Tuning the entanglement between orbital reconstruction and charge transfer at a film surface

B. Cui, C. Song, F. Li, G. Y. Wang, H. J. Mao, J. J. Peng, F. Zeng & F. Pan

Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

The interplay between orbital, charge, spin, and lattice degrees of freedom is at the core of correlated oxides. This is extensively studied at the interface of heterostructures constituted of two-layer or multilayer oxide films. Here, we demonstrate the interactions between orbital reconstruction and charge transfer in the surface regime of ultrathin (La,Sr)MnO₃, which is a model system of correlated oxides. The interactions are manipulated in a quantitative manner by surface symmetry-breaking and epitaxial strain, both tensile and compressive. The established charge transfer, accompanied by the formation of oxygen vacancies, provides a conceptually novel vision for the long-term problem of manganites—the severe surface/interface magnetization and conductivity deterioration. The oxygen vacancies are then purposefully tuned by cooling oxygen pressure, markedly improving the performances of differently strained films. Our findings offer a broad opportunity to tailor and benefit from the entanglements between orbit, charge, spin, and lattice at the surface of oxide films.

Results

Strain dependent Mn valence state. La₀.₇Sr₀.₃MnO₃ (001) (LSMO) films ranging from 5 unit cells (u.c.) to 125 u.c. under tensile to compressive strain states are obtained by growth on different substrates. MgO, Pb(Mg₀.₃Nb₀.₇)₀.₇₂Ti₀.₂₈O₃ (PMN-PT), and SrTiO₃ (STO) are substrates used for tensile strain, while LaAlO₃ (LAO) and LaSrAlO₄ (LSAO) are used for compressive strain and result in the following strain values: ε₀ = 8.9%,
The most eminent features in Fig. 1b occur for the peaks of Mn-are used to acquire XLD data, as explained in the following analysis. The out-of-plane components exhibit the same peak positions and plane (E//c) polarization components, respectively, as shown in 90° performed to study the manganese valence of LSMO films grown far exceed the critical thickness (see Supplementary Fig. S3).

The effects of strain and surface symmetry-breaking on orbital reconstruction. To elucidate charge redistribution in LSMO, we investigate the orbital occupancy of manganites on different substrates firstly. Representative XAS and XLD results, where XLD is the difference between the XAS in-plane and out-of-plane components, $I_{x}-I_{c}$, of LSMO on MgO and LAO substrates, are presented in Fig. 2a–f, giving information for the occupancy of Mn-3d orbits. The XAS with two incident angles are normalized according to the $I_{3}$ peak and the area under XLD around the $I_{2}$ peak (647.5 eV–660.0 eV) ($A_{XLD}$) is used to represent the difference between the relative occupancies of the 3$z^{2}-r^{2}$ and x$^{2}-y^{2}$ orbits [$A_{XLD} = P(3z^{2}-r^{2}) - P(x^{2}-y^{2})$] (Ref.12). The XLD signal around the $I_{2}$ peak derived from the normalized XAS spectra is negative for the films on MgO, indicating enhanced x$^{2}-y^{2}$ electron occupancy for films strained under tension (Fig. 2a–c). In contrast, compressive strain stabilizes the 3$z^{2}-r^{2}$ orbit, resulting in positively valued XLD signals for the LSMO on LAO (Fig. 2d–f). The effect of strain on orbital reconstruction is further confirmed in LSMO on PMN-PT, STO, and LSAO substrates (see Supplementary Fig. S4).

The relationship of film thickness and $A_{XLD}$ for the LSMO films on all substrates is displayed in Fig. 2g (symbols, left axis). Notably, $A_{XLD}$ for 5 u.c. LSMO on PMN-PT and STO is unexpectedly positive, substantiating that strain is not the sole driving force for orbital occupancy in these ultrathin films. The origin of this anomalously positive signal is the surface symmetry-breaking attributed to the absence of apical oxygen coordination12,22,23, which brings about an additional out-of-plane occupancy and counterbalances the tensile strain favoring in-plane orbits22. Given that the contributions of MnO$_2$ slabs depend on both their positions with respect to the surface and the attenuation depth ($\delta$), the intensity of the XLD signal can be fitted as follows12:

$$A_{XLD} \sim I_{XLD, norm} = \frac{\sum_{i=1}^{n} \left[P_{i}(3z^{2}-r^{2}) - P_{i}(x^{2}-y^{2})\right] \exp(-t_{i}/\delta)}{\sum_{i=1}^{n} \exp(-t_{i}/\delta)}$$

where $P_{i}(3z^{2}-r^{2})$ and $P_{i}(x^{2}-y^{2})$ are the relative occupancies of the 3$z^{2}-r^{2}$ and x$^{2}-y^{2}$ orbits, respectively, for the MnO$_2$ slab at a distance $t_{i}$ from the free surface. For the fully strained films (see Supplementary Fig. S2), the XLD signal of Eq. (1) can be calculated by three parameters: the occupation of the surface, $P_{S} = P_{0}(3z^{2}-r^{2}) - P_{0}(x^{2}-y^{2})$, the occupation of the bulk, $P_{B} = P_{0}(3z^{2}-r^{2}) - P_{0}(x^{2}-y^{2})$, and the attenuation depth $\delta$ (see Supplementary Fig. S5). For thicknesses less than 30 u.c., curves fitted using the experimental data are shown by the dashed lines in Fig. 2g (dashed lines, right axis), and the corresponding $P_{S}$ and $P_{B}$ are summarized in Table 1. The attenuation depth $\delta$ approximately equals to 4.6 nm, in agreement with previous works12,17.

Notably, experimental points are well fitted under 30 u.c, whereas for thicker films, considerable strain relaxation weakens the orbital reconstruction, leading to experimental values with $A_{XLD}$ far above (below) fitted curves for tensile (compressive) strain. These discrepancies may be attributed to the critical thickness for strain relaxation (see Supplementary Fig. S2). The bulk component is dependent on the strain: $P_{B}$ increases from negative to positive sequentially for MgO, PMN-PT, STO, LAO and LSAO, as listed in Table 1. In contrast, the surface electron occupancy, $P_{S}$, is found to always be pre-

Charge transfer and the formation of oxygen vacancies. As the orbital and electronic structure of LSMO under the influence of

Figure 1 | Shift of Mn $I_{3}$ edge peak position. (a), Schematic of experimental configuration for XAS measurements with different x-ray incident angles. (b) and (c), Normalized XAS (in-plane) at Mn-$I_{3}$ absorption edge for 15 u.c. and 125 u.c. LSMO grown on different substrates, respectively.
strain and surface symmetry-breaking is clarified, we develop an electrostatic model in Fig. 3 to describe the charge transfer in the films. In the absence of strain and surface effects, each Mn $e_g$ orbit obtains $1/3e^-$ from the adjacent La$_{2/3}$Sr$_{1/3}$O layer ($1/6e^-$ for the surface Mn $e_g$ orbit), as shown in Fig. 4a. Although the crystalline quality of the LSMO films grown on other substrates are not as good as that on STO, they are quasi-epitaxial without any phase and composition separation at a thickness of 15 u.c.$^2$. It is also noteworthy that the influence of the lattice distortion due to the film/substrate mismatch on the charge transfer has been taken into account in the orbital reconstruction in our model. The splitting of $e_g$ orbits leads to the rearrangement of uniformly distributed electrons within or between the layers. For the bulk part of LSMO films, the orbital occupancies are changed according to $P_b$ (Table 1) without external charge transfer and valence variation. For the surface layer, $3z^2 - r^2$ orbital energy levels are much lower than that of bulk ones$^{23}$; hence, electrons at the second MnO$_2$ layer ($i = 2$) are transferred to the surface energetically favorable $3z^2 - r^2$ orbit through the out-of-plane Mn-O-Mn covalent bonds. These bonds are hybridized by the O-$2p$ orbit and two adjacent Mn $3z^2 - r^2$ orbits and serve as a preferential high-mobility passageway for electron transfer due to their highly overlapped electron cloud$^{23}$, as displayed in Fig. 4b. With fixed $1/6$ electrons at the surface $x^2 - y^2$ orbits, the maximum transfer of electrons between MnO$_2$ (from the $i = 2$ to $i = 1$) layers ($n_2$) via (La,Sr)O is 2/3, which generates an extreme orbital component described by $P_s(3z^2 - r^2) = 5$ and an ionic Mn$^{3+}$ state at the surface. However, for larger out-of-plane orbital components, the transfer of electrons from the surface $x^2 - y^2$ to $3z^2 - r^2$ ($n_2$) is allowed, and the effects should be considered. Given that the orbital component $P_s(3z^2 - r^2) / P_s(x^2 - y^2)$ shown in Table 1 determines the

Figure 2 | X-ray linear dichroism and XLD signal versus sample thickness. (a–c) and (d–f), Normalized XAS and XLD of LSMO with different thicknesses of 5 u.c., 15 u.c. and 125 u.c. grown on MgO and LAO substrates, respectively. (g), Left axis (symbols): integrated area of the XLD signal of the samples grown on different substrates. Right axis (dashed lines): best fits of area under XLD signal to Eq. (1) as explained in the text.
The surface charge redistribution, the relationship between the number of transferred electrons and orbital components can be expressed by

\[
\frac{n_1 + n_2}{6} = \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)}
\]

From Eq. (2), we can derive the following equations to calculate the transferred electrons between the layers \( n_1 \) and the orbits in the surface layer \( n_2 \):

\[
\begin{align*}
&n_1 = \begin{cases} 
\frac{1}{6} \left( \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} - 1 \right) & \text{if } \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} \leq 5 \\
\frac{2}{3} & \text{if } \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} > 5
\end{cases} \\
&n_2 = \begin{cases} 
\frac{1}{6} \left( \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} + 1 \right) & \text{if } \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} \leq 5 \\
0 & \text{if } \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} > 5
\end{cases}
\end{align*}
\]

The values of \( n_1 \) and \( n_2 \) for various substrates calculated by Eqs. (3) and (4) are also listed in Table 1. The valence state of Mn (\( m \)) at the surface is determined by the interlayer charge transfer, \( m = \frac{2}{3} - n_1 \).

Consequently, the estimated valence states of Mn are 3.394, 3.333, 3.306, 3.167 and 3.000 for LSMO grown on MgO, PMN-PT, STO, LAO and LSAO substrates, respectively, in accordance with the shift of the Mn-L\(_3\) peak in Fig. 1b. Similarly, the charge transfer difference (\( \Delta n_1 = 0.394e^- \)) between MgO and LSAO substrates exactly coincides with the charge variation of the Mn ions (0.4e^-) mentioned above. It is therefore concluded that the coherence of the valence state characterization and the electrostatic model with respect to XLD results provides compelling evidence for the coupling between orbital reconstruction and charge transfer.

The polar discontinuities play a dominant role in the charge transfer at the film/substrate interface, as seen in LaAlO\(_3/SrTiO_3\). The effect of such charge transfer commonly affects the valence state of the constituent in the vicinity of the interface, for example, Ti\(^{4+} \rightarrow Ti^{3+}\) in SrTiO\(_3\) close to the LaAlO\(_3/SrTiO_3\) interface. Because the interfacial effect near the surface is quite weak, it is highly unlikely—although not impossible—that charge transfer originates primarily from charge redistribution in this region. Instead, the charge transfer in 15 u.c. LSMO is more feasibly motivated by orbital reconstruction. In addition, the present charge transfer model for the 15 u.c. thick sample is based on orbital reconstruction, which is detected by XDL measurements in TEF mode with an attenuation depth of ~4 nm, outside of the scope of the interfacial regime. As the LSMO film thickness is reduced to 5 u.c., the Mn-L\(_3\) peaks shift toward a lower energy in sequential order for MgO, PMN-PT, and STO substrates with decreasing tensile stress, similar to the 15 u.c. samples. Nevertheless, the possibility of electronic phase separation and polar discontinuities might complicate Mn valence investigations for several monolayer thick LSMO grown on LAO (see Supplementary Fig. S6).

The surface charge redistribution results in an electric potential offset (V) with an amplitude proportional to the amount of transferred charge. The potential before (black dashed lines) and after (red lines) surface charge redistribution can be clearly delineated in the electric potential diagrams in Fig. 3a and b. Specifically, \( n_1 \) is equally constituted by electrons from two (La,Sr)O layers adjacent to a MnO\(_2\) layer (\( i = 2 \)), while \( n_1/2 \) electrons from the (La,Sr)O layer nearest to the surface contribute to the electric potential of surface MnO\(_2\) (\( i = 1 \)). Hereby, after the surface charge redistribution, the electric potential of the (La,Sr)O layer nearest to the surface is \((n_1/2 - 1/6)\) eV, while the potential difference between the surface MnO\(_2\) and its adjacent (La,Sr)O layer is \((1/3 + n_1/2)\) eV. This sum is the absolute electric potential of the surface MnO\(_2\) layer, in contrast to the 1/6 eV before redistribution, described by

\[
V = \frac{1}{3} + \frac{n_1}{2} + \left( \frac{1}{6} - \frac{1}{6} \right) = n_1
\]

Corresponding results for potential offsets can be found in Table 1 for various substrates. We note that the internal charge redistribution in the LSMO film maintains the same electric potential between the substrate and surface. The ordered oxygen vacancy (\( V_{O_{\text{O}}} \)) in alternate MnO\(_2\) layers allow more electrons in the (La,Sr)O layer to be transferred to the stoichiometric MnO\(_2\) layers as the Mn valence should be uniform in the bulk films\(^{24,25}\), providing an effective avenue for the elimination of potential offset. Such charge redistribution reduces the Mn valence in both MnO\(_2\) and MnO\(_{2-x}\) layers, as shown in the bottom of Fig. 3c and d (blue arrows and potential lines). For films strained under tension, the oxygen deficiencies are less and the Mn valence is comparatively higher with a smaller offset, while the compressive ones possess more \( V_{O_{\text{O}}} \) and lower Mn valence. Quantitatively, each MnO\(_{2-x}\)-(La,Sr)O-MnO\(_2\) unit reduces the electrical potential by 2x eV. \( V_{O_{\text{O}}} \) in bulk MnO\(_{2-x}\) layers (\( x \)) is determined in the film with a thickness of 15 u.c., \( x = V/14 = n_1/14 \) (the bulk includes 14 layers in the 15 u.c. sample), producing values of \( x = 0.019, 0.024, 0.026, 0.036, \) and 0.048 for MgO, PMN-PT, STO, LAO and LSAO substrates, respectively (Table 1). The formation of additional \( V_{O_{\text{O}}} \) weakens the double exchange in the reconstructed surface and results in an antiferromagnetic phase, leading to the loss of ferromagnetism and metallic conductivity at the surface or, when ultrathin, in the entire film. It is noteworthy that the charge transfer in our case is in a single LSMO film rather than in heterostructures such as LaAlO\(_3/SrTiO_3\) (Ref. 19). However, strain relaxation would weaken the difference in surface orbital reconstruction (Fig. 2g), thus suppressing the charge transfer between MnO\(_2\) slabs and the concomitant Mn valence variation in the 125 u.c. samples. Hence, the results in Fig. 1c are well supported. We therefore summarize that charge redistribution is driven by the orbital reconstruction through the orbital component \( \frac{p_z(3z^2 - r^2)}{p_z(x^2 - y^2)} \) in 15 u.c. thick LSMO with different strain states, reaching a consistent charge transfer value with the Mn valence variation in XAS.

**Table 1 | Calculated results of the orbital occupation, charge transfer, electric potential offset, and oxygen vacancy concentration**

| Substrate  | \( P_5 \) | \( P_6 \) | \( \frac{P_5(3z^2 - r^2)}{P_5(x^2 - y^2)} \) | \( n_1 \) | \( n_2 \) | \( m \) | \( V/eV \) | \( x \) |
|------------|----------|----------|-----------------|--------|--------|-------|--------|-------|
| MgO        | 0.450    | -0.220   | 2.636           | 0.273e-| 0.000  | 3.394 | 0.273  | 0.019 |
| PMN-PT     | 0.500    | -0.100   | 3.000           | 0.333e-| 0.000  | 3.333 | 0.333  | 0.024 |
| STO        | 0.520    | -0.080   | 3.167           | 0.361e-| 0.000  | 3.306 | 0.361  | 0.026 |
| LAO        | 0.600    | 0.160    | 4.000           | 0.500e-| 0.000  | 3.167 | 0.500  | 0.036 |
| LSAO       | 0.720    | 0.230    | 6.143           | 0.667e-| 0.027e-| 3.000 | 0.667  | 0.048 |

Oxygen vacancy manipulation for high performance of manganite. Thus far, the electrostatic model has described both the charge redistribution and the introduction of \( V_{O_{\text{O}}} \) in the charge deviation of Mn valence from its ideal value, which serves as the intrinsic origin of
the severe deterioration of surface ferromagnetism and conductivity. It has been demonstrated previously that several methods, such as electrostatic doping and ferroelectric polarization, provide an opportunity to tune electronic and magnetic properties of manganite through the manipulation of carrier concentration. We now address \( V_O \) manipulation and its effect on performance enhancement in LSMO. Because the electric potential offset is sensitive to oxygen deficiencies (MnO\(_5\)) at the surface, the oxygen pressure used in the sample cooling process is expected to effectively control both the potential offset and \( V_O \). Consequently, samples of 15 u.c. on various substrates with different cooling oxygen pressures, \( p_C = 50, 300 \) and 550 Torr, are prepared, in which 300 Torr was employed for the samples discussed above. Concomitant O-K edge XAS of LSMO on MgO, STO and LAO substrates cooled under different oxygen pressures are normalized according to the feature peak of the Mn-3d orbit at approximately 530 eV and shown in Fig. 5. The pre-edge spectral region extending from 529 to 533 eV represents the Mn 3d unoccupied states and the second band of Mn 3d at approximately 533 eV (marked by the dashed line) is quite sensitive to the valence of Mn\(^{2+}\). Compared with the LSMO on STO and LAO, the second band of Mn 3d is much more prominent for films on MgO with a higher Mn valence. On the other hand, as \( p_C \) increases, the peaks at approximately 533 eV are apparently enhanced regardless of the substrate, indicating the reduction of \( V_O \) and Mn\(^{3+}\) (which can be found in the magnified view in Supplementary Fig. S7).

As a typical sample showing tensile strain (Fig. 3c), LSMO on MgO substrate with less intrinsic \( V_O \) exhibits a higher \( T_C \) and lower resistivity under a lower cooling oxygen pressure (\( p_C = 50 \) Torr), which causes more \( V_O \) (Fig. 6a and d). Similar to the samples with the MgO
substrate, a reduced $V_O$ has a negative effect on the magnetic and electric properties of films grown on STO (Fig. 6b and e). However, when the oxygen cooling experiments are performed on the samples with compressive strain, the situation changes dramatically. The films with compressive strain grown on LAO exhibit semiconducting behavior because the resistance is seen to increase with decreasing temperature, in analogy to the case on MgO and STO, when $p_{C} = 50$ and 300 Torr. As the cooling oxygen pressure increases to 550 Torr, it is surprisingly found that the films on LAO show a typical character of metallic conductivity (Fig. 6f). This behavior is opposite to that of the films under tensile strain. Generally, high oxygen pressure annealing would lead to a resistance increase. In the present case, however, the transition from semiconducting to metallic conductivity with increasing oxygen pressure confirms that oxygen compensates for the $V_O$ induced by the elimination of the potential offset. This process strengthens the double-exchange effect in LSMO. Accordingly, the films exhibit robust magnetization, and the $T_C$ of LSMO is greatly enhanced from ~200 K to 250 K by increasing $p_{C}$ from 50 to 550 Torr, as shown in Fig. 6c. The results from the effective manipulation of the magnetization and conductivity of LSMO by tensile and compressive strains indicating that our electrostatic model for the both charge redistribution and $V_O$ is confirmed by an elegant experimental design, shedding promising light on the development of manganite-based spintronics.

**Discussion**

The present results verify the existence of interactions between orbit (orbital reconstruction), charge (charge transfer), lattice (epitaxial strain), and spin (magnetization) in the surface regime of a single LSMO film. Surface symmetry-breaking and strain, as well as changing the orbital energy levels and occupancies of Mn ions, lead to charge redistribution throughout the films. The quantitative dependence of charge transfer on orbital reconstruction ($P_O(3z^2−r^2)/P_O(x^2−y^2)$) established in an electrostatic model sheds promising light on the preparation of a single oxide film where the four degrees of freedom act on each other, including but not limited to the manganite perovskite we have presented here. The understanding of the interactions at the film surface serves as the compass to improve the performance at the surface or throughout ultrathin LSMO films. The charge redistribution associated with the introduction of $V_O$ to modify the potential offset, which depends on the strain state, is then verified to be tunable by a facile, reliable, and efficient design—the oxygen pressure control in the cooling process, leading to an enhancement of the magnetization and conductivity at a lower (higher) oxygen pressure for the tensile (compressive) case. Thus, this aspect would optimize the interface between manganite/non-magnetic materials (such as LSMO/SrTiO$_3$ in magnetic tunnel junctions and LSMO/graphene in spin injection devices) that ultimately restricted the performances of oxide spintronics. At last, we note that the improvements introduced in this work can be readily generalized to other oxide films, and thus has the potential to generate a variety of unprecedented properties at film surface.

**Methods**

**Sample preparation.** All of the samples were grown using pulsed laser deposition (PLD) from a stoichiometric La$_{2/3}$Sr$_{1/3}$MnO$_3$ target by applying a KrF excimer laser at a rate of 1.16 nm/min. During growth, the substrate was held at 700 °C and in an oxygen background pressure of 200 mTorr. The growth was monitored in situ by RHEED (reflection high-energy electron diffraction) analysis allowing precise control of the

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**Figure 4 | Schematic of charge transfer through Mn-O-Mn covalent bond.** (a), Sketch for the charge distribution (left column) and orbit information (right column) of Mn $e_g$ and O $2p$ orbit near the surface without consideration of strain and surface symmetry-breaking effect. (b), The charge transfer schematic from bulk to surface for the films under tensile or compressive strain (left column) and corresponding high-mobility charge transfer passageway formed by two $3z^2−r^2$ orbit and O $2p$ orbit (right column). The electron at bulk orbits ($x^2−y^2$ or $3z^2−r^2$) are transferred to the surface $3z^2−r^2$ orbit through the out-of-plane Mn-O-Mn covalent bond as the arrows shown, leaving less filled orbits (washi in the schematic) in the bulk.

**Figure 5 | O-K edge of LSMO under different cooling pressure.** (a–c), O-K edge of 15 u.c. LSMO cooled in different oxygen pressures ($p_{C}$ = 50, 300 and 550 Torr) grown on representative substrates, MgO, STO and LAO. The dashed lines mark the Mn 3d relevant absorption peak around 533 eV. The peaks marked by arrows at 536 eV and 545 eV are assigned to the bands with La 5$d$/Sr 4$d$ and Mn 4$s$p character, respectively.
thickness at the unit cell scale and accurate characterization of the growth dynamics. Without special instruction, the samples were slowly cooled to room temperature in 300 Torr of oxygen at a rate of ~5 °C/min to improve the oxidation level after growth.

**Sample characterization.** A Quantum Design superconducting quantum interference device (SQUID) measurement system (QD MPMS-7) was used to measure the magnetic properties along the (100) direction of the substrate in the temperature range 5–400 K, which could detect the slight variation of magnetization with a resolution of 10–8 emu. All the field-cooling M–T (magnetization versus temperature) measurements in this work were carried out without any magnetic field after cooling down to 5 K in 20 kOe. Conductivity was determined in a Van der Pauw four-probe configuration by the ET9000 electric transport measurement system. XAS measurements were performed in total electron yield (TEY) mode at the Beamline BL08U1A in Shanghai Synchrotron Radiation Facility. The polarization directions of the circularly polarized x-rays were tuned by rotating the x-ray incident angle, with 90° and 30° corresponding to in-plane (E//a, I_ab) and majority of out-of-plane (E//c, I_cd), respectively. The spectra normalization was made by dividing the spectra by a factor such that the I_1 pre-edge and I_2 post-edge have identical intensities for the two polarizations. After that, the pre-edge spectral region was set to zero and the peak at L_3 pre-edge was set to one. X-ray linear dichroism (XLD), the difference between the pre-edge and post-edge have identical intensities for the two polarizations. After that, the pre-edge spectral region was set to zero and the peak at L_3 edge was XAS measured with an incidence angle of 90°. The measurement temperature for XAS and XLD is 300 K.

**Figure 6** | Magnetization and conductivity of LSMO films cooled under various oxygen pressures. (a–c), Magnetization versus temperature curves for 15 u.c. LSMO cooled in different oxygen pressures (p = 50, 300, and 550 Torr) grown on representative substrates, MgO, STO and LAO, respectively. Corresponding resistivities as a function of temperature are shown in (d–f).

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Author contributions
B.C. and G.Y.W. prepared the samples. B.C. and C.S. carried out the measurements. B.C. and F.L. were responsible for the simulation. C.S. and F.P. conceived and directed the project. F.Z., H.J.M. and J.J.P. provided advice on the experiments. All authors participated in discussing the data and writing the manuscript.

Additional information
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