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A THEORY OF FERROELECTRIC 90 DEGREE DOMAIN WALL

Yoshihiro Ishibashi

Aichi Shukutoku University, Nagakute-cho, Aichi 480-1197, Japan
Fax: 81-561-63-9308, e-mail: yishi@asu.aasa.ac.jp

A phenomelogical theory of the 90° ferroelectric domain wall is presented. It is the depolarizing field that distinguishes the stable head-to-tail wall from the unstable head-to-head wall energetically. The increment in the domain wall energy due to the depolarizing field is discussed.

Key words: ferroelectrics, 90° domain wall, depolarization field

1. INTRODUCTION

With the advent of the ferroelectric thin film memories,[1] the studies of domains and domain walls in ferroelectric materials have become more important than before, because the polarization reversal in ferroelectrics is caused by growth and shrink of domains.[2,3]

Among materials used for such application the perovskite-type oxide ferroelectrics are most important. It is known that in their tetragonal phase there are two kinds of domain walls, the 180° wall and the 90° wall. Though there are so many theoretical studies on the 180° walls, there is only few on the 90° walls in spite of much experimental observations.[4-7] In contrast to the case of the 180° wall, which can be analyzed with only one order parameter, in the case of 90° wall at least two order parameters and their spatial modulation must be involved in stabilizing the structure.

Under this situation, the present author has proposed a tentative theory of the 90° wall.[8] To examine the validity of the model previously proposed, here we discuss the effect of the depolarization field.

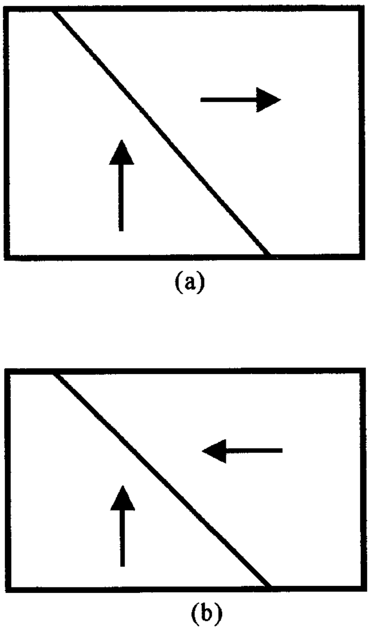

Fig. 1. The 90 degree domain wall. (a) The stable head-to-tail wall, and (b) the unstable head-to-head wall.

2. A MODEL FREE ENERGY DENSITY

The 90° wall is the boundary between a c-domain and an a-domain. Two types of the 90° walls, i.e., the head-to-tail wall and the head-to-head wall are depicted in Fig. 1(a) and (b), respectively. It can be easily guessed that due to the effect of the depolarization field the energy of the head-to-head wall is much higher than that of the head-to-tail wall. Of course, the head-to-head wall may not be realized because of its high energy nature.

The model free energy density, which the present author has proposed,[8] is applicable to the $m\bar{3}m$-to-$4mm$ transition of the second order in many perovskite-type oxide ferroelectrics, and is written as

$$
\begin{aligned}
f = & \frac{\alpha}{2}(p_x^2+p_y^2+p_z^2)+\frac{\beta_1}{4}(p_x^4+p_y^4+p_z^4) \\
& +\frac{\beta_2}{2}(p_x^2p_y^2+p_y^2p_z^2+p_z^2p_x^2) \\
& +\frac{\kappa_1}{2}\left[\left(\frac{\mathrm{d}p_x}{\mathrm{d}x}\right)^2+\left(\frac{\mathrm{d}p_y}{\mathrm{d}y}\right)^2+\left(\frac{\mathrm{d}p_z}{\mathrm{d}z}\right)^2\right] \qquad (1) \\
& +\frac{\kappa_2}{2}\left[\left(\frac{\mathrm{d}p_y}{\mathrm{d}x}\right)^2+\left(\frac{\mathrm{d}p_z}{\mathrm{d}x}\right)^2+\left(\frac{\mathrm{d}p_x}{\mathrm{d}y}\right)^2\right.
\end{aligned}
$$

$$+(\frac{\mathrm{d}p_z}{\mathrm{d}y})^2 + (\frac{\mathrm{d}p_x}{\mathrm{d}z})^2 + (\frac{\mathrm{d}p_y}{\mathrm{d}z})^2],$$

where $\alpha < 0$, $\beta_2 > \beta_1 > 0$, which is required for the stabilization of the tetragonal phase below the transition temperature (When $\beta_1 > \beta_2$ and $\beta_1 + 2\beta_2 > 0$, the rhombohedral phase is more stable than the tetragonal phase), and $\kappa_1 > 0$ and $\kappa_2 > 0$ for stabilizing the homogeneous structure. The free energy can be simplified as

$$f = \frac{\alpha}{2}(p_x^2 + p_y^2) + \frac{\beta_1}{4}(p_x^4 + p_y^4) + \frac{\beta_2}{2} p_x^2 p_y^2$$
$$+ \frac{\kappa_1}{2}[(\frac{\mathrm{d}p_x}{\mathrm{d}x})^2 + (\frac{\mathrm{d}p_y}{\mathrm{d}y})^2] \qquad (2)$$
$$+ \frac{\kappa_2}{2}[(\frac{\mathrm{d}p_y}{\mathrm{d}x})^2 + (\frac{\mathrm{d}p_x}{\mathrm{d}y})^2],$$

since in the concerned 90° walls there is no z-component of polarization p_z, and no z-dependence in p_x and p_y, either (See Fig.2 for the coordinates). Furthermore, eq.(2) can be transformed into

$$f = \frac{\alpha}{2}(p_x^2 + p_y^2) + \frac{\beta_1}{4}(p_x^4 + p_y^4) + \frac{\beta_2}{2} p_x^2 p_y^2$$
$$+ \frac{\kappa_1 + \kappa_2}{4}[(\frac{\mathrm{d}p_x}{\mathrm{d}X})^2 + (\frac{\mathrm{d}p_y}{\mathrm{d}X})^2], \qquad (3)$$

if we take a new X-Y coordinate system, rotated by 45° from the original x-y coordinate system (The components of the polarization are still denoted according to the x-y coordinate) and take into account that there appears no modulation along the Y-axis.

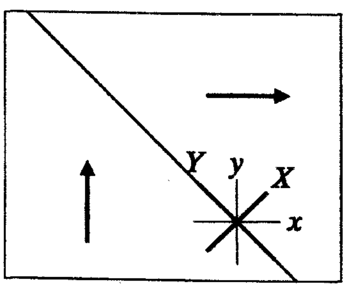

Fig. 2. The x-y and the X-Y coordinates.

To see how the polarization changes spatially, we have to solve the Euler-Lagrange equations for p_x and p_y;

$$\alpha p_x + \beta_1 p_x^3 + \beta_2 p_x p_y^2 - \kappa \frac{\mathrm{d}^2 p_x}{\mathrm{d}X^2} = 0,$$
$$\alpha p_y + \beta_1 p_y^3 + \beta_2 p_y p_x^2 - \kappa \frac{\mathrm{d}^2 p_y}{\mathrm{d}X^2} = 0, \qquad (4)$$

where

$$\kappa = \frac{\kappa_1 + \kappa_2}{2}. \qquad (5)$$

Let us first discuss the head-to-tail wall shown in Fig. 1(a). In this case the boundary conditions are

$$p_x = 0, \quad p_y = p_s \quad \text{at} \quad X = -L,$$
$$p_x = p_s, \quad p_y = 0 \quad \text{at} \quad X = L, \qquad (6)$$

where $p_s = (-\alpha / \beta_2)^{1/2}$. The boundaries at $X = +L$ can be regarded at infinity, since the assumed boundaries are far from the center of the wall, or if the system size which we have in mind is much larger than the wall thickness. There are no analytical solutions known to eqs.(4) in general cases, numerical calculations must be undertaken.

However, since it is not our aim to show detailed solution numerically, instead of solving the Euler-Lagrange equations, we rather resort to the variation method, where a set of plausible trial functions is adopted, with the symmetry being fully respected.

In the following the center of the 90° wall is placed at $X = 0$ and L is regarded as infinity, and let us adopt the trial functions as

$$p_x = (1 + \tanh KX + b\ \mathrm{sech}\ KX)\, p_s / 2,$$
$$p_y = (1 - \tanh KX + b\ \mathrm{sech}\ KX)\, p_s / 2, \qquad (7)$$

where b and K are the variational parameters to be determined so that the total wall energy is minimal. An approximate feature of p_x and p_y is shown in Fig. 3.

Now, let us turn to the case of the head-to-head 90° wall shown in Fig. 1(b). The boundary conditions in this case seem to be

$$p_x = 0, p_y = p_s \quad \text{at} \quad X = -L$$
$$p_x = -p_s, p_y = 0 \quad \text{at} \quad X = L. \qquad (8)$$

Respecting the symmetry and regarding L as infinity, as a set of plausible trial functions we can adopt

$$p_x = -(1 + \tanh KX + b\ \mathrm{sech}\ KX) p_s / 2,$$
$$p_y = (1 - \tanh KX + b\ \mathrm{sech}\ KX) p_s / 2. \qquad (9)$$

The energies to be obtained with the trial functions (7) and (9) put into (3) are exactly the same, though they should never be physically so, since the symmetry nature of them is quite different, as is easily seen from

Figs.1 (a) and (b). Thus, it turns out that something is missing in our consideration. In fact, the effect of the depolarization field should be taken into account.

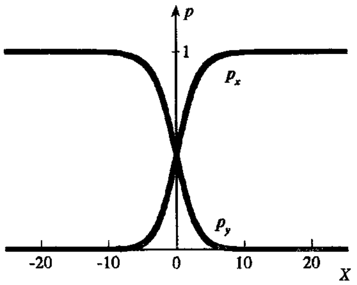

Fig. 3. The spatial modulation of the order parameters in the head-to-tail wall.

3. A MODEL WITH THE DEPOLARIZATION FIELD

First, let us consider the depolarization field, E_d, along the X-direction, because the spatial modulation of the polarization occurs in the X-direction, thst is, the modulation is a longitudinal type. The polarization component along the X-direction as p_X is expressed as

$$p_X = \frac{1}{\sqrt{2}}(p_x + p_y). \tag{10}$$

Since there is no free charge in the completely insulating ferroelectrics, we have

$$\mathrm{div}\,(E_d + 4\pi p_X) = 0\,, \tag{11}$$

from the integration of which we see

$$E_d = -4\pi p_x + c_1, \tag{12}$$

where c_1 is an integration constant.

On adding the depolarization field energy $-E_d\,dp_x = 2\pi p_X^2 - c_1 p_x$ to (3), the free energy becomes

$$f = \frac{\alpha}{2}(p_x^2+p_y^2)+\frac{\beta_1}{4}(p_x^4+p_y^4)+\frac{\beta_2}{2}p_x^2p_y^2 + \frac{k_1+k_2}{4}\left[\left(\frac{dp_x}{dX}\right)^2+\left(\frac{dp_y}{dX}\right)^2\right] + 2\pi p X^2 - c_1 p_X\,, \tag{13}$$

where the depolarization energy is expressed in terms of p_X for the sake of clarity. Then, the Euler-Lagrange equations (5) become

$$\alpha p_x+\beta_1 p_x^3+\beta_2 p_x p_y^2-\kappa\frac{d^2 p_x}{dX^2}+\frac{1}{\sqrt{2}}(4\pi p_X-c_1)=0$$
$$\alpha p_y+\beta_1 p_y^3+\beta_2 p_y p_x^2-\kappa\frac{d^2 p_y}{dX^2}+\frac{1}{\sqrt{2}}(4\pi p_X-c_1)=0 \tag{14}$$

and by integration we obtain

$$\frac{\kappa_1+\kappa_2}{4}\left[\left(\frac{dp_x}{dX}\right)^2+\left(\frac{dp_y}{dX}\right)^2\right] = \frac{\alpha}{2}(p_x^2+p_y^2)+\frac{\beta_1}{4}(p_x^4+p_y^4)+\frac{\beta_2}{2}p_x^2p_y^2 + 2\pi pX^2 - c_1pX - c_2\,, \tag{15}$$

where c_2 is an integration constant. These integration constants, c_1 and c_2, must be determined by the boundary conditions or by other physical conditions.

First, let us consider the head-to-tail wall. From the boundary conditions, we find that

$$c_1 = \frac{4\pi}{\sqrt{2}}\,p_s\,, \tag{16}$$

$$c_2 = -\frac{\alpha^2}{4\beta_1} - \pi p_s^2\,. \tag{17}$$

Regarding c_1, this is equivalent to consider that there is no field due to the depolarization at infinity.

The local energy increment due to the depolarizing field, f_d, is given as

$$f_d = 2\pi p_X^2 - \frac{4\pi}{\sqrt{2}}\,p_s p_X + \pi p_s^2 = \pi p_s^2\, b^2\, \mathrm{sech}^2\, KX\,. \tag{18}$$

For the head-to-head 90° wall, it is easily found from eqs. (14) that c_1 must be zero, i.e., $c_1 = 0$, because p_x is an odd function of X. Then, as is seen from eq. (15), the second integration constant c_2 depends upon the boundary conditions. Unless very artificial boundary conditions should be taken, the ferroelectricity must be suppressed if $\alpha + 4\pi > 0$, as is usually the case. Thus, this wall is found to be unsuitable under these conditions.

4. DISCUSSIONS

In the present paper we discussed the 90° wall well known to the perovskite-type oxide ferroelectrics. By reviewing the theory previously proposed,[8] it turned out that the depolarization field has to be taken into account, because the depolarization field is the very factor which differentiates the head-to-tail wall from the head-to-head wall distinctly, prohibiting the appearance of the latter wall.

The contribution from the depolarization field to the whole wall energy in the head-to-tail wall is found to depend on b introduced in eq.(7). It has been clarified[9] that b should be small if the free energy function is isotropic in the order parameter space, and in this case the contribution of the depolarizing field to the whole wall energy may be negligible, while b is large if the free energy function is anisotropic, implying that the contribution may not be negligible.

The process of the polarization reversal of ferroelectrics including the 90° walls is an interesting problem to study. Although a scenario has been proposed for it,[7] we need more experimental and theoretical information on the motion of the 90° wall.

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