A CONTRIBUTION TO THE THEORY OF DOMAIN WALLS IN FERROELECTRICS

V. A. ZHIRNOV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 19, 1958; resubmitted June 30, 1958


Transition regions in the 180° and 90° boundaries of ferroelectric domains in barium titanate are considered. The equilibrium variation of the spontaneous-polarization vector is deduced from the condition of minimum thermodynamic potential. Explicit expressions are obtained for the thickness and surface energy of the domain boundaries, and numerical estimates are made. The 180° domain boundary in Rochelle salt crystals is discussed.

Numerous experiments performed by different investigators have shown that in the domain structures of single crystals of barium titanate the directions of spontaneous polarization in neighboring domains form angles of 180° or 90°, which we shall call 180° and 90° domains. Little concluded from optical observations that the thickness of the transition region between 180° domains is of the order of the lattice constant \( d = 4 \times 10^{-8} \) cm, whereas for 90° domains it is \( 5 \times 10^{-5} \) cm. She also noted the dominant generation and growth of 90° domains and the relatively greater ease with which 90° boundaries are moved by external mechanical stresses. This latter effect is evidently the result of lower surface energy of 90° boundaries compared with 180° boundaries.

It may be of interest to obtain quantitative results for the thicknesses of transition layers and surface energies of 180° and 90° domain walls. We shall use the method suggested by Landau and Lifshitz for investigation of the domain structure of ferromagnets. The variation of polarization in an intermediate region is determined under thermodynamic equilibrium in the absence of an external field, and explicit expressions are obtained for the thickness of the transition layer and for the surface energy density which plays a part as the "coefficient of surface tension" of domain walls.

We shall obtain the contributions to the thermodynamic potential which are associated with the anisotropy energy, elastic energy, and electrostriction for cubically symmetrical barium titanate near the Curie point. In a transition region, an essential part is also played by the energy associated with nonuniform distribution of the polarization vector \( \mathbf{P} \):

\[
\frac{\kappa}{2} \left[ (\nabla \mathbf{P}_x)^2 + (\nabla \mathbf{P}_y)^2 + (\nabla \mathbf{P}_z)^2 \right].
\]

This expression can reasonably be used so long as the thickness of the transition layer is considerably greater than the lattice constant. The thermodynamic potential in the transition layer is thus given by

\[
\Phi = \Phi_0 + \frac{\kappa}{2} \left[ (\nabla \mathbf{P}_x)^2 + (\nabla \mathbf{P}_y)^2 + (\nabla \mathbf{P}_z)^2 \right] + \kappa (P_4^2 + P_5^2 + P_6^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2)
\]

\[
+ \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2)
\]

\[
+ \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2)
\]

\[
+ \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2) + \frac{\kappa}{2} (P_1^2 + P_4^2 + P_5^2)
\]

... (1)

where \( u_{ik} \) is the deformation tensor. The parameter \( \kappa \) can be evaluated by assuming that the energy \( (\kappa/2)(\nabla \mathbf{P})^2 \) is of the order of the exchange energy \( \alpha \mathbf{P}^2 \) far from the transition point if \( \mathbf{P} \) varies essentially only at distances of the order of the lattice constant \( d \). Then the lower limit of \( \kappa \) is given by \( \kappa \sim | \alpha(0) | d^2 \), where \( \alpha(T) = 3.8 \times 10^{-3} (T - \Theta) \). A reasonable range of values is \( \kappa \sim 3 \times 10^{-16} \) to \( 3 \times 10^{-14} \) cm².

In the theory of domain structure the essential difference between ferroelectrics and ferromagnets is provided by two factors. The exchange interaction in ferromagnets results in a constant absolute value of the magnetization so that the only change which occurs is a continuous rotation of the direction of magnetization in the intermediate region. In the case of ferroelectrics we must take into account the fact that the absolute value of the spontaneous polarization in the intermediate region can change from the very beginning.

It must be remembered, however, that in any real ferroelectric crystal the conductivity is dif-

822
ferent from zero. Therefore free charges can generally accumulate on crystal boundaries or domain walls. For this reason a flat ferroelectric in a condenser cannot be divided into domains.

For the 180° and 90° domains of interest here, assuming equal magnitude of the polarization throughout both domains, we can have the condition $\nabla \mathbf{P} = 0$. Therefore the absence of free charges on domain walls, that is, $\nabla \mathbf{D} = 0$, is consistent with zero value of the electric field $\mathbf{E}$, as is required for equilibrium when conduction occurs. We shall consider this case.

Let us consider the 180° domain wall of a BaTiO$_3$ single crystal when, for example, the polarization of neighboring domains is parallel and antiparallel to the $z$ axis and the separating wall is in the (100) crystallographic plane. Then $\nabla \mathbf{P} = 0$ leads to $P_x = 0$. Furthermore, since the interior of each domain can be regarded as unstressed all components of the stress tensor $\sigma_{ij} = -\partial\mathcal{F}/\partial x_{jk}$ will be zero far from the transition layer, that is, for $x = \pm \infty$.

The deformation tensor in the interior of the domains is then given by

$$u_{xx} = u_{yy} = \mu P_y^2, \quad u_{zz} = \rho P_z^2, \quad u_{xy} = u_{xz} = u_{yz} = 0,$$

where the measurements of Caspary and Merz give the following values of the constants: $\mu = -10.5 \times 10^6$ cm$^4$/coulomb$^2$ and $\rho = 24.0 \times 10^6$ cm$^4$/coulomb$^2$. Since the polarization distribution in the transition layer depends only on $x$ the deformation tensor also can depend only on $x$; therefore $u_{yy}$, $u_{zz}$, and $u_{yz}$ remain constant and equal to their boundary values. The other deformation components are determined from the equilibrium equations of an elastic body, $\partial \sigma_{ij}/\partial x_k = 0$, which in our case become

$$\sigma_{xx} = 0, \quad \sigma_{yy} = 0, \quad \sigma_{zz} = 0.$$

We thus obtain

$$u_{xx} = \mu P_y^2 - (q_{12}/c_{11})(P_y^2 + P_z^2 - P_0^2), \quad u_{yy} = u_{zz} = 0,$$

and all components of the deformation tensor in the transition layer satisfy St. Venant’s continuity conditions.

Inserting the deformations into (1), we obtain the variable part of the thermodynamic potential in the form

$$\mathcal{F} = \Phi_0 + \frac{x}{2}(\nabla P_y)^2 + \frac{4}{a}(\nabla P_z)^2$$

$$+ \frac{a}{2} P_y^2 + \frac{b}{2} P_z^2 + \frac{c}{4}(P_y^4 + P_z^4) + \frac{d}{2} P_y^2 P_z^2,$$

$$a/2 = a + \frac{q_{12}}{c_{11}} + q_{12} - (q_{12} c_{11}/c_{11}) (p + q), \quad b = -\frac{q_{12}}{c_{11}},$$

$$c/2 = 0, \quad d/2 = q_{12}^2/c_{11}.$$

On the basis of Devonshire’s results we can assume the following values of the constants:

$$a \approx 1.5 \times 10^{-2}, \quad b = -5.6 \times 10^{-2},$$

$$c \approx 1.5 \times 10^6 \text{cm}^4/\text{coulomb}^2,$$

$$d \approx -5 \times 10^7 \text{cm}^4/\text{coulomb}^2.$$

Near the Curie point, where and only where an expansion of the thermodynamic potential is valid, the temperature-dependent coefficient $\alpha = 3.8 \times 10^{-8} (T - \Theta)$ gives a small contribution to the coefficients $a$ and $b$, which are entirely determined by electrostriction and have opposite signs, with $b$ essentially negative. All of this is true only for the transition layer, since within a domain $P_y = 0, |P_z| = P_0$ and in the expression

$$\frac{b}{2} P_z^2 = aP_y^2 + (q_{12}^2 - q_{12} c_{11}/c_{11}) (p + \mu) P_0^2,$$

the coefficient of $P_y^2$ vanishes at the Curie point, which is in accordance with the phenomenological theory.

The condition of thermodynamic equilibrium, which is the minimization of $\int \Phi (P_y, P_z) \, dV$, reduces to the equations

$$xP_y^2 = aP_y^2 + cP_y^4 + dP_y^2 P_z^2, \quad xP_z^2 = bP_y + cP_z^2 + dP_y P_z^2,$$

which must be supplemented by the following boundary conditions at $x = \pm \infty$:

$$P_y = P_z = 0, \quad P_x = -P_0.$$

Besides the “trivial” solution $P_y = 0, P_z = -P_0$, which represents uniform polarization in the absence of domain walls, there exists an exact solution representing the presence of a transition layer and satisfying the boundary conditions

$$P_y = 0, \quad P_z = P_0 \tanh(x/\delta),$$

where $P_0^2 = |b|/c$ determines the equilibrium polarization within the domains and $\delta = P_0^2 \sqrt{2\alpha/\delta}$ determines the effective size of a transition region for 180° domains. When $d$ is sufficiently small to be neglected by comparison with $c$, the equations are separable and the solution is unique. In the general case the proof of uniqueness requires further examination.

We note that the foregoing solution differs essentially from the solution for a 180° transition region in the case of ferromagnetism:

$$M_y = M_0 \sin \theta, \quad M_z = M_0 \cos \theta, \quad \sinh(x/\delta) = D \cot \theta.$$

This is associated with the fact that the spin exchange energy gives an “infinitely” larger contribution (10$^5$ times larger) to the thermodynamic potential than the elastic energy and higher terms of the expansion. This insures a constant absolute value of the magnetic moment in the transition re-
region. Therefore in the ferromagnetic case the
original set of equations is highly degenerate, with
\( a = b, c = 0 \), so that its first integral gives the re-
quired solution.

The solution for \( \text{BaTiO}_3 \) gives \( \delta \approx 2 \times 10^{-7} -
5 \times 10^{-8} \text{ cm} \) for the thickness of 180° domain walls,
which is several times the lattice constant, and thus
agrees with experimental results.\(^1\)

We can also obtain an expression for the excess
surface energy associated with the existence of a
180° domain wall:
\[
s = \int_{-\infty}^{\infty} (\Phi - \Phi_0) \, dx = \frac{1}{2} P_0^2 V_{2\alpha c} \approx 10 \text{ erg/cm}^2.
\]
This agrees with the value given by Merz.\(^7\)

We shall now consider a 90° domain wall of
barium titanate in the (101) plane with the polariza-
tion in neighboring domains directed along the z
and x axes, respectively. For ease of calculation
we shall turn the coordinate system around the y
axis through \( \pi/4 \) so that the domain wall will lie
in the plane \( x = 0 \). The notation will now refer to
the new coordinate system. The condition \( \text{div} \, \mathbf{P} = 0 \)
now reduces to conservation of the component nor-
tal to the wall, \( P_x = P_y / \sqrt{2} \); thus all variations,
as in the case of the 180° layer, will be associated
with the dependence of \( P_y \) and \( P_x \) on \( x \). The previous method
is used to determine the compo-
ents of the deformation tensor in the
90° layer. These components satisfy St. Venant’s continuity
condition and are given by
\[
\begin{align*}
  u_{xx} &= \left( c_{44} (\mu + \rho) - c_{14}^2 \right) P_x^2 - 2 q_{12} P_y^2 \\
  &\quad - (q_{11} + q_{12} - 2 q_{44}) P_x^2 \left( c_{11} + c_{12} + 2 c_{44} \right)^{-1}, \\
  u_{yy} &= \frac{\mu + \rho}{2} P_x^2, \quad u_{xz} = -\sqrt{2} \frac{c_{44}}{c_{14}} P_x P_y, \\
  u_{zz} &= \frac{q_{11} - q_{12} - \frac{c_{11} - c_{12}}{2}}{c_{11} - c_{12}} P_x P_z, \quad u_{xy} = 0.
\end{align*}
\]
The variable part of the thermodynamic potential
can be written as
\[
\Phi = \Phi_0 + \frac{2}{3} \left( \nabla P_y \right)^2 + \left( \nabla P_x \right)^2
+ \frac{q_{11}}{2} P_x^2 + \frac{b_1}{2} P_z^2 + \frac{b_2}{4} P_y^2 + \frac{c_1}{4} P_x^4 + \frac{c_2}{4} P_x^4 + \frac{d_1}{2} P_y^4 P_x^2,
\]
with the condition for the minimum given by the equations
\[
\begin{align*}
  xP_y' &= a_1 P_y + c_1 P_x^2 + d_1 P_y^2 P_x^2, \\
  xP_y' &= b_1 P_x + c_1 P_x^2 + d_2 P_x^2 P_y^2.
\end{align*}
\]
The only solution which satisfies the boundary condi-
tions \( P_y = 0, \quad P_x = 0, \quad P_z = P_0 / \sqrt{2} \)
at \( x = -\infty \) is given by
\[
\begin{align*}
P_y &= 0, \quad P_x &= -\frac{P_0}{\sqrt{2}} \tanh \frac{x}{\delta_1},
\end{align*}
\]
where
\[
P_0 = 2 |b| / c_1; \quad \delta_1 = (2/\rho_0) V x / c_1.
\]
A numerical estimate gives
\[
\delta_1 \approx 10^{-6} \text{ to } 10^{-5} \text{ cm},
\]
from which we obtain \( \delta_1 \sim 10^{-6} \text{ to } 5 \times 10^{-7} \text{ cm} \),
which is one order of magnitude larger than for the
180° case. The disagreement with the experi-
mental value \( \delta_1 \sim 10^{-5} \text{ cm} \) may result from the
fact that the 90° domains observed in reference 1
were comparable in size with the thickness of the transition
layer, in which case the crystal cannot
be regarded as unstressed inside a domain.

For the surface energy of a 90° transition layer
of barium titanate we obtain the expression
\[
\sigma_1 = \frac{1}{2} \sqrt{\alpha c_2} P_0^2.
\]
For this case an estimate gives \( \sigma_1 \approx 2 \text{ to } 4 \text{ erg/cm}^2 \).
Comparison with 180° domains shows that
in the 90° transition layer a change of the polarization
vector is favored energetically since the mini-
mum absolute value is \( P_x = P_y / \sqrt{2} \) rather than
zero. This evidently accounts for the ease with
which 90° domain boundaries are produced and
moved.

We shall now consider a 180° domain wall in the
actually observable case of a Rochelle salt
single crystal where the polarization in neighbor-
ing domains is directed parallel and antiparallel
to the y axis and all changes occur along the z
axis. As previously, the condition \( \text{div} \, \mathbf{P} = 0 \)
reduces to the relation \( P_x = 0 \). The thermodynamic
potential will receive contributions from the energy
of nonuniform polarization, anisotropy, elastic en-
ergy (taking account of the orthorhombic symme-
try), linear piezoelectric effect, and quadratic
electrostrictive effect:
\[
\Phi = \Phi_0 + \frac{x_{\text{xx}}}{2} (\nabla P_y)^2 + \frac{x_{\text{yy}}}{2} (\nabla P_x)^2 + x_{\text{zz}} P_y^2 + x_{\text{xz}} P_x P_y
+ \frac{x_{\text{yz}}}{2} P_x^2 + \frac{x_{\text{x}}}{2} P_x^2 + \frac{x_{\text{yy}}}{2} P_y^2 + \frac{x_{\text{zz}}}{2} P_z^2
+ c_{11} U_{xx}^2 + c_{12} U_{xx} U_{yy} + c_{13} U_{xx} U_{zz} + c_{22} U_{yy}^2 + c_{23} U_{yy} U_{zz}
+ c_{33} U_{zz}^2 + h_{11} U_{yz} U_{xx} + h_{22} U_{yx} U_{xx} + h_{33} U_{yz} U_{xx}
+ (q_{11} P_y^2 + q_{12} P_x^2) U_{xx} + (q_{22} P_y^2 + q_{23} P_x^2) U_{yy}
+ (q_{33} P_z^2) U_{zz} + 2 q_{12} P_x P_y U_{yz}.
\]
In the absence of an external electric field the
stress tensor \( \sigma_{ik} \) is given by \( \sigma_{ik} = -\partial \Phi / \partial U_{ik} \).
If the crystal can be regarded as unstressed in-
side the domains the deformations are determined
from the equations \( \sigma_{ik} = 0 \), \( P_Y = P_x = 0, \quad P_z = \pm P_0 \)
with \( x = \pm \infty \) and are found to be
CONTRIBUTION TO THE THEORY OF DOMAIN WALLS IN FERROELECTRICS

where the constants \( \rho, \mu, \lambda \) are solutions of the equations

\[ c_{i1} \rho + c_{i2} \mu + c_{i3} \lambda = - q_i \quad (i = 1, 2, 3). \]

In the transition layer, as previously, \( u_{yy}, u_{zz} \) and \( u_{yz} \) retain their boundary values, and the other components of \( u_{ik} \) are obtained from the equilibrium equations \( \sigma_{11} = 0 \):

\[ u_{xx} = \frac{(c_{15} \mu + c_{16} \lambda)}{c_{11}} P_0^2 - \frac{q_1}{c_{11}} P_0^2 - \frac{q_1}{c_{11}} P_z, \]

\[ u_{xx} = \frac{\rho_{11}}{c_{15}} P_y, \quad u_{xy} = \frac{\rho_{15}}{c_{15}} P_z. \]

These deformations give the following form to the variable part of the thermodynamic potential:

\[ \Phi = \Phi_0 + \frac{x_1}{2} (\nabla P_y)^2 + \frac{x_2}{2} (\nabla P_z)^2 \]

\[ + \frac{A}{2} P_y^2 + \frac{B}{2} P_z^2 + \frac{C}{4} P_y^4 + \frac{D}{4} P_z^4 + \frac{F}{2} P_y P_z, \]

\[ \frac{A}{2} = \alpha_2 - \frac{h_1^2}{2c_{15}} + \left[ \lambda q_{12} + \left( \frac{\mu + c_{18} \mu - c_{18} \lambda}{c_{11}} \right) q_{18} \right] P_0^2, \]

\[ \frac{B}{2} = \alpha_3 - \frac{h_2^2}{2c_{15}} + \left[ \lambda q_{33} + \mu q_{23} - \left( \frac{c_{15} \mu + c_{15} \lambda}{c_{11}} \right) q_{15} \right] P_0^2, \]

\[ \frac{C}{2} = \beta_3 - \frac{h_3^2}{2c_{15}} + \left[ \lambda q_{33} - \mu q_{23} \right] P_0^2, \]

\[ \frac{D}{2} = \beta_3 - \frac{h_3^2}{2c_{15}} + \left[ \lambda q_{33} - \mu q_{23} \right] P_0^2, \]

\[ F = -q_{15} q_{15} / c_{11}. \]

The minimum of \( \int \Phi \, dV \) reduces to the equations

\[ \kappa_2 P_y'' = AP_y + CP_y + FP_y P_z, \]

\[ \kappa_2 P_z'' = BP_z + DP_z + FP_z P_y, \]

with one solution that satisfies the boundary conditions \( P_y' = P_y = 0, \ P_z' = 0, \ P_z = -P_0 \) when \( x = -\infty \):

\[ P_y = 0; \ P_z = P_0 \tan \frac{x}{\delta}; \quad \delta = \frac{1}{P_0} \sqrt{\frac{2k_3}{D}}. \]

For the density of the surface energy associated with a domain wall in Rochelle salt we obtain

\[ \sigma = \sigma_0 V \kappa_3 D P_0^3. \tag{2} \]

It is known that at \( T = 0^\circ C \)

\[ P_0 = 2.5 \times 10^{-7} \text{ coulomb/cm}^2, \quad \alpha_3 = -2 \times 10^{-4}, \]

\[ \beta_3 = 3.3 \times 10^{11} \text{ cm}^4 / \text{coulomb}^2, \quad q_{15} \sim 90, \]

and at \( T = 20^\circ C \)

\[ P_0 = 1.4 \times 10^{-7} \text{ coulomb/cm}^2, \quad \alpha_3 = -8 \times 10^{-4}, \]

\[ \beta_3 = 4 \times 10^{11} \text{ cm}^4 / \text{coulomb}^2, \quad q_{15} \sim 150. \]

In addition, using the values \( \kappa \sim Q \sim 10^{-14} \text{ cm}^2, \ c_{11} = 4 \times 10^{-6} \text{ coulomb}^2 / \text{cm}^4 \), we obtain

\[ \kappa_3 = 1.2 \times 10^{-7} \text{ erg/cm}^2; \quad \kappa_3 \sim 2.2 \times 10^{-6} \text{ erg/cm}^2 \]

\[ \kappa_3 \sim 1.2 \times 10^{-3} \text{ erg/cm}^2. \]

These values agree with the results of reference 8, where, however, electrostriction is not taken into account consistently and the deformations do not satisfy the St. Venant's compatibility conditions.

The given values of the surface energy of domain boundaries in ferroelectrics enable us to investigate different domain configurations corresponding to the minimum thermodynamic potential.

In conclusion the author wishes to thank Prof. V. L. Ginzburg and I. E. Dzialoshinskii for valuable suggestions and fruitful discussions.

6 A. F. Devonshire, Phil. Mag. 40, 1040 (1949).
7 W. J. Merz, Phys. Rev. 95, 690 (1954).

Translated by I. Emin 249