Observation of Uncompensated Bound Charges at Improper Ferroelectric Domain Walls

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ABSTRACT: Low-temperature electrostatic force microscopy (EFM) is used to probe unconventional domain walls in the improper ferroelectric semiconductor Er$_{0.99}$Ca$_{0.01}$MnO$_3$ down to cryogenic temperatures. The low-temperature EFM maps reveal pronounced electric field gradients generated by partially uncompensated domain-wall bound charges. Positively and negatively charged walls display qualitatively different fields as a function of temperature, which we explain based on different screening mechanisms and the corresponding relaxation time of the mobile carriers. Our results demonstrate domain walls in improper ferroelectrics as a unique example of natural interfaces that are stable against the emergence of electrically uncompensated bound charges. The outstanding robustness of improper ferroelectric domain walls in conjunction with their electronic versatility brings us an important step closer to the development of durable and ultrasmall electronic components for next-generation nanotechnology.

KEYWORDS: Electrostatic force microscopy, domain walls, improper ferroelectric, cryogenic temperatures, hexagonal manganites

Surfaces and interfaces in complex oxide materials can be electrically polar, which leads to unusual physical behavior beyond the bulk properties. These include local electronic reconstruction phenomena such as emergent quasi-2D magnetism, multiferroicity, and superconductivity. Recently, it has been demonstrated that polarity-driven reconstruction also occurs at ferroelectric domain walls, that is, natural interfaces that separate regions with a different orientation of the spontaneous ferroelectric polarization. Domain walls in ferroelectrics develop, for example, diverse dc transport characteristics ranging from highly conducting to strongly insulating states and unusual ac conductivity and can be used to implement elementary digital operations. Furthermore, as an advantage to artificially designed interfaces, the domain walls can be injected, moved, and erased on demand, opening up completely new opportunities for interface engineering and nanoelectronics applications.

The spontaneous formation of charged domain walls is rare in proper ferroelectrics such as BaTiO$_3$ and PbZr$_{0.2}$Ti$_{0.8}$O$_3$ because of the high electrostatic costs. Using special preparation methods, charged walls can be created, but their stability critically depends on the material’s ability to screen the associated diverging electrostatic potential.

A different situation arises in so-called improper ferroelectrics; in this class of materials, the polarization is a byproduct that evolves as a secondary effect, whereas the primary symmetry-breaking order parameter can be, for example, of structural or magnetic origin. As a result, charged domain walls naturally arise in the as-grown state, enforced by the primary order parameter, which is responsible for the symmetry breaking and domain formation. Because of the secondary nature of the polar order, charged walls are

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significantly more stable in improper ferroelectrics than in proper ferroelectrics, and theory even predicts that they may exist without screening, representing a rare example of a stable, electrically uncompensated oxide interface.\(^5,18\)

In this Letter, we report on the observation of electrically uncompensated charged domain walls in hexagonal manganites. Using low-temperature scanning probe microscopy (SPM) and analytical modeling, we investigate the electronic domain-wall transport, carrier distribution, and electrostatics at positively (head-to-head) and negatively (tail-to-tail) charged improper ferroelectric walls at temperatures down to 4.2 K. By decreasing the temperature, we observe the emergence of pronounced electric far fields that originate from partially unscreened bound charges at the domain walls. The magnitude and temperature dependence of these fields are qualitatively different for head-to-head and tail-to-tail walls, which we explain based on the local distribution of screening carriers. Our low-temperature study provides new insight into the electrostatics at domain walls in improper ferroelectrics and demonstrates a new aspect of their outstanding robustness.

**Ferroelectric Domain Walls in Er\(_{0.99}\)Ca\(_{0.01}\)MnO\(_3\).** For our study, we choose the p-type hexagonal semiconductor Er\(_{0.99}\)Ca\(_{0.01}\)MnO\(_3\). The system exhibits improper ferroelectricity below \(T_c \approx 1470\) K, with a spontaneous polarization \(P_s \approx 6\) \(\mu\)C cm\(^{-2}\) at room temperature.\(^19,20\) In the ferroelectric phase, the system develops all fundamental types of ferroelectric domain walls, namely, neutral (side-by-side) as well as negatively (tail-to-tail) and positively (head-to-head) charged walls; the atomic structure and basic transport phenomena at these walls are now well understood.\(^3,21,22\) At tail-to-tail walls, hole carriers accumulate to screen the negative bound charges, giving rise to enhanced conductance. In contrast, the screening at head-to-head walls is explained by hole depletion and the subsequent formation of an electronic inversion layer. The latter governs the conductivity at high voltage, enabling switching between insulating (low-voltage) and conducting (high-voltage) domain-wall behavior.\(^23\) Compared with the parent compound ErMnO\(_3\), the doping of Ca\(^2+\) enhances the bulk conductivity and hence improves the screening efficiency at the walls.\(^24\) Single crystals of Er\(_{0.99}\)Ca\(_{0.01}\)MnO\(_3\) are grown by the pressurized floating-zone method.\(^24\) A specimen is orientated by Laue diffraction and prepared into a 70 \(\mu\)m thick platelet with the ferroelectric polarization (P\(_{\perp}\)) lying in the surface plane. To achieve the flat surface required for our measurements, the sample is chemically mechanically polished using silica slurry, yielding a root-mean-square roughness of \(<1\) nm. Platinum markers with a distance of \(20\) \(\mu\)m are patterned on the surface by electron beam lithography in positive tone resists and subsequent electron beam evaporation of platinum for navigation and for reliably tracking regions of interest in the SPM measurements. The latter are performed on an NT-MDT NTEGRA Prima atomic force microscopy (AFM) system (room temperature) and an attocube attoLIQUID2000 AFM (low temperature).

**Temperature-Dependent Transport at Tail-to-Tail and Head-to-Head Walls.** We begin with piezoresponse force microscopy (PFM) and conducting atomic force microscopy (cAFM) measurements gained on Er\(_{0.99}\)Ca\(_{0.01}\)MnO\(_3\) at room temperature. The PFM data in Figure 1a show a pattern of ferroelectric 180° domains (in-plane P) with meandering domain walls and six-fold meeting points.\(^2,22,25\) The cAFM scans obtained at the same sample position (Figure 1b) with a tip voltage \(V_{\text{bias}} = 3\) V show conducting tail-to-tail (bright) and insulating head-to-head walls (dark), confirming that our Er\(_{0.99}\)Ca\(_{0.01}\)MnO\(_3\) sample develops the peculiar domain and domain-wall properties common to hexagonal manganites.\(^3,10\) Figure 1c–e displays selected cAFM scans recorded as a function of temperature around a six-fold domain-wall meeting point. Analogous to Figure 1b, a pronounced conductance contrast is observed at both tail-to-tail and head-to-head walls at 295 K (Figure 1c). With decreasing temperature, the conductance contrast decreases along with the bulk conductance. Around 235 K, the cAFM signal at the head-to-head walls reaches the noise level of our setup (\(<1\) pA), whereas the tail-to-tail walls are still visible (Figure 1d). By increasing \(V_{\text{bias}}\), that is, driving a higher...
current through the sample, the temperature range in which the walls are detectable can be expanded. For $V_{bias} = 10$ V, which is the highest bias we apply in our experiments, it is possible to resolve the tail-to-tail walls down to $\sim 160$ K (Figure 1e).

An overview of the temperature-dependent cAFM measurements is presented in Figure 1f. Data points are extracted from cAFM maps, as in Figure 1c−e, and bulk and domain-wall values correspond to the mean value averaged over areas of $2 \times 2 \mu$m$^2$ and $10 \times 30$ nm$^2$, respectively. Figure 1f shows that the bulk conductance decreases exponentially with decreasing temperature, as expected for a semiconductor. The evolution of the corresponding band gap is displayed in the inset of Figure 1f, derived by optical transmission spectroscopy, as explained in SI Note 1. It is important to note that cAFM records both variations in conductivity as well as changes in the Schottky barrier formed at the tip−sample interface (SI Note 1), and either contribution can yield exponential scaling as a function of temperature. In this work, however, we investigate emergent electrostatics so that we do not pursue this convolution of conduction contributions further.

Most importantly, Figure 1 shows that semiconducting behavior, with conductance dropping exponentially as the temperature decreases, is measured in both domain and domain wall regions. The latter is intriguing because it potentially leads to the emergence of partially unscreened domain walls at low temperatures: Upon cooling, the increase in bulk polarization due to the pyroelectric effect yields additional bound charges at the walls. The screening of such additional bound charges, however, is substantially hindered by the reduced conductivity at low temperatures.

**Electrostatic Response at Charged Domain Walls.** To investigate the domain-wall screening at cryogenic temperatures, we perform low-temperature electrostatic force microscopy (EFM) measurements. Figure 2a presents a cAFM image ($T = 295$ K) showing the distribution of conducting and insulating domain walls similar to Figure 1b. To record EFM data, an oscillating platinum-coated tip (grounded) is scanned across the surface with a typical lift height of 30 nm. Uncompensated charges create an image charge in the tip that leads to an additional charge-induced attractive force, $F_{attr}$, which is detectable as a change in the phase of the tip oscillation,

$$F_{attr} \propto \frac{d}{r^2}$$

scaling with the out-of-plane force gradient.

EFM images obtained after cooling the sample to $T = 4.2$ K at $\sim 2.5$ K min$^{-1}$ reveal distinct line-like features, as shown in Figure 2b (see SI Note 2 for a topography image). These features coincide with the domain walls in the cAFM image taken at room temperature (Figure 2a), as indicated by the dashed lines, corroborating that the domain pattern remains stable down to $4.2$ K.

Upon heating, the EFM wall contrasts decrease, as presented in Figure 3a,b. On a closer inspection, we also find that tail-to-tail and head-to-head walls exhibit different temperature
dependencies in EFM. At $\sim 80$ K, the contrast at tail-to-tail walls (blue dashed line) first inverts (dark $\rightarrow$ bright) and then vanishes; a similar behavior is observed at head-to-head walls (red dashed line), which are resolved up to higher temperature, that is, $\sim 120$ K (Figure 3b,c). At 160 K, the walls are no longer resolved, and we detect a homogeneous potential.

In summary, the EFM response at head-to-head and tail-to-tail walls vanishes at different temperatures. The distinct temperature dependencies demonstrate a qualitative difference in the electrostatic fields associated with the two types of domain walls.

Electrostatic Far Fields at Head-to-Head and Tail-to-Tail Walls. The measured EFM domain-wall signals can be rationalized by combining analytical and numerical calculations in which $E_{\text{R}}(0.09\text{Ca}_{0.01}\text{MnO}_3)$ is considered as a $p$-type semiconductor similar to previous studies.\textsuperscript{2,15,31} The calculated band diagram in Figure 4a is in good agreement with previous analytical\textsuperscript{2} and DFT-based\textsuperscript{15} investigations. The negative bound charge of the tail-to-tail walls is screened by the accumulation of mobile holes within a few unit cells. In contrast, screening of the positive bound charge at head-to-head walls is achieved by means of a hole depletion layer and an electronic inversion layer.\textsuperscript{15}

We note that in the considered doping regime, the width of the depletion layer at head-to-head walls does not depend on the domain-wall charge, that is, the spontaneous polarization of the domains, and is given by $w = \sqrt{2eE_F/(\epsilon^2 N_A)}$ with $\epsilon = 13\epsilon_0$ in our system.\textsuperscript{32} For the values of acceptor density used in the calculations, that is, $2 \times 10^{18}$ to $2 \times 10^{19}$ cm$^{-3}$, the depletion layer screens about 15% to 50% of the maximum bound charge $2P_0$ of the head-to-head walls. The rest of the charge is screened by the electronic inversion layer within a few unit cells.\textsuperscript{15}

According to refs 33 and 34, the spontaneous polarization of the domains increases as the temperature decreases at a rate of $\sim 1.5$ nC cm$^{-2}$/K, leading to an increase in the domain-wall charge.\textsuperscript{22,34} The extra electric fields measured in Figures 2 and 3 are likely due to the inability of the system to screen the respective extra pyroelectric charge resulting from the exponentially growing relaxation time of the mobile carriers $\tau = \epsilon/(em \mu) \propto \exp(E_F/(k_B T))$. Here $\mu$ is the hole mobility, $n_h$ is the density of mobile holes in the bulk, and $E_F$ is the Fermi energy. In particular, as $\tau$ exceeds the data acquisition time of our experiment, the electrostatic equilibrium cannot be reached, and the extra domain-wall charge remains uncompensated. The latter happens at a characteristic temperature $T^*$, which we estimate as $T^* \approx 60$ K for the aforementioned parameters and the typical acquisition time $\sim 10^4$ s of our EFM experiments. This value is in reasonable agreement with the temperature, $\sim 120$ K, below which the additional contribution to the electric far fields is detectable (Figure 3c, signal at the head-to-head walls).

The attractive force on the EFM tip resulting from the charge distribution across the domain walls is shown in Figure 4b. At $T > T^*$, the material is in electrostatic equilibrium (all charged domain walls are fully screened), and the band diagram in Figure 4a determines the charge distribution. In this regime, only head-to-head walls are able to generate a weak and temperature-independent attractive force, which originates from the quadrupolar-like charge distribution associated with the hole depletion layer and the electronic inversion layer.
Because we do not resolve such a temperature-independent attractive force in our EFM data (Figure 3), we conclude that this contribution is below the detection limit of our experiment.

However, for $T < T^*$, uncompensated pyroelectric charges appear at both head-to-head and tail-to-tail walls with a surface density $\sigma = \pm 2p_p(T^*-T)$, where $p$ is the pyroelectric constant, leading to a pronounced attractive force between the tip and sample surface at both wall types. These pyroelectric charges provide an additional contribution that adds to the aforementioned weak attractive force at the head-to-head walls, which leads to a stronger EFM response compared with the tail-to-tail walls. The difference in signal strength is in agreement with our experimental observations, explaining why the head-to-head walls are detected at higher temperature than tail-to-tail walls in sensitivity-limited EFM measurements (Figure 3).

We note that the presence of impurities and crystallographic defects in the sample can increase the relaxation time, $\tau$, and hence give rise to a higher $T^*$. Furthermore, the EFM contrast inversion observed at the walls can be modeled by including a nonzero surface potential. As we show in Figure 4c, the contrast inversion observed at head-to-head walls is reproduced by assuming an additional surface potential, $\delta V_s$ which we model by a finite voltage, $V_s$, between probe tip and sample surface.

In conclusion, our work establishes an extraordinary robustness of charged domain walls in hexagonal manganites, which is crucial for domain-wall engineering$^{26,27}$ and to develop them into durable electronic components for domain-wall nanoelectronics. Using low-temperature EFM, we demonstrate the emergence of uncompensated bound domain-wall charges in $\text{Er}_{0.99}\text{Ca}_{0.01}\text{MnO}_3$. In contrast with domain walls in proper ferroelectrics, the charged domain walls in this system readily withstand a lack of screening charges, representing a striking example for the unique properties of domain walls in improper ferroelectrics.

The exponentially decaying conductance observed at the domain walls in conjunction with previous magnetic force microscopy studies$^{28,29}$ suggests that domain boundaries in hexagonal manganites act as 2D ferromagnetic semiconductors in their ground state. Such a behavior is intriguing as ferromagnetic semiconductors are capable of providing near-total spin polarization, a concept that has not been addressed in connection with functional (multi)ferroic domain walls yet, opening up new research opportunities in the field of functional ferroic domain walls.

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**REFERENCES**


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