of phase transitions into inhomogeneous states in organic ferroelectrics in an external electric field

E. V. Chenskiĭ and V. V. Tarasenko

Institute of Radio Engineering and Electronics, USSR Academy of Sciences

(Submitted 16 February 1982)
Zh. Eksp. Teor. Fiz **83**, 1089–1099 (September 1982)

Phase transitions are considered in a ferroelectric located in an external electric field near the Curie temperature. It is shown that states of three types are possible: homogeneous, stripe, and hexagonal domain structures. The spectra of small oscillations in the stability region of each of these states are determined. In the absence of a field, a ferroelectric can go over from the homogeneous state only into a stripe domain structure via a second-order phase transition. In an external electric field, a ferroelectric goes over first from the homogeneous state into a state with a hexagonal-domain lattice via a first-order phase transition. With further lowering of the temperature, the hexagonal structure turns into a stripe one.

PACS numbers: 77.80.Bh, 77.80.Dj

INTRODUCTION

It is well known that ferroelectrics break up into domains below the phase-transition point. This is due to the need for decreasing the energy of the polarizing field, and periodically disposed regions (domains) with oppositely directed spontaneous polarization are produced as a result. A decrease in the period of the domain structure lowers the energy of the depolarizing field and increases simultaneously the energy of the polarization inhomogeneity, so that there exists a definite period that minimizes the electric-field energy and the gradient energy.

Far from the phase-transition temperature, the depolarizing field is localized near the crystal surface, and the transition layers between the domains are thin domain walls. At the center of the domains the electric field is close to zero, and the polarization is close to spontaneous. In this case it is easy to calculate[1,2] the two indicated energies and find the period of the domain structure. When the phase transition temperature is approached, the depolarizing field penetrates into the interior of the crystal. The polarization at the center of the domain begins to depend strongly on this field, and the field itself depends in turn on the polarization at the center of the domain. The calculation of the domain structure in this case must therefore be made self-consistent. This was already done by one of us.[3] The shift of the phase-transition temperature, the temperature dependence of the polarization, and the singularities of the heat capacity during the phase transition were all obtained.

It must be noted that an exact calculation of the domain-structure parameters is a very complicated problem because of the nonlinearity of the obtained equations. Near the phase-transition temperature, however, when the amplitude of the resultant polarization is still small, there exists a small parameter proportional to the square of the polarization amplitude and making it possible to solve consistently the problem posed with arbitrary degree of accuracy with respect to the small parameter. In the absence of an external field, such a problem was first solved in Refs. 4 and 5 for ferromagnetic crystals. It was shown, in particular, that within the framework of the Landau theory of phase transitions a transition from a homogeneous into an inhomogeneous state is of second order for bounded crystal of arbitrary shape. Exact analytic expressions were obtained for all the thermodynamic quantities near the phase-transition temperature.

It is known that in infinite ferroelectric (ferromagnetic) crystals there is no temperature phase transition in an external electric (magnetic) field, i.e., the Curie point is an isolated singular point on the temperature-field phase diagram. In bounded crystals, however, a possibility appears for the existence of stable inhomogeneous states and of phase transitions, in an external field, from a homogeneous to an inhomogeneous state, as well as between different inhomogeneous states.

One of us has considered also phase transitions from homogeneous states in a stripe domain structure in a ferromagnet in an external magnetic field.[6]

In this paper we examine the influence of an external electric field on a phase transition in a ferroelectric planced in a capacitor with gaps.

1. STABILITY OF HOMOGENEOUS STATE OF A FERROELECTRIC IN A CAPACITOR

We consider a uniaxial ferroelectric crystal in the form of a plane-parallel plate of thickness l, placed in capacitor with metallic electrodes to which a voltage U is applied. We assume that gaps of thickness $d/2$ are present between the electrodes and the ferroelectric. Let the ferroelectric axis be perpendicular to the plate surface along the z axis.

We can then write for the free energy of the system

$$F=V^{-1}\left\{\int dv[{}^1/_2\varkappa(\nabla_\perp P_z)^2+{}^1/_2\varkappa_1(\nabla_z P_z)^2-{}^1/_2\alpha P_z{}^2+{}^1/_4\beta P_z{}^4 +{}^1/_2\alpha_\perp P_\perp^2+E^2/8\pi]+\sum_{i=1}^{2}\int_{S_i} dS_i\sigma_i U_i\right\}, \quad (1)$$

where $\alpha=(T_0-T)\alpha';\beta>0$, $\mathbf{P}$ is the polarization and $\varkappa$ and $\varkappa_1$ are parameters for the gradient energy, $\alpha_\perp{}^{-1}$ is the polarizability in the plane of the plate, $\mathbf{E}$ is the electric field strength, eU_i and σ_i are respectively the chemical potential

 0038-5646/82/090618-06$04.00 © 1983 American Institute of Physics

and the surface charge density on the i-th electrode, e is the electron charge, and V is the volume of the ferroelectric. The integration in the first term of (1) is over the volumes of the ferroelectric and the gaps. In the expression for the gradient energy we have confined ourselves to terms containing P_z, so that the longitudinal susceptibilty is considerably larger than the transverse near the phase-transition temperature, and consequently $|\mathbf{P}_z| \gg |\mathbf{P}_\perp|$.

The equations of state that follow from (1) are

$$E_{zf} = -\varkappa \nabla_\perp^2 P_z - \varkappa_1 \nabla_z^2 P_z - \alpha P_z + \beta P_z^3, \quad \mathbf{E}_{\perp f} = \alpha_\perp \mathbf{P}_\perp. \tag{2}$$

Here E_f is the electric field intensity in the ferroelectric.

The distribution of the polarization and of the electric field should satisfy the Maxwell equations

$$\operatorname{div} \mathbf{D} = 0, \quad \mathbf{E} = -\nabla \varphi, \tag{3}$$

where $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ is the induction and φ is the potential. From (2) and (3) we obtain an expression for P_z:

$$4\pi \nabla_z^2 P_z/\varepsilon_\perp = (\nabla_\perp^2 + \varepsilon_\perp^{-1}\nabla_z^2)(\varkappa \nabla_\perp^2 P_z + \varkappa_1 \nabla_z^2 P_z + \alpha P_z - \beta P_z^3), \tag{4}$$

where $\varepsilon_\perp$ is the dielectric constant in the plane of the plate. It can be shown that when $\alpha \ll 4\pi$ (this is always the case for ferroelectrics), we can neglect the derivatives with respect to z in the right-hand side of (4), and we arrive at the following equation for P_z:

$$4\pi \varepsilon_\perp^{-1} \nabla_z^2 P_z = \nabla_\perp^2 (\varkappa \nabla_\perp^2 P_z + \alpha P_z - \beta P_z^3) \tag{5}$$

with the boundary conditions

$$E_{zd}\left(\frac{l}{2}\right) = D_{zf}\left(\frac{l}{2}\right), \quad \mathbf{E}_{\perp d}\left(\frac{l}{2}\right) = \mathbf{E}_{\perp f}\left(\frac{l}{2}\right), \quad \mathbf{E}_{\perp d}\left(\pm\frac{l+d}{2}\right) = 0, \tag{6}$$

where $\mathbf{E}_d$ is the electric field in the gap.

Using Eqs. (2) and (3) we transform (1) into

$$F = V^{-1}\left[-\frac{\beta}{4}\int dv P_z^4 + \sum_{i=1}^{z}\int dS_i \sigma_i (\varphi_i + U_i)\right]. \tag{7}$$

The free energy (7) for a homogeneously polarized ferroelectric ($P = P_0$) takes the form

$$F_0 = -{}^1/_4 \beta P_0^4 - P_0[E_0 - 2\pi d P_0/l + {}^1/_2(\alpha P_0 - \beta P_0^3)]. \tag{8}$$

We have put here $E_0 = U/l$; $U = U_1 - U_2$. Minimizing F_0 with respect to P_0, we obtain an equation for P_0:

$$E_0 = (4\pi d/l - \alpha) P_0 + \beta P_0^3. \tag{9}$$

We consider now the stability of the homogeneous state of the ferroelectric. We assume that a certain homogeneous polarization P_0 is present in the ferroelectric, and we introduce a small periodic inhomogeneous increment $P_1(x,z)$:

$$P_1(x, z) = P_0 + P_1(z)\cos kx. \tag{10}$$

Substituting (10) in the equation (5) for the polarization, we obtain in equation for $P_1(z)$

$$4\pi P_1''(z) + \varepsilon_\perp k^2 (\tilde{\alpha} - \varkappa k^2) P_1(z) = 0, \tag{11}$$

where $\tilde{\alpha} = \alpha - 3\beta P_0^2$. We seek the solution of (11) in the form $P_1(z) = P_1 \cos qz$, after which we obtain an equation that connects $\tilde{\alpha}$, q, and k:

$$\tilde{\alpha} = \varkappa k^2 + 4\pi q^2/\varepsilon_\perp k^2. \tag{12}$$

In addition, the solution (10) must satisfy the boundary conditions (6). To this end, we write out the expressions for the intensities of the inhomogeneous part of the electric field $\mathbf{E}_f^{(1)}$ in the ferroelectric:

$$E_{zf}^{(1)} = -(\tilde{\alpha} - \varkappa k^2) P_1 \cos qz \cos kx,$$

$$E_{xf}^{(1)} = \frac{k}{q}(\tilde{\alpha} - \varkappa k^2) P_1 \sin qz \sin kx$$

and $\mathbf{E}_d^{(1)}$ in the gap:

$$E_{zd}^{(1)} = [a_1 e^{-k(z-l/2)} + a_2 e^{k(z-l/2)}]\cos kx,$$

$$E_{xd}^{(1)} = [a_1 e^{-k(z-l/2)} - a_2 e^{k(z-l/2)}]\sin kx.$$

We then obtain from the boundary condition an equation that relates q and k:

$$q \operatorname{tg}(ql/2) = \varepsilon_\perp k \operatorname{th}(kd/2). \tag{13}$$

The system (12) and (13) can be easily solved in two limiting cases, $kd \ll 1$ and $kd \gg 1$. Expressing k in terms of q from (13) and substituting in (12), we obtain

$$\tilde{\alpha} = \frac{4\pi d}{l} y(\operatorname{ctg} y + \lambda^2 \operatorname{tg} y), \quad kd \ll 1,$$

$$\tilde{\alpha} = 4\pi\varepsilon_\perp(\operatorname{ctg}^2 y + \gamma^2 y^2 \operatorname{tg}^2 y), \quad kd \gg 1, \tag{14}$$

where $y = ql/2; \lambda^2 = x/\pi\varepsilon_\perp d^2; \gamma^2 = \varkappa/\pi\varepsilon_\perp {}^2 l^2 \ll 1$. The value of q at which the homogeneous state of the ferroelectric first loses stability is determined from the condition that $\tilde{\alpha}(\partial\tilde{\alpha}/\partial y = 0)$ be a minimum. Minimizing expressions (14) with respect to y, we obtain for y the equations

$$(2y - \sin 2y)\cos^2 y = \lambda^2(2y + \sin 2y)\sin^2 y, \quad kd \ll 1, \tag{15}$$

$$2\gamma^2 y(2y + \sin 2y)\sin^4 y = \cos^4 y, \quad kd \gg 1. \tag{16}$$

If $\lambda^2 > 1/3$ ($d < d_f \equiv (3\varkappa/\pi\varepsilon_\perp)^{1/2}$), Eq. (15) has a single root $y = 0$, corresponding to the homogeneous state ($q = k = 0$). A second-order phase transition takes place then in a short-circuited crystal at a temperature at which $\alpha = \alpha_f^{(0)} \equiv 4\pi d/l$, and there is no phase transition at all at $U \neq 0$. At $d > d_f$ Eq. (15) acquires, besides the root $y = 0$, a second solution $y \neq 0$, which corresponds to a transition into an inhomogeneous state ($k, q \neq 0$). Thus, for $0 < d - d_f \ll d_f$ we obtain

$$\tilde{\alpha} = \alpha_f^{(0)}\left[1 - \frac{5}{16}\left(1 - \frac{d_f^2}{d^2}\right)^2\right],$$

$$ql = \left[\frac{15}{2}\left(1 - \frac{d_f^2}{d^2}\right)\right]^{1/2}, \tag{17}$$

$$k = \left[\frac{15}{2\varepsilon_\perp dl}\left(1 - \frac{d_f^2}{d^2}\right)\right]^{1/2}.$$

It can be seen from (17) that at $d > d_f$ the transition to the inhomogeneous state takes place at $\tilde{\alpha} = \alpha_f < \alpha_f^{(0)}$. It follows therefore that the inhomogeneous state becomes favored over the inhomogeneous. We note that $d_c = (3\varkappa/\pi\varepsilon_\perp)^{1/2} \sim 10^{-8}$ cm, so that in a real situation the gap width $d \gg d_f$. This is exactly the case we shall consider hereafter. At $d \ll d_f$, as follows from (15) and (16),

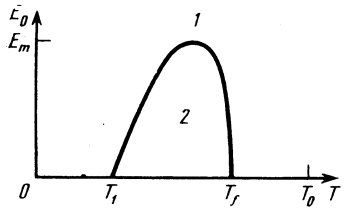

FIG. 1. Stability region of homogeneous state on the (E_0, T) phase diagram. The value of T_f corresponds to $\alpha = \alpha_f$; $T_1 - \alpha = 6\pi d/l - \alpha_f/2$; 1) homogeneous state, 2) inhomogeneous state.

$$ql \approx \pi, \quad k = k_f \equiv \left(\frac{4\pi^3}{\varepsilon_\perp \varkappa l^2}\right)^{1/4}, \quad \tilde{\alpha} = \alpha_f \equiv 4\left(\frac{\pi^3 \varkappa}{\varepsilon_\perp l^2}\right)^{1/2}. \tag{18}$$

Solving Eq. (9) simultaneously with the equation $\tilde{\alpha} = \alpha_f$ we obtain on the (E_0, T) phase diagram the line on which the homogeneous state loses stability:

$$E_0 = \frac{2}{3\sqrt{3}\beta}(\alpha - \alpha_f)^{1/2}\left(\frac{6\pi d}{l} - \frac{\alpha_f}{2} - \alpha\right), \tag{19}$$

which is shown in Fig. 1. From (19) it follows that at

$$E_0 > E_m \equiv \frac{1}{3}\left(\frac{2}{3\beta}\right)^{1/2}\left(\frac{4\pi d}{l} - \alpha_f\right)^{3/2}$$

the homogeneous polarization is stable at all temperatures. At $E_0 < E_m$, a phase transition into the inhomogeneous state is possible. It is interesting that in a zero field the homogeneous state is stable not only in the paraphase $(\alpha < \alpha_f)$, but also in the temperature region $\alpha > 6\pi d/l - \alpha_f/2$. This is well known experimental fact. If the crystal is polarized in a field and cooled to temperatures low enough compared with the Curie temperature, the single-domain state remains stable also in a short-circuited crystal. When the crystal is heated it breaks up first into domains, and only then does the polarization vanish at the Curie point.

2. INHOMOGENEOUS STATES OF THE FERROELECTRIC

In the preceding section, in the analysis of the stability of the homogeneous state, we have assumed the inhomogeneous addition to be infinitely small. To describe the domain states we must recognize that the amplitude of the inhomogeneous part is finite. The distribution of the polarization in a plate with a periodic domain structure is described in the general case by two reciprocal-lattice vectors, $\mathbf{k}_1$ and $\mathbf{k}_2$. The polarization can be expressed in terms of a double Fourier series with z-dependent coefficients:

$$P_z(\mathbf{r}, z) = \sum_{m,n=-\infty}^{+\infty} A_{mn}(z) \exp[i(m\mathbf{k}_1 + n\mathbf{k}_2)\mathbf{r}]. \tag{20}$$

This distribution can have twofold, or sixfold symmetry axes. These axes correspond respectively to a stripe domain structure, a quadratic domain lattice, and to a hexagonal domain lattice.

Near the phase-transition temperature we can confine ourselves in expression (20) for the polarization to first order in the amplitude of the domain structure

$$P_z(\mathbf{r}, z) = P_0 + {}^1/_2 P_1(z) \sum_{j=1}^{n} e^{i\mathbf{k}_j \mathbf{r}},$$

where the vectors $\mathbf{k}_j$ form a Wigner star, and n is equal to the order of the lattice symmetry. The free energy connected with the inhomogeneous part of the polarization is given by

$$F_1 = -(\beta/4l)\int_{-l/2}^{+l/2} dz f(z), \tag{21}$$

where

$$f(z) = {}^3/_8 P_1^4(z) \quad \text{for} \quad n=2,$$
$$f(z) = {}^9/_4 P_1^4(z) \quad \text{for} \quad n=4,$$
$$f(z) = 3P_0 P_1^3(z) + {}^{45}/_8 P_1^4(z) \quad \text{for} \quad n=6.$$

A. Stripe structure

For a stripe domain structure Eq. (5) takes the form

$$4\pi P_1''(z) + \varepsilon_\perp k^2(\tilde{\alpha} - \varkappa k^2) P_1(z) - \frac{3}{4}\beta\varepsilon_\perp k^2 P_1^3(z) = 0. \tag{22}$$

If we seek the solution in the form of a series

$$P_1(z) = \rho + a\cos qz + b\cos 2qz + c\cos 3qz + \ldots, \tag{23}$$

then the principal term in (23), if the conditions $\beta a^2/\alpha_f$ and $\beta P^2 0/\alpha_f \ll 1$ are satisfied, is $a\cos qz$. The remaining terms in (23) are small to the extent that the parameters indicated above are small. Thus, for example $c/a = -3\beta a^2/64\alpha_f$.

Substituting the solution (23) in Eq. (22) and recognizing that it follows from the boundary conditions it follows that $ql \approx \pi$, we obtain an equation for the amplitude a:

$${}^9/_{16}\beta a^2 = \tilde{\alpha} - \varkappa k^2 - \varkappa k_f^4/k^2. \tag{24}$$

The free energy (21) then becomes equal to

$$F_1 = -(9/256)\beta a^4. \tag{25}$$

The free energy (25) is a minimum at the maximum a^2, reached when $k = k_f$ [see (18)]. From (24) we then obtain (Fig. 2)

$${}^9/_{16}\beta a^2 = \tilde{\alpha} - \alpha_f = \Delta\tilde{\alpha}. \tag{26}$$

An expression for α_f was obtained above. Substituting a^2 from (26) in (25) we obtain the free-energy increment due to the inhomogeneous part of the polarization:

$$F_1 = -(\Delta\tilde{\alpha})^2/9\beta. \tag{27}$$

It follows from (27) that the jump of the heat capacity in the phase transition from the homogeneous state to the stripe structure is equal to

$$C = T_f \alpha'^2/9\beta = {}^4/_9 C_0,$$

where C_0 is the heat-capacity jump in an infinite crystal.

B. Hexagonal lattice

For the state with hexagonal lattice Eq. (5) takes the form

$$\frac{4\pi}{\varepsilon_\perp k^2} P_1''(z) + (\tilde{\alpha} - \varkappa k^2) P_1(z) - 3\beta P_0 P_1^2(z) - \frac{15}{4}\beta P_1^3(z) = 0. \tag{28}$$

We seek the solution of Eq. (28), just as for the stripe structure, in the form (23), after which we have the equation

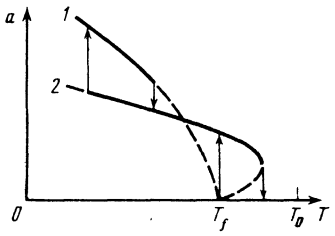

FIG. 2. Temperature dependence of the amplitude of a stripe (1) and hexagonal (2) domain structure. The dashed curves show the instability region, and the arrows show the points of transition from one state to another.

$$\frac{45}{16}\beta a^2=\tilde{\alpha}-\varkappa k^2-\frac{4\pi q^2}{\varepsilon_\perp k^2}. \tag{29}$$

It follows from the boundary condition $P_1(z=\pm l/2)=0$ that

$$ql\approx\pi+4\beta P_0 a/(\tilde{\alpha}-\varkappa k^2), \tag{30}$$

and from (29) we obtain the temperature dependence of the wave amplitude (see Fig. 2);

$$a=-\frac{64P_0}{45\pi}\left[1\pm\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{1/2}\right], \quad \alpha_0=\frac{256}{45\pi^2}\beta P_0^2. \tag{31}$$

The free energy for a hexagonal structure, as follows from (21), is

$$F_1=-\frac{\beta P_0}{\pi}a^3-\frac{135}{256}\beta a^4. \tag{32}$$

It follows from (31) and (32) that the hexagonal structure is produced via a first-order phase transition with temperature hysteresis. The domain structure sets in at $\Delta\tilde{\alpha}=0$ and vanishes at $\Delta\tilde{\alpha}=-a_0$. Comparing the free energies for the stripe and hexagonal structures we find that the thermodynamic phase transition from the stripe to the hexagonal structure occurs at

$$\Delta\tilde{\alpha}=(14+6\sqrt{6})\alpha_0\approx 16.54\beta P_0^2, \tag{33}$$

with the stripe structure favored when $\Delta\tilde{\alpha}<16.54\beta P^2{}_0$. From (32) it follows that the free energy of the hexagonal structure becomes comparable with that of the homogeneous state at

$$\Delta\tilde{\alpha}=-(2048/405\pi^2)\beta P_0^2=-{}^8/_9\alpha_0, \tag{34}$$

and the instability of the hexagonal structure, with transition into the homogeneous state, sets in at

$$\Delta\tilde{\alpha}=-\alpha_0. \tag{35}$$

The heat capacity of the system with hexagonal structure is

$$C=\frac{2}{15}\frac{T\alpha'^2}{\beta}\left[1+\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{-1/2}\right]. \tag{36}$$

It follows hence that when the stability-loss line is approached the heat capacity has a square-root divergence.

The susceptibility of the system is in this case

$$\chi=-\frac{\partial^2 F}{\partial E_0^2}=\chi_0\left[1+\frac{135\pi^2}{2048}\left(3-\frac{256}{45\pi^2}\right)^2\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{-1/2}\alpha_0\right], \tag{37}$$

where $\chi_0=l/4\pi d$. It can be seen from (37) that when the instability point is approached the susceptibility also has a square-root divergence.

3. OSCILLATION SPECTRUM OF DOMAIN STRUCTURE

In the preceding section we have considered static solutions for the polarization distributions in a stripe and hexagonal domain structure. The stability analysis for each structure is simplest to carry out by investigating the polarization-oscillation spectrum.

The equation of motion for the polarization can be written in the form

$$\mu\ddot{\mathbf{P}}=\mathbf{f}(\mathbf{P}), \tag{38}$$

where μ is a coefficient corresponding to the effective mass and $\mathbf{f}$ is the force that arises when the polarization deviates from the equilibrium position:

$$\mathbf{f}=-\delta F/\delta\mathbf{P}. \tag{39}$$

Using expression (1) for the free energy, we get from (38) and (39)

$$\mu\ddot{P}_z=E_{zf}-\varkappa\nabla_\perp{}^2P_z+\alpha P_z-\beta P_z{}^3, \quad \mu\ddot{\mathbf{P}}_\perp=\mathbf{E}_{\perp f}-\alpha_\perp\mathbf{P}_\perp \tag{40}$$

The equations of motion (40) and Maxwell's equations constitute a system that determines, together with the boundary conditions, the spectrum of the polarization oscillations. This system of equations can be reduced to single equation for ρ_z:

$$4\pi\nabla_z{}^2\rho_z-\varepsilon_\perp\nabla_\perp{}^2(\varkappa\nabla_\perp{}^2+\alpha-3\beta P_z{}^2+\mu\omega^2)\rho_z=0, \tag{41}$$

where ρ_z is the small deviation of P_z from the equilibrium position.

We consider first the spectrum of the stripe structure. The static distribution of the polarization is subject in this case to the relation [see (23) and (26)]

$$P_z(x,z)=P_0+P_1(z)\cos k_f x, \quad P_1(z)={}^4/_3(\Delta\tilde{\alpha}/\beta)^{1/2}\cos qz.$$

The term $3\beta P_z^2$ in (41) plays the role of a certain periodic potential for ρ_z with harmonics k_f and $2k_f$.

We seek the solution for ρ_z in the form[7]

$$\rho_z=e^{iQ_y y}\sum_{n=-\infty}^{\infty}e^{ik_n x}\Psi_n(z);$$
$$k_n=Q_x+nk_f, \quad |Q_x|\leq k_f/2. \tag{42}$$

Substituting the solution (42) in (41) and gathering terms with like harmonics, we obtain a system of equations for $\Psi_n(z)$:

$$\left[\tilde{\alpha}-\varkappa(k_n{}^2+Q_y{}^2)-\frac{3}{2}\beta P_1{}^2(z)+\mu\omega^2\right]\Psi_n(z)$$
$$+\frac{4\pi}{\varepsilon_\perp(k_n{}^2+Q_y{}^2)}\Psi_n{}''(z)$$
$$=3\beta P_0P_1(z)[\Psi_{n-1}(z)+\Psi_{n+1}(z)]$$
$$+\frac{3}{4}\beta P_1{}^2(z)[\Psi_{n-2}(z)+\Psi_{n+2}(z)]. \tag{43}$$

We seek the function $\Psi_n(z)$ in the form

$$\Psi_n(z)=a_n+b_n\cos qz+c_n\cos 2qz, \tag{44}$$

after which we obtain a system of equations for the coefficients a_n, b_n, and c_n:

$$\begin{aligned}
&[4\pi q^2/\varepsilon_\perp(k_n^2+Q_y^2)+\varkappa(k_n^2+Q_y^2)-\alpha_c+\Delta\tilde{\alpha}-\mu\omega^2]\\
&\quad\cdot\ +\Delta\tilde{\alpha}(b_{n-2}+b_{n+2})\\
&\quad +2P_0(\beta\Delta\tilde{\alpha})^{1/2}(2a_{n-1}+2a_{n+1}+c_{n-1}+c_{n+1})=0,\\
&\quad [\varkappa(k_n^2+Q_y^2)-\alpha_c+{}^1/_3\Delta\tilde{\alpha}-\mu\omega^2]a_n+{}^1/_3\Delta\tilde{\alpha}(2a_{n-2}\\
&\quad +2a_{n+2}+c_{n-2}+c_{n+2}+2c_n)+2P_0(\beta\Delta\tilde{\alpha})^{1/2}(b_{n-1}+b_{n+1})=0,\\
&\quad [16\pi q^2/\varepsilon_\perp(k_n^2+Q_y^2)+\varkappa(k_n^2+Q_y^2)-\alpha_c+{}^1/_3\Delta\tilde{\alpha}-\mu\omega^2]c_n\\
&+{}^2/_3\Delta\tilde{\alpha}(a_{n-2}+a_{n+2}+2a_n+c_{n-2}+c_{n+2})\\
&\quad +2P_0(\beta\Delta\tilde{\alpha})^{1/2}(b_{n-1}+b_{n+1})=0.
\end{aligned} \tag{45}$$

From the system (45) it follows that the frequency ω is a minimum when the vectors satisfy the condition $k_n^2+Q_y^2=k_f^2$. From this we find that at $Q\ll k_f$ the modes $n=\pm 1$ become strongly coupled, and at $Q\approx k_c^2$ ($Q_x=k_f/2$ and $Q_y=\sqrt{3}k_f/2$) the modes $n=0$ and $n=\pm 1$ become coupled. Solving the system of equations for the vectors indicated above, we obtain the frequency spectrum:

$$\left.\begin{aligned}\mu\omega_1^2&=2\Delta\tilde{\alpha}+4\varkappa Q_x^2\\ \mu\omega_2^2&=4\varkappa Q_x^2\end{aligned}\right\}\quad\text{for}\quad |Q_x|\ll k_f, \tag{46}$$

$$\mu\omega_{1,2}=\Delta\tilde{\alpha}\pm\frac{32\beta^{1/2}P_0}{3\pi}(\Delta\tilde{\alpha})^{1/2}\quad\text{for}\quad Q_x=\frac{k_c}{2},\quad Q_y=\frac{\sqrt{3}\,k_f}{2}. \tag{47}$$

It follows from (47) that the stripe structure is unstable with respect to a transition into a hexagonal structure at

$$\Delta\tilde{\alpha}=(1024/9\pi^2)\beta P_0^2=20\alpha_0. \tag{48}$$

The oscillation spectrum of the hexagonal structure should be found from Eq. (41) with a value of P_z

$$P_z(\mathbf{r},z)=P_0+P_1(z)[\cos\mathbf{k}_1\mathbf{r}+\cos\mathbf{k}_2\mathbf{r}+\cos(\mathbf{k}_1+\mathbf{k}_2)\mathbf{r}], \tag{49}$$

where $P_1(z)$ is determined from (23) and (31).

We seek the solution for ρ_z in the form

$$\begin{aligned}\rho_z&=\sum_{n,m}\exp(i\mathbf{k}_{nm}\mathbf{r})\Psi_{nm}(z),\\ \Psi_{nm}(z)&=a_{nm}+b_{nm}\cos qz+c_{nm}\cos 2qz,\end{aligned} \tag{50}$$

where $\mathbf{k}_{nm}=\mathbf{Q}+n\mathbf{k}_1+m\mathbf{k}_2$.

Near the center of the Brillouin zone ($Q\ll k_f$), the most strongly coupled modes Ψ_{nm} are those with the indices (10); ($\bar{1}0$); (01); ($0\bar{1}$); (11); ($\bar{1}\bar{1}$). Substituting the solution (50) in (41) and taking (49) into account, we obtain a system of homogeneous equations for the coefficients b_{nm}, which can be conveniently written in matrix form

$$\hat{D}\mathbf{b}=0. \tag{51}$$

The matrix $\hat{D}$ and the vector $\mathbf{b}$ are given by

$$\hat{D}=\begin{vmatrix}\Omega_{10}&1&2&2&2&2\\ 1&\Omega_{\bar{1}0}&2&2&2&2\\ 2&2&\Omega_{01}&1&2&2\\ 2&2&1&\Omega_{0\bar{1}}&2&2\\ 2&2&2&2&\Omega_{11}&1\\ 2&2&2&2&1&\Omega_{\bar{1}\bar{1}}\end{vmatrix},\qquad \mathbf{b}=\begin{vmatrix}b_{10}\\ b_{\bar{1}0}\\ b_{01}\\ b_{0\bar{1}}\\ b_{11}\\ b_{\bar{1}\bar{1}}\end{vmatrix}, \tag{52}$$

where

$$\Omega_{nm}=\frac{16\mu}{9\beta a^2}(\omega_{nm}^2-\omega^2),$$

$$\mu\omega_{nm}^2=-\tilde{\alpha}+\varkappa k_{nm}^2+\frac{4\pi q^2}{\varepsilon_\perp k_{nm}^2}+\frac{27}{8}\beta a^2,$$

and a is determined from Eq. (31).

From the condition that a nontrivial solution exist for the vector $\mathbf{b}$, we obtain the dispersion equations

$$\det\hat{D}=0, \tag{53}$$

from which we determine the connection between the quantities q, Q, and ω:

$$\Omega_i=\Omega\equiv\frac{16\mu}{9\beta a^2}(\omega_0^2-\omega^2),\quad i=1,2,\ldots,6. \tag{54}$$

Here

$$\begin{aligned}\mu\omega_0^2&=-\Delta\tilde{\alpha}+\frac{27}{8}\beta a^2+\frac{\alpha_f}{\pi}ql+2\varkappa Q^2,\\ \Omega_1&=-9-{}^3/_{16}\Delta^2,\quad \Omega_{2,3}=3\mp\Delta,\\ \Omega_4&=1-2\Delta,\quad \Omega_{5,6}=1+\Delta,\quad \Delta=-16\varkappa Q^2/9\beta a^2.\end{aligned}$$

Equation (53) is in fact the dispersion equation for an unbounded medium. The boundary conditions on the surface of the plate and on the electrodes lead to the equation

$$\sum_{i=1}^{6}\Psi_{nm}^{(i)}(z=\pm l/2)=0, \tag{55}$$

which yields an additional connection between ω and q. Defining $\varphi_i=(1-q_i l/\pi)$, we write down (55) in matrix form

$$\sum_{i=1}^{6}\hat{\Phi}^{(i)}\mathbf{b}^{(i)}=0, \tag{56}$$

where the matrix $\hat{\Phi}^{(i)}$ is of the form

$$\hat{\Phi}^{(i)}=\begin{vmatrix}\varphi_i&0&0&\lambda&\lambda&0\\ 0&\varphi_i&\lambda&0&0&\lambda\\ 0&\lambda&\varphi_i&0&\lambda&0\\ \lambda&0&0&\varphi_i&0&\lambda\\ \lambda&0&\lambda&0&\varphi_i&0\\ 0&\lambda&0&\lambda&0&\varphi_i\end{vmatrix},\qquad \lambda=\frac{8\beta P_0 a}{\pi\alpha_c},$$

and the quantities φ_i are defined by Eq. (54). From the condition that a nontrivial solution of (56) exist, we obtain six low-frequency branches for the polarization oscillations

$$\begin{aligned}\mu\omega_1^2&=2\alpha_0\left[1+\frac{\Delta\tilde{\alpha}}{\alpha_0}+\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{1/2}\right]+2\varkappa Q^2,\\ \mu\omega_2^2&=\frac{16}{5}\alpha_0\left[1-\frac{\Delta\tilde{\alpha}}{8\alpha_0}+\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{1/2}\right]+\varkappa Q^2,\\ \mu\omega_3^2&=\mu\omega_2^2+2\varkappa Q^2,\quad \mu\omega_4^2=6\alpha_0\left[1+\left(1+\frac{\Delta\tilde{\alpha}}{\alpha_0}\right)^{1/2}\right]+2\varkappa Q^2,\\ \mu\omega_5^2&=3\varkappa Q^2,\quad \mu\omega_6^2=\varkappa Q^2.\end{aligned} \tag{57}$$

The remaining branches of the spectrum have high frequencies and are separated in energy from the considered low-frequency branches by a gap $\mu\omega^2\sim\alpha_f$. We recall that the small parameters of our problem are the quantities $\Delta\tilde{\alpha}/\alpha_f$

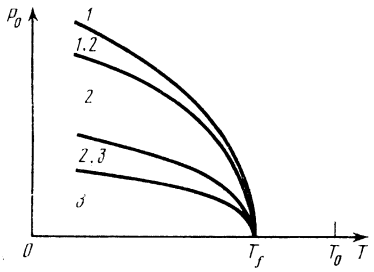

FIG. 3. Stability regions near the phase-transition temperatures of the homogeneous state (1) and of the hexagonal (2) and stripe (3) domain structure on the (P_0, T) phase diagram.

and α_0/α_f. The instability of the system corresponds to vanishing of some frequency from the presented spectrum. From the expression for ω_1^2 in (57) we can see that ω_1^2 vanishes at $\Delta\tilde{\alpha} = -\alpha_0$, corresponding to instability of the hexagonal structure to a transition into the homogeneous state. This agrees with the results of the thermodynamic analysis in Sec. 2 [see (35)].

The frequencies $\omega_{2,3}^2$ vanish at $\Delta\tilde{\alpha} = 80\,\alpha_0$. This corresponds to a transition from the hexagonal to the stripe structure. The complete phase diagram of a ferroelectric in an external magnetic field is shown in Fig. 3. We note that ω_5 and ω_6 are respectively the longitudinal and transverse acoustic branches. The longitudinal sound velocity is $\sqrt{3}$ times larger than the transverse. We have thus found that in the absence of an external field only a stripe domain structure can be stable. A hexagonal structure can arise only in an external electric field and in a limited temperature interval. When the temperature is lowered the hexagonal structure becomes unstable at a temperature determined by the equation $\Delta\tilde{\alpha} = 80\alpha_0$, and goes over into a stripe structure. We have thus found that phase transitions are possible between three states: homogeneous state and stripe and hexagonal domain structures. A quadratic lattice is not realized at all.

Examinaton of the domain structure with allowance for the anisotropy of the dielectric constant in the plane of the plate shows that the anisotropy determines the direction of the domain walls and expands the region of existence of the stripe domain structure. The domain walls of the stripe structure are directed along the axis with the lower dielectric constant. A hexagonal structure arises only in sufficiently strong fields. In the case of strong anisotropy the hexagonal structure may not occur at all, and there exists only one phase transition from the ground state into a stripe domain structure. Following Ref. 6, we can show that at $0 < \alpha_0 < \alpha_{cr} \equiv 16\alpha_f/15\pi^2$ this transition is of second order, and that at $\alpha_0 > \alpha_{cr}$ a first-order phase transition takes place. The point defined by the equalities $\tilde{\alpha} = \alpha_f$ and $\alpha_0 = \alpha_{cr}$ on the field-temperature phase diagram is the critical point.

The authors thank V. B. Sandomirskiĭ, D. G. Sannikov, and N. A. Tikhomirova for helpful discussions.

[1]T. Mitsui and I. Furuichi, Phys. Rev. **90**, 193 (1953).
[2]C. Kittel, transl. in Usp. Fiz. Nauk **16**, 452 (1950).
[3]E. V. Chenskiĭ, Fiz. Tverd. Tela (Leningrad) **14**, 2241 (1972) [Sov. Phys. Solid State **14**, 1940 (1973)].
[4]V. V. Tarasenko, E. V. Chenskiĭ, and I. E. Dikshteĭn, Zh. Eksp. Teor. Fiz. **70**, 2178 (1976) [Sov. Phys. JETP **43**, 1136 (1976)].
[5]V. V. Tarasenko, E. V. Chenskiĭ, and I. E. Dikshteĭn, Fiz. Tverd. Tela (Leningrad) **18**, 1576 (1976) [Sov. Phys. Solid State **18**, 916 (1976)].
[6]V. V. Tarasenko, *ibid.* **22**, 503 (1980) [**22**, 294 (1980)].
[7]V. G. Bar'yakhtar, B. A. Ivanov, and A. L. Sukstanskiĭ, *ibid.* **21**, 3003 (1979) [**21**, 1729 (1979)].

Translated by J. G. Adashko