A CONTRIBUTION TO THE THEORY OF DOMAIN WALLS IN FERROELECTRICS

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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[1,2] 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[1] concluded from optical observations that the thickness of the transition region between 180° domains is of the order of the lattice constant (d = 4×10^{-8} cm), whereas for 90° domains it is 5×10^{-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[3] 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 essentail part is also played by the energy associated with nonuniform distribution of the polarization vector P:

$$\frac{\varkappa}{2} [(\nabla P_x)^2 + (\nabla P_y)^2 + (\nabla P_z)^2].$$

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

$$\Phi = \Phi_0 + \frac{\varkappa}{2} [(\nabla P_x)^2 + (\nabla P_y)^2 + (\nabla P_z)^2]$$
$$+ \alpha (P_x^2 + P_y^2 + P_z^2) + \frac{\beta_1}{2} (P_x^4 + P_y^4 + P_z^4)$$
$$+ \beta_2 (P_x^2 P_y^2 + P_x^2 P_z^2 + P_y^2 P_z^2) + \frac{c_{11}}{2} (u_{xx}^2 + u_{yy}^2 + u_{zz}^2)$$
$$+ c_{12} (u_{xx}u_{yy} + u_{xx}u_{zz} + u_{yy}u_{zz}) + \frac{c_{44}}{2} (u_{xy}^2 + u_{xz}^2 + u_{yz}^2)$$
$$+ q_{11} (u_{xx}P_x^2 + u_{yy}P_y^2 + u_{zz}P_z^2)$$
$$+ q_{12} [u_{xx} (P_y^2 + P_z^2) + u_{yy}(P_x^2 + P_z^2)$$
$$+ u_{zz}(P_x^2 + P_y^2)] + 2q_{44} (u_{xy}P_xP_y + u_{xz}P_xP_z + u_{yz}P_yP_z), \quad (1)$$

where u_{ik} is the deformation tensor. The parameter $\varkappa$ can be evaluated by assuming that the energy $(\varkappa/2)(\nabla P)^2$ is of the order of the exchange energy αP^2 far from the transition point if P varies essentially only at distances of the order of the lattice constant d. Then the lower limit of $\varkappa$ is given by $\varkappa \sim |\alpha(0)| d^2$, where $\alpha(T) = 3.8 \times 10^{-5}(T - \Theta)$. A reasonable range of values is $\varkappa \sim 3 \times 10^{-15}$ to 3×10^{-16} cm^2.

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-

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.[4] For the 180° and 90° domains of interest here, assuming equal magnitude of the polarization throughout both domains, we can have the condition div $\mathbf{P} = 0$. Therefore the absence of free charges on domain walls, that is, div $\mathbf{D} = 0$, 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 div $\mathbf{P} = 0$ leads to $P_x = 0$. Furthermore, since the interior of each domain can be regarded as unstressed all components of the stress tensor $\sigma_{ik} = -\partial\Phi/\partial u_{ik}$ 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

$$u_{xx} = u_{yy} = \mu P_0^2, \quad u_{zz} = \rho P_0^2, \quad u_{xy} = u_{xz} = u_{yz} = 0,$$

where the measurements of Caspari and Merz[5] 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, $\partial\sigma_{ik}/\partial x_k = 0$, which in our case become

$$\sigma_{xx} = 0, \quad \sigma_{xy} = 0, \quad \sigma_{xz} = 0.$$

We thus obtain

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

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

$$\Phi = \Phi_0 + \frac{\varkappa}{2}[(\nabla P_y)^2 + (\nabla P_z)^2]$$
$$+ \frac{a}{2}P_y^2 + \frac{b}{2}P_z^2 + \frac{c}{4}(P_y^4 + P_z^4) + \frac{d}{2}P_y^2 P_z^2,$$
$$a/2 = \alpha + [q_{11}\mu + q_{12}\rho - (q_{12}c_{12}/c_{11})(\rho + \mu)]P_0^2,$$
$$b/2 = \alpha + [q_{11}\rho + q_{12}\mu - (q_{12}c_{12}/c_{11})(\rho + \mu)]P_0^2,$$
$$c/2 = \beta_1 - q_{12}^2/c_{11}, \quad d/2 = \beta_2 - q_{12}^2/c_{11}.$$

On the basis of Devonshire's results[6] we can assume the following values of the constants:

$a \approx 1.5 \times 10^{-2}$, $b \approx -5.6 \times 10^{-2}$,
$c \approx 1.5 \times 10^8$ cm^4/coulomb^2,
$d \approx -5 \times 10^7$ cm^4/coulomb^2.

Near the Curie point, where and only where an expansion of the thermodynamic potential is valid, the temperature-dependent coefficient $\alpha = 3.8 \times 10^{-5}$ ($T - \Theta$) 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

$$\frac{b}{2}P_z^2 = \alpha P_0^2 + \left[q_{11}\rho + q_{12}\mu - q_{12}\frac{c_{12}}{c_{11}}(\rho + \mu)\right]P_0^4$$

the coefficient of P_0^2 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

$$\varkappa P_y'' = aP_y + cP_y^3 + dP_y P_z^2, \quad \varkappa P_z'' = bP_z + cP_z^3 + dP_z P_y^2,$$

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

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

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 $\delta = P_0^{-1}\sqrt{2\varkappa/c}$ 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:[3]

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

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-

gion. 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 required solution.

The solution for $BaTiO_3$ gives $\delta \approx 2 \times 10^{-7} - 5 \times 10^{-8}$ 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:

$$\sigma = \int_{-\infty}^{\infty} (\Phi - \Phi_0) \, dx = \tfrac{4}{3} P_0^3 \sqrt{2 \varkappa c} \approx 10 \text{ erg/cm}^2.$$

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 polarization 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 div **P** = 0 now reduces to conservation of the component normal to the wall, $P_X = P_0/\sqrt{2}$; thus all variations, as in the case of the 180° layer, will be associated with the dependence of P_y and P_z on x. The previous method is used to determine the components of the deformation tensor in the 90° layer. These components satisfy St. Venant's continuity condition and are given by

$$u_{xx} = [(c_{44}(\mu + \rho) - c_{12}\mu - q_{44}) P_0^2 - 2q_{12}P_y^2$$
$$- (q_{11} + q_{12} - 2q_{44}) P_z^2](c_{11} + c_{12} + 2c_{44})^{-1},$$

$$u_{yy} = \mu P_0^2, \quad u_{zz} = \frac{\mu + \rho}{2} P_0^2, \quad u_{xy} = -\sqrt{2}\frac{q_{44}}{c_{44}} P_0 P_y,$$

$$u_{xz} = \frac{q_{12} - q_{11}}{c_{11} - c_{12}} \frac{P_0}{\sqrt{2}} P_z, \quad u_{yz} = 0.$$

The variable part of the thermodynamic potential can be written as

$$\Phi = \Phi_0 + \frac{\varkappa}{2}[(\nabla P_y)^2 + (\nabla P_z)^2]$$
$$+ \frac{a_1}{2} P_y^2 + \frac{b_1}{2} P_z^2 + \frac{c_1}{4} P_y^4 + \frac{c_2}{4} P_z^4 + \frac{d_1}{2} P_y^2 P_z^2,$$

with the condition for the minimum given by the equations

$$\varkappa P_y'' = a_1 P_y + c_1 P_y^3 + d_1 P_y P_z^2,$$
$$\varkappa P_z'' = b_1 P_z + c_2 P_z^3 + d_2 P_z P_y^2.$$

The only solution which satisfies the boundary conditions $P_y' = P_y = 0$, $P_z' = 0$, $P_z = P_0/\sqrt{2}$ at $x = -\infty$ is given by

$$P_y = 0, \quad P_z = -\frac{P_0}{\sqrt{2}} \tanh \frac{x}{\delta_1},$$

where

$$P_0^2 = 2|b|/c_2; \quad \delta_1 = (2/P_0)\sqrt{\varkappa/c_2}.$$

A numerical estimate gives

$$c_2 = \beta_1 + \beta_2 - (q_{11} - q_{12} - 2q_{44})^2/(c_{11} + c_{12} + 2c_{44})$$
$$\approx 10^7 \text{ cm}^4/\text{coulomb}^2,$$

from which we obtain $\delta_1 \sim 10^{-6}$ to 5×10^{-7} cm, which is one order of magnitude larger than for the 180° case. The disagreement with the experimental value $\delta_1 \sim 10^{-5}$ 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

$$\sigma_1 = \tfrac{2}{3}\sqrt{\varkappa c_2}P_0^3.$$

For this case an estimate gives $\sigma_1 \approx 2$ to 4 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 minimum absolute value is $P_X = P_0/\sqrt{2}$ 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 neighboring domains is directed parallel and antiparallel to the y axis and all changes occur along the z axis. As previously, the condition div **P** = 0 reduces to the relation $P_X = 0$. The thermodynamic potential will receive contributions from the energy of nonuniform polarization, anisotropy, elastic energy (taking account of the orthorhombic symmetry), linear piezoelectric effect, and quadratic electrostrictive effect:

$$\Phi = \Phi_0 + \frac{\varkappa_1}{2}(\nabla P_y)^2 + \frac{\varkappa_2}{2}(\nabla P_z)^2 + \alpha_2 P_y^2 + \alpha_3 P_z^2$$
$$+ \frac{\beta_2}{2} P_y^4 + \frac{\beta_3}{2} P_z^4 + \frac{1}{2}(c_{11}u_{xx}^2 + c_{22}u_{yy}^2 + c_{33}u_{zz}^2$$
$$+ c_{44}u_{yz}^2 + c_{55}u_{xz}^2 + c_{66}u_{xy}^2) + c_{12}u_{xx}\,u_{yy} + c_{13}u_{xx}u_{zz}$$
$$+ c_{23}u_{yy}\,u_{zz} - h_{14}u_{yz}P_x - h_{25}\,u_{xz}\,P_y - h_{36}u_{xy}P_z$$
$$+ (q_{12}P_y^2 + q_{13}P_z^2)\,u_{xx} + (q_{22}P_y^2 + q_{23}P_z^2)\,u_{yy}$$
$$+ (q_{23}P_y^2 + q_{33}P_z^2)\,u_{zz} + 2q_{44}P_yP_zu_{yz}.$$

In the absence of an external electric field the stress tensor σ_{ik} is given by $\sigma_{ik} = -\partial \Phi/\partial u_{ik}$. If the crystal can be regarded as unstressed inside the domains the deformations are determined from the equations $\sigma_{ik} = 0$, $P_X = P_y = 0$, $P_z = \pm P_0$ with $x = \pm \infty$ and are found to be

$$u_{xx} = \rho P_0^2, \quad u_{xz} = 0, \quad u_{yy} = \mu P_0^2, \quad u_{yz} = 0,$$

$$u_{zz} = \lambda P_0^2, \quad u_{xy} = \pm h_{36} P_0 / c_{66},$$

where the constants ρ, μ, λ are solutions of the equations

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

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 $\sigma_{1i} = 0$:

$$u_{xx} = -\left(\frac{c_{12}}{c_{11}}\mu + \frac{c_{13}}{c_{11}}\lambda\right)P_0^2 - \frac{q_{12}}{c_{11}}P_y^2 - \frac{q_{13}}{c_{11}}P_z^2,$$

$$u_{xz} = \frac{h_{25}}{c_{55}}P_y, \quad u_{xy} = \frac{h_{36}}{c_{66}}P_z.$$

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

$$\Phi = \Phi_0 + \frac{\varkappa_1}{2}(\nabla P_y)^2 + \frac{\varkappa_2}{2}(\nabla P_z)^2$$

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

$$\frac{A}{2} = \alpha_2 - \frac{h_{25}^2}{2c_{25}} + \left[\lambda q_{23} + \left(\mu - \frac{c_{12}}{c_{11}}\mu - \frac{c_{13}}{c_{11}}\lambda\right)q_{12}\right]P_0^2,$$

$$\frac{B}{2} = \alpha_3 - \frac{h_{36}^2}{2c_{66}} + \left[\lambda q_{33} + \mu q_{23} - \left(\frac{c_{12}}{c_{11}}\mu + \frac{c_{13}}{c_{11}}\lambda\right)q_{13}\right]P_0^2,$$

$$\frac{C}{2} = \beta_2 - q_{12}^2/c_{11}, \quad \frac{D}{2} = \beta_3 - q_{13}^2/c_{11}, \quad F = -q_{12}q_{13}/c_{11}.$$

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

$$\varkappa_2 P_y'' = AP_y + CP_y^3 + FP_y P_z^2, \quad \varkappa_3 P_z'' = BP_z + DP_z^3 + FP_y^2 P_z,$$

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

$$P_y = 0; \quad P_z = P_0 \tanh\frac{x}{\delta}; \quad \delta = \frac{1}{P_0}\sqrt{\frac{2\varkappa_3}{D}}.$$

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

$$\sigma = {}^4/_3 \sqrt{\varkappa_3 D}\, P_0^3. \tag{2}$$

It is known[8] that at $T = 0°C$

$$P_0 = 2.5 \cdot 10^{-7} \text{ coulomb/cm}^2, \quad \alpha_3 = -2 \cdot 10^{-2},$$

$$\beta_3 = 3.3 \cdot 10^{11} \text{ cm}^4/\text{coulomb}^2, \quad q_{13} \sim 90,$$

and at $T = 20°C$

$$P_0 = 1.4 \cdot 10^{-7} \text{ coulomb/cm}^2, \quad \alpha_3 = -8 \cdot 10^{-2},$$

$$\beta_3 = 4 \cdot 10^{11} \text{ cm}^4/\text{coulomb}^2, \quad q_{13} \sim 150.$$

In addition, using the values $\kappa \sim d^2 \sim 10^{-14} \text{ cm}^2$, $c_{11} = 4 \times 10^{-8} \text{ coulomb}^2/\text{cm}^4$, we obtain

at $T = 0°C$: $\delta \simeq 1.2 \cdot 10^{-7}$ cm, $\sigma \sim 6 \cdot 10^{-2} \text{ erg/cm}^2$;
at $T = 20°C$: $\delta \simeq 2.2 \cdot 10^{-6}$ cm, $\sigma \sim 1.2 \cdot 10^{-2} \text{ erg/cm}^2$.

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.

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