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Highly mobile vortex structures inside polar twin boundaries in $SrTiO_3$

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We present computer simulations of previously unknown polarization singularities (vortexes) inside polar $SrTiO_3$ twin boundaries. Usually polarity in twin walls is ferri-electric, whereas vortex excitations lead to true ferroelectricity on a very local scale. As a result, in-plane electric fields can selectively stabilize one of the vortex polarization states and enhance the ability of the walls to move. This behavior can explain the well-known and uniquely high, mobility of twin boundaries in $SrTiO_3$. For nanoscale ferroelectric memory devices, we envisage a precisely controllable device, where a desired domain wall pattern is manipulated by shifting the vortex position electrically. [http://dx.doi.org/10.1063/1.4866859]

As devices become smaller and smaller, their functionality will be constrained to ever smaller dimensions.[1,2] The future goal will be to produce multifunctional elements (such as memory devices) with a length scale of 1–10 nm, rather than the currently available 500 nm. The most promising way forward is to use, as a host, a ferroelastic material which will produce very high densities of functional twin boundaries. Typical examples are superconducting domain boundaries in insulating materials,[3,4] twin boundaries with high defect mobilities,[5–7] two-dimensional electron gases at interfaces,[8–10] unusual vortices near twin boundaries,[11–13] or multiferroicity and chirality at domain boundaries.[14–16] The design and the development of such interfaces is at the heart of "domain boundary engineering"[17,18] and this paper is probably one of the biggest advances in multiferroic material design: We show that twin boundaries in $SrTiO_3$ have exactly the required functionalities for ferroelectric nanodevices.

Functional ferroelectric twin boundaries can be polar with dipole moments aligned in direction of the apex of the twin wall.[19] This is not the only solution, however, and, as we show in this letter, some segments of a polar wall in $SrTiO_3$ have dipole moments pointing towards the twin-apex, while other segments have dipole moments pointing in the opposite direction. Both solutions are compatible with the symmetry of the twin boundary. A unique structural element is that a vortex connects these two segments. The vortex rotates the dipole moment out of the twin wall and hence breaks the symmetry. Moreover, this rotation generates another degree of freedom: A vortex can rotate clockwise or counterclockwise, therefore, the resulting symmetry breaking dipoles can enhance or compensate for other vortexes.

Twin boundaries in $SrTiO_3$ are indeed polar, with dipole moments in the twin plane. This alone is not sufficient, however, because it only implies ferri-electricity (as previously found in $CaTiO_3$ (Ref. 20)). In the present work, we detected an unusual feature: the dipoles frequently reverse direction inside the wall. The switching behavior is not like an Ising wall, but instead follows the trajectory of a Bloch wall: the dipole rotates out of the twin plane. During the rotation, dipoles point in a direction perpendicular to the wall and hence become switchable! Due to improved functionality offered by this process, the vortexes of the rotating dipoles become the more suitable functional elements, rather than the polarity of the walls, as previously anticipated. The most spectacular consequence is that the twin walls have a lower symmetry than the bulk (P1). Thus, the asymmetry of the atomic positions in the walls may promote superconductivity and we may speculate that the unexplained superconductivity in $SrTiO_3$ indeed has its origin in the mixing of spin singlet and triplet states when the inversion symmetry is broken.[21] Moreover, the optical phonon density of states available for Cooper pairs will be substantially increased. This scenario could follow the path of wall related superconductivity as found in another perovskite crystal.[3]

Research during recent years has shown that the discovery of interfacial ferroic properties is often triggered by computer simulations and theoretical exploration of extreme physical properties in materials design. The first and main report of polar interfaces in non-polar materials was in $CaTiO_3$: A large spontaneous polarization was predicted in {100} twin walls of $CaTiO_3$, a definitely non-polar material.[20] Subsequent experimental studies using transmission electron microscopy[22] and second harmonic generation (SHG) confirmed such wall polarity.[23,24] Similar behavior was attributed to multidomain boundaries with distinct polar and oxygen octahedral tilting in $BiFeO_3$ *ab initio* simulations.[25]

The latest experimental advance was reported[26] in resonant piezoelectric spectroscopy (RPS) experiments for strontium titanate at cryogenic temperatures, well below the ferroelastic transition (105 K). The signals were too weak to be related to bulk piezoelectricity. Instead it was argued that standing mechanical waves were excited by the shift of twin boundaries in an oscillating electric field. Together with previous work showing that elastic resonances in $SrTiO_3$ are heavily influenced by moving twin boundaries with a dramatic change of the pinning behavior below 50 K,[27] it constitutes a direct evidence of twin boundary polarity in $SrTiO_3$, but the physical mechanism for the field effect is still unknown.

In this paper, we show that polar twin boundaries do indeed spontaneously form at low temperatures without any

subsidiary help from defects or external strain fields, and can be moved by electric fields. $SrTiO_3$ has a non-polar bulk structure.[28,29] Wall polarity requires coupling between the local lattice deformation (as expressed by the ferroelastic order parameter Q) and a dipole moment P. If symmetry allowed, coupling λQ^2P^2 is mainly repulsive ($\lambda > 0$),[14] or if suitable gradient couplings occur,[30] the polarization is suppressed inside the bulk but not in the domain walls. This effect localizes P to the wall. The open question is then how specific coupling schemes of this type follow from the local interatomic interactions.

To investigate twin walls in $SrTiO_3$, we conducted atomistic simulations in tetragonal and cubic samples, comprised of 40 000 atoms, exploiting the MD package LAMMPS.[31] Typical geometry was $\sim 80\,\text{Å} \times 80\,\text{Å} \times 80\,\text{Å}$ and a timestep of 2 fs was used. We imposed periodic boundary conditions in all three directions, verifying that they have minimal impact on the twin structure. The global cutoff for non-Coulombic interactions was chosen to be 12 Å. In isothermal simulations, the temperature was controlled by a Langevin thermostat[32] with damping parameter $\tau = 0.2$ ps at initial equilibration and by a Nosé-Hoover thermostat[33] with $\tau = 0.1$ ps, at data sampling. In isobaric simulations, the pressure was controlled using a Berendsen[34] barostat at equilibration and Nosé-Hoover[35] with $\tau_P = 1$ ps at sampling.

The strontium titanate interatomic interactions were modeled by the Buckingham potential, previously parameterized by Akhtar *et al.*[36] The corresponding lattice constant was estimated to be within 0.5% of experimentally obtained 3.905 Å[37,38] at room temperature. By fixing the lattice parameter at the experimental values, we estimated the elastic constants in good correspondence with previous experiments.[39]

Below 105 K,[28,29] the high-symmetry cubic perovskite structures undergoes a second-order phase transition to a tetragonal structure with symmetry $I4/mcm$. The tetragonal cell consists of two pseudocubic cells with the cubic cell face diagonals as cell vectors and ratio $c/a \simeq 1.0006$ determined experimentally.[37,40–42] As a primary order parameter Q, we examined bulk rotations of octahedra. For bulk $SrTiO_3$, the octahedral rotation is 2° in experiments,[43] and 8°–10° in simulations with shell model pair potentials.[36] The discrepancy, caused by polarization terms, between experimental determination and available classical pair potentials is well known and described elsewhere.[44] Employing standard definitions of octahedral tilting,[7,8,20,45] we found a tilt angle of 9°–11°, formed around each Ti atom in the annealed bulk tetragonal system.

A twin boundary was created by merging two supercells along the diagonal [−101], one with conventional tetragonal a along x and c along z and the other one with short a along z and long c along x. The two structures were rotated by a small angle around the y axis to match the lattice periodicity of the two pieces. The resulting structure was relaxed using steepest descent and further equilibrated in canonical ensemble NVT runs for 2 ns at 20 K. The final twin was described in terms of order parameter Q and an off-centering distance δ across the twin boundary.

After equilibration, the octahedra located far from the twin boundary were rotated as previously in the bulk samples, while in the diagonal plane a twin wall appeared,

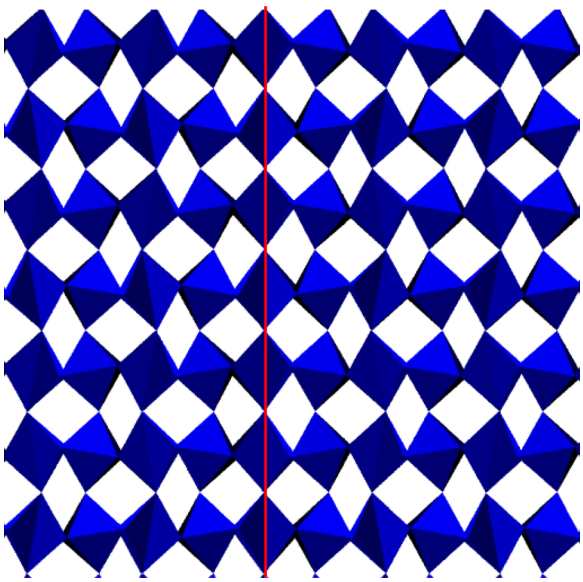

FIG. 1. A snapshot of the TiO_6 octahedral tilts in the vicinity of the twin wall (vertical red line). Notice the change of the tilting angles across the boundary.

characterized by zero tilting angles (as shown in Figs. 1 and 4). It remained stable throughout time evolution. Its thickness was measured as $2\omega = 9.4$ Å by fitting Q to a wall profile given by a hyperbolic tangent. The atomic displacement pattern exhibited two kinds of behavior (see Fig. 2). Ti atoms have a significant correlated repulsive shift from the in-plane centre of the polarization vortex, but remain randomly displaced beyond the boundary. In the planes directly adjacent to the twin, Ti atoms move towards the polarization vortex, while Sr atoms shift away from the vortex. An additional structural examination around the walls indicates a decrease by ∼4.5 pm of Ti-Ti nearest neighbor distances perpendicular to the walls (similar to the dipole moment 6 pm in $CaTiO_3$ (Ref. 45)) and an increase by ∼1.0 pm of Sr-Sr distances at the wall, as shown in Fig. 3.

In summary, we modelled a phenomenon of switchable polarity in $SrTiO_3$, occurring due to the fact that opposing polarities are connected by highly mobile vortexes. In turn,

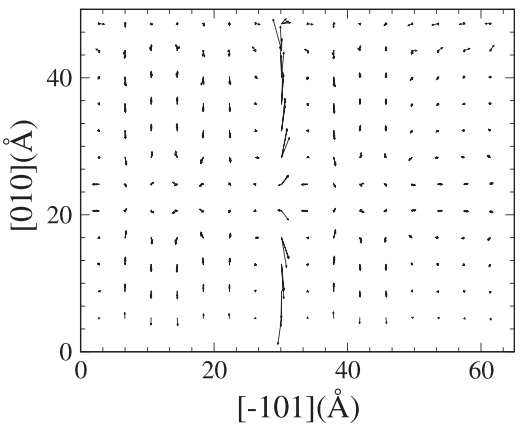

FIG. 2. In-plane displacements of Ti-atoms with respect to the centre of oxygen octahedra. The twin boundary is characterized by the appearance of a vortex. All arrows are amplified by factor of 20.

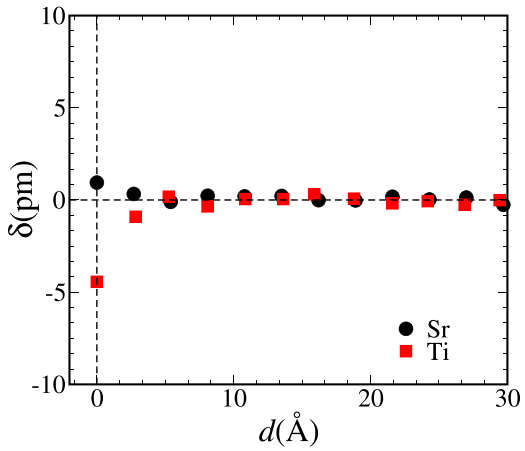

FIG. 3. The variation of the Sr-Sr and Ti-Ti nearest-neighbor distances in the bulk and near the twin wall against the distance perpendicular to the wall.

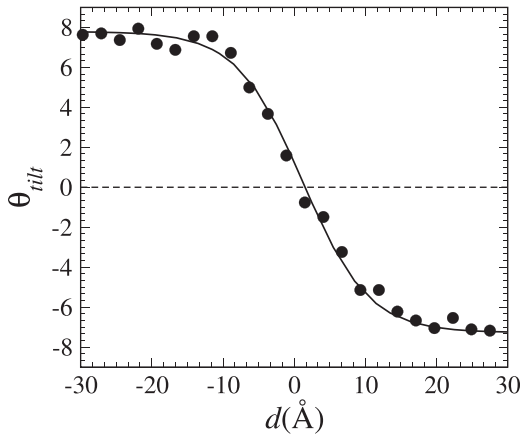

FIG. 4. Octahedral tilting angle, used as an order parameter plotted against the distance perpendicular to the twin wall. The points represent simulation results at 20 K, while solid line represents a fit to the hyperbolic tangent with the wall width $2\omega = 9.4$ Å.

the twin walls are highly mobile under external strain and electric fields,[26] causing a rapid change of the dipole moment. An upcoming objective of our research is to model an electric field in simulations to emulate these conditions. A possible application could be in controlled nanoscale memory devices (e.g., non-volatile[46] or reversible electronic switches used in resistive RAM[47]), where a desired domain wall pattern is traced by the vortex position between the electrodes. These vortex structures have many similarities to the "racetrack" arrangement, where magnetic boundaries are shifted inside a magnetic nanowire.[48] The shift of the vortex line can then be monitored electrically (an electric dipole perpendicular to the twin boundary) or magnetically if the velocity of the vortex allows electromagnetic coupling. Developing such a nano-device clearly still requires that some obstacles are overcome, such as the optimization of wall pinning, but our study elucidates that the fundamental physical effects exist and that local ferroic vortex switching will become a realistic possibility in the future.

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