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Interfacial coupling-induced ferromagnetic insulator phase in manganite film

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ABSTRACT:

Interfaces with subtle differences in atomic and electronic structures in perovskite ABO_3 heterostructures often yield intriguingly different properties, yet their exact roles remain elusive. Here, we report an integrated study of unusual transport, magnetic, and structural properties of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film on SrTiO_3 substrate. The variations in the out-of-plane lattice constant and BO_6 octahedral rotation across the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{SrTiO}_3$ interface strongly depend on the thickness of the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film. In the 12-nm film, a new interface-sensitive ferromagnetic polaronic insulator (FI') phase is formed during the cubic-to-tetragonal phase transition of SrTiO_3 , apparently due to the enhanced electron-phonon interaction and atomic disorder in the film. The transport properties of the FI' phase in the 30-nm film are masked because of the reduced interfacial coupling and smaller interface-to-volume ratio. This work demonstrates how thickness-dependent interfacial coupling leads to the formation of a theoretically predicted ferromagnetic-polaronic insulator, as illustrated in a new phase diagram, that is otherwise ferromagnetic metal (FM) in bulk form.

Table of Contents Graphic: The phase diagram of $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ film; The MnO_6 octahedral distortion and rotation around PSMO/STO interface.

Interfacial phenomena of perovskite ABO_3 epitaxial heterostructures have attracted much attention in enhanced ordering temperature,¹ interfacial magnetism,² and improved device performance.³ Interfacial structural asymmetry significantly affects the local unit cell dimension and BO_6 octahedral rotation/distortion.^{4,5} Experimental bond angle, bond length and magnetic ordering temperature of thin manganite films drastically deviate from that of bulk.⁴⁻¹⁰ To date, understanding of correlations between interfacial structures and properties is still in its infancy. To resolve this critical and complex problem, experimental exploration of the intimate relationship between the interface-depth profile of atomic structures and material properties is greatly warranted.

In perovskite-manganite $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln is a trivalent rare earth element and A is a divalent metal), the effect of colossal magnetoresistance (CMR) coincides with the paramagnetic insulator (PI)-to-ferromagnetic metal (FM) phase transition for doping of $\sim 0.25 < x < \sim 0.5$.¹¹ Depending on x , competition between electron-phonon interaction and double-exchange interaction¹²⁻¹⁴ leads to the formation of a FM or a ferromagnetic insulator (FI). The FI phase was observed in bulk for low doping concentration x , for example, $\text{La}_{0.85}\text{Ca}_{0.15}\text{MnO}_3$ and $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$.¹⁵⁻¹⁶ Theoretical work on bulk manganite at $x \sim 0.3$ predicts a metal-to-polaronic insulator phase transition controlled by the strength of electron-phonon interaction (λ) and/or quenched disorder (Δ).¹⁷⁻²⁰ Polaron melting and ordering have been proposed as a key mechanism for CMR effects.²¹⁻²²

In this work, the octahedral rotation, the interface and depth-profile of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films deposited on (001) SrTiO_3 (STO) substrate were measured using half-integer x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). Correlating the structural information with the transport and magnetic properties, we report the experimental

observation of a theoretically predicted ferromagnetic-polaronic insulator FI' phase in $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. This novel FI' phase was formed during the cubic-to-tetragonal phase transition of STO. A high resistivity cusp was observed at completion of the STO phase transition at ~ 105 K, which was attributed to the STO-induced phonon softening, affecting interfacial structural coupling between TiO_6 and MnO_6 octahedra that enhanced the electron-phonon interactions and site disorders. On further cooling to below 105 K, a ferromagnetic metal phase with high resistivity (FM') existed. The new phase diagram with thickness-sensitive FI' phase was proposed. A thicker film diminished these effects due to the reduced interfacial coupling and smaller interface-to-volume ratio.

At room temperature bulk STO is cubic with lattice constant of $3.905 \text{ \AA}$, without TiO_6 ²³ octahedral rotation and labelled as $a^0a^0a^0$ according to Glazer's designation.²⁴⁻²⁵ The cubic-to-tetragonal transition commences at $\sim 150\text{K}$ and completes at $\sim 105\text{K}$, with accompanying $a^0a^0c^-$ TiO_6 octahedral rotation.²⁶⁻²⁷ Bulk $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, a strong correlated-electron system with intermediate band-gap, is orthorhombic at room temperature with $a = 5.479 \text{ \AA}$, $b = 7.705 \text{ \AA}$, $c = 5.450 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, and MnO_6 octahedral rotation $a^+b^-b^-$.²⁸⁻²⁹ The lattice constant of pseudo-cubic unit cell is $\sim 3.860 \text{ \AA}$ and the estimated MnO_6 rotation angle is 9.6° , 9.6° and 12° around three axes, respectively. Besides the PI-to-FM transition at $\sim 280 \text{ K}$,²⁹ there is no structural phase transition observed with decreasing temperature to 50 K .²⁸⁻³⁰ The difference in crystal structure between $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and STO substrate, including the 1.1% lattice mismatch and BO_6 rotation, results in structural asymmetry and special properties at the interface.

Figure 1A shows the resistivity-temperature (ρ - T) and magnetization-temperature (M - T) of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films with different thicknesses on STO substrate. The $p1$ position (black arrows), corresponding to the onset of ferromagnetic ordering in cooling from the high temperature PI phase, shifts to a higher temperature with increasing film thickness; and $p2$

(brown arrows) remains constant near 105 K. The positions of $p1$ and $p2$ for different phase transitions are obtained using the first derivative, i.e., $\frac{d\rho}{dT} = 0$, when a clear peak is present. In the event of a shoulder on the curve (no clear peak), the second derivative, i.e., $\frac{d^2\rho}{dT^2} = 0$, is used to determine the position of the phase transition. Similar observations of $p1$ and $p2$ are found in the derivative of the M - T curves (Fig. S1A). In bulk $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ the PI phase transforms to FM phase when cooling to $\sim 280 \text{ K}$ ²⁹; in 30-nm $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film, $p1$ at $\sim 180 \text{ K}$ corresponds to the PI -to- FM transition; in 12-nm film $p1$ at $\sim 150 \text{ K}$ is attributed to the PI -to- FI' phase transition and the FI' -to- FM' transition occurs below 105 K. The saturated magnetizations of all films decrease and the resistivity increase (Fig. S2), compared to that of bulk ($\sim 3.5 \mu_B/\text{Mn}$ at low temperature²⁹ and the resistivity is $< 5 \times 10^{-3} \Omega/\text{cm}$ from 300 K to 50 K³¹). This phenomenon is common in manganite film and several factors may contribute to it, such as the change of crystal structure.⁴ The term FM' denotes a metallic phase that has much higher resistivity compared to the traditional FM phase.

Figures 1B-1C show the effects of Sr concentration for the 30-nm and 12-nm films, respectively. The bulk phase diagram²⁹ was shown in Fig. 1D, which reveals the paramagnetic-to-ferromagnetic phase transition with decreasing temperature at different Sr concentrations. Compared to bulk (Fig. 1D), the paramagnetic-to-ferromagnetic transition temperature of films decreases with decreasing thickness. For the phase diagram of 12-nm film at $T > 50 \text{ K}$, the FI phase (Fig. 1F) extends to a higher doping concentration. At $x = 0.33$, a novel intermediate FI' phase exists between $p1$ and $p2$. At around $x = 0.40$, although the $p2$ feature around 105 K (thick red horizontal line in Fig. 1F) still exists in the ρ - T and derivative of M - T curves (Fig. S1C), the FI' phase tends to fade away. The approximate phase boundary is indicated by the red dashed curve (Fig. 1F). The FI' phase depends on the doping concentration and temperature. The FI'

phase depends on the doping concentration x and temperature. Note that FI' and FI are used to denote the ferromagnetic insulator phase of different doping concentrations x , considering that the FI' phase would change to the FM' phase with decreasing temperature, whereas the conventional FI phase does not show such phase transition. Hereafter the films with $x = 0.33$ are used to discuss the novel FI' phase.

At first glance, the origin of the FI' phase may be attributed to **electron transfer from Mn in $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film to STO substrate across the interface** that reduces the effective dopant x to the left FI region. However, the appearance of the FM' phase eliminates this scenario. We further verify the weak charge transfer across the interface by first principles calculations (Fig. S3). All films were fabricated under the same conditions and the FI' phase could not have resulted from the oxygen vacancy or different chemical valence, as verified by the Mn *K*-edge XANES showing the same peak position in the spectra³²⁻³⁴ (Fig. S4). **Another possible factor is the misfit strain (1.1%) between PSMO and STO that may increase resistivity and decrease the PI-to-FM phase transition ($p1$) temperature in manganite film¹²⁻¹³. The effect of misfit strain will gradually diminish in thicker film experiencing strain relaxation. Note that strain relaxation was not observed in both 12 nm and 30-nm films, as shown in the following STEM results. The effect of misfit strain therefore cannot be used to explain large difference in resistivity and the same value of $p2$ in these films.** Hence, it is more likely that other mechanisms, especially those associated with interfacial structural coupling, are responsible. In the 12-nm film, $p1$ moves to a higher temperature with increasing magnetic field, whereas $p2$ remains constant at the cubic-to-tetragonal phase transition temperature of STO at 105 K (Fig. S1B). Considering that STO phase transition commences at ~ 150 K³⁵ (Fig. S1D) and the robust thickness-dependence of FI' region observed in Fig. 1A, the new FI' phase should be related to the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ /STO interfacial coupling around the STO cubic-to-tetragonal phase transition. The effects of the phase transition

of the STO substrate on $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films were observed. To confirm these effects of the STO substrate, $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films with different thicknesses were also deposited on the cubic (001) $(\text{LaAlO}_3)_{0.3}\text{-(Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT, 3.868 Å) substrate. The $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films on the LSAT substrate however do not show the same features at 105 K, as shown in Fig. S5. Hence, retrieving structural information about the interface in order to understand the microscopic mechanisms is highly desirable, but challenging due to difficulty in measuring oxygen positions. We resolved this issue by combining XRD with high-resolution electron microscopy.

Room temperature, volume-averaged, half-integer synchrotron XRD suggests MnO_6 octahedral rotation $(a^-a^-c^-)^{36}$ for both 12-nm and 30-nm films (Fig. S4 and Table. S1). A corresponding structural model of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ based on XRD is shown in Figs. 2A-2B, i.e. $a^-a^-c^-$ MnO_6 octahedra and $a^0a^0a^0$ TiO_6 octahedra. The fitted MnO_6 rotation angles for 12-nm and 30-nm films are $\alpha=\beta=4.5^\circ\pm0.4^\circ$, $4.2^\circ\pm0.4^\circ$, and $\gamma=8^\circ\pm0.3^\circ$, $8.2^\circ\pm0.4^\circ$, respectively. These two films do not show a significant difference in rotation angles of the MnO_6 octahedra and XRD results are clearly insufficient to explain the different transport properties of these films. To reveal the structural depth-profile, measurements of MnO_6 octahedra rotation and lattice parameter as a function of distance from the substrate-film interface were carried out using position-sensitive annular bright field (ABF) and high-angle dark field (HAADF) imaging in STEM.

The alternately rotated U-MnO_6 and V-MnO_6 octahedra overlap when projected along the [100] or [010] direction as shown in Fig. 2A. When projected along the $[\bar{1}10]$ direction in Fig. 2B, however, U-MnO_6 or V-MnO_6 octahedra aligns and the apical oxygen atoms form a zigzag chain along the [110] direction due to the octahedral rotation, as shown by the pink lines in Fig. 2B. Fig. 2D shows an ABF-STEM image from the cross-section sample of the 30-nm film viewed

along the $[\bar{1}10]$ direction. Short and long oxygen distances (d_1 and d_2) arranged alternately along both $[001]$ and $[110]$ directions are observed due to $\mathbf{a}^*/\mathbf{b}^*$ rotation. The effect of rotation around out-of-plane axis ($\mathbf{c}^*$) on the oxygen spacing is not visible in this view and **the details are discussed in Fig. S6**. However, the oxygen position is inconsistent with the simulated ABF image in Fig. 2E based on the model with symmetric MnO_6 octahedron of Fig. 2B, suggesting that the MnO_6 octahedra consists of not only rotation but also distortion.

From the ABF-STEM images, an asymmetric octahedron is proposed, as shown in Fig. 2C and Fig. S7. The simulated image in Fig. 2F, based on this asymmetric model, agrees very well with the experimental observation in Fig. 2D. Density function theory simulation³⁷ using the supercell including STO and $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ confirms that the asymmetric octahedral rotation is indeed energetically favorable (Fig. S3). Our image simulations further confirm that the intensity peak in ABF-STEM and HAADF-STEM images correspond to the projected atomic position when the film is viewed along the $[\bar{1}10]$ zone axis over a large range of sample thickness (a few nm to 30 nm). This allows us to measure the projected atomic positions directly from the ABF-STEM and HAADF-STEM image pairs.

Figures 3A-3B show the typical HAADF and ABF images from the 30-nm film simultaneously acquired with ABF and HAADF detectors. The interface between the STO and the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ film is sharp without interfacial dislocations. To improve the signal-to-noise ratio, the ABF image is averaged vertically, as shown in Fig. 3C. The inset in Fig. 3E shows the intensity scan line (black circles) from the yellow dash line in the panel II of Fig. 3D, and the complete line scan from the oxygen row is shown in **Fig. S8**. The oxygen position is refined individually, e.g. only refining the data in the shadow area with a Gaussian function (red line in the inset of Fig. 3E). The Pr/Sr position is refined based on the intensity scan line from the

Pr/Sr/Ti row (Fig. S8) for calculating the center of each unit cell as the reference. The oxygen displacement (d_O), calculated by subtracting the face center of the unit cell from the oxygen position, is plotted in Fig. 3E. There are four sets of data for the oxygen displacement from these two oxygen rows, as indicated by the four types of triangles (see the II of Fig. 3D). Solid-up-black and open-down-red triangles represent “initial” oxygen site with large oxygen displacement, while solid-up-red and open-down-black triangles represent “distorted” oxygen site with small oxygen displacement. This displacement further confirms the proposed asymmetric MnO_6 octahedral rotation; otherwise they should have the same value with opposite direction of motion. The “distorted” and “initial” oxygen sites of asymmetric MnO_6 rotation are discussed in Fig. S7. Interestingly, the d_0 value does not trend towards a value of zero in the STO substrate, which is due to the interaction between the PSMO film and STO substrate, yielding a structural modification in the interfacial region. Similar asymmetric oxygen displacement is observed in the 12-nm $Pr_{0.67}Sr_{0.33}MnO_3$ (Fig. S9).

The calculated rotation angles of the octahedra from the above STEM for both films are shown in Fig. 4A. The rotation angle in the STO substrate is the same for both samples. However it is quite different for the two $Pr_{0.67}Sr_{0.33}MnO_3$ films with different thicknesses. The rotation angle increases considerably with distance from the film-substrate interface to the film surface in the 12-nm film, but the rotation angle increases only slightly from the interface in the 30-nm film. The observed oscillation of rotation angle for the 12-nm film in the first 20 unit cells (Fig. 4A) should be related to the short-range and long-range strain field around the interface⁴¹, which warrants future investigation. The c lattice parameter is calculated from the measured position of the Pr/Sr atoms, as shown in Fig. 4B. The c -lattice parameter is inversely proportional to the distance from the interface for the 12-nm film; for the 30-nm film it decreases within a few unit cells in the interfacial region and then becomes flat. The change of the c -lattice parameter in STO

near the interface can be attributed to the interfacial structure modification from the interaction between STO and PSMO film. The c -lattice parameter variation along the normal direction in the interfacial region is further confirmed by high quality synchrotron XRD, as shown in Fig. 4C. The (002) peak of the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ for both 12-nm and 30-nm films are fitted using two Pseudo-Voigt³⁹ functions ($L1$ and $L2$). The fitting results are shown in Table S2. The film may be viewed as two different layers ($L1$ and $L2$) stacked on the substrate: $L1$ refers to the interfacial layer and $L2$ the layer away from the interface towards the film surface. The large variation of the MnO_6 octahedral rotation and lattice parameter c in $L1$ layer indicate a strong interfacial structural coupling between the $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and STO. Note that the small variation of MnO_6 rotation and c -lattice parameter in $L2$ layer indicates diminishing effects of interfacial coupling in this layer. Interestingly, oxygen rotation (Fig. 4A) and lattice parameter (Fig. 4B) of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ near the interface are unexpectedly different for both films. These results unequivocally demonstrate that the atomic structure of interface is film-thickness dependent, contrary to traditional understanding.

The different film-substrate interfaces of the two films at room temperature are expected to persist with decreasing temperature as both are constrained to the STO substrate. The STEM measurements of oxygen positions at low temperature do not provide a solid conclusion due to adverse sample drift. Thus, electron diffraction at room temperature and 90 K was employed instead (Fig. S10). It shows the change of c lattice parameter of the 12-nm film follows that of STO, whereas that of the 30-nm film does not. Fig. 4D shows the temperature-dependent XRD measurement of c -lattice parameter for the two films and STO. The c value of the 12-nm film has the same temperature dependence as the STO substrate in the entire temperature range of 50 to 300 K. For the 30-nm film, however, the c value starts to increase at $\sim 180\text{K}$ near the PI-to-FM phase transition. The STO cubic-to-tetragonal phase transition has a stronger influence on the

crystal structure of the 12-nm film than that in the 30-nm film. The gradual change of temperature behavior of c-lattice constant with increasing thickness mirrors the gradual disappearance of $p2$ feature.

For the high-temperature PI phase, the thickness-dependent resistivity difference may be due to structural differences (Figs. 4A-4B). The softening of Γ_{25} phonon modes ($a^0 a^0 c^-$ TiO₆ rotation) commences with STO cubic-to-tetragonal phase transition at ~ 150 K (Fig. S1D). Earlier theoretical work⁴⁰ reported that the Γ_{25} phonon mode decays exponentially with a decay length of 2.3 unit cells into the LSMO film deposited on STO substrate, and the LSMO relaxes to its bulk-like octahedral rotations within 2-3 unit cells. They attributed the high resistivity cusp near 105 K to evanescent cross-interface coupling between the charge carriers in the film and a soft-phonon mode in the STO with decreased carrier relaxation times, mediated through corresponding oxygen octahedral motions. Our experimental results show that the interfacial coupling is strong between the STO substrate and Pr_{0.67}Sr_{0.33}MnO₃ film, with penetration depth at least 20 unit cells in the 12-nm Pr_{0.67}Sr_{0.33}MnO₃ (Fig. 4A), which may be caused by the larger difference in crystal structure between bulk Pr_{0.67}Sr_{0.33}MnO₃ and STO (See ‘Methods’ for details). The large variation of lattice constant and MnO₆ rotation/distortion in the 12-nm film suggests a non-uniform interfacial environment that may enhance the site disorder strength (Δ) with contribution from random local TiO₆ rotation near the STO interface at the onset of STO phase transition.³¹ Increasing softening of the Γ_{25} phonon mode with decreasing temperature may strengthen electron-phonon interaction (λ) of Pr_{0.67}Sr_{0.33}MnO₃ film through interfacial coupling (Fig. 4D) by decreasing carrier relaxation⁴⁰ time (S11). Both enhanced λ and Δ could induce formation of theoretically predicted polaronic insulator¹⁷⁻²⁰ FI’ as shown in 12-nm film and Fig. 1A. **The formation of polaron insulator FI’ phase is supported by temperature dependence of resistivity,**

which could be well-fitted using small polaron model⁴¹ as shown in Fig. S12. Between $p1$ and $p2$, the resistivity shows film-thickness dependence: ferromagnetic insulator behavior in the 12-nm film and ferromagnetic metallic behavior in the 30-nm film. The resistivity value of $p2$ of the 30-nm film is much lower compared to that of the 12-nm film. Why does the STO substrate not significantly affect properties of the 30-nm film? A possible reason can be found in the low temperature XRD data (Fig. 4D). The temperature dependence of c -lattice parameter of the 30-nm film significantly deviates from that of STO, indicating that the 30-nm film does not couple as strongly with the STO as compared to the 12-nm film, due to smaller interface-to-volume ratio in the 30-nm film. A weaker interfacial coupling will likely weaken the effects of phonon-softening induced scattering. Below 105 K, the 12-nm film shows ferromagnetic metallic behavior but with high resistivity. This may be explained by decreased effects of phonon softening (λ) away from the STO transition temperature at 105 K (Fig. S1D), and/or reduction in disorder strength (Δ) as TiO_6 rotations near the STO surface become fully cooperative below 105 K.

In summary, the STO phonon softening, enhanced interfacial electron-phonon interactions and site disorders are responsible for the FI' phase of the 12-nm $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ at ~105 K. The disappearance of this FI' phase in the 30-nm film can be attributed to different interfacial structure and smaller interface-to-volume ratio compared to the 12-nm film. Understanding and controlled-design of complex interfaces in heterostructure may lead to novel material properties for potential electronic devices.

Methods

Sample fabrication

$\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ targets were prepared using stoichiometric amounts of Pr_6O_{11} , SrCO_3 and Mn_2O_3 powders with purity better than 99.9%. The mixtures were heated in air at 600 °C for 4 h

for de-carbonization. The mixture powders were ground and then heated at 1350 °C for 8 h, followed by re-grinding to ensure homogeneity. The powders were pressed into a 2-in diameter target and sintered at 1350 °C for 12 h in air. $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ films with different thicknesses were grown on (001) SrTiO_3 (STO) and (001) $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) by pulsed laser deposition at 100 mTorr oxygen pressure at a substrate temperature of 780°C. After deposition, the samples were cooled down at 15°C /min in a 200 mTorr oxygen atmosphere. The energy density of the 248 nm KrF excimer laser beam on target was 1.5 J/cm² with pulse frequency 2 Hz. The deposition rate for different compositions were checked by scanning electron microscope using films ~ 60 nm, ranging from 1.8 ~ 2 nm/min. The thickness of samples discussed in this paper was then controlled using deposition time for each respective deposition rate. The stoichiometry was confirmed by Rutherford backscattering spectrometry.

Transport and magnetic properties

The magnetic properties were measured by a superconducting quantum interference device (SQUID), and the transport properties were measured by the Physical Property Measurement System (PPMS) using linear four point probe. During measurement, the magnetic field was applied along the in-plane (100) direction.

XRD

The crystallographic texture of the films at room temperature was studied using a four-circle diffractometer at the Singapore Synchrotron Light Source (SSLS), with x-ray wavelength equal to Cu $K_{\alpha 1}$ radiation. Low temperature XRD was performed using Philips PANalytical X-ray diffractometers equipped with Cu $K_{\alpha 1}$ radiation.

X-ray absorption

The X-ray absorption near edge structure (XANES) measurements were carried out using linear polarized X-rays at the undulator beamline 20-ID-B of the Advanced Photon Source

(APS), Argonne National Laboratory, USA. The Si (111) monochromator with resolution $\delta E/E = 1.3 \times 10^{-4}$ was used. The XANES was collected in fluorescence mode using a 12-element Ge solid-state detector. A Mn metal foil, placed to intercept a scattered beam, was used as an online check of the monochromator energy calibration.

High resolution STEM

High-resolution STEM-ADF/ABF imaging and electron diffraction were performed using the double aberration-corrected JEOL-ARM200CF microscope with a cold-field emission gun and operated at 200 kV, at Brookhaven National Laboratory, USA. The microscope was equipped with JEOL and Gatan HAADF and ABF detectors for incoherent Z-contrast and phase imaging for heavy atoms and light atoms, respectively. The cross-section TEM samples were prepared by focused ion beam (FIB) followed by gentle ion-milling at low operating voltages. The HAADF and ABF images were acquired with condense aperture of 21.2 mrad and collection angle of 67-275 mrad for HAADF and 11-22.4 mrad for ABF images, respectively. To assist interpretation of the HRSTEM images, image simulations were carried out using our own computer codes based on the multislice method with frozen phonon approximation.

ASSOCIATED CONTENT

Supporting Information. Additional experimental and calculation details, figures, and tables.

This material is available free of charge via the Internet.

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Notes

The authors declare no competing financial interest.

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Figure 1

Figure 1. (A) The resistivity-temperature (ρ - T , upper) and magnetization-temperature (M - T , low) curves of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{SrMnO}_3$ films of different thicknesses. In magnetic measurements, an in-plane magnetic field of 500 Oe was applied along [100] direction. The 12-nm thick film undergoes a phase transition from paramagnetic insulator (PI) to new ferromagnetic insulator (FI') phase at ~ 150 K; and from FI' to ferromagnetic metal (FM') at ~ 105 K. The ρ - T (upper) and M - T (low) curves of 30-nm (B) and 12-nm (C) $\text{Pr}_{1-x}\text{Sr}_x\text{SrMnO}_3$ films with different Sr doping concentration x . (D) is phase diagram of bulk $\text{Pr}_{1-x}\text{Sr}_x\text{SrMnO}_3$ after Ref. 29. The phase diagrams of the 30-nm (E) and the 12-nm (F) $\text{Pr}_{1-x}\text{Sr}_x\text{SrMnO}_3$ films at $T > 50$ K. Open diamond symbols correspond to different doping concentration from (B-C). In (F) the horizontal red solid line indicates the temperature boundary between the FI' and FM' region, which is at ~ 105 K based on the current work. The dashed red line shows the approximate phase boundary of FI' to FM and FM' to FM transitions.

Figure 2

Figure 2. Perspective view (from XRD data) along (A) $[100]$ direction, and (B) $[\bar{1}\bar{1}0]$ projection of BO_6 octahedra tilt. In (A), the 8 octahedra (grey) on the left have no TiO_6 tilt, while the 12 MnO_6 octahedra (green and burgandy color) on the right have $a^-a^-c^-$ octahedral tilt. Green spheres represent Ti in STO; Golden, blue and yellow spheres represent Pr/Sr, Mn and O in $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{SrMnO}_3$, respectively. The green and burgundy octahedra represent counter-clockwise rotation $\mathcal{O}$ - MnO_6 and clockwise rotation $\mathcal{U}$ - MnO_6 , respectively. (C) $[\bar{1}\bar{1}0]$ projection with asymmetric/distorted MnO_6 octahedra (from STEM data). (D) STEM Annular bright field (ABF) image viewed along $[\bar{1}\bar{1}0]$ direction from the 30-nm PSMO film, showing the projection of Pr/Sr (golden), Mn (blue) and O (yellow) atoms. (D) is a portion of the averaged image of the film near the interface. The projected oxygen columns are consistent with asymmetric/distorted MnO_6 octahedral rotation in (C), rather than symmetric MnO_6 octahedral rotation in (B). Image simulations with (E) Symmetric MnO_6 model as shown in (B), and (F) Asymmetric/distorted MnO_6 model as shown in (C). The red rectangles outline the supercell. The simulated image in (F) agrees with the experimental image in (D) very well.

Figure 3

Figure 3. Simultaneously acquired (A) high angle annular dark field (HAADF) and (B) annular bright field (ABF) images in STEM mode for 30-nm $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{SrMnO}_3$ (PSMO) film. The interface between the 1st layers of PSMO and STO is easy to identify from HAADF image contrast because $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{SrMnO}_3$ has strong contrast while STO has weak contrast. The vertical dash line indicates the Pr/Sr layer at the interface. (C) ABF

image after averaging the ABF image vertically in **(B)** for enhanced signal/noise ratio. **(D)** The I, II and III are the magnified images from the interface (pink rectangle), the film (green rectangle) close to interface and film (blue rectangle) away from the interface in **(C)**, respectively. The golden circles mark the Pr/Sr columns and the red rectangle outlines the supercell. There are four sets of data for the oxygen displacement (d_O), as indicated by the four kinds of triangles in the II. **(E)** Deviation of oxygen (d_O) from the face center of ABO_3 unit cell along [001] direction. The blue lines are for viewing guide only. The inset shows the intensity profile (circles) from the horizontal scan line (yellow dash line in II of **D**). The red line is the fitting curve by fitting the individual oxygen peak with a Gaussian function within the shadow region.

Figure 4

Figure 4. (A) BO_6 octahedra a^-/b^- rotation angle and (B) Out-of-plane c -lattice parameter as a function of distance from the interface. The vertical dashed line corresponds to the PSMO/STO interface. The octahedral rotation angle increases with the distance for the 12-nm PSMO film, but almost does not change for the 30-nm PSMO film. (C) XRD of 002 peaks for 30 nm (black squares) and 12 nm (red circles) films at room temperature, which were fitted using two Pseudo-Voigt functions ($L1$ and $L2$). The orange, magenta, cyan lines are fitted curves of $L1$, $L2$ and $L1+L2$ for 30-nm film; the green, violet, and blue lines are fitted curves of $L1$, $L2$ and $L1+L2$ for 12-nm film. (D) Averaged c -lattice parameter of STO substrate and PSMO films with different thicknesses as a function of temperature measured by XRD.