Bloch-type Domain Walls in Rhombohedral $BaTiO_3$

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Introduction

The properties and structure of ferroelectric domain walls (FDW) play an important role in the performance of many ferroelectric devices. Among many others it impacts on their mechanical and electrical properties such as dielectric permittivity, piezoelectric constant, and polarization switching phenomena.

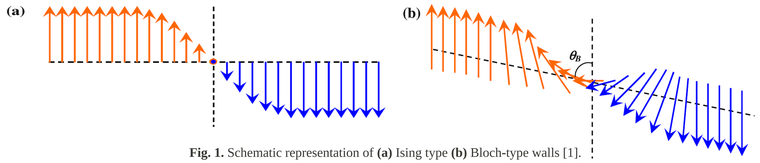


Fig. 1. Schematic representation of **(a)** Ising type **(b)** Bloch-type walls [1].

Untill recently, ferroelectric domain walls (FDWs) were usually considered to be of Ising type, in which P‖, the projection of the polarization vector onto the plane of the domain wall, simply reverses itself by passing through zero along a high-symmetry path as one scans through the domain wall. Ising FDWs tend to be favored because ferroelectrics are generally strongly electrostrictive, so that a rotation of P‖ away from this high-symmetry path would entail a significant elastic energy cost. However, there have been some theoretical predictions of the presence of Bloch and even Neel components in some FDWs [2,3]. Most recently, it has been predicted, in the framework of a phenomenological Ginzburg-Landau-Devonshire (GLD) model, that the 180° FDWs in rhombohedral $BaTiO_3$ are of Bloch type [4].

In the low-temperature rhombohedral phase of $BaTiO_3$, the possible mechanically compatible and electrically neutral FDWs are of three types: R71°, R109°, and R180°, where the angle denotes the rotation relating the polarizations on either side of the wall. The plane of the domain wall can be either {-211} or {1-10} for the 180° FDW. We have investigated the R71°, R109°, and R180°{1-10} FDWs in $BaTiO_3$ using first-principles calculations within the local-density approximation (LDA).

Geometry

The investigated mechanically compatible and electrically neutral FDWs are shown in the left column of Fig.2. On the right panel, the symmetry-adopted coordinate system (r,s,t) for each of these walls are shown. The unit vector normal to the wall is denoted by **s**. Being electrically neutral implies that the difference between the spontaneous polarization on the two sides of the wall P(∞)-P(-∞) is normal to **s**. The unit vector **r** ‖ [P(∞)-P(-∞)] is chosen in this direction. The third basis vector **t**, is defined as **t** = **r** × **s.**

The first-principles calculations are set up by considering a supercell that is extended along the wall's normal **s**. The unit vector normal to the R109° FDW is in the [100] direction, so a supercell can be easily made by stacking the 5-atom rhombohedral primitive cells in this direction. The R71° and R180°[1-10] walls on the other hand are parallel to the diagonal plane in the primitive cell. So a 10-atom unit is considered which is rotated by 45° around the *z*-axis with respect to the parent cubic unit cell and supercell is made by stacking these units in the **s** direction as shown in Fig.3.

The periodic boundary condition imposed by the computational method requires a supercell with two FDWs. For simplicity we consider two walls related by two-fold screw symmetry along the stacking direction **s**. If these walls are well separated, their effect on each other is small and leaves the general features of the walls unaffected.

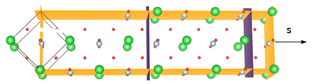


Fig. 3. A supercell with four 10-atom rotated units.

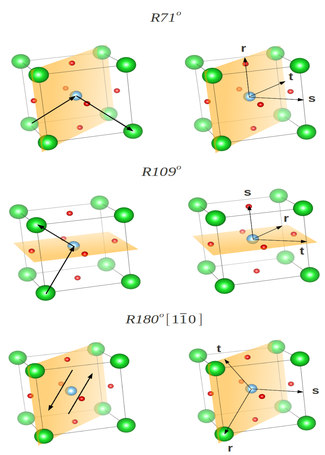


Fig. 2. The Domain walls' Geometry and coordinate system.

Computational Method

The calculations are done using the ABINIT implementation of density functional theory [5] with projector augmented-wave (PAW) pseudopotentials [6]. The plane wave cut-off and the energy cut-off for the fine FFT grid are set to 25 Ha and 40 Ha respectively. The tolerance on the difference of forces is set to 5×10^{-17} N. The structural optimizations are done using the Broyden-Fletcher-Goldfarb-Shanno minimization (BFGS).

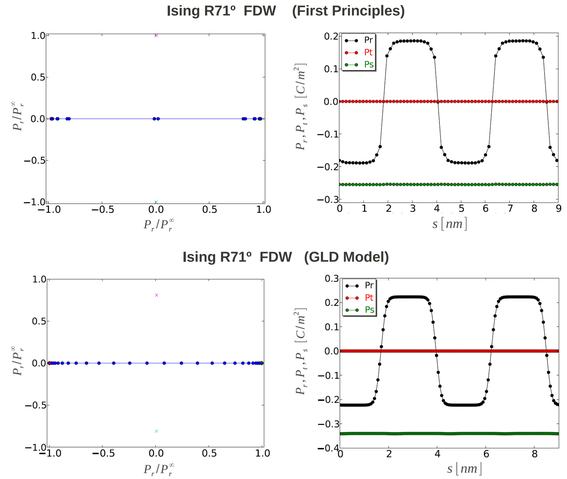
GLD Model

The GLD free energy density f is given by a functional of Cartesian components of P_i, its spatial derivatives $p_{i,j}=\partial P_i/\partial x_j$, and strain components e_{ij}:

$$f = f_L[P_i] + f_c[e_{ij}] + f_q[P_i, e_{ij}] + f_G[P_{i,j}]$$

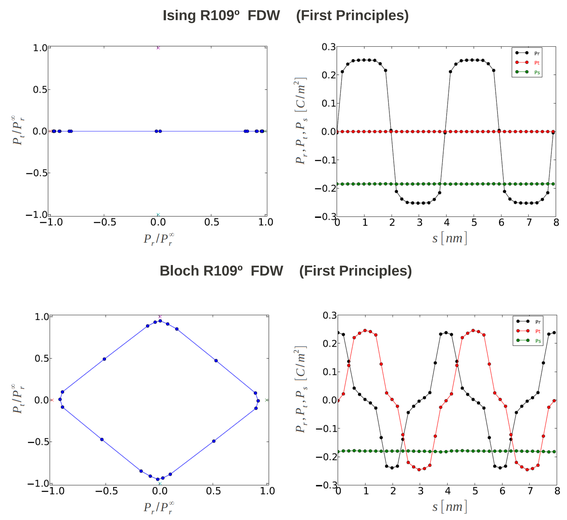
Landau Term · Elastic Term · Electrostriction Term · Gradient Term

R71° FDW



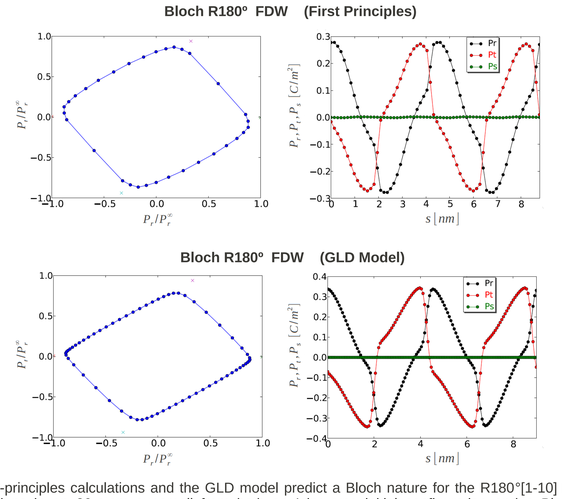
Both first-principles results and GLD model confirm the Ising nature of the R71° FDW. The polarization profile in an 80-atom supercell are calculated by first principles, and by the GLD model are shown above. As is clear from both figures, the P_t component remains zero everywhere in the supercell, which indicates the Ising nature of this FDW. The energy and width of the wall calculated from first principles are 3.7 mJ/m^2 and 0.60 nm, respectively.

R109° FDW



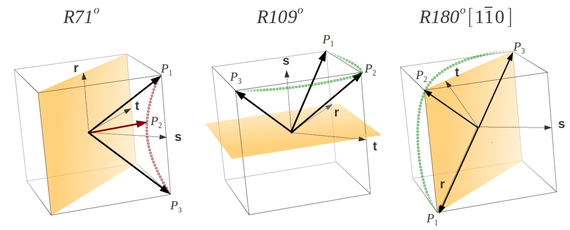
The R109° FDW has an Ising-type solution like the R71° FDW, but relaxing the atomic positions from a Bloch-type domain wall initial configuration leads to a Bloch-type R109° FDW. The energy of this Bloch-type FDW differs from that of the Ising-type R109° FDW by only a few meV. Similar results are found using the GLD model. The energy and thickness of this wall are 7.8 mJ/m^2 and 0.7 nm, respectively. The Bloch-type domain walls are typically broader than the Ising ones. The Bloch R109° FDW is about 1 nm thick.

R180° FDW



Both first-principles calculations and the GLD model predict a Bloch nature for the R180°[1-10] FDW. Relaxing the atomic positions in an 80-atom supercell from both an Ising-type initial configuration and a Bloch-type one under rhombohedral strain leads to the same solution, which means the Bloch-type solution for this FDW is a global minimum. Furthermore, comparison of the first-principles results and the GLD model [2] suggests that a 40% reduction in the gradient term in the GLD model is needed to bring agreement with the first-principles results.

Summary and Conclusion



Among the three investigated FDWs, the polarization vector rotates by the smallest angle in the R71º FDW, and by the biggest angle in the R180º FDW, so it is not surprising that the former has the smallest energy and the latter the biggest, as summarized in the table below. It appears that there is also a simple explanation for the fact that the R71º FDW is of Ising type, the R180º is of Bloch type, and the R109º FDW has both solutions with a very small difference in energy. As can be seen in the above figure, the polarization vector in a hypothetical Bloch R71º FDW would pass through a tetragonal polarization state, which is not energetically favorable in the rhombohedral phase. On the other hand, the Bloch 109º FDW and Bloch 180º FDW can be considered as a combination of two R71º FDWs, and an R71º FDW plus an R180º FDW, respectively. As can be seen from the table below, the total energy of two Ising R71º FDWs is comparable to the energy of one Bloch 109º FDW, while the total energy of a combination of one Ising R71º FDW and one Ising 109º FDW is much lower than that of an Ising 180º FDW. This can explain why the 109º FDW can be of either type, and the R180º FDW can only adopt a Bloch form.

FDW	Ising R71	Ising 109	Ising 180	Bloch 71	Bloch 109	Bloch 180
Energy $[mJ/m^2]$	3.7	7.8	36	————	7.7	28

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