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ORIGINAL REPORT



# High-spin state and magnetic coupling induced through interfacial orbital reconstruction observed in SrRuO<sub>3</sub>/LaNiO<sub>3</sub> superlattice

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## ABSTRACT

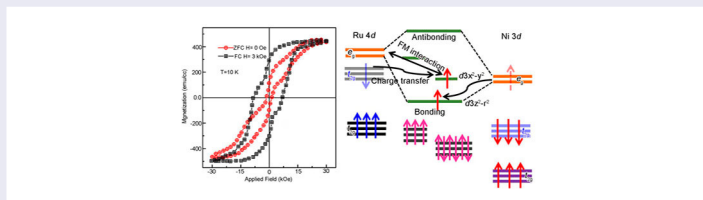
A high-spin state of SrRuO<sub>3</sub> at the interface and large magnetic coupling were observed in SrRuO<sub>3</sub>/LaNiO<sub>3</sub> superlattices. X-ray absorption spectroscopy and X-ray linear dichroism results show preferential occupation of the  $d_{3z^2-r^2}$  orbitals. The origin of the high-spin state in SrRuO<sub>3</sub> and the large-scale magnetic coupling is closely related to the orbital reconstruction. The reduced energy of the  $d_{3z^2-r^2}$  orbitals and enhanced densities of the  $e_g$  of SrRuO<sub>3</sub> contribute to the interface magnetic moment. The orbital occupancy is strongly correlated with the interface magnetic properties, thereby extending the concept of orbital degrees of freedom modulation on magnetic coupling properties.

## ARTICLE HISTORY

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## KEYWORDS

High-spin-state; orbital reconstruction; exchange bias; XAS; XLD



## IMPACT STATEMENT

Impact statement A high-spin state in SRO at the interface and large magnetic coupling is observed in SRO/LNO superlattices and the origin of these properties is closely related to orbital reconstruction.

## Introduction

The electronic structure at the perovskite-oxide interface between two transition metal oxides features complex interactions among the lattice, charge, spin, and orbital degrees of freedom and shows many emergent physical properties, including high-temperature superconductivity [1], magnetoresistance [2], exchange bias (EB) [3], and ferroelectricity [4]. With regard to these complex oxide structures, many of which are epitaxially compatible, the past decade has seen rapid growth in materials science at the atomic level with the creation of heterostructures with unique properties [5]. The capacity to fabricate superlattices (SLs), in which the component materials host systems of interacting electrons, has allowed experimental researchers to understand interfacial orbital reconstruction in efforts

to develop new electronic and magnetic functionalities at heterointerfaces for electronics and spintronics applications [6].

Macroscopically, charge transfer and orbital reconstruction appear to be of major importance in controlling the electronic phases in strongly correlated electron systems [7] because the magnetic and transport properties are closely related to the charge and orbital degrees of freedom [8]. For example, in ferromagnetic/superconducting systems such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>/La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>/SrRuO<sub>3</sub>, charge transfer and orbital reconstruction both play important roles in the interfacial magnetic proximity [9,10]. The magnetic coupling in manganite/LaNiO<sub>3</sub> and manganite/NiO systems such as LaMnO<sub>3</sub>/LaNiO<sub>3</sub>, LaMnO<sub>3</sub>/NiO, and La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/LaNiO<sub>3</sub> also involves charge transfer

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and orbital reconstruction, which both promote magnetic interactions at the interfaces [11–13].

Recently, investigations of  $3d$ – $4d$  and  $3d$ – $5d$   $ABO_3$  oxide interfaces have triggered renewed interest when magnetism [14], spin-glass [15], and topological phases [16] have been found at these interfaces. However, at the  $3d$ – $4d$  and  $3d$ – $5d$   $ABO_3$  oxide interfaces, which exhibit large spin–orbit interactions when compared with  $3d$ – $3d$  ions [17], the corresponding orbital hybridization and orbital occupancy remain unclear because of a lack of adequate information. In this paper, we present the results of a detailed study of the electronic structure and orbital occupancy in the  $SrRuO_3/LaNiO_3$  (SRO/LNO) SL with the aim of understanding the relationship between orbital reconstruction and the magnetic states at the  $3d$ – $4d$  oxide interface. Specifically, we show that, when compared with single-layer LNO, a different ionic charge distribution between the Ni–O and Ru–O layers modifies the sequence of energy levels within the  $e_g$  manifolds and consequently varies the orbital occupancy and magnetism state. Our findings are of direct relevance to the orbital occupancy of the  $3d$ – $4d$  heterostructures and provide an experimental demonstration of how orbital occupancy at the  $3d$ – $4d$ –metal sites can be altered and potentially engineered through appropriate design of successive ionic layers.

## Materials and experimental methods

The SL of  $[SRO_n/LNO_m]_7$  ( $n = 1, 2, 4, 8, 12, 20$  unit cells (u.c.);  $m = 1, 2, 5, 8, 12, 20$  u.c.) and single layer SRO (1, 2, 4, 8, 12, 20 u.c.) and LNO (1, 2, 4, 8, 12, 20 u.c.) reference samples were grown on STO (001) substrates by pulsed laser deposition. The SRO and LNO layers were grown at  $750^\circ\text{C}$  in an oxygen atmosphere under 30 Pa with a laser repetition rate of 5 Hz and energy density of  $1\text{ J/cm}^2$ . Structural quality and superlattice characterization of the samples was performed by X-ray diffraction (Rigaku, D8 Discover) analysis. A transmission electron microscope (JEM-2400FCS, JEOL) equipped with a high-angle-annular-dark-field (HAADF) detector was used for  $Z$ -contrast imaging analysis. Energy-dispersive X-ray spectroscopies (STEM-EDS) were performed using a monochromatic aberration-corrected scanning transmission electron microscope (STEM). Magnetization measurements were performed in a superconducting quantum interference device magnetometer. Linearly polarized soft X-rays tuned to the Ni  $L$  edge were used to perform X-ray absorption spectroscopy (XAS) in beamline BL08U1A of the Shanghai Synchrotron Radiation Facility in total-electron-yield mode.

## Results and discussion

The X-ray diffraction pattern of the  $[SRO_8/LNO_5]_7$  SL (Figures 1(a)) shows the periodically modulated structures of satellite peaks around the STO (002) peak for the SRO/LNO SL. The SL period  $\Lambda$  shows good agreement with the 8-u.c. of SRO and 5-u.c. of LNO in one stacked bilayer. The low surface roughness of the SL was confirmed by atomic force microscopy (Figures 1(b)). TEM images of  $[SRO_8/LNO_5]_7$  (Figures 1(c)) confirmed that the  $[SRO_8/LNO_5]_7$  SL thickness is approximately 35 nm for seven bilayers. Figures 1(d) shows an atomically-resolved HAADF-STEM image of  $[SRO_8/LNO_5]_7$ . In this image, the SRO/LNO interface was sharp. Figures 1(e) shows an STEM-EDS image of La  $L_\alpha$ , Sr  $K_\alpha$ , and O  $K_\alpha$  atoms that reveals that the electronically abrupt SRO/LNO interface was also chemically abrupt.

Figures 2(a) shows the magnetic hysteresis characteristics of the  $[SRO_8/LNO_5]_7$  SL measured at 10 K after zero-field-cooling (ZFC) and field-cooling (FC) with an applied magnetic field of 3 kOe applied perpendicular to the film plane from 300 K. The SL shows enhancement of the coercive field ( $H_C$ ) for the FC loop after FC (Figures 2(a)). A similar enhancement in  $H_C$  is also observed for other multilayers with different SRO thicknesses. The magnetic hysteresis loops of these SLs in the out-of-plane (Figure S1) direction after FC at 10 K were measured under an external field of  $\pm 30$  kOe. A high EB field ( $H_E$ ) of approximately 780 Oe was observed in this SRO/LNO SL. The observed EB and the coercivity enhancement in the heterostructures unambiguously indicate the existence of interfacial magnetic coupling. Interestingly, Figures 2(b) shows that the SL has a large saturated moment value of  $2.2\text{ }\mu_B/\text{Ru}^{4+}$  that exceeds the values for the low-spin state with an electron configuration of  $t_{2g}$  ( $3\uparrow, 1\downarrow$ ) for the pure films [18]. The enhanced saturation moment ( $M_S$ ) values for Ru in these SLs make them extremely difficult to picture as a low-spin moment plus a small orbital moment [19]. Figures 2(b) shows that these saturated moment values decrease with increasing film thickness, demonstrating the strong correlation between the moment enhancement and the interface coupling effects. In the absence of magnetic impurities at the interface, orbital reconstruction was found to play a crucial role in inducing both magnetic coupling and unidirectional anisotropy in the heterostructures [20]. Here, we propose the stabilization of a high-spin  $4\text{ }\mu_B/\text{Ru}^{4+}$   $t_{2g}$  ( $3\uparrow, 1\uparrow$ ) configuration at the interface to explain the EB effect, the coercivity enhancement, and the Ru moment in the SRO/LNO SL.

To obtain further insight into this magnetic behavior, the temperature dependences of the magnetization of the samples after FC were measured under an out-of-plane

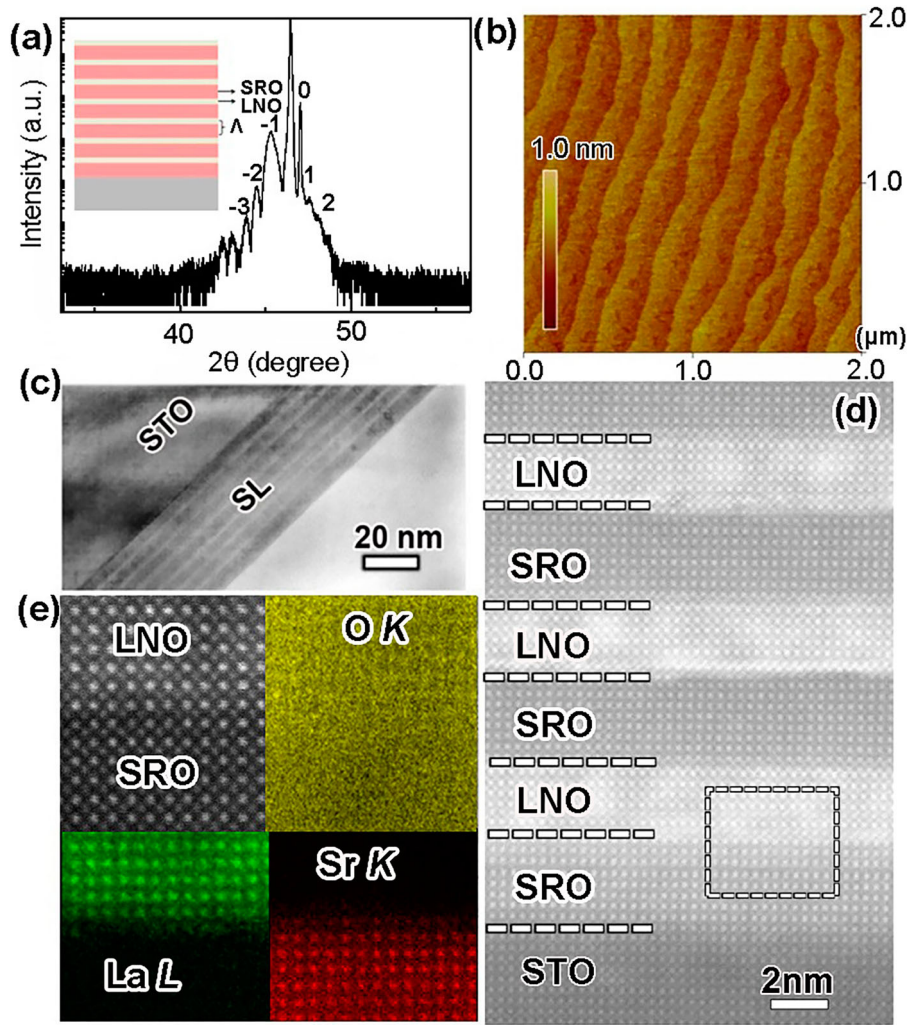


**Figure 1.** (a) XRD patterns of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. The inset shows a schematic of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. (b) AFM image of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. (c) Cross-sectional TEM image of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. (d) STEM image of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. (e) Magnified HAADF-STEM image and STEM-EDS image of a typical SRO/LNO bilayer.

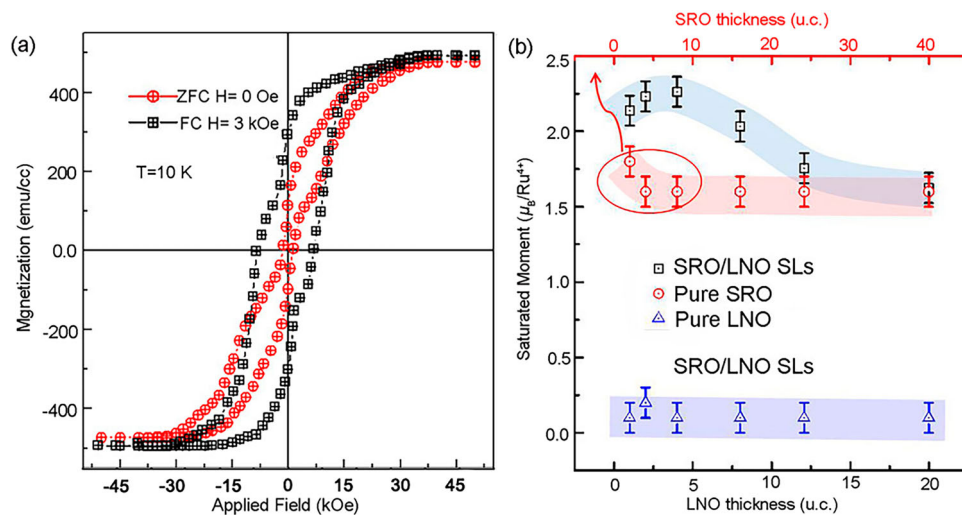


**Figure 2.** (a) Magnetic hysteresis loops of [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL measured at 10 K after ZFC from 300 K (black line) and FC (red line). (b) Saturated moments of [SRO<sub>n</sub>/LNO<sub>5</sub>]<sub>7</sub> SLs ( $n = 1, 2, 4, 8, 12, 20$  u.c.) and single SRO (1, 2, 4, 8, 12, 20 u.c.) and LNO (1, 2, 4, 8, 12, 20 u.c.) reference samples.

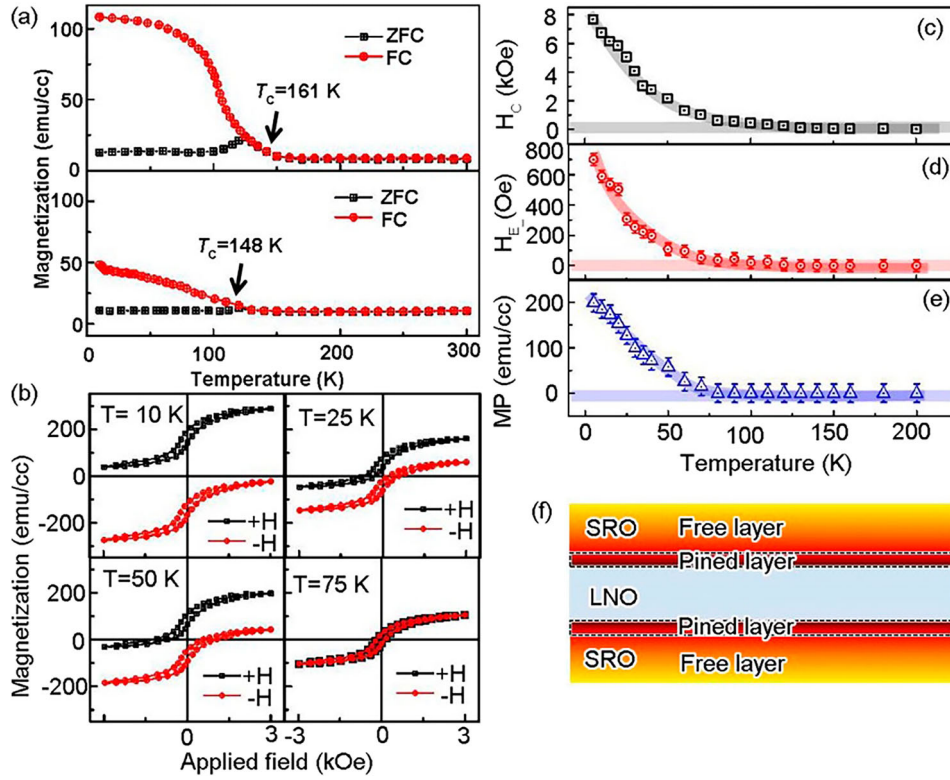


**Figure 3.** (a) Temperature dependence of magnetization measured under a 500 Oe applied field under ZFC and FC conditions for [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL and single layer SRO films. (b) FC minor loops, measured under a magnetic field of  $\pm 3$  kOe, which is smaller than the coercivity of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. (c)–(e)  $H_C$ ,  $H_E$  and  $MP$  of the SRO/LNO SL as functions of temperature, respectively. (f) Schematic of the cross-section of the interface across the SRO/LNO multilayer.

magnetic field of 500 Oe, as shown in Figures 3(a). The Curie temperature ( $T_C$ ) values are 161 and 148 K for the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL and the single-layer SRO film, respectively. The increased  $T_C$  values for [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> can be attributed to correlation effects caused by the strongly hybridized  $p$  and  $d$  orbitals across the interface [21]. A robust exchange interaction has been demonstrated to mediate both the Ru valence states and the orbital occupancy induced by orbital reconstruction [22]. Additionally, the hysteresis loop features a distinctive two-step magnetization reversal. This phenomenon is similar to the results for the SRO/NiO SL [23]. We have shown that a pinned layer exists at the interface (Figures 3(f)) [24]. Here, the small low-field step in Figures 2(a) arises from switching of the free SRO layers and the high-field step can be attributed to the pinned SRO layers at the interface. We also note that the FC minor loop gives coercivity  $H_C \sim 800$  Oe, which is almost the same as that for a single layer SRO film. To enable further understanding of the switching process underlying the hysteresis loop, several FC minor and saturation loops with different temperatures were measured. Figures 3(b) shows the FC minor loops measured under a magnetic field of  $\pm 3$  kOe, which is smaller than the coercivity

of the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL. All the minor loops are symmetrical along the field axis. However, the loops are shifted along the magnetization axis and show different bias moments ( $MP$ s). The absolute  $MP$  value was calculated using the relation  $MP = |M_1 + M_2|/2$  introduced by Padhan et al. [24], where  $M_1$  and  $M_2$  are the magnetization values at which the magnetic field becomes zero. The  $MP$  stems from the pinned SRO layer and the minor loop represents the magnetization of the free SRO added to this value. In addition, the two-step magnetization reversal disappears with increasing measured temperature ( $\sim 75$  K), as shown in Figures 3(b). Figures 3(c–e) present the temperature dependences of  $H_C$ ,  $H_E$  and  $MP$  for the [SRO<sub>8</sub>/LNO<sub>5</sub>]<sub>7</sub> SL after various training runs. We find that the blocking temperature ( $T_B$ ), above which  $H_E$  vanishes, is approximately 75 K, which is much lower than the  $T_C$  of the SRO layer. The fact that  $T_B < T_C$  strongly suggests that the EB observed in SRO/LNO is dependent on the presence of ferromagnetic (FM) ordering at the interfaces.  $H_C$  and  $MP$  also approach zero around the same temperature, indicating that the variations in these properties, which occur because of the pinned moments, are strongly correlated with each other.

The pinned layer thicknesses ( $t_p$ ) were calculated from the experimental saturation magnetization values of Ru and MP using the pinned model reported by Padhan [24]. Interestingly, with increasing LNO (SRO) thickness and fixed SRO (LNO) thickness, the pinned layer thickness initially increased and then remained nearly constant (approximately 2 u.c.). It was noted that the pinned layer thickness decreased rapidly with increasing temperature and vanished at approximately 75 K, as shown in Figures 4(a). Therefore, the pinned layer effect is an interfacial effect and should have an effective length at low temperature. More interestingly, the pinned SRO layer reached a large saturated moment value ( $\sim 4 \mu_B/\text{Ru}^{4+}$ ) when the SRO thickness was 2 u.c., but decreased with increasing SRO thickness (Figures 4(b)). Interfacial effects could represent a plausible explanation for the magnetization enhancement—both Ru valence states and orbital occupancy induced through orbital reconstruction can mediate the Ru spin states.

To enhance our understanding of the electronic structure across the interface, we combined XAS and X-ray linear dichroism (XLD)—extremely sensitive probes of the electronic structure and the orbital occupancy of

distinct  $e_g$  orbitals—to investigate the origin of ferromagnetism at the interface quantitatively [25]. Figures 5(a,b) show that  $e_g$  band splitting ( $\Delta E$ ), which can be estimated using the peak XAS energy shift (between  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$ ), was observed for the SL (but not for the single layer LNO film). Note that the in-plane energy absorption is  $\sim 0.13$  eV higher than the out-of-plane absorption (illustrated schematically in Figures 5(a–b)). Note that the  $\Delta E$  values increase gradually with decreasing temperature (Figure S2) for the SL; however, in contrast, the sign of  $\Delta E$  reverses for the single layer LNO films and it decreases with decreasing temperature, as shown in Figures 5(e). Here, we interpret the differences in energy splitting as arising from bond length changes and Ni–O–Ru hybridization at the SRO/LNO interface. We investigated the orbital properties on the Ni sites further and the orbital polarization was measured via XLD. The area under the XLD curve for the  $L_2$  peaks ( $I_A$ ) represents the difference between the relative occupancies of the  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$  orbitals [26]. Figures 5(c) shows that a negative  $I_A$  exists in the spectra of the single-layer LNO films grown on tensile STO substrates (Figures 4(c)), indicating that  $d_{x^2-y^2}$  orbital occupation is preferred. In contrast, for the SRO/LNO SL, a positive  $I_A$  is observed in the spectra, indicating that  $d_{3z^2-r^2}$  orbital occupation is preferred.

We used density functional theory (DFT) to calculate the density of states (DOS) of the Ni 3d orbitals and Ru spin-up and spin-down states for LNO, SRO, and the SRO/LNO SLs (detailed information is provided in the Supplemental Material). The SRO/LNO SLs showed enhanced  $d_{3z^2-r^2}$  hole density relative to  $d_{x^2-y^2}$ . This orbital polarization  $P$  is defined as:

$$P = \frac{n_{x^2-y^2} - n_{3z^2-r^2}}{n_{x^2-y^2} + n_{3z^2-r^2}}$$

In the SRO films, the  $e_g$  orbitals have higher energies than the  $t_{2g}$  orbitals. The  $t_{2g}$  orbitals are degenerate and the splitting between the up- and down-spin states is large, as illustrated in Figures 5(f). However, in the SRO/LNO SLs, the bandwidth of the  $d_{xy}$  states decreased, while the values of the  $d_{xz}/d_{yz}$  states and the splitting between the up- and down-spin states is smaller than in the SRO film. In particular, supported by DFT calculations, these data indicate the formation of a strong chemical bond between Ru and Ni atoms across the interface. Note that, because of the hybridization of the Ru–O–Ni,  $e_g$  shows enhanced densities below the Fermi level, which contributes to the system's magnetic moment because the occupation of  $e_g$  orbitals is split for the spin-up and spin-down channels.

In this context, we now explore the orbital reconstruction at the SRO/LNO interface and the resulting FM interaction. The  $t_{2g}$ -orbitals of  $\text{Ru}^{4+}$  ions are higher than

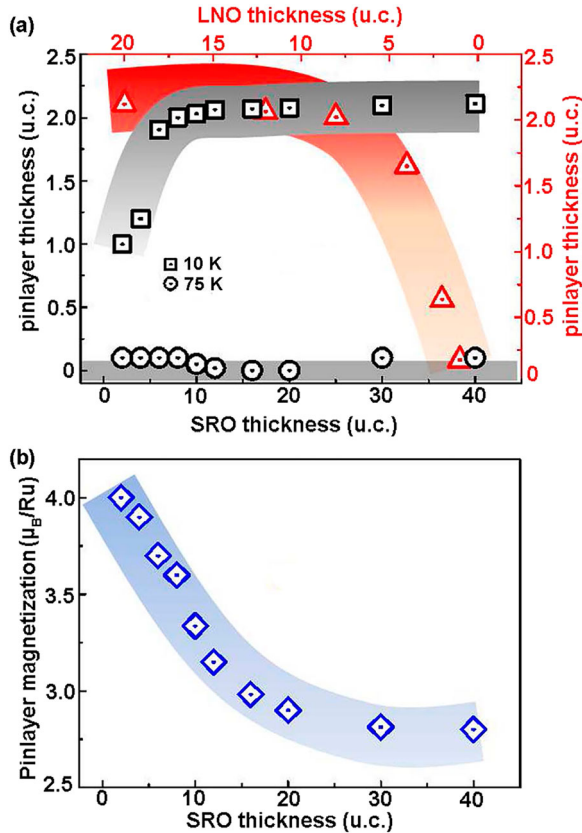


**Figure 4.** (a) Pinned layer thickness as a function of the  $[\text{SRO}_n/\text{LNO}_m]_7$  ( $n = 1, 2, 4, 8, 12, 20$  u.c.;  $m = 1, 2, 5, 8, 12, 20$  u.c.) SL thicknesses. (b) Saturated moment values of the pinned layer for the  $[\text{SRO}_n/\text{LNO}_m]_7$  as a function of SRO thickness.

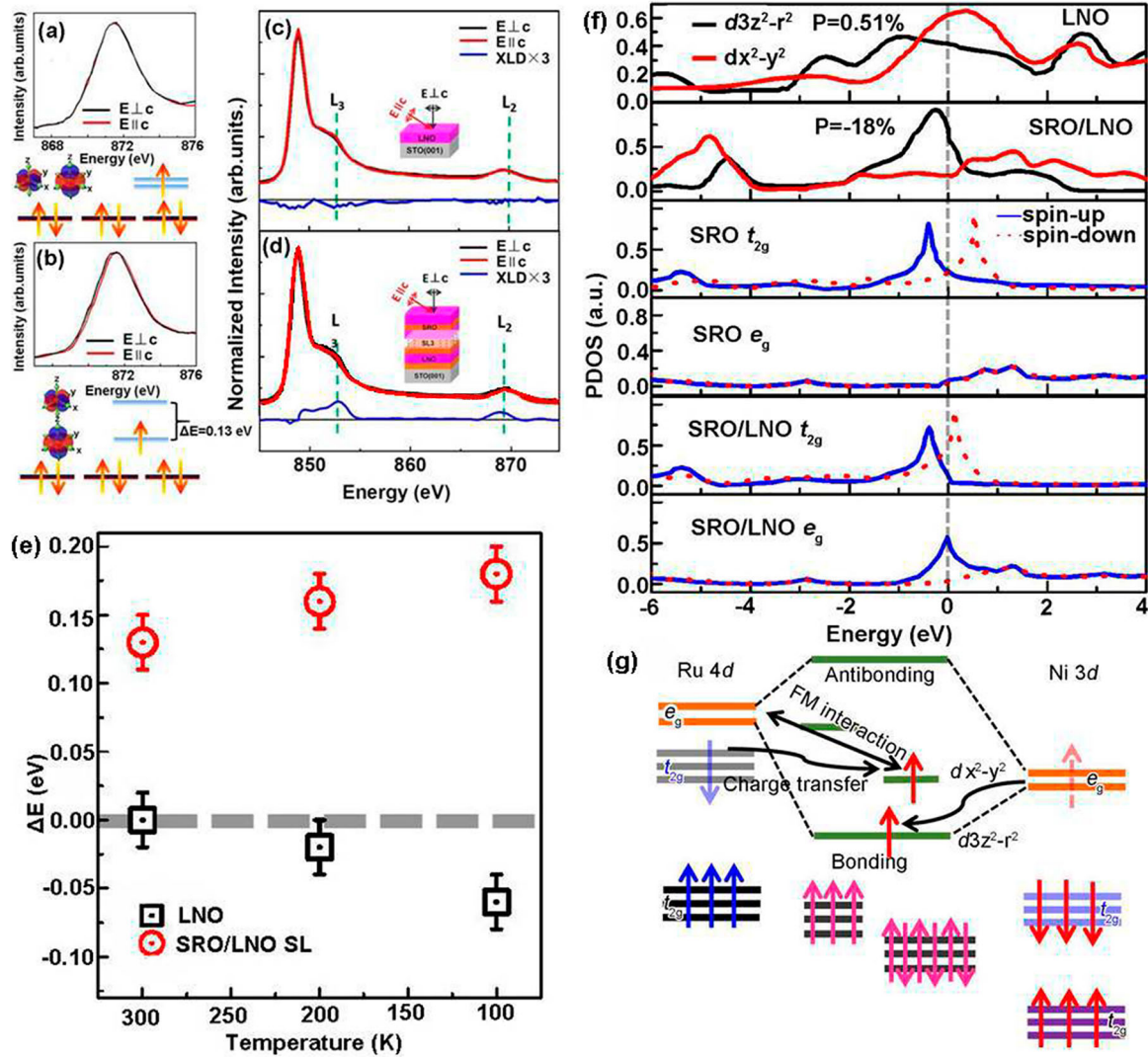


**Figure 5.** (a)–(b) XAS spectra of single layer LNO and  $[\text{SRO}_8/\text{LNO}_5]_7$  at the Ni  $L_2$ -edge showing Ni  $e_g$  band splitting of the  $d_{3z^2-r^2}$  (black line) and  $d_{x^2-y^2}$  (red line) orbitals. (c), (d) XAS spectra of single layer LNO films and  $[\text{SRO}_8/\text{LNO}_5]_7$ , respectively. The normalized differences in the peak are shown for each film. (e) Splitting values of the  $e_g$  orbitals ( $\Delta E$ ) as a function of temperature. (f) DFT calculation of the PDOS of the Ni  $3d$  orbitals and the Ru spin-up (blue straight lines) and spin-down (red dash-dotted lines) states for LNO, SRO and the SRO/LNO SL. (g) Schematic energy diagram showing orbital reconstruction at the SRO/LNO interface.

those of the Ni ions because of the low electronegativity; according to the Allred-Rochow electronegativity scale, the value is approximately 0.2 eV [27]. At  $E_g$  symmetry, strong hybridization between the  $4d$   $e_g$ -orbitals of  $\text{Ru}^{4+}$  and  $3d$   $e_g$ -orbitals of Ni forms bonding (lower energy) and antibonding (higher energy) orbitals consisting of  $e_g$ - $d_{3z^2-r^2}$  orbitals with an admixture of  $p_z$  orbitals, as shown in Figures 5(g). Figures 5(g) shows that the bonding orbital  $e_g$ - $d_{3z^2-r^2}$  is occupied by an electron from the Ni  $e_g$ - $d_{x^2-y^2}$ , as demonstrated by the XLD and DFT results; this occurs because they are sufficiently low in energy when compared with the  $4d$   $t_{2g}$ -orbitals of  $\text{Ru}^{4+}$ . On the one hand, alternating occupation of the  $e_g$  orbitals of Ru and Ni on neighboring lattice sites favors double exchange interaction, as shown in Figures 5(g), which

produces magnetic regions that pin the FM SRO and promotes EB at the SRO/LNO interface. On the other hand, at the interface, electrons transfer from Ru  $t_{2g}$  to the new  $e_g$  orbitals, effectively placing Ru in a high-spin state with an enhanced magnetic moment.

## Conclusion

A peculiar high-spin state for SRO at the interface and large magnetic coupling was observed in SRO/LNO SLs that can be attributed to interfacial orbital reconstruction. XAS and XLD results show preferential occupation of the  $d_{3z^2-r^2}$  orbitals. Furthermore, the origins of the high-spin state SRO and large magnetic coupling are closely related to the orbital reconstruction. Orbital

reconstruction is found to be important in engineering of the interface between transition metal oxides to develop potentially useful electronic and magnetic properties at these interfaces.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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