Order-Parameter Symmetries of Domain Walls in Ferroelectrics and Ferroelastics

Pierre Tolédano,1 Mael Guennou,2 * and Jens Kreisel2

1Laboratoire des Systèmes Complexes, Université de Picardie, 80000 Amiens, France
2Département Science et Analyse des Matériaux, CRP Gabriel Lippmann, 41 rue du Brill, L-4422 Luxembourg

(Dated: January 23, 2014)

The symmetry of boundaries between ferroelectric, ferroelastic and antiphase domains is a key element for a theoretical understanding of their properties. Here, we derive this symmetry from their organic relation to the symmetry of the primary transition order-parameters. The domain wall symmetries are shown to coincide with directions of the order-parameter n-dimensional vector space, corresponding to sum of the vectors associated with adjacent domain states. This property is illustrated by the determination of the domain wall maximal symmetries in BaTiO3, LaAlO3, SrTiO3 and Gd2(MoO4)3. Besides, the domain pattern in YMnO3 is interpreted as resulting from an annihilation-creation process, the annihilation of the antiphase domains walls creating six ferroelectric domain walls merging at a single point.

Keywords: Domain walls, ferroelectricity, ferroelasticity, Landau theory, symmetry

There is currently a renewed interest for investigating the structure and physical properties of domain walls in ferroic elements, as they may represent active functional devices [1, 2]. Domain walls can have different physical properties from those of the domains they separate, their symmetry combining the intersecting symmetries of the adjacent domains plus additional symmetries transforming one domain into another [3]. A number of experimental results confirm the existence of different physical properties of the domain walls with respect to the bulk phase such as reports on (super)conducting walls separating insulating domains [4] and polar walls separating paraelectric domains [5–7] and polar walls separating paraelectric domains [8, 9]. However, it is no yet clear if all those results reflect intrinsic properties of the domain walls, or if they are related to the complex minimization of the different energy ingredients, such as surface energy, residual stresses, shape anisotropy, structural defects, impurities or stoichiometry issues, contributing to their stabilization. Theoretical tools are needed to distinguish intrinsic effects and properties. Here, we propose an approach which allows deriving the symmetry of the domain walls from their organic relationship with the primary transition order-parameter giving rise to the domain pattern. We show that although in most cases the symmetry of domain walls as obtained by geometrical considerations [4] can be straightforwardly deduced from the symmetry of the corresponding order-parameter, in a number of specific situations, considering or ignoring the order parameter symmetry leads to different predictions.

Our proposed approach for determining domain wall symmetries is based on the following property: The symmetry of the domain wall between two adjacent domains associated with the vectors \( \mathbf{V}_1 \) and \( \mathbf{V}_2 \) in the n-dimensional order-parameter vector space is an isotropy subgroup of the symmetry group of the domain state corresponding to \( \mathbf{V}_1 + \mathbf{V}_2 \). This is inferred from the property that the symmetry group of a domain wall leaves the domain pair invariant: the common symmetry operations of adjacent domains represented by \( \mathbf{V}_1 \) and \( \mathbf{V}_2 \) as well as the operations exchanging the two vectors also leave their sum invariant. Therefore, the symmetry group \( G_0 \) of \( \mathbf{V}_1 + \mathbf{V}_2 \) contains the isotropy subgroup \( G \) corresponding to the symmetry of the domain-wall. \( G \) may coincide with \( G_0 \) or be a proper isotropy subgroup of \( G_0 \). The symmetry can be further reduced for a particular choice of domain wall orientation, which in practice is not only dictated by the order-parameter symmetry but also follows from considerations such as minimization of bound charges or elastic compatibility and by the history and preparation of the sample.

As a first illustrative example of our approach, we consider the ferroelectric domains of the three ferroelectric-ferroelastic phases of barium titanate BaTiO3 having the 4mm, 3m and mm2 point groups [10]. Table 1 lists the set of stable states associated with the primary polarization order-parameter and the corresponding symmetries of each domain state [11, 12]. Figure 1 (a) shows the vectors associated with one domain of each state in the 3-dimensional order-parameter space \( E_3 \).

In the tetragonal phase the sum of the vectors of \( E_3 \) associated with a pair of ferroelectric domains at 90° coincides with the symmetry of the orthorhombic domain states. Choosing e.g. \( \mathbf{V}_1^\pm = (\pm P, 0, 0) \) and \( \mathbf{V}_2^\pm = (0, \pm P, 0) \), we have four possible combinations and two equivalent point-group symmetries \( m \sigma_m m \pm 2 \epsilon_y \) and \( m \sigma_x m \pm 2 \epsilon_y \) corresponding to the symmetry of \( \mathbf{V}_1^\pm + \mathbf{V}_2^\pm = (\pm P, \pm P, 0) \) (Table 1). Depending on the orientation of the domain wall, each sum can yield the four configurations (head-to-head, tail-to-tail, tail-to-head and head-to-tail) observed experimentally [13], as illustrated in figure 1 (b) for the \( (P, P, 0) \) case. For head-to-tail configurations, the symmetry reduces from \( m \sigma_x m \pm 2 \epsilon_y \) to \( m \).

The domain wall symmetries separating the 71° and

*Electronic address: guennou@lippmann.lu
Table I: Equilibrium states induced by the 3-component polarization-order-parameter associated with the ferroelectric transitions in BaTiO$_3$ and the improper ferroelastic transitions in LaAlO$_3$ and SrTiO$_3$: labelling of the state, equilibrium values of the order-parameter components for one domain state, space-group of the domain state.

| Domain State | Symmetry | Order-Parameter Components |
|--------------|----------|---------------------------|
| BaTiO$_3$    |          |                           |
| 0 (0,0,0)    | Pm3m     |                           |
| I (P,0,0)   | P44mm    | I (η,η,0) 14/mcm          |
| II (P,P,0)  | Ammm2    | II (η,η,η) Imma           |
| III (P,P,P) | R3m      | III (η,η,η) R3c           |
| IV (P,P,P)  | Pm       | IV (m,m,0) C2/m           |
| V (P,P,P)   | Cm       | V (η,η,η) C2/c            |
| VI (P,P,P)  | P1       | VI (η,η,η) C2/m           |
| VII (P,P,P) | P1       | VII (η,η,η) P1            |

Figure 1: (a) Directions representing one domain of the equilibrium states induced by the 3-dimensional order-parameter of BaTiO$_3$. Red arrows correspond to the observed states. (b)-(d) Vectors associated with domain walls (blue arrows) between adjacent domains (red arrows) in the tetragonal (b), rhombohedral (c) and orthorhombic (d) phases of BaTiO$_3$. The detailed meaning of the figures is in the text. In Fig. (b) black arrows show the orientations of the polarization on both sides of a domain wall.

109° rhombohedral domains of BaTiO$_3$ are obtained in the same way: putting $V_1 = (P,P,P)$ and $V_2 = (-P,P,P)$ the sum $\vec{V}_1 + \vec{V}_2^+ = (0,2P,2P)$ corresponds to the orthorhombic domain state of symmetry $m_x m_y m_z 2\pi_2$ providing the 71°-domain wall symmetry (Fig. 1 (c)). With $\vec{V}_2^- = (P,-P,-P)$, the sum $\vec{V}_1 + \vec{V}_2^- = (2P,0,0)$ coincides with the direction of the tetragonal domain state of symmetry 4 mm, the 109°-domain wall symmetry corresponding to $m_x m_y m_z 2\pi_2$ (Fig. 1 (c)), which is a maximal isotropy subgroup of 4 mm.

Neighbouring orthorhombic domains present a variety of domain wall symmetries. For the domain states $V_1 = (P,P,0)$ and $V_2^+ = (P,-P,0)$ the sum $\vec{V}_1 + \vec{V}_2^+ = (2P,0,0)$ is associated with the tetragonal domain 4 mm (Fig. 1 (d)). The domain wall having the maximal isotropy subgroup $m_x m_y m_z 2\pi_2$. For $\vec{V}_2^- = (-P,0,-P)$ the domain wall symmetry $m_x m_y m_z 2\pi_2$ is that of one of the twelve orthorhombic domain states $\vec{V}_1 + \vec{V}_2^- = (0,0,0)$ (Fig. 1 (d)). For $\vec{V}_2^+ = (P,0,P)$ the sum $\vec{V}_1 + \vec{V}_2^+ = (2P,P,P)$ yields a domain wall symmetry $\pi_2$ corresponding to the monoclinic domain state denoted IV in Table I which is not stabilized in bulk BaTiO$_3$ although its presence has been disputed in literature [14].

For determining the domain wall symmetries between the 180° ferroelectric domains of BaTiO$_3$, one has to take into account the reduction of the order-parameter space $E_3 = E_2 + E_1$. In the 2-dimensional order-parameter space $E_2$, spanned by the bases $\vec{V}_1 = (\pm P,0)$, $\vec{V}_2 = (0,\pm P)$ or $\vec{V}_1 = (\pm P,\pm P)$, $\vec{V}_2 = (\pm P,\mp P)$, the sum $\vec{V}_1 + \vec{V}_2$ provides the domain-wall orientations $\pi_y$, $\pi_x$, $\pi_x$, and $x$ having the respective monoclinic symmetries $2\pi_y/m\pi_x$, $2\pi_y/m\pi_y$, $2\pi_x/m\pi_x$ and $2\pi_y/m\pi_y$. They correspond to the four 180° domains configurations shown in Fig. 2 (d). In the one-dimensional order-parameter space $E_1$ the basic vector $\vec{V}$ coincides with the single domain state $\pm P$ of tetragonal symmetry $4\gamma/m\gamma$ which is the symmetry of the head-to-head and tail-to-tail domain walls (Fig. 2 (a)).

As a second example we describe the domain wall symmetries separating the ferroelastic domains in LaAlO$_3$ and SrTiO$_3$ which undergo improper ferroelastic transitions [15, 16] leading, respectively, to rhombohedral and tetragonal phases for different equilib-
Figure 2: Orientation of the polarization (red arrows) on each side of the 180° domain walls in the tetragonal ((a), (d)), rhombohedral (b) and orthorhombic (c) phases of BaTiO₃. The detailed meaning of the figures is in the text.

The two-component order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17]. The two-component order-parameter symmetry as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].

Although the domain-wall symmetry derived from the order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].

The two-component order-parameter symmetry as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17]. The two-component order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].

Although the domain-wall symmetry derived from the order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].

Although the domain-wall symmetry derived from the order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].

Although the domain-wall symmetry derived from the order-parameter symmetry often coincides with the symmetry resulting from the geometrical approach in terms of layer groups [4], such coincidence is not always realized as, for example, at the improper ferroelectric-ferroelastic (FF) transition in gadolinium molybdate (GMO) [17].
I–II and II–III can produce an annihilation of the FF domain walls and creation of an antiphase domain wall I–III: I–II + II–III → I–III. A striking illustration of the annihilation-creation process is found in the vortex-like domain pattern of Y MnO$_3$ [10] which shows the existence of a 6-domain state point at which annihilation of the antiphase domains results in the creation of six adjacent ferroelectric domains (Fig. 3 (c)). The two component order-parameter associated with the cell-tripled $P6_4/mmc$($\vec{a}, \vec{b}, \vec{c}$) → $P6_3cm$(2$\vec{a} + \vec{b}$, $\vec{b} - \vec{a}$, $\vec{c}$) improper ferroelectric transition in YMnO$_3$ gives rise to a total of six domain states combining three antiphase domains, resulting from the loss of the paraelectric translations ($\vec{a}, \vec{b}$), with two opposite ferroelectric 180° domains along $\vec{c}$. The corresponding cloverleaf domain pattern contains alternating ± and π 180° ferroelectric domain walls merging at a single point but no antiphase domain walls.

In summary, it has been shown on selected examples of transitions that the symmetries of ferroelectric, ferroelastic and antiphase domain walls can be directly derived from the symmetry of the corresponding adjacent domains in the order-parameter vector space. In some cases, such as the walls between the 180°-domains in BaTiO$_3$, one has to take into account a reduction of the parent order-parameter space. In all cases the domain-wall symmetry is an isotropy subgroup coinciding with the sum of the vectors associated with adjacent domains. Although only the point-group symmetry of the domain-walls has been worked out, the procedure also provides the space-group symmetries of the domain walls from which one can deduce the Bravais lattice along the two crystallographic directions preserved by the orientation of the domain wall. In our illustrative examples the maximal symmetry induced by the primary order-parameter has been considered for the domain walls without taking into account specific constraints which may reduce their symmetry. Let us finally emphasize that our proposed theoretical approach of domain walls applies to higher-order ferroics in which higher rank macroscopic tensors emerge spontaneously [21] or to non-ferroic transitions [22] involving exclusively antiphase domains. By contrast the domain wall symmetry of magnetic ferroics and multiferroics will be described elsewhere as it requires taking into account time-reversal symmetry.

The authors are grateful to B. Mettout for very helpful discussions.

[1] H. Bea and P. Paruch, Nat Mater 8, 168 (2009).
[2] E. K. H. Salje, ChemPhysChem 11, 940 (2010).
[3] G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, Rev. Mod. Phys. 84, 119 (2012).
[4] V. Janovec and J. Privratská, International Tables for Crystallography, volume D, chapter 3.4 - Domain structures, pages 449–505, 2006.
[5] A. Aird, M. C. Domenechetti, F. Mazzi, V. Tazzoli, and E. K. H. Salje, J. Phys.: Condens. Matter 10, L569 (1998).
[6] J. Seidel et al., Nat Mater 8, 229 (2009).
[7] J. Guyonnet, I. Gaponenko, S. Gariglio, and P. Paruch, Advanced Materials 23, 5377 (2011).
[8] S. Van Aert et al., Advanced Materials 24, 523 (2012).
[9] E. K. H. Salje, O. Aktas, M. A. Carpenter, V. V. Laguta, and J. F. Scott, Phys. Rev. Lett. 111, 247603 (2013).
[10] M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics, Clarendon Press, Oxford, 1977.
[11] H. T. Stokes and D. M. Hatch, Isotropy Subgroups of the 230 Crystallographic Space Groups, World Scientific, 1988.
[12] P. Tólédano and V. Dmitriev, Reconstructive Transitions in Crystals and Quasicrystals, World Scientific, Singapore, 1996.
[13] W. J. Merz, Phys. Rev. 95, 690 (1954).
[14] D. S. Keeble and P. A. Thomas, Journal of Applied Crystallography 42, 480 (2009).
[15] S. Bueble, K. Knorr, E. Brecht, and W. W. Schmahl, Surface Science 400, 345 (1998).
[16] J. F. Scott, Phys. Rev. 183, 823 (1969).
[17] L. E. Cross, A. Fouskova, and S. E. Cummins, Phys. Rev. Lett. 21, 812 (1968).
[18] J.-C. Tólédano and P. Tólédano, The Landau Theory of Phase Transitions, World Scientific, 1987.
[19] S. C. Chae et al., Proceedings of the National Academy of Sciences 107, 21366 (2010).
[20] V. A. Meleshina, V. L. Indenbom, K. S. Bagdasarov, and T. M. Polkhovskaya, Sov. Phys. Crystallogr 18, 764 (1974).
[21] P. Tólédano and J.-C. Tólédano, Phys. Rev. B 16, 386 (1977).
[22] P. Tólédano and J.-C. Tólédano, Phys. Rev. B 25, 1946 (1982).