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**Coexistence of antiferrodistortive and polar order in a superconducting
SrTiO₃ film**

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Abstract

Strontium titanate (SrTiO_3) can exhibit multiple orders, including superconductivity, an antiferrodistortive instability and ferroelectricity. The cooperation or competition between these orders in samples that undergo all three transitions is of great fundamental interest. Here we report scanning transmission electron microscopy imaging of the antiferrodistortive and ferroelectric structural distortions in a compressively strained SrTiO_3 film that was previously shown to become superconducting at ~ 410 mK. The experiments are complemented by first-principles simulations. Unlike the polar ferroelectric phase, which is suppressed by dopants, the antiferrodistortive order is insensitive to the presence of the free carriers. The single domain nature of the antiferrodistortive phase excludes any role of antiferrodistortive domain walls in the superconductivity. A previously reported low temperature resistance anomaly is associated with the ferroelectric transition, not the antiferrodistortive transition.

Strontium titanate (SrTiO_3) exhibits several symmetry-breaking transitions that are associated with the softening of transverse optical (TO) phonon modes. One of these is a zone boundary mode that results in a transition to an antiferrodistortive (AFD) structure near 105 K and the other, at $k = 0$, is a ferroelectric (FE) instability [1]. Numerous theoretical proposals have attempted to explain the still enigmatic superconductivity of doped SrTiO_3 with the presence of the ferroelectric soft mode or its fluctuations [2-11]. Recent experiments support a cooperative relationship between the polar and superconducting instabilities [12-22], although fluctuations of the polar soft mode as a pairing mechanism appear less likely, as samples that are deep in the ferroelectric state also become superconducting [14,15,19].

The AFD transition results in a rotation of the TiO_6 octahedra, with neighboring octahedra rotating in opposite directions along the tetragonal c -axis (see Fig. 1), and involves no loss of inversion symmetry. The AFD order is not believed to directly influence the superconducting transition. Nevertheless, the AFD transition may play an indirect role because it affects the polar soft mode [23] and details of the electronic band structure [24,25]. Moreover, without an externally applied stress, samples contain multiple ferroelastic AFD domains. Some studies have suggested that the AFD domain structure and/or the domain walls could locally enhance superconductivity [26-28].

Samples without AFD domains would allow for clarifying the intrinsic electrical transport behaviors. Epitaxial SrTiO_3 thin films that are under an in-plane, biaxial compressive stress undergo an AFD transition from a high symmetry tetragonal phase ($P4/mmm$) to a single-domain AFD $I4/mcm$ phase [29,30]. In *undoped* SrTiO_3 films that are under $\sim 1\%$ biaxial compressive stress, this transition occurs above room temperature [30-32]. When doped, compressively stressed films undergo a ferroelectric transition followed by a superconducting transition, allowing

for elucidating the effect of polar order on the superconductivity [14,15,20-22,33,34]. The AFD order is, however, more challenging to characterize, as the associated oxygen octahedra rotations only displace the oxygen ions. As we will show here, a state-of-the-art aberration corrected scanning transmission electron microscope (STEM) is needed to image the AFD structure.

In this study, we use annular bright field (ABF) STEM to image oxygen displacements associated with the AFD transition in a compressively strained SrTiO_3 film that undergoes successive ferroelectric and superconducting transitions at low temperatures, which were studied in prior reports [14,15,21]. Simultaneously, we also map locally polar nano domains within the AFD phase by quantifying the Ti column positions in high-angle annular dark-field (HAADF) STEM. These polar nanodomains were studied previously in similar films as a function of carrier density and were shown to be a necessary precursor to the ferroelectric phase transition [22]. We show that at room temperature, the film consists of a single AFD c -domain, similar to undoped films. Thus, long range AFD order persists even at high carrier densities, unlike the nano polar order, whose length scale is already significantly reduced at these carrier densities, consistent with earlier observations [22]. We compare the experimental results to first-principles simulations and a free energy model and find excellent agreement with the experiments. We conclude that AFD domains or domain walls play no role in the enhanced superconducting transition temperature observed in these films.

The film studied here is a 70-nm-thick, Sm-doped SrTiO_3 thin film grown by molecular beam epitaxy (MBE) on a (001) $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) substrate, as described elsewhere [14,35]. The substrate imposes a biaxial in-plane strain of $\sim -0.9\%$. The carrier density is $9 \times 10^{19} \text{ cm}^{-3}$. The carrier density places the film near the peak of the superconducting dome. The sample is film A of ref. [21], which reports on its electrical and ferroelectric properties, and

also shows x-ray data that confirms that the film is coherently strained. As discussed in ref. [21], the film undergoes successive ferroelectric and superconducting transitions, at 100 K and 410 mK, respectively. STEM images of the SrTiO₃/LSAT interface show that the film remains coherently strained to the substrate even after all cross-section samples were prepared (see Figure S1 in ref. [36]). Thinner films were also studied in ref. [21], but they are not superconducting or ferroelectric (possible reasons were discussed in ref. [21]).

Figure 1 shows the orientation of the (01 $\bar{1}$) and ($\bar{1}$ 10) planes parallel to which cross-section TEM samples were prepared (for details see Supplementary Information [36]). While ($\bar{1}$ 10) is parallel to [001] (the film growth direction), (01 $\bar{1}$) is tilted by 45° against [001]. Images for analysis of the AFD oxygen octahedral tilts were thus acquired from the center of the film to avoid overlap with the substrate (see Fig. S1c in ref. [36]). HAADF and ABF images were acquired on a 5th order aberration corrected STEM equipped with a cold field emitter and operated at 200 kV (Thermo Fisher Spectra). The semi-convergence angle was 30 mrad. The ranges of collection semi-angles for the HAADF and ABF imaging were 45 mrad – 200 mrad and 16 mrad – 32 mrad, respectively. To improve the signal-to-noise ratio, 20 images (1024 × 1024 pixels, 1 μs dwell time) were sequentially recorded and cross-correlated. Position averaged convergent beam electron diffraction was employed to precisely align the zone axis for imaging [37]. The position of every atomic column in the HAADF and ABF images was determined by fitting to a two-dimensional (2D) Gaussian function using the Atomap package [38]. All images were acquired at room temperature, i.e., above the ferroelectric phase transition (~ 100 K, see ref. [21]).

Calculations of the polar and AFD orders were performed using density functional theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP) [39,40] (also see ref. [41]). We used the supplied projector-augmented wave potentials within the generalized gradient

approximation and Perdew-Burke-Ernzerhof scheme [42]. Electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cutoff of 800 eV, and reciprocal space was sampled using an $8 \times 8 \times 8$ Γ -centered mesh for a single five-atom unit cell. The carrier concentration was varied by setting the number of valence electrons in VASP using NELECT with a compensatory background charge applied to maintain charge neutrality. The doping dependence of the phonon frequencies associated with the polar and AFD instabilities were calculated from phonon dispersions of the strained, centrosymmetric, unrotated reference structure using the finite displacement method within the PHONOPY code [43]. We used Monte Carlo simulations in combination with a free energy model, described in ref. [44], to simulate the polar and AFD order at room temperature on a $32 \times 32 \times 32$ lattice with periodic boundary conditions. The rotation order parameter is defined as the average of octahedral rotation between neighboring cells, while the global polarization order parameter is defined as the eigenvector of the polarization, comprised of the three components: the titanium, axial in-plane oxygens, and apical out-of-plane oxygen displacements. More details on the AFD and polar order parameters can be found in the Supplementary Information [36]. More information on the model free energy and technical details of the Monte Carlo simulation can be found elsewhere [44].

Figure 2 shows our analysis of annular bright-field ABF images recorded along $[\bar{1}10]$ (top row) and $[01\bar{1}]$ (bottom row), respectively. The Sr, Ti, and O columns are all resolved in the ABF images [Figs. 2(a,b) and 2(e,f)]. Schematic projections along these two directions are shown in Figs. 2(c) and 2(g) for the case of an AFD structure whose tetragonal c -axis is along the film normal. Along $[01\bar{1}]$, two characteristic oxygen-oxygen distances, denoted $d1$ and $d2$ in Fig. 2(g), give rise to extra intensity maxima in the Fourier transform (FFT) of the ABF image [see red arrows in the inset in Fig. 2(e)]. In contrast, along $[\bar{1}10]$, there are only small oxygen

displacements, which are not resolved and which do not produce alternating oxygen-oxygen spacings. Figures 2(d) and 2(h) show histograms of the relevant oxygen-oxygen distances. Consistent with the FFTs, the $[\bar{1}10]$ projection shows a single spacing (a single peak in the histogram), while the broad distribution in Fig. 2(h) can be decomposed into two spacings, 391 ± 4 pm and 403 ± 4 pm, respectively. From the measured spacings, the octahedra rotation angle θ (see Fig. 1) can be determined. Here, $\theta \sim 0.9\pm0.6^\circ$ [36].

In all images investigated (> 100), the superlattice peaks in the FFT are only observed in the tilted cross section along $[01\bar{1}]$. Thus, the compressively strained SrTiO_3 film consists of a single c -domain. Conversely, the single domain nature makes the preparation of tilted cross sections necessary to detect the characteristic AFD displacements in the ABF images. To further confirm the interpretation, samples along the same directions were prepared from a SrTiO_3 single crystal, which, at room temperature, is far above the AFD transition. No superlattice reflection spots could be detected (see Supplementary Information [36]).

We next briefly turn to the polar order, which was already extensively characterized in compressively strained SrTiO_3 films in prior publications [15,21,22,33]. Previous studies [22,33] showed polar nanodomains at room temperature, i.e., above the ferroelectric transition. In films with relatively high carrier densities, such as the ones studied here, the size of these polar nanodomains is just a few unit cells [22]. HAADF images of the sample investigated here confirms these prior findings. Figure 3 shows Ti-O column displacement (polarization) vectors presented in several different ways to aid in direct comparison with the prior publications. The displacement vectors are defined as the difference between the center of mass of four neighboring Sr columns and the Ti-O column position, which is determined by Gaussian fitting [22,33]. Figure 3(a) shows a map of the Ti-O column displacement vectors in 30° intervals, while their length and orientation

quantified by arrows in Fig. 3(b). Also shown are a contour map [Fig. 3(c)] that shows the predominance of displacement vectors that are below average, further indication of the disruption of nanodomains, and a histogram [Fig. 3(d)].

We now compare the experimental results to first-principles simulations using a free energy model with near DFT-level accuracy [44]. In Fig. 4(a), ground state displacements associated with the polar and AFD orders, respectively, are displayed as a function of the free carrier concentration at 0 K. As the carrier concentration is increased, the Ti displacements are reduced until the polar order is eventually destroyed. The AFD rotation angles, however, remain virtually unaffected by doping (a small increase is associated with the destruction of polar order). Figure 4(b) shows the calculated imaginary phonon frequencies of the polar and AFD instabilities as a function of carrier concentration. The polar instability is markedly suppressed by increasing carrier density, while the AFD phonon frequency hardens slightly. Thus, while the polar distortion is strongly affected by doping, the rotation of the oxygen octahedra is essentially independent of the carrier density.

To visualize the domain structure at 300 K, representative simulation snapshots of the polar and AFD order parameters are shown in Fig. 4(c) for a film with a carrier density of $1.4 \times 10^{20} \text{ cm}^{-3}$. Each pixel represents a single 5-atom unit cell, with the color scale indicating the magnitude of the order parameter normalized to the ground state value of the undoped system. The rotation order parameter has been multiplied by a phase factor to eliminate the checkboard pattern of out-of-phase rotations. Small variations of AFD order are primarily due to thermal fluctuations at 300 K; the rotation order parameter averaged over 500,000 Monte Carlo iterations shows small variations, as summarized in the Supplementary Information [36]. Additionally, because the AFD

and polar order parameters are weakly coupled, polar domains may contribute to a small non-uniformity of the AFD order.

To briefly summarize, our experiments and simulations show that the AFD transition in compressively strained, doped SrTiO_3 films occurs above room temperature, similar to what has previously been observed for undoped films [30,31]. Also similar to undoped films [30], the film consists of a single, AFD c -domain. The single domain nature of these films excludes any role of AFD domain walls in the enhanced superconducting transition temperature found in compressively strained films [14], since they do not exist in this superconducting film. The results also show that the low temperature resistance anomaly, which is seen in these films [14] and other ferroelectric SrTiO_3 samples [19], is not associated with the AFD transition or domain walls (as seen elsewhere [45]). The results thus confirm our previous conclusions [14], namely that it is associated with the ferroelectric transition.

Our experiments and simulations also show that the AFD transition is relatively insensitive to the presence of free carriers. This is apparent from the simulations, which only consider the effect of free carriers, and in the experiments, which show that the AFD transition temperature is above room temperature, similar to undoped, strained SrTiO_3 films studied in the prior literature [30]. The insensitivity to carrier density suggests that there is no connection to the superconducting transition, which strongly depends on the carrier density. In addition to film strain, alloying elements with a valence mismatch can also increase the AFD transition temperature [46]. While the concentration of trivalent Sm here is small, it may cause an additional small increase in the AFD transition temperature in the experiments.

The film studied here also undergoes a ferroelectric transition [21], for which the polar nanodomains are a necessary precursor [33]. Our findings show that these polar nanodomains

form within a single AFD domain. As shown previously [15,22], the nanodomains and the transition to the globally ordered polar state are strongly suppressed by the presence of dopants and free carriers. The two transitions therefore co-exist and are mostly independent of each other, in the sense that suppression of the polar domains and polar long range order by free carriers does not suppress the AFD transition, though there is some weak coupling of the order parameters apparent in the simulations (as also discussed in the literature for undoped SrTiO₃ [47-49]). Taken together, these findings highlight the differences between the two transitions: unlike the AFD transition, the polar transition involves long range Coulomb interactions, as is evident from the formation of the nanodomains that precede it, which are strongly screened by free carriers. While both transitions involve a TO phonon mode that does not strongly couple to free carriers, theory has shown that the polar transition is closely coupled with the splitting between the TO and longitudinal optical (LO) phonon modes [50]. In contrast to the TO modes, LO modes can couple strongly to the free carriers, as can also be seen in transport experiments [51]. These considerations explain the much greater sensitivity of the polar transition to the presence of free carriers and, conversely, the insensitivity of the AFD transition to them.

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Figure Captions

Figure 1: Schematic showing the AFD structure (top left) and the planes parallel to which the TEM cross-sections were prepared. The two planes, $(01\bar{1})$ and $(\bar{1}10)$, respectively, are shaded in blue and red, respectively. While the $(\bar{1}10)$ is parallel to $[001]$, $(01\bar{1})$ is inclined by 45° against $[001]$.

Figure 2: ABF imaging of the AFD domain structure using two cross sections along $[\bar{1}10]$ (a-d) and $[01\bar{1}]$ (e-h), respectively. (a) ABF-STEM image along $[\bar{1}10]$ and FFT (inset). (b) Magnified section of (a) with oxygen columns marked by red dots. (c) Schematic of the AFD structure along $[\bar{1}10]$. (d) Histogram of oxygen-oxygen distances. (e) ABF-STEM image along $[01\bar{1}]$. The FFT (inset) shows additional intensities indicated by the red arrows. Note the zigzag pattern of oxygen columns in this projection. (f) Magnified section of (e) with oxygen columns marked by red dots. (g) Schematic of the AFD structure along $[01\bar{1}]$, showing the zigzag pattern of oxygen columns and the resulting two distinct oxygen-oxygen distances, $d1$ and $d2$. (h) Histogram of the oxygen-oxygen distances, which has two peaks corresponding to $d1$ and $d2$.

Figure 3: Polar order quantified via the off-centering of Ti-O columns in HAADF-STEM images along $[100]$. (a) Polarization orientation maps. The color scale corresponds to 30° intervals of polarization directions. (b) Displacement vectors of the Ti-O column off-centering from the area outlined by the box in (a). The displacement vectors are depicted 12 times of their actual values. (c) Color contour map of Ti-O column off-centering for the (a). (d) Histogram of the displacement vectors.

Figure 4: First-principles simulations of AFD and polar order. (a) Magnitude of ground state Ti displacements (orange) and AFD rotation angles (blue) as a function of carrier concentration. (b)

Imaginary phonon frequencies associated with the polar (orange) and AFD (blue) instabilities as a function of carrier concentration. (c-f) Representative snapshots calculated from Monte Carlo simulations at 300 K of the polarization (c,d) and rotation (e,f) order parameters for a $32 \times 32 \times 32$ supercell with carrier density $1.4 \times 10^{20} \text{ cm}^{-3}$. The polarization snapshots show small domains with opposite polarization (orange and purple patches), while the rotation snapshots show a large single domain.

Figure 1

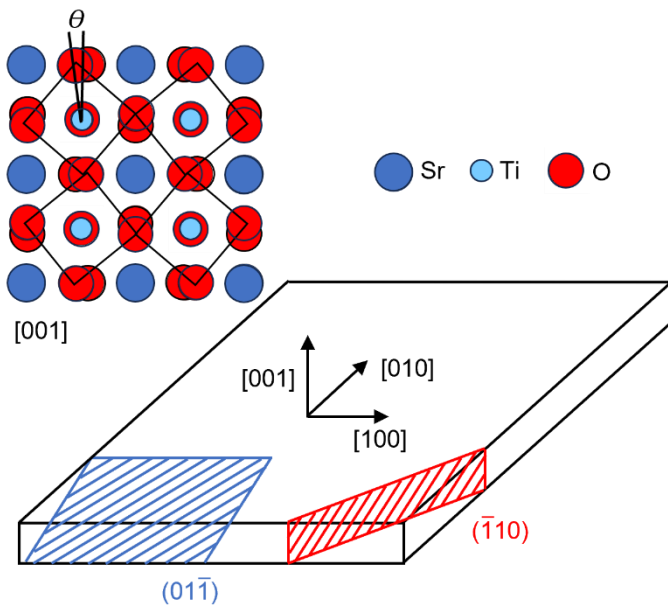


Figure 2

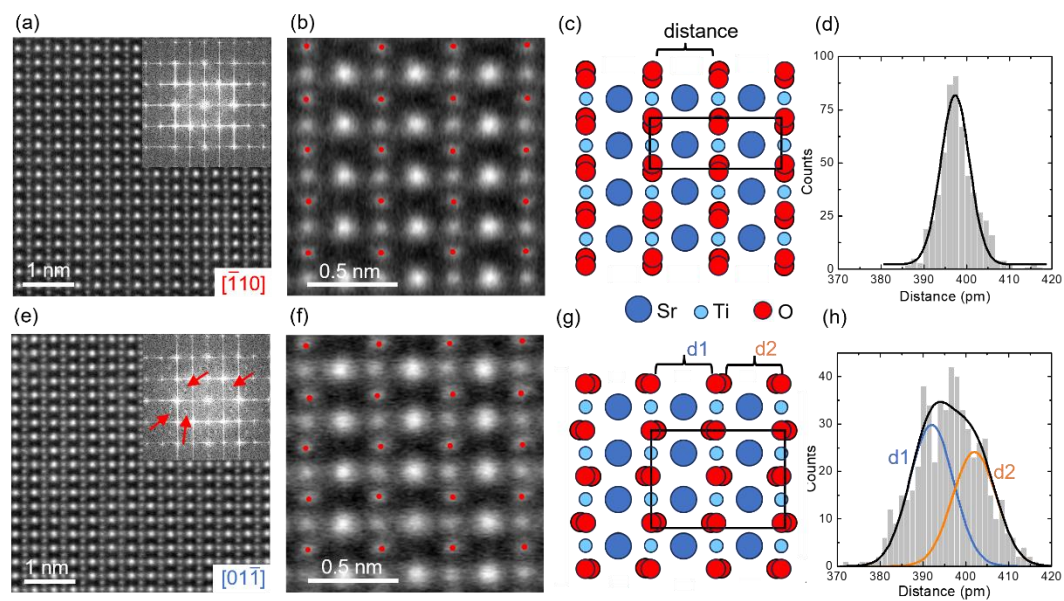


Figure 3

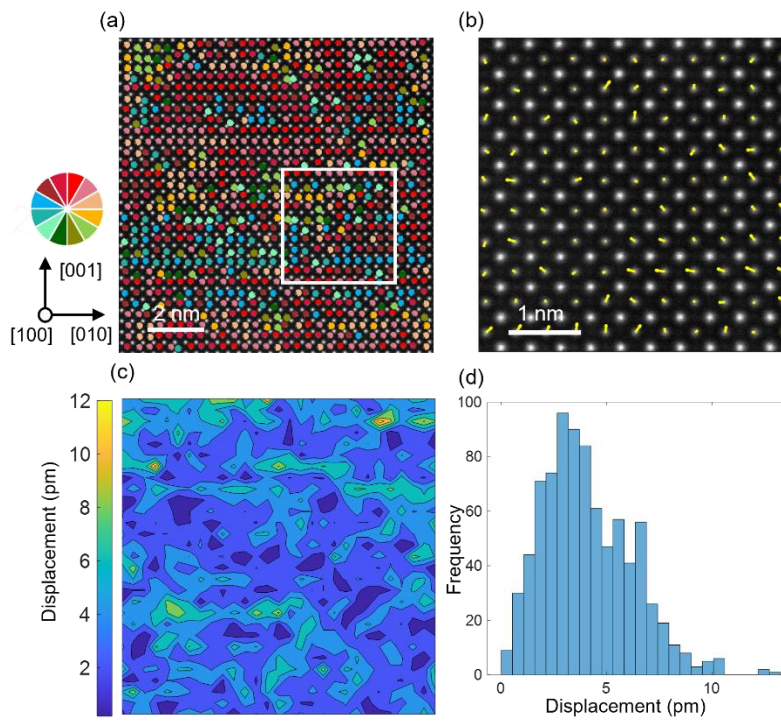


Figure 4

