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Wall thickness dependence of the scaling law for ferroic stripe domains

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Abstract

The periodicity of 180° stripe domains as a function of crystal thickness scales with the width of the domain walls, both for ferroelectric and for ferromagnetic materials. Here we derive an analytical expression for the generalized ferroic scaling factor and use this to calculate the domain wall thickness and gradient coefficients (exchange constants) in some ferroelectric and ferromagnetic materials. We then use these to discuss some of the wider implications for the physics of ferroelectric nanodevices and periodically poled photonic crystals.

The generic term 'ferroic' designates crystalline materials that are ordered either ferroelectrically, ferromagnetically or ferroelastically (also including antiferroic configurations). Ferroic materials usually display domains, that is, regions that are either ordered along different polar axes, or along the same axis but with opposite polarity, the latter being known as 180° domains. Ferroic domains often form regular stripe patterns. Landau [1] first, and Kittel [2] later, showed that the width of magnetic 180° stripe domains (w) is correlated to the thickness of a crystal in a very well defined manner: the domain width (w) is directly proportional to the square root of the crystal thickness (d). This law was later extended by Mitsui and Furuichi for ferroelectric materials [3], and by Roytburd for epitaxially clamped ferroelastic ones [4].

Recently, Schilling *et al* [5] have shown that the constant of proportionality between w^2 and d is a defining characteristic of the type of ferroic transition being considered, with ferromagnets having generally bigger domains than ferroelectrics for crystals of the same thickness. These experimental results were discussed by Scott [6], who observed that the differences between ferroelectric and ferromagnetic domain periodicity essentially disappeared once the domain wall thickness was incorporated as a scaling factor. Mathematically this can be expressed as $\frac{w^2}{Td} = M$, where T is the thickness of the domain wall and d is the crystal thickness; since domain walls tend to be narrow (a few unit cells) for all ferroelectrics, and

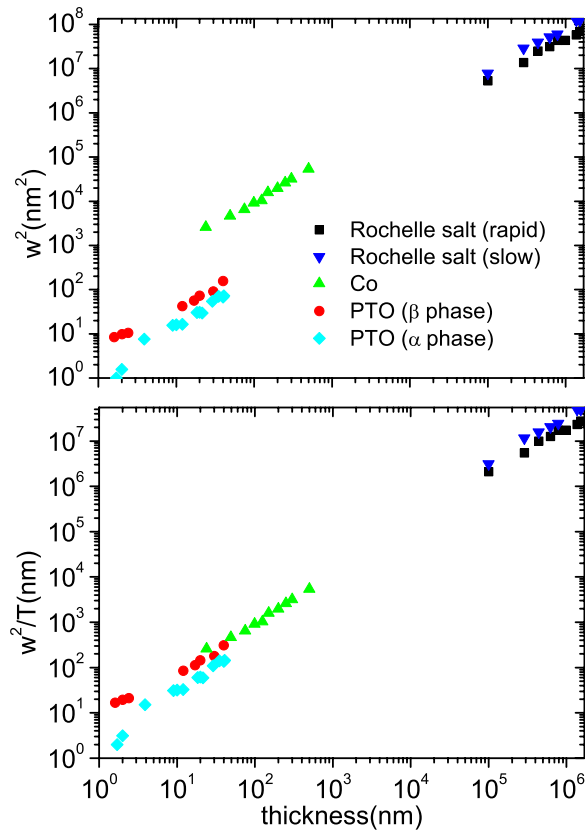


Figure 1. Above: square of the 180° domain width as a function of crystal thickness for some ferroics (data extracted from [3, 18, 25]). Below: when the square of the domain size is divided by the wall thickness, all data fall on the same parent curve. The wall thicknesses used for the scaling have been extracted from [3, 8, 22].

(This figure is in colour only in the electronic version)

broader for ferromagnets (tens of nanometres), the dimensionless factor M ends up being pretty much the same for both. This is illustrated in figure 1: the different characteristics for w^2 as a function of crystal thickness of ferroelectrics and ferromagnets fall on the same parent curve once the square of the domain width is scaled by the domain wall thickness T .

Using well known results from the theory of ferroics it is possible to derive a simple analytical expression for this dimensionless scaling constant M . Here we do this and then use the result to (a) calculate the thickness of the domain walls and the gradient coefficients in some ferroic materials, and (b) discuss the implications of our results for the physics of ferroelectric nanodevices and periodically poled photonic crystals.

We begin by writing the Landau thermodynamic potential of a ferroic with a second-order phase transition. For simplicity's sake, we have limited ourselves to the case of 180° walls in a uniaxial ferroic, so a single order parameter will suffice. We call this order parameter Q , and it can be either the polarization of a ferroelectric or the magnetization of a ferromagnet. Across a domain wall there is a change of the sign of the order parameter, which means that there is necessarily a gradient whose associated energy must be incorporated into the thermodynamic potential. Assuming that Q points along the z -direction and that the domain

wall is perpendicular to the x -axis, the thermodynamic potential is

$$\Delta G = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{k}{2}\left(\frac{\partial Q}{\partial x}\right)^2. \quad (1)$$

For a mono-domain state, and also at the centre of the domains, we can neglect the gradient term, and minimization then leads to the familiar result for the order parameter in the ferroic state:

$$Q_0^2 = -\frac{a}{b}. \quad (2)$$

The second derivative of the free energy with respect to the order parameter is the stiffness. In the ferroic state, the result is $\chi^{-1} = -2a$ or, relating this to the order parameter,

$$\chi_c^{-1} = 2bQ_0^2. \quad (3)$$

Here the term ‘stiffness’ has different meanings depending on the ferroic context, being inverse permittivity for ferroelectrics and inverse susceptibility for magnets.

The energy density of the domain wall is calculated by minimizing the energy difference between a mono-domain state and a state with one domain wall. That is, one has to minimize the following [3, 7]:

$$\sigma = \int_{-\infty}^{+\infty} \left(\frac{a}{2}(Q^2 - Q_0^2) + \frac{b}{4}(Q^4 - Q_0^4) + \frac{k}{2}\left(\frac{\partial Q}{\partial x}\right)^2 \right) dx \quad (4)$$

where Q_0 is given by equation (2). Minimization of σ with the boundary conditions $Q(x = \pm\infty) = \pm Q_0$ leads to the solution of the profile of the order parameter across the domain wall $Q(x) = Q_0 \tanh(x/\delta)$; the domain wall thickness can then be defined as $T \equiv 2\delta$, where δ is given by

$$\delta = \frac{1}{Q_0} \sqrt{\frac{2k}{b}} = \sqrt{-\frac{2k}{a}} \quad (5)$$

and the energy density of the domain wall is

$$\sigma = \frac{4}{3}Q_0^3\sqrt{2kb} = \frac{4}{3}Q_0^2\sqrt{-2ka}. \quad (6)$$

Several simplifications have been made in the above treatment. First, in constraining the order parameter to just one dimension we have implicitly discarded the possibility of Bloch walls and Néel walls. This is in principle wrong for magnetic materials—though not for ferroelectrics. However, the analysis of such walls in magnetic materials actually arrives at the same solutions for δ and σ [8]. Second, in limiting our Landau expansion to the Q^4 order, we are limiting ourselves to second-order transitions, which is not the case for several important ferroelectrics such as PbTiO_3 and BaTiO_3 , although in thin films of these two materials epitaxial clamping (regardless of strain) changes the transition from first to second order [9, 10]. The exact solution of the first-order domain wall can be found in [11]. And third, we have neglected the elastic coupling to the lattice distortions (strain terms), which is particularly important in ferroelectrics as they are generally also ferroelastic. However, the effect of strain can be incorporated by a renormalization of the coefficients in the Landau expansion [7, 9, 10, 12], so our analysis is valid once the renormalized coefficients are used.

Regarding the physical interpretation of equation (5), k represents an ‘exchange’ constant, as its energy contribution is proportional to the mismatch of spins/dipoles with respect to their neighbours (gradient term), whereas a and b represent the ‘anisotropy’ contributions, as they indicate the strength of the alignment of the order parameter with respect to the crystallographic axes. Quite naturally, it follows that if the anisotropy terms are big, the domain walls will tend to be narrow so as to minimize the number of misaligned spins/dipoles, whereas if the exchange

k is big the domain walls will tend to be wide so that the gradient is as small as possible. In magnets, the exchange interaction wins, whereas in ferroelectrics the opposite is true: hence the generally observed difference in domain wall thickness [5, 7].

The exchange constant k is well characterized for most magnetic materials, but that is not the case for ferroelectrics [13], a problem which has so far complicated the analysis based on equations (5) and (6). It is therefore interesting to write the energy density as a function of wall thickness, which removes the dependence on k :

$$\sigma = \frac{4}{3} Q_0^4 b \delta = -\frac{4}{3} Q_0^2 a \delta. \quad (7)$$

This expression will be used later.

We turn now to the relation between domain periodicity and crystal thickness in a slab cut perpendicular to the polar direction. The uncompensated dipoles/spins at the surface generate a large electrostatic/magnetostatic energy, which is reduced by creating domains of opposite polarity. The depolarization/demagnetization energy of the two crystal surfaces as a function of domain width is

$$F_{\text{surface}} = \frac{7\zeta(3)Q_0^2}{\pi^3} \sqrt{\chi_a \chi_c} w \quad (8)$$

where $\zeta(3)$ is Riemann's zeta function $\zeta(3) \simeq 1.202$,³ and χ_a is the permittivity/susceptibility perpendicular to the polar direction. Although the physical forces involved (electrostatic, magnetostatic) are different, the Maxwell equations for the energy are analogous, and thus the resulting expression for the surface energy ends up being much the same [2, 3, 8, 14–16]; the difference between the two ferroics is thus not contained in the shape of the equation, but only in the magnitudes involved: the order parameter Q (polarization/magnetization) and the permittivity/susceptibility χ .

The reduction in surface energy achieved by introducing domains is partly offset by the energy cost of the domain walls, which is proportional to σ , to the wall size (itself proportional to the crystal thickness d) and to the number density of domain walls (inversely proportional to the domain width w). Hence, $F_{\text{wall}} = \sigma d/w$. Adding the two energy components and minimizing with respect to the domain width w leads to

$$w^2 = \frac{\pi^3 \sigma \sqrt{\chi_a \chi_c}}{7\zeta(3)Q_0^2} d. \quad (9)$$

If we now substitute the order parameter Q_0 and the energy density σ by their respective expressions from equations (2) and (7), the final expression for the dimensionless factor is

$$M \equiv \frac{w^2}{d\delta} = \frac{2}{3} \frac{\pi^3}{7\zeta(3)} \sqrt{\frac{\chi_a}{\chi_c}} \simeq 2.455 \sqrt{\frac{\chi_a}{\chi_c}}. \quad (10)$$

The experimental observation that M is generally a number in the range 1–10 for any ferroic is thus explained: the result is a numerical constant ($\simeq 2.455$) modified by the square root of either the dielectric or the susceptibility anisotropy⁴ depending on whether the material is ferroelectric or ferromagnetic. This generalized expression is appealingly simple, but it has some limitations. First, the polarization at the surface has been assumed to be well described by a square-wave of amplitude P and wavelength $2w$. This implicitly assumes that the thickness of the domain wall is negligible in comparison with the domain width, which is not true

³ Calculating the energy involves integrating the Fourier series of a square-wave of period $2w$ and amplitude proportional to Q^2 ; the zeta function appears as follows: $\sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} = (1 - \frac{1}{2^3}) \sum_{n=1}^{\infty} \frac{1}{n^3} = \frac{7}{8}\zeta(3)$.

⁴ A similar equation, implicitly normalized in terms of the extrapolation length, has been reported for ferroelectric films by Luk'yanchuk and co-workers [17]. While mathematically the extrapolation length and the wall half-thickness δ are the same, we believe the wall thickness to be a more experimentally meaningful parameter.

Table 1. Calculated thickness of the domain walls (compared with previously published results) and calculated value of the exchange constant k using the experimental slope ($=\delta M$) of w^2 as a function of d for 180° domains in two different ferroelectrics. The Landau coefficients used in the calculations have been extracted from [3] and [9].

Material	δM (nm)	ϵ_x	ϵ_z	δ (Å)	δ_{previous} (Å)	k ($\text{m}^3 \text{F}^{-1}$)
Rochelle salt	21	445	9.8	13	12–22 [3]	9×10^{-11}
PbTiO ₃	3.5	124	66	2.45	$\simeq 2$ [22]	2.8×10^{-11a}

^a The coefficient k of PTO was calculated using the formula for first-order phase transitions [11].

for extremely small domain periods (e.g., in ultra-thin films), or in the immediate vicinity of the phase transition. Also, it has been implicitly assumed that the material is a perfect insulator, so that there is no charge screening the surface polarization. Generally speaking, the first approximation holds well for 180° walls in ferroelectrics, which are thinner than those of ferromagnets, while the second approximation is better for ferromagnets, as the magnetic interaction is not screened. Equation (10) is nonetheless quite successful at describing the results plotted in figure 1, and thus it can be used as a rough guide to explore some practical problems.

It has been a long-standing and challenging problem to directly measure the thickness of domain walls in ferroics, and particularly in ferroelectrics, as the latter tend to be very thin and hard to observe experimentally [19–21]⁵. On the other hand, theoretical approaches based on phenomenological models suffer from the fact that the coefficient k of the gradient term is also hard to characterize experimentally [13]. Our analysis provides a way out by combining an easy (but indirect) experimental measurement (domain period versus crystal thickness) with an equation where the gradient coefficient has been eliminated (10). So, measuring the domain width and knowing the dielectric constants of a material should in principle be enough to estimate the domain wall width.

In figure 1 we have shown the square of the domain width as a function of crystal thickness for 180° domains in ferroelectric PbTiO₃ (PTO) and Rochelle salt, and ferromagnetic Co. All of them can be analysed with the present treatment, although in the case of the PTO films a correction due to the effect of the substrate must be taken into account [15, 18]. The measured slope, the permittivities and the calculated thickness of the 180° domain walls are shown in table 1, compared to previous values extracted from the literature.

Our predicted value for δ of the Rochelle salt is 13 Å (and thus the wall thickness is $T = 2\delta = 26$ Å), compatible with the results of Mitsui and Furuichi ($T = 24\text{--}47$ Å) [3], and Zhirnov ($\delta = 12\text{--}220$ Å) [7]. As for the predicted value for the domain walls of PTO, once the effect of the SrTiO₃ substrate has been taken into account [15, 18] we obtain that $\delta = 2.45$ Å or $T = 4.9$ Å, in excellent agreement with the first-principles calculations of Meyer and Vanderbilt [22]. The combination of our model with experimental data thus agrees with previous estimates, and supports the view that ferroelectric 180° domain walls are atomically sharp [23, 24].

The above equations apply to magnetic materials too. Fitting the data for Co [25] to our model, the calculated domain wall thickness is 20 nm, which is somewhat thicker than previous theoretical estimates that yield a value of 5–10 nm, but thinner than the experimentally determined values of 46 nm [26]. All in all, the results suggest that the method is quite robust.

Moreover, once the domain wall thickness has been determined, one can go back to equation (5) and determine the value of the exchange constant (k) for the material. This

⁵ We note here that while diffraction analysis for KTiOPO₄ (KTP) assumed atomically sharp domain walls [20]; these authors have later observed their calculations to be tolerant of thicker domain wall assumptions, so the actual thickness of the domain wall for KTP remains to be experimentally measured.

constant is in fact important for ferroelectric thin films and nanostructures, and also for graded ferroelectrics: it comes up in the term associated with the surface depolarization [27–31] and the compositional gradients [32], both of which have a strong effect on functional properties. Our calculated values of k for PbTiO_3 and Rochelle salt are included in table 1.

Parenthetically, we note also that regular domains in ferroelectric crystals have important applications in photonics, where they are used for frequency conversion through quasi phase matching [33]. At present, the regularly spaced stripe domains are achieved through periodic poling, which has limitations due to the large coercive field—and sometimes finite conductivity—of some of the most important photonic crystals, such as LiNbO_3 and KTiOPO_4 . Importantly also, artificially fabricated domain structures are not in thermodynamic equilibrium, and switchback can occur [34]. While in practice periodic poling is always likely to be required (e.g. to maximize registration), one can help stabilize the patterned domain structure by choosing a crystal of the right thickness. Assuming $\delta = 3 \text{ \AA}$ and anisotropy = 1, a periodic domain structure with a domain width of for example $5 \mu\text{m}$ would be most stable for a crystal $\simeq 3 \text{ cm}$ thick or, conversely, a 0.5 mm crystal can have domains as small as $0.6 \mu\text{m}$. This suggests that the known difficulty in stabilizing narrow domains in thick crystals is not due to an intrinsic factor: indeed, experiments that exploit the depolarizing effect of backswitching voltages have achieved self-patterned sub-micron domains in LiNbO_3 crystals 0.5 mm wide [35].

In sum, the scaling law for ferroic domains provides a versatile and powerful tool for analysing the physical properties of ferroic materials in general, and ferroelectrics in particular. Our own analysis of existing data supports the view that the thickness of 180° domain walls in ferroelectrics is extremely narrow (of the order of one unit cell), and that regular patterns of sub-micron size domains can be achieved in photonic crystals. More studies of stripe-domain periodicity as a function of crystal thickness should be carried out to establish domain wall thickness and exchange parameters for other relevant ferroelectrics such as LiNbO_3 and BaTiO_3 .

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