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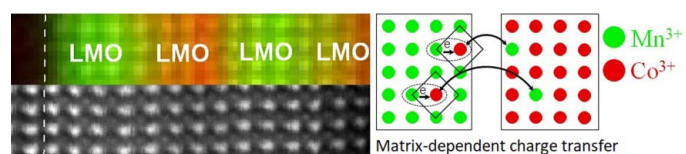
Ferromagnetism and matrix-dependent charge transfer in strained $\text{LaMnO}_3\text{--LaCoO}_3$ superlattices

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ABSTRACT

Interfacial magnetism at transition-metal oxide interfaces is of tremendous interest. The emergence of ferromagnetism and a matrix-dependent charge transfer between Co and Mn ions in the interdiffusion region of compressively strained $\text{LaMnO}_3\text{--LaCoO}_3$ superlattices (SLs) were studied. The SLs exhibit considerable ferromagnetism, which is negligible in both constituents. This is explained by the matrix-dependent charge transfer between Co and Mn ions. That is, the valence state of diffused Co ions into LaMnO_3 shifts from $3+$ to $2+$ by adopting one electron from Mn^{3+} , inducing the same amount of Mn^{4+} , while the Mn ions that diffuses into LaCoO_3 remains Mn^{3+} .



IMPACT STATEMENT

Matrix-dependent charge transfer effect was induced by the interplay between intrinsic and extrinsic effect in transition-metal oxides superlattices, which could be used to site-selectively modulate the electronic and magnetic states.

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1. Introduction

Benefiting from the tremendous advances in oxide thin film fabrication techniques, precise control of the intrinsic interplay of charge, spin, orbit and lattice degrees of freedom at oxide interfaces has reached an unprecedented level [1]. As a consequence, novel interfacial functionalities, which are absent in the constituent materials, were intensively studied [2,3]. Empowered by potential spintronic applications, interfacial magnetism is of

particular interest [4], especially the ones made of ABO_3 perovskite transition-metal oxides (TMO) [5–7].

In addition to intrinsic properties, the extrinsic modulations, such as off-stoichiometry and interdiffusion, play an important role as well. They can locally alter the B -site chemical surroundings, such as valence state and $B\text{--}O\text{--}B'$ bond angles, which essentially govern the magnetic behaviors of the perovskite TMOs and their interfaces [8]. Generally, these extrinsic effects were thought to

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be inimical to distracting or even concealing the intrinsic properties, which are inevitable to some degree at real interfaces. The incapability to eliminate the extrinsic effects stimulates us to explore the opposite direction. If harnessed properly, these extrinsic effects could contribute new degrees of freedom and spawn tailored functionalities. Among the various extrinsic effects, interdiffusion is known for its deviation from ideally abrupt interfaces, which is uniform near the interface and thus easy to tame.

In this *Letter*, we demonstrate the emergence of ferromagnetism and matrix-dependent charge transfer of *B*-site ions, observed in the interdiffusion region of compressively strained superlattices (SLs). A series of LaMnO_3 (LMO) and LaCoO_3 (LCO) SLs on LaAlO_3 substrates were fabricated in consideration of two factors hereinafter. Firstly, the compressive strain imposed by LAO predominantly suppress the ferromagnetism in LMO [9] and LCO [10]. Hence, ferromagnetic distraction from each constituent was diminished when studying the ferromagnetism of their SLs. Secondly, LMO, LCO and LAO share the same *A*-site element, La. The shared *A*-site element eliminates the effect of *A*-site interdiffusion [11,12], which could also impact the local valence state of *B*-site.

2. Experimental section

2.1. Sample fabrication

Both LMO and LCO thin films were prepared by pulsed laser deposition on $5 \times 5 \text{ mm}^2$ and 0.5 mm-thick LAO (001) substrates from polycrystalline stoichiometric LMO and LCO targets, respectively. A growth temperature of 800°C, oxygen background pressure of 10 mTorr, an excimer laser with a wavelength of 248 nm, a repetition rate of 1 Hz and energy density of 1.8 J cm^{-2} were used. After deposition, all samples were cooled down to room temperature at a rate of $10^\circ\text{C min}^{-1}$ in an oxygen environment the same as the deposition pressure. Both LMO and LAO growth followed the uc-by-uc growth mode and were monitored by *in situ* reflection high energy electron diffraction.

2.2. Magnetic properties measurement

The magnetic properties were measured using superconducting quantum interference device (SQUID, Quantum Design) magnetometry, with an external magnetic field applied along to the in-plane LAO [100] direction. Magnetization versus applied fields (M - H) ranging from -3 to $+3$ T was measured at 10 K. All M - H data were normalized by subtracting the temperature-independent

paramagnetic and diamagnetic signals of LAO substrates. Magnetization versus temperature (M - T) measurement ranging from 10 to 300 K was measured at 0.1 T after a 3 T field cooling process. A constant diamagnetic contribution was subtracted in all M - T data.

2.3. X-ray absorption spectroscopy measurements

A series of Mn and Co L-edge soft X-ray absorption spectroscopy (XAS) measurements were performed at Beamline 4.0.2 of Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL) in total electron yield mode at room temperature under high-vacuum condition ($\sim 10^{-8}$ Torr). The spectra have been normalized to the photon flux measured by the photocurrent of a clean gold mesh.

2.4. STEM

High-resolution STEM-HAADF and EELS spectrum imaging were performed using the JEOL-ARM200F microscope equipped with ASCOR aberration corrector and cold-field emission gun operated at 200 kV. The cross-section TEM samples were prepared by focused ion beam with a 2 kV cleaning step. The HAADF and ABF images were acquired with condenser aperture of 30 mrad and collection angle of 68–280 mrad for HAADF mode. EELS spectra were recorded using a Gatan Quantum ER spectrometer attached to the STEM with a 0.25 eV/channel energy dispersion.

2.5. Ab initio calculation

All calculations were performed by density functional theory based on the Vienna *Ab initio* Simulation Package [13,14] with Perdew–Burke–Ernzerhof approximation for the exchange-correlation functional [15] and the frozen-core all-electron projector-augmented wave method [16] for the electron–ion interaction. On-site Coulomb interaction $U = 2.7$ eV and on-site exchange interaction $J = 1.0$ eV were applied to Mn. The cutoff energy for the plane wave expansion was set to 500 eV. For bulk LMO, a gamma-centered $7 \times 7 \times 7$ *k*-point grid for Brillouin zone sampling was found to be sufficient. A G-type antiferromagnetic orthorhombic (*Pnma*) structure was used for LMO with relaxed lattice parameters of $a = 5.93 \text{ \AA}$, $b = 5.57 \text{ \AA}$ and $c = 7.67 \text{ \AA}$.

3. Results and discussion

LMO, LCO and LAO possess the pseudocubic lattice parameters of 3.95, 3.805 and 3.787 Å, respectively, which result into a moderate LMO/LAO lattice mismatch of

−4.3% and a small one in LCO/LAO of −0.48%. In our study, LMO/LCO SLs with a periodicity of (4 uc-LMO/4 uc-LCO) n (n indicates periodic repetitions), was labeled as SL44 n . SLs with varied n from 1 to 4 and 16 uc LMO and LCO films were grown for magnetic measurements. Detailed structure characterizations can be found in Figure S1.

Figure 1(a) illustrates that both individual LMO and LCO thin films grown on LAO showed negligible magnetic moment. As for SLs, the ferromagnetic signal apparently emerged. Figure 1(c) summarizes the magnetic moments after removing the substrate contribution. The magnetic moment of SLs increased linearly with interfaces/layers ratio (or interface-area-to-volume ratio, see Figure 1(d)), which indicates the interfacial origin of the ferromagnetism. Figure 1(b) also supports our observations that no discernible sign of ferromagnetic transitions were observed in LMO and LCO thin films. It

is noteworthy that, the shapes of M - H loops and M - T curves of all the SLs are nearly identical, which indicates the same ferromagnetism origin.

The magnetic state of TMOs is highly dependent on the valence state of the transition-metal elements. To reveal the role of intrinsic and extrinsic effects on the appearance of ferromagnetism in the SLs, global characterization of XAS and local characterization of STEM-EELS were employed to examine the valence state of both Mn and Co ions. Figure 2 shows the XAS results of 8 uc LMO, 8 uc LCO, SL441 and SL444. The 8 uc LMO and LCO films were chosen here to ensure that the films are thin enough to allow the detection of possible film-substrate interfacial effect. As shown in the left insert of Figure 2, the main Mn- L_3 peaks of both of the SLs shifted to an energy higher than that of 8 uc LMO (~ 641.2 eV), clearly indicating the presence of Mn⁴⁺ induced by the SL structure. Similar to the magnetic

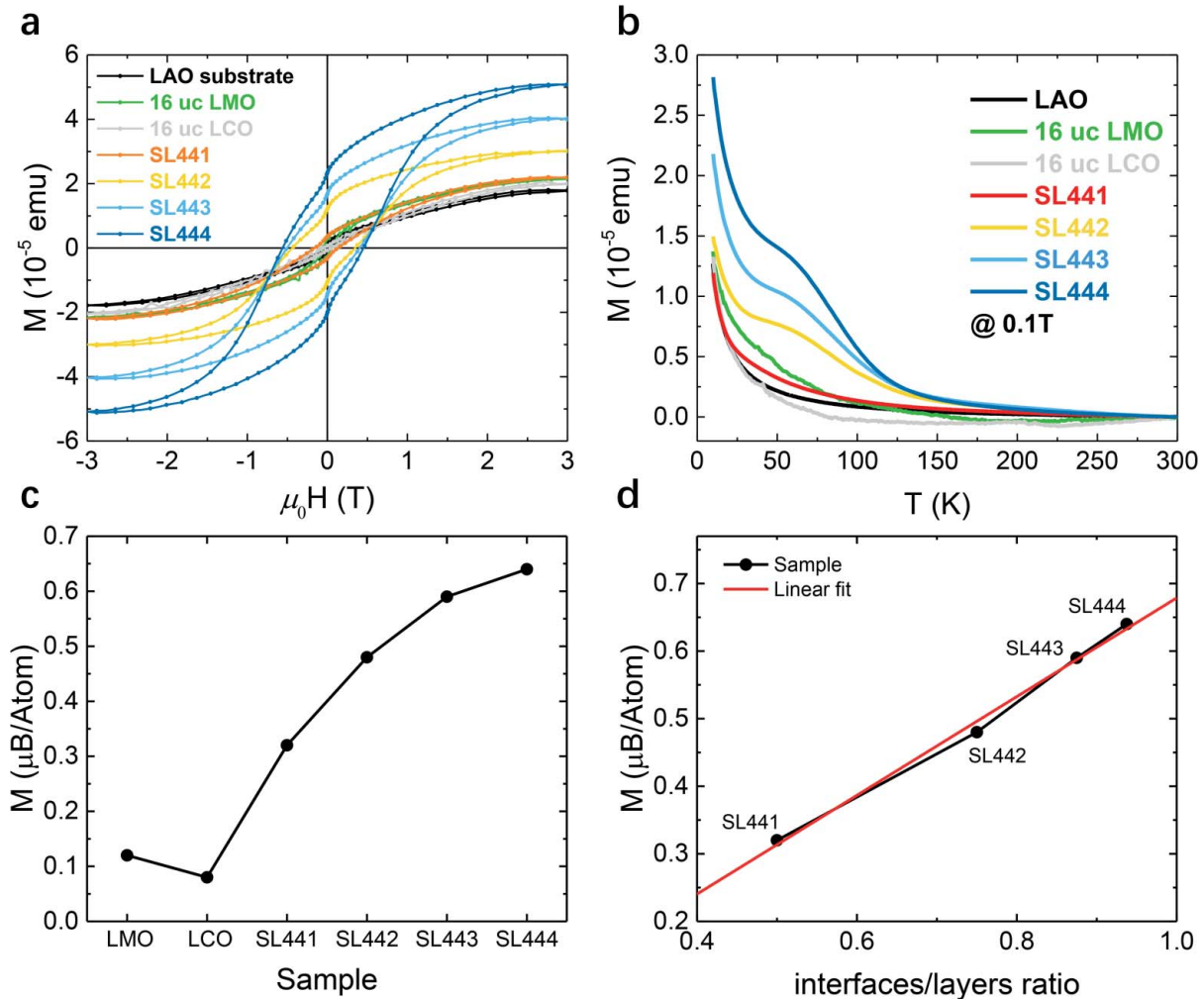


Figure 1. Emergence of ferromagnetism in LCO/LMO SLs on LAO substrate attained by SQUID. (a) M - H loops of SLs, individual LMO, LCO layers and LAO substrate at 10 K after a zero field cooling. (b) 3 T field cooling M - T curves measured at 0.1 T of the same samples. (c) A summary of magnetic moments of all samples at 10 K. (d) The linear fit of magnetic moments of SLs as a function of interfaces/layers ratio.

properties, this blue shift of Mn- L_3 peak of SL444 was more significant than that of SL441, as a result of more charge transferred in SL444 due to its larger interface-area-to-volume ratio. Meanwhile, the Co^{2+} fingerprint shoulder peaks in the SLs was apparently higher than that of 8 uc LCO (~ 775.7 eV) (see the right inset of Figure 2), demonstrating that the valence state of a small portion of Co ions in the SLs changed their valence from $3+$ to $2+$. In consideration of the higher Mn ion and lower Co ion valence state observed in the SLs, a charge transfer effect [17] between B -site ions (from Mn^{3+} to Co^{3+}) was unambiguously demonstrated. The coexistence of Co^{2+} , Co^{3+} , Mn^{3+} and Mn^{4+} ions in the SLs makes the origin of this emerging ferromagnetism rather intricate. As suggested by the Goodenough–Kanamori rules [18,19] and the insulating nature of the SLs (Figure S2), the favorable scenario is the ferromagnetic super-exchange effect such as $\text{Mn}^{4+}-\text{O}^{2-}-\text{Co}^{2+}$.

Figure 3(a) shows the atomically resolved HAADF image of SL442 projected onto the (010) plane of LAO substrate. The SLs were coherently grown on LAO substrate. Figure 3(b) illustrates the EELS elemental maps corresponding to the La- $M_{4,5}$, Mn- $L_{2,3}$ and Co- $L_{2,3}$ edges, which shows a 2–3 uc interdiffusion of Mn and Co ions. In Figure 3(c), we demonstrated the EELS line profiles of Mn ions uc-by-uc along [001] direction to determine their valence state by estimating the relative shift of the strong Mn- L_3 peak. EELS line profiles of Co ions were not shown because the Co^{2+} fingerprint shoulder peak was not detectable by EELS owing to the lower energy resolution of EELS than XAS. By combining the results of both the XAS and EELS, the local valence state of Co ions could be determined based on the charge conservation

law since the charge transfer only happened between B -site elements. Two reference samples of thick LMO and CaMnO_3 films were measured to calibrate the Mn^{3+} and Mn^{4+} peaks (see Figure 3(c)). The red dash line indicates the value of energy loss for the Mn^{3+} reference peak, which is at the same position as Line 8 and 15 (The diffused Mn ions in LCO matrix, labeled as Mn@LCO). This illustrated that valence state of Mn@LCO remained a $+3$ valence state, indicating the valence state of Co@LCO was $3+$ as well. Nonetheless, the green dash line shows the value of energy loss of the peak position of Line 4 and 12 (Mn@LMO), which is between the Mn^{3+} and Mn^{4+} references. This manifested the higher valence state of Mn@LMO, which also induced Co^{2+} @LMO. These findings reveal that the emergence of the Mn^{4+} @LMO and Co^{2+} @LMO was matrix-dependently triggered by the diffusion of Co^{3+} into LMO matrix only, rather than the diffusion of Mn^{3+} into LCO matrix (see Figure 3(d)).

To explain the experimentally observed matrix-dependent charge transfer between Co and Mn ions, we performed first-principles calculations. The significantly different lattice parameters of LMO and LCO impose different octahedral crystal fields on the Mn ions. To study the hierarchies of Mn $3d$ orbital levels for these two cases, we can simply model them with LMO (mimicking Mn ions under the LMO crystal field) as shown in Figure 4(a) and LMO with 4% compressive strain (mimicking Mn ions under the LCO crystal field) as shown in Figure 4(b), respectively. Notice that LMO layers suffer in-plane strain imposed by the LAO substrate, and have Jahn–Teller (JT) distortions which are not considered in these model. This is because the in-plane strain and the JT distortions do not affect the out-of-plane dz^2 orbitals, which are the

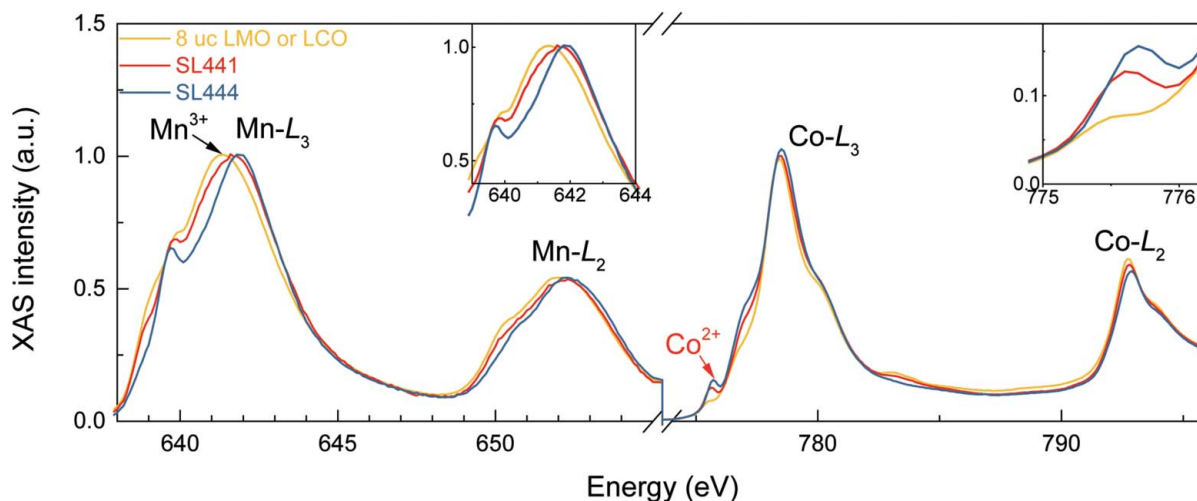


Figure 2. Charge transfer effect in SLs revealed by Mn and Co L -edge spectra. The red arrow indicates the Co^{2+} shoulder peak, while the black arrow indicates the Mn^{3+} peaks. The blue shift of the Mn- L_3 , which proves the presence of Mn^{4+} , is zoomed in the left inset. The bulge pre-peaks at 775.7 eV, which indicate the existence of Co^{2+} , is zoomed in the right inset.

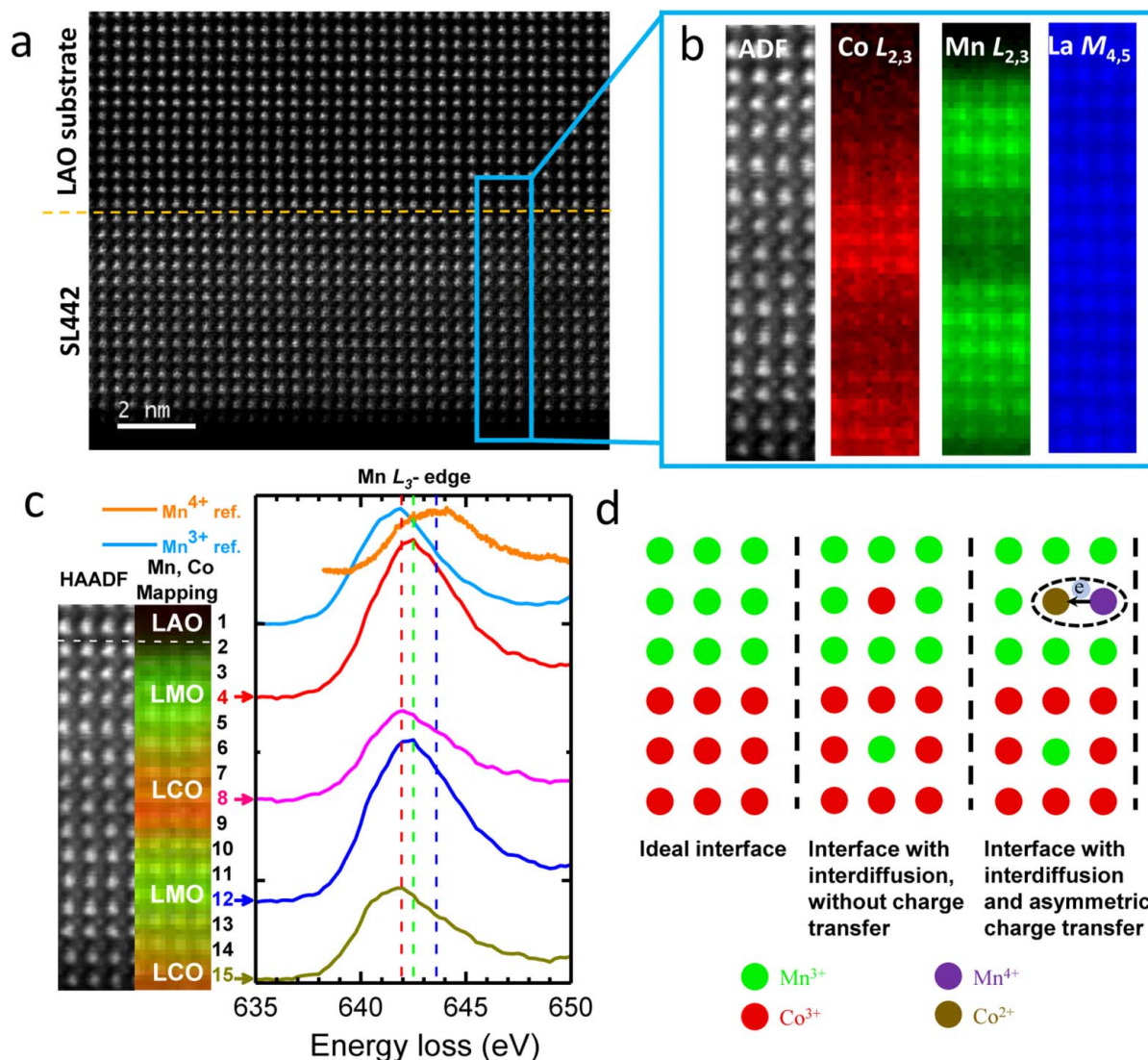


Figure 3. Matrix-dependent charge transfer obtained by STEM in combination with EELS. (a) HAADF images of SL442. (b) Enlarged HAADF, and EELS elemental maps corresponding to the La- $M_{4,5}$, Mn- $L_{2,3}$ and Co- $L_{2,3}$ edges. The Mn and Co spread in the whole region of the SL, which demonstrate the interdiffusion effect. (c) The EELS elemental line profiles of Mn- L_3 edges across the interface to surface. Line 4 and 12 represented Mn@LMO, showing a higher oxidation state than Mn³⁺. Whereas, Line 8 and 15 represented Mn@LCO, which remained to be Mn³⁺. The red dash line indicates the value of Mn³⁺, Line 8 and 15 peaks. The green dash line indicates the value of Line 4 and 12 peaks. The blue dash line indicates the value of Mn⁴⁺ peak. (d) Schematic views of an ideal interface, an interface with interdiffusion, and an interface with interdiffusion and matrix-dependent charge transfer.

main contribution of e_g states of Mn under the octahedral crystal field.

The 3d orbital levels of Mn mainly split into an e_g doublet and a t_{2g} triplet under the LMO octahedral crystal field (see the left side of Figure 4(c,d)). Figure 4(e) shows the calculated splitting energy between t_{2g} and e_g states for Mn@LMO is 0.54 eV. In such a moderate case, a high spin-polarization state is favorable with the four electrons of Mn³⁺ occupying the three t_{2g} and one e_g states. In presence of Co ions diffusion into LMO, the same orbital symmetry of the e_g orbitals allows charge transferring

from the occupied Mn e_g orbitals to the empty e_g electrons of Co@LMO, resulting valence change from Mn³⁺ to Mn⁴⁺ and from Co³⁺ to Co²⁺ (Figure 4(c)).

Whereas, for the Mn@LCO surrounded by Co ions, the Mn@LCO experienced a larger compressive octahedral crystal fields than Mn@LMO. Hence, oxygen octahedral rotations would be induced in order to accommodate such a compressive strain [20,21]. Consequently, the electronic property of LMO changes accordingly. The calculations showed that the splitting energy between t_{2g} and e_g states for the Mn@LCO was enhanced from 0.54 to

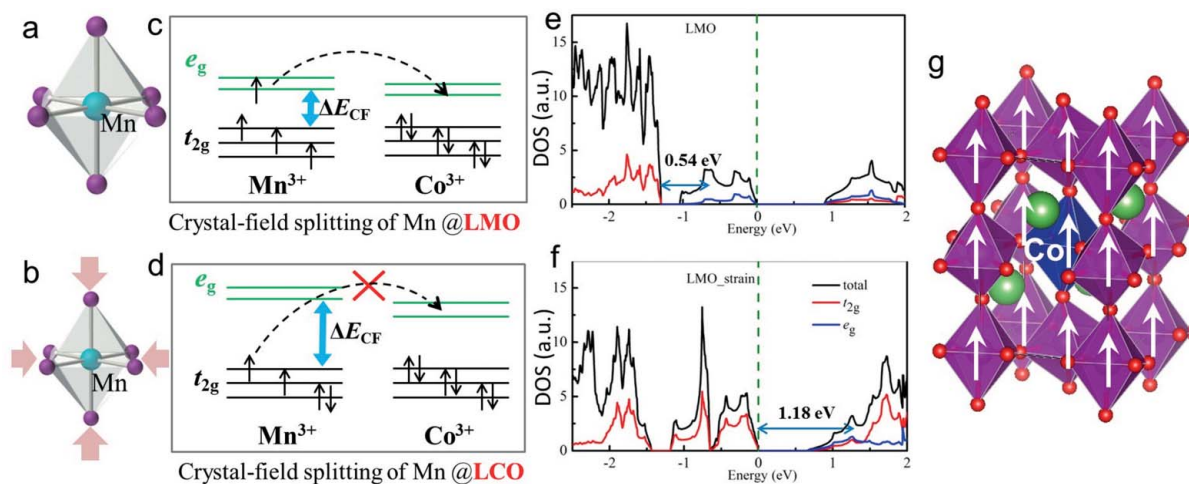


Figure 4. The origin of the matrix-dependent charge transfer and ferromagnetism. The octahedral structure of MnO_6 in (a) LMO and (b) LCO. (c) Mn d -electron configuration under the octahedral crystal field of LMO, where a high spin state of Mn^{3+} can transfer its one e_g electron to the unoccupied e_g of Co^{3+} . (d) Mn d -electron configuration under the octahedral crystal field of LCO which the Mn ions diffused into. The compressive strain forces the Mn^{3+} to stay in a low spin state, and forbids any charge transfer from t_{2g} of Mn^{3+} to e_g of Co^{3+} by the orbital asymmetry. (e,f) The partial density of states corresponding to (a) and (b), respectively, show the splitting energy between t_{2g} and e_g . (g) Schematic diagram of ferromagnetic coupling between a diffused Co ion and its surrounding Mn ions in the LMO layers.

1.18 eV (see Figure 4(f)). Such a large energy gap is energetically unfavorable to the occupation of e_g states, resulting in a low spin-polarization state with all four electrons of Mn^{3+} occupying only the t_{2g} states. In this case, the difference in the symmetry of t_{2g} and e_g orbitals forbids any charge transfer from the t_{2g} states of Mn^{3+} to the empty e_g orbitals of the Co^{3+} (Figure 4(d)), remaining Mn^{3+} and Co^{3+} in the interdiffusion region of LCO layers.

To investigate the relationship between the emergence of ferromagnetism and this matrix-dependent charge transfer effect, we model a supercell of Co-doped LMO by replacing an Mn ion by Co with an according to Co concentration of 25% in a form of $\text{LaMn}_{0.75}\text{Co}_{0.25}\text{O}_3$ (Figure 4(g)). Our calculations show that a ferromagnetic state is energetically more stable than an antiferromagnetic one, with $\Delta E_{\text{FM-AFM}} = -66.4 \text{ meV}$. The calculated magnetic moment of Mn and Co is 3.45 and $2.19 \mu_B$, respectively. This proves that the charge-transfer is responsible for the ferromagnetic coupling between Mn and Co ions observed in our experiment.

4. Conclusion

In summary, the ferromagnetism and a matrix-dependent charge transfer effect between Mn and Co were triggered in the interdiffusion region of strained LMO–LCO SLs grown on LAO. In the matrix-dependent charge transfer, only the Co diffused into LMO matrix contributes to the charge transfer, as attested by XAS and

EELS, and further explained by DFT calculations. As a subsequent effect of interdiffusion, ferromagnetism was induced as the DFT calculations indicate. These findings manifest the complex interplay between intrinsic and extrinsic effect in TMO SLs, provide a novel way to region-selectively modulate the electronic and magnetic states of TMO SLs, and underline the importance of extrinsic effect, which could contribute new degrees of freedom and spawn tailored functionalities for future spintronics.

Disclosure statement

No potential conflict of interest was reported by the authors.

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