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ABSTRACT

The interface reconstruction in perovskite heterostructures caused by interfacial octahedral tilt/rotation and its effects on the spin, charge, and orbital degrees of freedom is a very attractive topic for correlated oxides. Here, we present a systematic investigation on tensely strained (110)-LaCoO$_3$/La$_{2/3}$Sr$_{1/3}$MnO$_3$/LaCoO$_3$ trilayers, focusing on orbital reconstruction and accompanied effects. The most remarkable finding is the reordering of the energy levels of Mn-3$d$ orbitals at the interface: the low-lying orbital becomes $d_{x^2-y^2}$ for sandwiched La$_{2/3}$Sr$_{1/3}$MnO$_3$ rather than $d_{3z^2-r^2}$ as expected for a bare La$_{2/3}$Sr$_{1/3}$MnO$_3$ film. Interlayer charge transfer via $d_{x^2-y^2}$ orbitals is further detected as a driving force of orbital reconstruction. Due to spin–orbit coupling, the charge/orbital reconstruction produces a chain effect on the spin degree of freedom of the La$_{2/3}$Sr$_{1/3}$MnO$_3$ layer, resulting in a dramatic spin reorientation by 90$^\circ$ in a film plane. The present work demonstrates how to tune macroscopic properties of correlated oxides via mutual coupling between different degrees of freedom.

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INTRODUCTION

Perovskite transition metal oxides (TMOs) with strongly coupled spin, charge, and orbital degrees of freedom provide a valuable playground for the exploration for emergent phenomena. What is of special importance is that the heterostructures are composed of different TMOs, which own unique interface phases with cooperatively distorted oxygen octahedra and reconstructed spin/charge/orbital orders. There are reports on dramatic variations in macroscopic properties for (001) oriented multilayers, produced by even a subtle octahedral tilt/rotation at interfaces. As shown by Liao et al., through transferring the octahedral rotation in NdGaO$_3$ to the La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) film, a giant anisotropic transport in ultrathin LSMO films as well as a realignment of the magnetic easy axis can result. In a recent work, Zhang et al. demonstrated how symmetry mismatch drove a spin reorientation for the LSMO/LaCoO$_{2.5}$ heterostructures. It was found that, at the interface, MnO$_6$ octahedra share the apical oxygen with neighboring CoO$_4$ tetrahedra, forming elongated octahedra which support perpendicular magnetic anisotropy. The strong effect of the engineered interface was also observed in magnetic oxides other than LSMO. As reported by Kan et al., the SrRuO$_3$/Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ combination led to a large Ru–O–Ti bond angle; thus, a unique SrRuO$_3$ phase with a substantially larger Ru–O–Ru bond angle than that of the bulk counterpart is observed.

These works clearly demonstrate the effects of octahedral tilt/rotation on spin ordering. Different from its bulk counterpart, the interface phase suffers from a spatial confinement in the out-of-plane direction. In addition to enhancing quantum fluctuation, this feature will allow a full use of the advantage of interlayer engineering, getting states available for either constituent of the heterostructure. In general, interface engineering takes the effect via modifying the multiple degrees of freedom of the interface phase. Due to the strong coupling between different degrees...
of freedom, any variation in one degree of freedom will cause a chain effect. Undoubtedly, a deep understanding of the interface effect will strengthen our capabilities to design materials on demand. In this work, we presented a systematic investigation on tensely strained (110)-LCO/LSMO/LCO trilayers (LCO = LaCoO$_3$), focusing on interface orbital reconstruction and accompanied effects associated with spin degrees of freedom. As reported by Chen et al., the (110)-orientated films exhibit a faster strain relaxation process along the [1 ¯10] direction than that along the [001] direction. That is to say that the tensile strain along the [001] direction dominates the lattice distortion of the LSMO film deposited on the (110)-STO substrate. This causes the elongation of MnO$_6$ octahedra along the in-plane [001] axis and the preferred occupation of the d$_{3z^2-r^2}$ orbital. Thus, the magnetic easy-axis of the (110)-LSMO/STO bare film aligns along the [001] axis. In this case, interlayer orbital hybridization and charge transferring are expected to hardly occur due to the absence of the Mn 3d$_{3z^2-r^2}$ and O 2p$_x$ (2p$_y$) overlap. Surprisingly, we observed a reversion of the energy levels of the d$_{x^2-y^2}$ and d$_{3z^2-r^2}$ orbitals: the low-lying orbital is d$_{x^2-y^2}$ in LSMO of the trilayers. Accompanying orbital reconstruction, a Mn-to-Co charge transfer via the d$_{x^2-y^2}$ orbitals takes place. It is this process that stabilizes the d$_{x^2-y^2}$ orbital. Accordingly, the magnetic easy axis of the LSMO layer undergoes a switching from the [001] to the [1 ¯10] direction due to the strong correlation between the orbital and spin degrees of freedom.

**METHODS**

LCO/LSMO/LCO trilayers [Fig. 1(a)] were grown on (110)-SrTiO$_3$ (STO) single crystal substrates ($5 \times 3 \times 0.5$ mm$^3$) using the technique of pulsed laser deposition (PLD). During deposition, the temperature of the substrate was maintained at 700°C (for LSMO) or 635°C (for LCO) and the oxygen pressure was fixed to 30 Pa. Here, a low growth temperature was adopted for the LCO layer to avoid recrystallization, which will cause rough interfaces. The repetition rate of the laser pulse was 2 Hz, and the fluence was 2 J/cm$^2$ (KrF excimer laser, wavelength = 248 nm). After deposition, the samples were cooled to room temperature at the rate of 10°C/min in an oxygen pressure of 100 Pa. The layer thickness was set to 7 nm for LCO and to 4 nm, 5 nm, 9 nm, 10 nm, 15 nm, and 19 nm for LSMO. A (110)-[LCO (3 m)/LSMO (3 m)]$_5$ ([LCO/LSMO]$_5$) superlattice sample was also prepared for the measurements of x-ray absorption spectroscopy (XAS), where m means a monolayer and it is $\sim$2.7 Å. For comparison studies, two bare LSMO films with the thicknesses of 6 nm and 10 nm, respectively, were also fabricated. Here, film thickness has been determined by the number of laser pulses, after a

![FIG. 1](https://example.com/figure1.png) (a) A sketch for the (110)-LCO/LSMO/LCO trilayers and the relationship between two coordinate systems of [110]-[1 ¯10]-[001] and [001]-[010]-[001]. (b) XRD spectra of the LCO/LSMO/Co trilayers with different LSMO thicknesses (black curves). Results of curve-fitting were also represented (red curves). (c) Reciprocal space mapping of the (222) (left panel) and (130) (right panel) reflections of the trilayers with $t_{LSMO} = 10$ nm. The vertical alignment of the reflections indicates a fully coherent growth of the trilayers on the substrate, without lattice relaxation. Here, “MLs” denote trilayers. The vertical dashed lines are guides to the eye.
careful calibration by the technique of small angle x-ray reflectivity (Fig. S1 of the supplementary material).

The surface morphology of the trilayers was measured by using an atomic force microscope (AFM, SPI 3800N, Seiko). The crystal structure of the films was determined by using a Bruker x-ray diffractometer equipped with thin film accessories (D8 Discover, Cu Ka radiation). Lattice images were recorded by using a high-resolution scanning transmission electron microscope (STEM) with double Cs correctors (JEOL-ARM200F). Magnetic measurements were conducted by using a quantum-designed vibrating sample magnetometer (VSM-SQUID) in the temperature interval from 5 K to 300 K and the magnetic field range up to 7 T.

The XAS spectra were collected at the Beam line BL08U1A in Shanghai Synchrotron Radiation Facility, in the total electron yield mode. The spectra were measured at the Mn $L$-edge for two polarization directions by setting x-ray polarization to [001] and [110] directions in sequence. The spectra normalization was made by dividing the spectra by a factor such that the $L_3$ pre-edge and $L_2$ post-edge have identical intensities for the two polarizations. After that, the pre-edge spectral region was set to zero and the peak at the $L_3$ edge was set to one. The XLD ($I_{[001]} - I_{[110]}$) is the intensity difference of normalized XAS along two measurement directions, which gives information on the empty Mn-3$d$ states. Co $L$-edge XAS was measured with the x-ray polarization to [001]. The measurement temperature for XAS and XLD is 300 K.

RESULTS AND DISCUSSION

Figure 1(a) is a sketch for the (110)-LCO/LSMO/LCO trilayers and the relationship between two coordinate systems of [110]-[110]-[001] and [001]-[010]-[001]. The trilayers are very smooth, with a root-mean-squared roughness around 0.4 nm (Fig. S2 of the supplementary material). Figure 1(b) shows the $\Theta$–2$\Theta$ x-ray diffraction (XRD) spectra for selected LCO/LSMO/LCO trilayers with the LSMO layer thicknesses of $t_{\text{LSMO}}$ = 5 nm, 10 nm, 15 nm, and 19 nm. The XRD spectrum is somewhat complex, composed of multiple broad peaks whose number grows with $t_{\text{LSMO}}$. As shown in Fig. 1(b), the calculated curve (red line) mimics the experimental one (black line) very well. Multiple XRD peaks are signatures of high crystal quality of the trilayers. According to the results of curve fitting, the out-of-plane lattice parameter defined by $d_{110} = \sqrt{2/2a_0}$ can be deduced, where $a_0$ is the lattice parameter of the perovskite unit cell for LSMO or LCO. It is noted that $d_{110} \approx 2.71$ Å for LSMO and $\approx 2.68$ Å for LCO, smaller than the bulk value ($\approx 2.74$ Å for LSMO and $\approx 2.70$ Å for LCO). As expected, both films are in-plane tensely strained.

To get the information about the in-plane lattice structure, the reciprocal space mappings (RSMs) of (222) and (130) reflections are measured. As shown in Fig. 1(c), multiple reflections of the trilayers are also detected by RSMs, aligning vertically with that of the substrate. In addition to a fully coherent growth of the film on the substrate, this result indicates that the trilayers share exactly the same in-plane lattice constant with STO, $a_{\text{STO}} = 3.905$ Å and $a_{\text{LCO}} = 5.522$ Å. Therefore, the trilayers are fully tensely strained. This conclusion is consistent with that drawn from curve fitting of the $\Theta$–2$\Theta$ scanning. Similar results are obtained for other trilayers investigated here (not shown).

Figure 2(a) shows the typical high-angle annular dark-field (HAADF) image of the cross section of the (110)-LCO/LSMO/LCO trilayers with $t_{\text{LSMO}} = 10$ nm, recorded along the [001] zone axis. Yellow dashed lines mark the LCO/LSMO interfaces. Inclined dark stripes can be observed in the left side LCO layer, which is a typical feature of the oxygen-deficient LCO film. (b) An enlarged view of the HAADF image and the corresponding electron energy loss spectroscopy (EELS) spectrum images of the Mn-$L_3$ and Co-$L_2$-$L_3$ edges, recorded along the white vertical line across the horizontal LSO(LCO) interface. The interface is of high quality, with only minor interlayer diffusion in the range around one unit cell.
show the Mn-XAS spectra of a bare LSMO film (6 nm in thickness) and a [LCO (3 m)/LSMO (3 m)]₅ superlattice, respectively. Here, the superlattice with an ultrathin layer thickness (3 m) was chosen to highlight the interface effect. Since magnetic signals mainly come from the LSMO layer, we only present the Mn-L₂ and L₃ absorption peaks. Two spectra are obtained for each sample by setting x-ray polarization to [001] and [110] directions in sequence. As shown by the upper right sketch in Fig. 3(a), the [001] and [110] planes are parallel to the dₓ²−ᵧ² and d₃z²−r² orbitals, respectively. Two broad peaks are observed in the interested energy range, corresponding to the L₂ and L₃ absorption edges of Mn 3d electrons. As reported, the L₂ peak contains important information on the orbital structure: a high (low) peak implies a low (high) orbital occupancy. To highlight the difference in the absorption peaks along two directions, x-ray linear dichroism (XLD) spectra, defined by the upper right sketch in Fig. 3(a), [001] and [110] planes are parallel to the dₓ²−ᵧ² and d₃z²−r² orbitals, respectively. Two broad peaks are observed in the interested energy range, corresponding to the L₂ and L₃ absorption edges of Mn 3d electrons. As reported, the L₂ peak contains important information on the orbital structure: a high (low) peak implies a low (high) orbital occupancy. To highlight the difference in the absorption peaks along two directions, x-ray linear dichroism (XLD) spectra, defined by the upper right sketch in Fig. 3(a), [001] and [110] planes are parallel to the dₓ²−ᵧ² and d₃z²−r² orbitals, respectively. Two broad peaks are observed in the interested energy range, corresponding to the L₂ and L₃ absorption edges of Mn 3d electrons. 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FIG. 4. (a) Normalized Mn- and Co-XAS spectra for the bare LSMO film and [LCO (3 m)/LSMO (3 m)]$_5$ superlatice. The arrow marks the direction for spectrum shift. (b) Sketch for the overlap of the $d_{x^2-y^2}$ orbitals of Mn-3$d$ and Co-3$d$ electrons, via the O 2$p_x$ (2$p_y$) orbital (left panel). It is this overlap that leads to the charge transfer across the LCO/LSMO interface. Due to the formation of the Mn–O–Co covalent bond, the $d_{x^2-y^2}$ orbital is stabilized (right panel). It is possible that the shared electron is closer to Co$^{3+}$. Consequently, signatures of charge transfer are detected by XAS.

\[ \Delta E_{SO} = \zeta \left[ \langle L \cdot S \rangle_{[001]} - \langle L \cdot S \rangle_{[\bar{1}10]} \right] = \frac{\zeta}{4\mu_B} \left( m_{0[110]} - m_{0[001]} \right), \]

where $\zeta$ is a parameter for spin–orbital coupling, $m_0$ is the orbital moment, and $\langle \rangle$ represents a thermodynamic average. For LSMO in trilayers, a direct calculation gives the orbital moment of 0 along the [001] direction and $\frac{1}{2} \left( \frac{\zeta}{\lambda_{x^2-y^2,yz}} + \frac{\zeta}{\lambda_{x^2-y^2,xz}} \right)$ along the [110] direction. According to Eq. (1), the easy axis has a larger orbital moment than the hard axis. This means that [110] is the easy axis. For the bare LSMO film, the corresponding values are $\frac{4\mu_B}{\zeta}$ and $\frac{1}{2} \left( \frac{\zeta}{\lambda_{x^2-y^2,yz}} + \frac{\zeta}{\lambda_{x^2-y^2,xz}} \right)$. Accordingly, the easy and hard axes are reversed (see Note 1 of the supplementary material for detailed calculations).

FIG. 5. (a) Thermomagnetic curves of the bare LSMO (10 nm) film, acquired in field-cooling mode with the fields along the [001] and [110] directions, respectively. Shaded areas highlight the magnetic difference along the two measuring directions. Clearly, magnetic moments prefer to align along the [001] direction, as shown by the sketch at the upper right corner. (b) Thermomagnetic curves of the (110) LCO (7 nm)/LSMO (10 nm)/LCO (7 nm) trilayers, measured with exactly the same condition as for the bare LSMO film. The magnetic easy axis at low temperature now is [110].
To quantitatively describe magnetic anisotropy, we converted the $M$–$T$ curves in Fig. 5 into a series of $M$–$H$ curves at different temperatures (see Fig. S4 of the supplementary material for directly measured $M$–$H$ loops). Figures 6(a) and 6(b) show two typical $M$–$H$ curves obtained at 10 K and 160 K along different directions. From first glance, the growth rate of $M$ with $H$ is obviously different along the [110] and [001] directions. Take the data of 10 K as an example. When measured along the [110] direction, the trilayers get magnetic saturation at very low fields (0.1 T), and further increase in magnetic field only causes minor variation in $M$ (see Fig. 5). In contrast, along the [001] direction, the saturation state is not gained until the field is above 1.5 T. The energy cost by orientating magnetic moment from easy hard axes, namely, the anisotropy constant, $K = 1.84 \times 10^6$ erg/cm$^3$ at 10 K, is calculated from the area encircled by the two $M$–$H$ curves. For the bare LSMO film, however, $K = 0.93 \times 10^6$ erg/cm$^3$ at 10 K. Obviously, the actual anisotropy constant of the trilayers should be larger than that observed here since it has to overcome the intrinsic anisotropy energy of the bare LSMO. A simple calculation yields $\Delta K = 2.77 \times 10^6$ erg/cm$^3$ for trilayers. This value is larger by a factor of three in magnitude than that of the bare LSMO layer. Obviously, the effect of interface reconstruction is much stronger than the strain effect.

Based on Eq. (1), we can get an estimation of anisotropic energy. For LSMO, Mn possesses a spin–orbital coupling coefficient of $\zeta = 0.045$ eV$\cdot$Å and an orbital magnetic moment of $-0.1$ μB. Based on the density functional theory calculations, the orbital magnetic moment difference along two orthogonal directions can be up to $\Delta \mu_z = 0.01$ μB. Adopting this $\Delta \mu_z$, the calculated anisotropy constant is $\sim 10^6$ erg/cm$^3$, which is consistent with the experimental value obtained for our LCO/LSMO heterostructure.

Following a similar procedure, the anisotropy constant at high temperatures can be obtained. As shown in Fig. 6(d), $K$ is maximal at low temperatures, nearly constant from 10 K to 100 K, and rapidly decreases upon further warming up above 100 K. The decrease in $K$ with temperature can be ascribed to the decrease in the magnetization of the LSMO layer. If the anomalous magnetic anisotropy stems from interface reconstruction, it should be dependent on the layer thickness of LSMO ($t_{\text{LSMO}}$). In Figs. 7(a)–7(c), we show the isothermal magnetization curves of the trilayers with different LSMO layers (see Fig. S5 of the supplementary material for $M$–$T$ curves measured under different applied fields). From first glance, the discrepancy of the two $M$–$H$ curves along two directions reduces as layer thickness grows. This feature is especially obvious as $t_{\text{LSMO}}$ increases from 10 nm to 19 nm. It implies a reduction in anisotropy energy. A direct calculation shows that $K = -2.55 \times 10^6$ erg/cm$^3$ for $t_{\text{LSMO}} = 5$ nm and $-0.6 \times 10^6$ erg/cm$^3$ for $t_{\text{LSMO}} = 19$ nm. The maximal anisotropy constant is $5.8 \times 10^6$ erg/cm$^3$, gained in the [LCO (3 nm)/LSMO (3 ml)]$_3$ superlattice. Figure 7(d) shows the anisotropy constant as a function of the reciprocal layer thickness of LSMO. Although the $K$/$t_{\text{LSMO}}$ relation is nonlinear, $K$ displays a clear tendency toward growth as $t_{\text{LSMO}}$ decreases. This result confirms the dominant role of the interface effect.

Finally, we emphasize that the effect of interface reconstruction on spin orientation is strong only for tensile trilayers. For compressive trilayers, charge transfer takes place via both $d_{x^2-y^2}$ and $d_{z^2}$ orbitals in the case, which orbital is more stable depends on the competition of these two orbitals. Consequently, the interface effect on the spin degree of freedom could be weakened. To investigate the effect of interface coupling in the
compressive state, we choose the combination of La$_{2/3}$Ba$_{1/3}$MnO$_3$ (LBMO) and (LaAlO$_3$)$_{0.3}$(SrAlO$_3$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT) substrates (the lattice constant is 3.91 Å for LBMO and 3.86 Å for LSAT). The compressive strain of the LBMO/LSAT film is about −1%, which is exactly opposite to that of the LSMO/STO film (tensile 1%). We have fabricated compressive trilayers LCO/LBMO/LCO on the LSAT substrate. As expected, the preferred spin orientation is [110]. The interface effect only enhanced anisotropy energy by $\Delta K = 2.2 \times 10^5$ erg/cm$^3$ (see Fig. S6 of the supplementary material) for La$_{2/3}$Ba$_{1/3}$MnO$_3$ ($T = 100$ K), while it causes an increment of $\Delta K = 2.7 \times 10^6$ erg/cm$^3$ for tensile LCO/LSMO/LCO at 100 K [Fig. 6(d)].

CONCLUSIONS

In conclusion, a systematic investigation on tensely strained (110)-LaCoO$_3$/La$_{2/3}$Sr$_{1/3}$MnO$_3$/LaCoO$_3$ trilayers is presented, focusing on the orbital reconstruction at interfaces and the effect stemming from spin–orbital coupling. It is found that the interlayer coupling makes Mn 3d$_{x^2-y^2}$ preferentially occupied, overcoming the effect of tensile strains which stabilizes d$_{3z^2-r^2}$. We present evidences for interlayer charge transfer via d$_{x^2-y^2}$ orbitals. This causes the formation of Mn–O–Co covalence, thus lowering the energy level of d$_{x^2-y^2}$. In response to orbital reconstruction, the spin orientation of La$_{2/3}$Sr$_{1/3}$MnO$_3$ undergoes a 90° switching in the film plane due to spin, charge, and orbital coupling. This work demonstrates how spin, charge, and orbital degrees of freedom couple with each other during the interface reconstruction, paving the way toward the exploration for novel materials.

SUPPLEMENTARY MATERIAL

See the supplementary material for the schematic representation of the x-ray reflectivity, surface morphology, thermomagnetic curves, and magnetic hysteresis loop of the LCO/LSMO/LCO trilayers; thermomagnetic curves and magnetic hysteresis loop of the [LCO/LSMO)$_5$ superlattice, LCO/LBMO/LCO trilayers, and bare LBMO; and the detailed calculations of orbital momentum.

AUTHOR’S CONTRIBUTIONS

F.H. and X.C. contributed equally to this work.

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There are no conflicts of interest to declare.

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