

Ferrielectric Twin Walls in CaTiO_3

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Sizeable spontaneous polarization has been found in the (100) twin walls of CaTiO_3 , a definitely nonpolar material. Theoretical simulations of these walls show an extremely rich texture of the local polarization at and close to the walls, including a strong antiferroelectric component, and local nonzero contributions perpendicular to the wall plane, which do not contribute to the net dipole. Individual Ti displacements of 2 pm off the octahedron center give rise to a net polarization corresponding to a displacement of 0.6 pm in the direction of the bisector of the twin angle.

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Within the generic field of phase transitions in solids, the competition between different instabilities is a subject of special importance. From the interplay between magnetism and superconductivity in high T_c superconductors, to the very active field of multiferroics [1], substantial efforts are dedicated to understand the coupling between different order parameters, with both fundamental and applied aims. Some efforts are directed towards promoting and understanding such couplings within homogeneous materials, while others explore the mutual interactions of different materials in nanosize superstructures of reduced dimensionality (e.g. superlattices) [2–7].

Twin walls represent a particularly interesting intermediate situation, since they represent a two-dimensional nanosized feature within a homogeneous solid. They are characterized by a primary order parameter, which dominates in the bulk of the uniform solid and disappears inside twin walls. Competing secondary order parameters often show the inverse behavior, appearing inside twin walls [8,9] but being suppressed in the bulk. This behavior has been explored extensively for ferroelastic walls, where quite remarkable phenomena are observed, e.g., twin walls that can support superconducting currents within an otherwise insulating material [10]. The theoretical rationale for such exotic internal wall structures is captured mainly by the Houchmandazeh-Laizerowicz-Salje coupling term $H_c = \frac{1}{2} \lambda Q^2 P^2$ (with $\lambda > 0$), which is always compatible with the crystal symmetry [11], or via equivalent gradient coupling analogous to a flexoelectric term.

Here we show that this coupling is physically realistic and sizeable for polar walls in nonpolar materials, where Q is the ferroelastic parameter as manifested by the relevant octahedral tilt, and P is the polarization appearing in the wall. The twin walls thus carry their own dipole moment inside a ferroelastic paraelectric matrix. Similar two-dimensional polarizations have been proposed in nanostructured materials [3–6], the main difference being that twin walls are mobile, which gives them an additional dynamic dimension and interesting possibilities for manipulation. Polar walls can be influenced by external elec-

tric fields, which could lead, for instance, to extremely fine scale dynamic memory devices, analogous to those recently proposed using magnetic domains [12], but based on domain walls instead of domains, and hence much finer. Also, the dynamics of the walls, and thus the response and dissipation when deforming, should be tunable with electric fields, since the motion mechanism [13] is affected by secondary order parameters [14].

While indirect evidence for the polar behavior of twin walls has been reported before [15], as well as in antiphase boundaries [16] and grain boundaries [17], here we present the first clear indication of twin wall polarity and propose an underlying structural mechanism for the coupling between strain and dipole moment. We have chosen CaTiO_3 as an example because its orthorhombic low-temperature form (space group $Pnma$) is purely ferroelastic and no ferroelectric features have ever been recorded for it. The TiO_6 octahedron, on the other hand, is well known for its tendency to form polar groups where the Ti position is off-centered with respect to the geometrical center of the surrounding oxygen atoms. Such polar structures exist in compounds such as BaTiO_3 , PbTiO_3 and others. The known competition with octahedral rotation [18] in the tetragonal and orthorhombic phases of CaTiO_3 suppresses the off-centering. It is, however, restored when the rotation angle vanishes or when the density of the material decreases. Both conditions are met inside the twin wall and it is thus not entirely unexpected that twin walls should show dipolar moments. What is unknown is the actual size of the polarization and the texture of the polarization field. Our findings indicate the development of off-center displacements comparable to the bulk values of common ferroelectric materials, and an extremely rich texture of polar ordering structure within the wall, with both antiferroelectric and ferroelectric components, displaying a final (ferrielectric) net polarization.

To investigate polar ordering in the ferroelastic walls of CaTiO_3 , numerical simulations have been performed based on an atomic-scale description of the walls in which atoms interact via empirically defined forces. This technique has

been chosen because, on the one hand, we do not need precise quantitative numbers but rather relative sizes and orientations, and, on the other hand, because a sufficiently large simulation box is needed. Periodic boundary conditions were used in three dimensions. Open boundary conditions in the direction perpendicular to the walls would imply surfaces, which would add unwanted complexity to the problem. Two twin walls are needed to conform to periodic boundary conditions. In the directions parallel to the walls, sufficient size is needed to allow for nontrivial textures of the polarization in the wall (different orderings of off-centering vectors). A supercell was built of 26 unit cells in the direction perpendicular to the walls (hereafter called x), six unit cells in the direction perpendicular to the plane of the twin angle (hereafter called z), and ten unit cells in the bisector of the twin angle (y , see Fig. 1). We are referring here to unit cells of the primitive cubic cell, with one formula unit per cell. This gives a total of 7800 atoms.

The twin walls considered are parallel to the (100) plane of the cubic high-temperature phase ($Pm\bar{3}m$), which is equivalent to the (110) plane in the orthorhombic low-temperature phase ($Pnma$). The initial structure was built by taking one half of the system in the equilibrium bulk orthorhombic structure, with the conventional \vec{a} , \vec{b} , and \vec{c} along the (110), $(1\bar{1}0)$, and (001) directions of the supercell axes, respectively, and rotating it around the z axis to generate the other half [19]. This procedure generated a ferroelastic twin wall with the primary order parameter Q being the octahedral rotation around the y axis and the twin

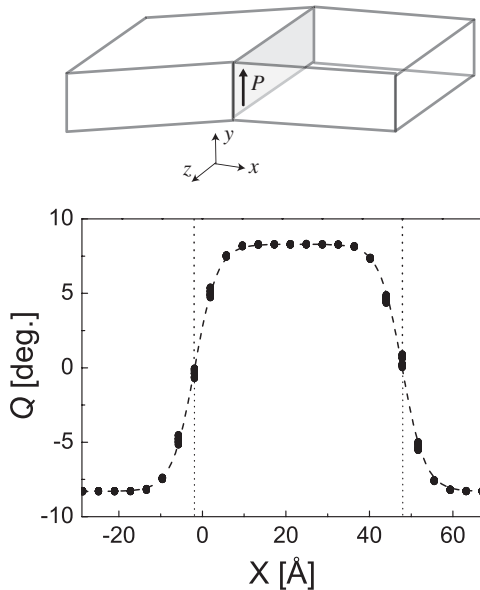


FIG. 1. Top panel: Sketch of the geometry and orientation of the twin wall (at $x \sim 48$ Å). P indicates the direction of the net ferroelectric moment. Bottom panel: Octahedral rotation as primary order parameter, Q , versus position perpendicular to the twin wall. The dashed line is a fit to the expected hyperbolic tangent. The vertical lines indicate the position of both walls.

angle in the xy plane. It also generated an antiphase boundary in the rotations around the z axis of no ferroelastic significance, which was annealed away dynamically (see below).

The results below are presented for the force field used in Ref. [19] for this material. It is based on a Buckingham potential (exponential core-core repulsion, r^{-6} attraction and Coulomb interaction between ionic charges) with parameters fitted to reproduce the experimental structure. The orthorhombic structure is obtained within 0.2% for the lattice parameters, and the tilt angles within 1° (more details will be presented elsewhere [20]). The orthorhombic phase has been found to be stable within this description (it represents an energy minimum with respect to atomic displacements and lattice deformations, and, so far, no lower energy minimum has been found). The robustness of the conclusions of this paper have been checked by using a different force field generated for the purpose [21] by fitting the parameters to reproduce structure, elastic constants, and zone-center phonons [20]. The conclusions of this work are unchanged by the choice of force field (relevant numbers are offered below for comparison). Although finer details might be different, there is no reason to expect that the qualitative picture obtained here would be altered if first-principles calculations were used instead.

The overall structure of the supercell was relaxed in two stages. Firstly, a mild thermal treatment (0–10 K) was applied to the prepared sample for 10 ps of molecular dynamics. The simulations used a time step of 1 fs, and were done for controlled temperature and pressure, allowing for variable cell shape [22]. This procedure removed the antiphase boundary and located the equilibrium basin. Secondly, a slow final quenching to zero temperature of 10 ps was performed to obtain the final structure with as little structural noise as possible.

Figure 1 shows the primary order parameter Q as a function of x , in the direction perpendicular to the wall. Q is a measure of the rotation around the y axis of the oxygen octahedra around each titanium atom, appropriately sign corrected. The dashed line indicates the fitted $Q_0 \tanh(x/w)$ functional form expected from Landau theory [23] (one such function for each barrier), with $Q_0 = 8.3^\circ$ and $2w = 10.9$ Å. The obtained wall width lies well within the experimental values as determined previously [24–26]. The second force field gives a width of $2w = 8.4$ Å and $Q_0 = 9.5^\circ$.

The secondary order parameter of interest here is the off-centering of Ti from the center of charge of the corresponding oxygen octahedron. The largest displacements are of 2.0 pm (2.6 pm for the second force field), mostly along the z direction. Two types of off-centering are seen (Fig. 2). The largest component is the one along the z direction, within the domain wall. This off-centering is antiferroelectric with alternating Ti positions shifted in opposite

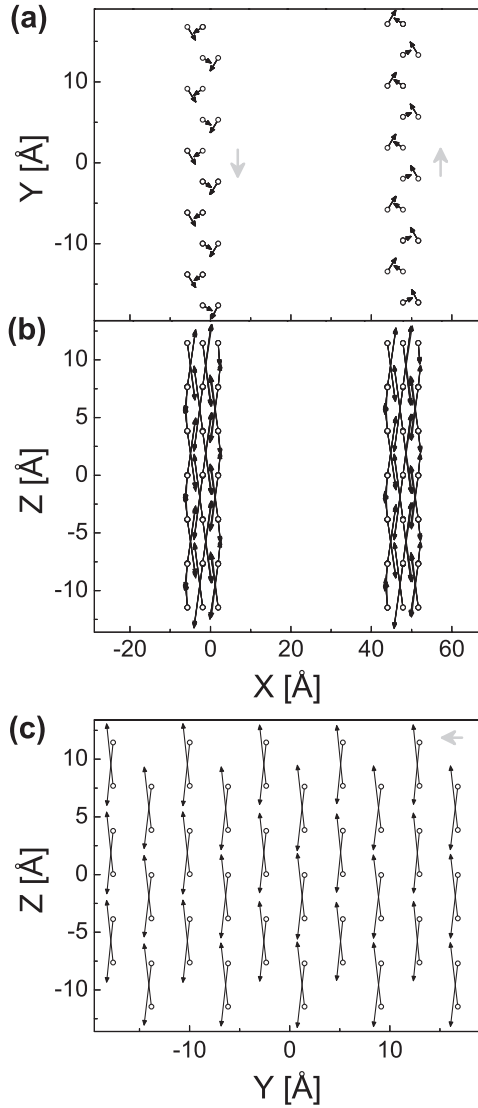


FIG. 2. Dipole moments and texture at twin walls, as projected onto (a) the xy , (b) the xz , and (c) the yz planes. The arrows indicate the Ti displacement from the center of the corresponding O octahedron. Their sizes have been scaled by a factor of 300 with respect to the scale in the axes. Panel (c) shows the twin wall plane. The gray arrows indicate the direction of the net polarization.

directions. In contrast the off-centering along the y direction is ferroelectric and produces a net dipole moment for each domain wall equivalent to a net displacement of 0.6 pm per Ti atom (0.9 pm for the second force field). There is also a smaller antiferroelectric component along the direction perpendicular to the wall, x . The direction of the net polarization with respect to the twin wall geometry is illustrated in Fig. 1.

Rather than polarization, each twin wall displays a net dipole density, defined as dipole moment per unit area. In a system defined by point charges like the one considered here, this dipole density is obtained by summing the dipole

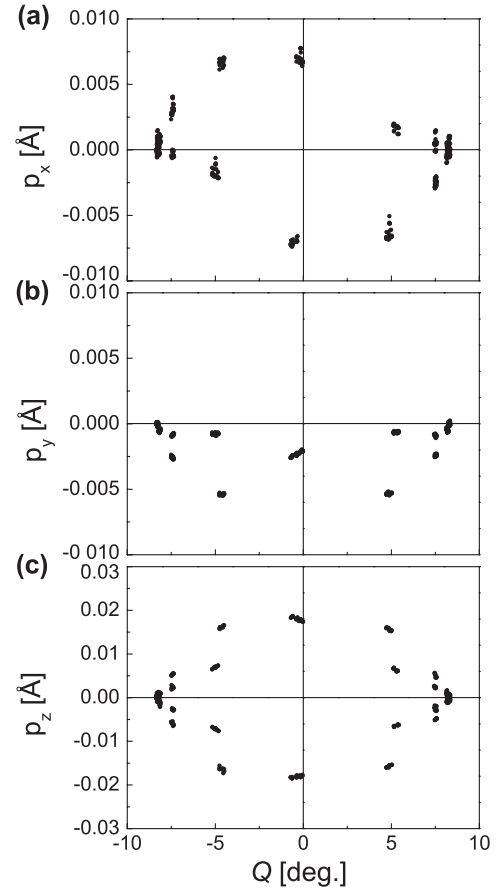


FIG. 3. Off-centering of Ti atoms within their corresponding O octahedra: Their Cartesian components are plotted against the primary order parameter Q .

moments associated with Ti atoms over all layers at and close to the twin wall, and dividing by the area considered (in this case the yz cross-sectional area of the simulation box). The local dipoles can be related to octahedral off-centerings by the effective charge on the Ti atoms, $\vec{d} = q_{\text{eff}} \delta \vec{r}$. This effective charge cannot be determined within the framework of these calculations (it could be obtained as the Born effective charge for a simulation with explicit electronic structure). We propose two different estimates: (i) the formal charge on Ti ($+4e$), and (ii) the effective charge that relates the experimental measures of off-centering and polarization in BaTiO_3 , which is $\sim +8e$. For formal charges the dipole per unit area is $5.1 \times 10^{-12} \text{ C/m}$ for model 1, and $2.2 \times 10^{-11} \text{ C/m}$ for model 2. These numbers would double for $q_{\text{eff}} = +8e$. It is also illustrative to give the effective polarization at the wall by taking these numbers and dividing them by the wall thickness, which gives 0.004 C/m^2 for model 1 and 0.02 C/m^2 for model 2, for $q_{\text{eff}} = +4e$ (twice as much for the other estimate).

Alternating domain walls show opposite dipole moments. This is a consequence of the fact that the net ferroelectric moment does not originate from a spontaneous

symmetry breaking process, but rather a consequence of the symmetry being already broken by the wall. A further consequence of this is that the signs of P and the twin angle are locked, and thus there will be no independent switching of either. In other words, the deformation (and shape) of the sample will be coupled to its polarization by the electromechanical coupling at the twin walls.

A plan view of the central Ti-layer of a domain wall in Fig. 2(c) clearly shows the zig-zag motion of the displacement in the direction of the z axis with a resulting ferrielectric dipole moment in the y direction. The rich texture displayed in Fig. 2 is reproduced by the second force field.

Figure 3 shows the behavior of the three off-centering components versus the primary order parameter. The small x component (perpendicular to the wall) for the off-centering gives an overall antisymmetric curve with respect to Q , as expected from symmetry considerations. In this particular case the main displacements along x point towards the wall from both sides. The other two curves are symmetric (within the accuracy of the relaxation), showing one the ferroelectric component, and the other the antiferroelectric one. It is interesting to note that the maximum ferroelectric component does not occur in the middle of the wall, but halfway toward the tails of the wall. This is very probably due to the interaction with other secondary order parameters (a slight enhancement of other tilt angles is observed in the walls, for instance [20]). Indeed, the complexity of the patterns in Fig. 3 is clearly beyond what is expected from a two-order-parameter Landau theory. In particular, off-centering appears multivalued for some values of Q in Fig. 3, which reflects the fact that inequivalent Ti atoms react differently to the presence of the wall at finite Q values. We hope these results will stimulate not only experiments and more sophisticated calculations, but also a theoretical model to capture the essentials of the obtained texture. The fact remains, however, that a net polarization is associated to each wall.

In summary, ferrielectric twin walls have been obtained from theoretical simulations for a nonferroelectric material. The sizeable Ti off-centering displays an intricate texture, with strong antiferroelectric components and a net polarization in the direction pointed by the chevron defined by the twin angle.

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