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Title

Controlling Magnetic Properties of LaMnO₃/SrTiO₃ Heterostructures by Stoichiometry and Electronic Reconstruction: Atomic-Scale Evidence

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Abstract

Interface driven magnetic effects and phenomena associated with spin-orbital coupling and intrinsic symmetry breaking are of importance for fundamental physics and device applications. How interfaces affect the interplay between charge, spin, orbital and lattice degrees of freedom is the key to boost the device performances. In $\text{LaMnO}_3/\text{SrTiO}_3$ (LMO/STO) polar-nonpolar heterostructures, electronic reconstruction leads to an antiferromagnetic to ferromagnetic transition, making them viable for spin filter applications. The interfacial electronic structures play a critical role in understanding the microscopic origins of the observed magnetic phase transition, from antiferromagnetic at 5 unit cells (ucs) of LMO or below to ferromagnetic at 6 ucs or above, yet such a study is missing. Here we offer an atomic scale understanding of LMO/STO ambipolar ferromagnetism by quantifying the interface charge distribution and first principle density functional theory (DFT) calculations across this abrupt magnetic transition. We find that the electronic reconstruction is confined within the first 3 ucs of LMO from the interface, and more importantly, it is robust against oxygen non-stoichiometry. When restoring stoichiometry, we achieve an enhanced ferromagnetic insulating state in LMO films with a thickness as thin as 2 nm (5 uc), making LMO readily applicable as barriers in spin filters.

Introduction

Charges and spins in strongly correlated systems determine the electronic and magnetic structures, further leading to the corresponding electronic and magnetic properties.^[1,2] Charge modulation, achieved through chemical and electrostatic doping, is a common technique to modify the band fillings status. These modified

electronic structures have an influence on the properties, e.g. high critical temperature superconductivity, electronic phase separation and charge ordering.^[2-4] Non-stoichiometry, which commonly exists in materials, results in an unintentional doping, altering their properties.^[5] For example, oxygen-deficient SrTiO_{3-x} becomes conductive,^[6] in contrary stoichiometric SrTiO_3 (STO) is a typical band insulator with a band-gap of 3.2 eV. In manganite-,^[7,8] cobalt-,^[9,10] iron- and nickel-based perovskites,^[11,12] the non-stoichiometry of oxygen not only introduces electron/hole doping but also affects the super-exchange or double-exchange interactions by modification of the metal-oxygen bond length and/or angle.^[13] One example is oxygen-deficient LaCoO_{3-x} which becomes a ferromagnetic (FM) insulator via modification of Co spin states,^[14] while stoichiometric LaCoO_3 is antiferromagnetic (AFM).

The arrangement of charge within a specific lattice structure determines the macroscopic polarity.^[15,16] For example, in ABO_3 perovskite oxides, the alternating stacking of AO^+ and BO_2^- layers makes them polar when both A and B cations are trivalent. Within heterostructures, a polarity mismatch occurs at a polar-nonpolar interface (e.g. a LaAlO_3 (LAO)/STO interface). Such electrostatic discontinuity boundary conditions can drive an electronic/atomic reconstruction.^[15-18] In real material systems, non-stoichiometry can coexist with polarity mismatch,^[19] but how they interact with each other and affect the electronic and magnetic properties are still unclear.^[20-21] Therefore, a quantitative description of the interaction between non-stoichiometry and polar mismatch at the atomic level is essential to achieve better electronic and spintronic devices.^[22,23]

One of the best systems for this study is LaMnO_3 (LMO)/STO heterostructures. LMO is an antiferromagnetic insulator in bulk form,^[24,25] however, with moderate doping, it becomes a ferromagnetic insulator.^[2,7,26] Along the [001] direction, LMO is a polar oxide due to the alternating charged $(\text{LaO})^+$ and $(\text{MnO}_2)^-$ layers while STO is non-polar. The polar discontinuity at the LMO/STO interface induces an electronic reconstruction, which drives the AFM to FM transition *via* electron doping.^[27] In addition, LMO tends to contain excess oxygen δ ($\text{LaMnO}_{3+\delta}$). Since oxygen cannot stay in the interstitial sites, excess oxygen is realized by cation vacancies, in the form of $\text{La}_{1-\varepsilon}\text{Mn}_{1-\varepsilon}\text{O}_3$ (**Fig. S1**), where $\varepsilon=\delta/(3+\delta)$.^[28] The excess oxygen (cation vacancies) leads to partial oxidation of Mn^{3+} to Mn^{4+} and hence ferromagnetism is favored due to double exchange in mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ system *via* hole doping.^[29,30] In the LMO/STO heterostructures, we therefore expect that both origins coexist.

In this paper, we provide an atomic-scale picture of the coexistence of non-stoichiometry and electronic reconstruction at the LMO/STO interface using atomic-resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), further validate the picture with DFT calculations. We show that electronic reconstruction is restricted to only 3 unit cells (ucs) *inside* the LMO from the LMO/ STO interface. We tune the oxygen stoichiometry by a vacuum annealing treatment, and successfully reduce the critical thickness for electronic reconstruction from 6 to 5 uc, which is consistent with the DFT calculations. Furthermore, the ferromagnetic insulating properties of LMO are significantly enhanced at a thickness of only 5 uc (~ 2 nm), making it possible to construct efficient and reliable spin filters.

Results

Figure 1a shows the reflection high energy electron diffraction (RHEED) intensity oscillations obtained during a 5 uc-LMO growing on a STO substrate. It suggests a layer-by-layer growth mode, in consistent with the atomic-terrace topography by atomic force microscopy (AFM) as shown in **Figure 1b**. An atomically sharp LMO/STO interface is observed in a high angle annular dark field (HAADF)-STEM image, **Figure 1c**. Obviously, the LMO film, perfectly epitaxially grown on the STO, shows minimal defects and are fully strained. In addition, atomic-resolution EELS elemental mappings of La, Mn and Ti are summarized in **Figure 1d**. The apparent inter-diffusion is limited to 1 uc, which further confirms the sharp interface across the heterostructure. Additional AFM and high-resolution X-ray diffraction (HRXRD) data confirm the good quality of film on a macroscopic scale (see **Fig. S2**).

Figure 2a shows the thickness-dependent in-plane magnetic moment, normalized by Mn atoms, measured at 10 K by a superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM). The transition from AFM to FM happens in as-deposited LMO/STO heterostructures with thickness from 5 to 6 ucs, in agreement with previous findings.^[27,31] To eliminate the excess oxygen in the LMO, the LMO/STO heterostructures, with the LMO thickness from 4 to 50 uc, were annealed at 1×10^{-6} Torr and 700°C for 2 hours. For simplicity, we named the LMO/STO heterostructures with LMO thickness of t uc before and after vacuum annealing as t uc sample and t uc-v.a. sample, respectively. In these vacuum-annealed samples, the magnetic moment is suppressed at the higher thicknesses but *enhanced* when the LMO thickness is in the region of 4 to 6 uc. Taking the 5 uc sample as an example, the magnetic moment increases from 0.2 to 0.4 μ_B/Mn at 10 K with the help of vacuum annealing, as shown both in the magnetic moment *versus* temperature curve (M-T curve, **Figure 2b**) and the magnetic hysteresis loop (**Figure**

2c). From the M-T curve, the Curie temperature (T_c) remains the same after vacuum annealing. At the LMO thickness of 24 ucs, the magnetic moment decreases from 1.1 to 0.4 μ_B/Mn after vacuum annealing (**Figure 2a**), while T_c also remains the same (~ 100 K in **Figure 2b**). When the LMO thickness increases to 50 ucs, the magnetic moment is suppressed down to ~ 0.22 μ_B/Mn , very close to the canted moment (~ 0.2 μ_B/Mn) of the bulk LMO antiferromagnetic state.^[25] Moreover, when we further extend the vacuum annealing duration to 4 hours, the magnetic moments remain the same as the 2-hour annealing results (**Fig. S3**). It means that a fully stoichiometric LMO state has been recovered *via* vacuum annealing, confirming that excess oxygen exists in the as-deposited films. Therefore, the as-deposited films can be denoted as $\text{LMO}_{3+\delta}$, where δ is estimated to be 0.1 from the magnetic moment changes *via* the vacuum annealing, as the moment and T_c values are comparable with previous studies on magnetic properties of $\text{LMO}_{3.1}$.^[32] Such an oxygen excess state for as-deposited samples is also confirmed by the HRXRD results. Previous studies show that $\text{LMO}_{3+\delta}$ cell volume decreases almost linearly with the value of δ .^[33] When we perform the vacuum annealing experiments, we observe a lattice expansion in out-of-plane lattice, meaning the cell volume increases (**Fig. S2**). The cell volume expansion indicates that the non-stoichiometric δ is reduced after vacuum annealing.

To investigate possible changes in atomic or electronic structure after vacuum annealing, we performed HAADF-STEM and EELS spectrum imaging on the 5, 6 and 24 uc samples, before and after vacuum annealing. We could not identify any structural changes from the HAADF and AFM images (see **Figure S4** and **S5**). The difference lies in the electronic state of Mn due to the vacuum annealing. **Figure 3a**, **c** and **e** present a series of uc-by-uc Mn- $L_{2,3}$ edge spectra across the LMO/STO interfaces with 5, 6 and 24 uc as-deposited films, respectively. For the 5 uc sample,

all Mn L_3 peaks are located at ~ 641.1 eV, indicating the same Mn valence throughout the film. In contrast, the 6 uc sample exhibits a red shift of 0.40 eV in the first 2 ucs from the interface, where the L_3 peaks are at 641.5 eV for the rest of MnO_2 layers. This red shift indicates the Mn valence change from Mn^{3+} to Mn^{2+} due to extra electrons, which are attributed from the electronic reconstruction caused by polar discontinuity. A similar red shift appears in the first 2 ucs next to the interface in the 24 uc sample. Therefore, the electronic reconstruction arises in the as-deposited samples with the LMO thickness of 6 ucs and above. For comparison, **Figure 3b, d** and **f** present the Mn EEL spectra of the vacuum-annealed 5, 6 and 24 uc samples, respectively. In the 5uc vacuum-annealed sample, a red shift of Mn EEL spectra in the first 2 ucs of LMO emerges, compared to the as-deposited sample. When the vacuum-annealed samples with the LMO film thickness of 6 ucs and above, the red shift of Mn EEL spectra remains the same. It proves that the electronic reconstruction starts from 5 uc, instead of 6 uc, after vacuum annealing. The reduced critical thickness of the electronic reconstruction directly correlates the magnetic results. This decrease in the critical thickness proves that vacuum annealing, which results in a change in the oxygen stoichiometry, has a direct influence on the electronic reconstruction. In addition, for samples with the LMO thickness of 6 uc and above, the electronic reconstruction is robust against a degree of non-stoichiometry.

To quantitatively analyze Mn EEL spectra, we extract the L_3 peaks and calculate the L_3/L_2 white-line intensity ratios to identify the Mn electronic configuration uc-by-uc. In a Mn EEL spectrum, L_3 and L_2 peaks correspond to $2p_{3/2} \rightarrow 3d$ and $2p_{1/2} \rightarrow 3d$ transitions, respectively. Therefore, the L_3/L_2 area ratio is sensitive to the number of electrons in the Mn $3d$ orbital, thus offering a useful method to determine the local Mn valence in the LMO films. The L_3/L_2 white-line ratio was calculated from a fitting by a

combination of Gaussian and Lorentzian functions sitting on a step function, after a power-law background subtraction (**Fig. S6**).^[33]

Figure 4a shows the L_3/L_2 ratios and L_3 peak positions for the 5, 6 and 24 uc samples before vacuum annealing. Three dashed lines represent the L_3/L_2 ratios for pure Mn^{2+} , Mn^{3+} and Mn^{4+} states (4.2 for Mn^{2+} , 3.0 for Mn^{3+} and 2.0 for Mn^{4+}), which are obtained from reference 34,^[34] our pulsed laser deposition (PLD) deposited thick LMO film after vacuum annealing and $CaMnO_3$ film as reference samples,^[35] respectively. For the 5 uc sample, the L_3/L_2 ratios for all MnO_2 layers are about 2.9; and all the L_3 peak positions remain at about 641.1 eV, proving negligible transferred electrons. When the LMO thickness increases to 6 ucs, the L_3/L_2 ratios increase to 3.1 in the first 2 ucs near the LMO/STO interface and then drop to 2.9 onwards. Meanwhile, the L_3 peak shifts from 641.0 (1st uc) to 641.3 eV (2nd uc) and saturates at 641.5 eV for the rest ucs. Using a linear approximation of the L_3/L_2 ratio dependence on Mn valence, we calculate the number of excess charges, relative to Mn^{3+} , for all the samples. In **Figure 4c**, there are less than 0.05 e⁻/uc excess charges in the entire 5uc as-deposited LMO film. When it comes to the 6 uc sample, ~ 0.15 e⁻/uc charges are present within the first 2 ucs near the interface which are regarded as the electron doped region. Then, the region from the 3rd uc, in which the L_3/L_2 area ratios are slightly less than 3 (a Mn^{3+}/Mn^{4+} mixed valence state), is hole doped. The excess charges are denoted as negative values (~0.2 hole/uc from the 3rd uc onwards). The same trends in the L_3/L_2 ratios and L_3 peak positions are observed in the 24 uc sample, with excess charges in the electron doped (0.6 and 0.3 e⁻/uc for the 1st and 2nd uc, respectively) and hole doped (~0.22 hole/uc from the 3rd uc onwards) regions. It is noteworthy that the 0.22 hole/uc is consistent with the previous estimated excess oxygen ($\delta = 0.1$), which contributes to the hole doping of

0.2 hole/uc. **Figure 4b** shows the L_3/L_2 ratios and L_3 peak positions of all vacuum-annealed samples. Compared with the samples before vacuum annealing, the electron doping is enhanced in the first 2 ucs near the interfaces (the green region), evidenced by large L_3/L_2 ratios (close to 3.9 for 6 and 24 uc vacuum-annealed samples). Moreover, from the 3rd uc onwards (the yellow region), the L_3/L_2 ratios increase slightly and saturate at about 3.0, which correspond to the pure Mn^{3+} state. Meanwhile, the L_3 peak positions also shift to the lower values, in consistent with the reduction of Mn valence by vacuum annealing. In the excess charge plot (**Fig. 4d**), the electron doping within the first 2 ucs (3 ucs for 24-v.a. sample) is enhanced while the hole doping (the yellow region) is eliminated. In addition, 24 uc and 24-v.a. sample uc-by-uc O K edge EEL spectra (**Fig. S7**) pre-peaks show consistent results of interfacial electron doping and bulk hole doping with the Mn EEL spectra analysis.

Discussion

Intermixing could also have a major effect on the Mn electronic state. Apparently, in the EELS mapping (**Fig. 1d**), the intermixing is limited to 1 uc across the interface which can be written as $(La,Sr)(Ti,Mn)O_3$. However, the Ti valence remains 4+ throughout the STO substrate for the 24 uc sample, even near the interface (**Fig. S8**), in agreement with the previous X-ray absorption spectroscopy and EELS measurements.^[38,39] To preserve charge neutrality, the valence of Mn in the intermixed region should increase from the 3+ to 4+, opposite to our experimental observations. Therefore, the intermixing is possibly due to the broadening of the electron probe as it propagates through the sample. Some lateral spreading can cause an atomically abrupt interface to appear interdiffused.^[40] From the atomic scale valence information of Ti and Mn, we provide a clear understanding of the role of electronic reconstruction on forming a ferromagnetic insulating interface (the

insulating transport behavior shown in **Figure S5**) rather than a conducting interface in LMO-STO heterostructures. This scenario is different from the case of the LAO/STO interface since LMO has a smaller band gap (1.1 eV) than STO (3.2 eV), whereas LAO has a larger band gap (5.6 eV). Therefore, the transferred electrons exist in the conduction band of LMO, instead of STO,^[27] the schematic electron reconstruction is shown in **Fig. S9**.

The magnetic properties of LMO is determined by the Mn spin exchange interactions within the perovskite lattice. In stoichiometric LMO, Mn^{3+} is a Jahn-Teller ion with $t_{2g}^3e_g^1$ occupancy, which creates a ground state of A-type AFM state, where in-plane interaction is ferromagnetic while out-of-plane interaction is AFM. When it is electron doped or hole doped, the filling becomes more isotropic, which increases the ferromagnetic interaction between quarter filled e_g orbitals and reduced anti-ferromagnetic super exchange interaction between half-filled t_{2g} orbitals. **Figure 5a** shows calculated magnetic moment of Mn ion as a function of electron or hole doping concentration while LMO is bi-axially strained (compressive strain ~2 % on STO substrate). When the doping concentration is low (less than 0.1 e/uc or 0.1 hole/uc), it remains in the AFM state. Once the doping surpasses the threshold, the moment increase suddenly as the FM state is energetically favored. The small moment we measured is due to doped FM state and undoped AFM tends to coexist in manganite oxides.^[1] Therefore, the experimental moment values are generally smaller compared to computed values.

In our experimental system, electron-doping comes from electronic reconstruction while hole-doping comes from excess oxygen. The former is an interfacial phenomenon while the latter is present in entire films. Hence, we expect the former to

dominate magnetic properties in the thin (no more than 6 ucs) films while the latter for thick (larger than 6 ucs) films. When the excess oxygen ($\delta=0.1$) is eliminated from the LMO film *via* vacuum annealing, the hole doping changes from 0.2 hole/uc to 0 hole/uc, it induces an FM to AFM transition (gray arrow for all thickness samples). Only a remnant $\sim 0.2 \mu_B/\text{Mn}$ canted moment is observed in the stoichiometric LMO film originated from the Dzyaloshinskii-Moriya interaction,^[29] as shown in the 50 uc-v.a. sample.

Oxygen stoichiometry determines the polar effective charge thus the electronic reconstruction induced FM. Schematics of the LMO and $\text{LMO}_{3+\delta}$ structures are illustrated in **Fig. 5b**. In the LMO films, the alternating charged layers of $(\text{LaO})^+$ and $(\text{MnO}_2)^-$ have +1 and -1 polar charges, respectively. While in the $\text{LMO}_{3+\delta}$ films, the charged sheets are $(\text{LaO}_{1+\delta/3})$ and $(\text{MnO}_{2+2\delta/3})$, with charges of $\{1-[3\delta/(3+\delta)]\}$ and $-\{1-[3\delta/(3+\delta)]\}$, which are smaller than 1, which is the stoichiometric case. When $\delta=0.1$, effect polar charge $Q_{\text{eff}} = \{1-[3\delta/(3+\delta)]\} = 0.903$, while is about 90% of stoichiometric value. Similar to the LAO/STO system,^[36,37] the polar effective charge determines (1) the critical thickness initiating the electronic reconstruction and (2) the number of transferred electrons at the LMO/STO interface. The critical thickness $t_c = E_g(\text{LMO})/E_0$, where $E_g(\text{LMO})$ is the band gap of LMO, ~ 1.1 eV, E_0 is the internal electric field determined by $E_0 = eQ_{\text{eff}}/[2A\epsilon_0\epsilon_r(\text{LMO})]$, where Q_{eff} is the effective polar charge, e is the elemental charge, A is the unit cell area, ϵ_0 and $\epsilon_r(\text{LMO})$ are permittivity of vacuum and LMO film respectively. Hence t_c is inversely proportional to the effective polar charge, $t_c = [2A\epsilon_0\epsilon_r(\text{LMO})]E_g(\text{LMO})/eQ_{\text{eff}}$, assuming the relative permittivity and band gap of LMO change is subtle.. When we do vacuum annealing, Q_{eff} changes from 0.903 to 1, we would expect the critical thickness reduces accordingly from 6 ucs to 5 ucs. It

corresponds to 5 uc-v.a. sample doping concentration increases beyond 0.1 e/uc (orange arrow in **Fig. 5a**) which stabilizes the FM phase. Q_{eff} effect on the number of transferred electrons is also very straightforward, $n(t)=0.5eQ_{\text{eff}}(1-t_c/t) = 0.5eQ_{\text{eff}} - [A_{\text{O}}\varepsilon_r(\text{LMO})E_g(\text{LMO})]/t$, where n is the transferred electrons at LMO thickness t with a critical thickness of t_c . Hence, n (6-v.a.) is enhanced as Q_{eff} changes to 1 from 0.903 compared to the as-deposited samples. Such enhanced e-doping leads to an enhanced magnetic moment as moment increase monotonically as electron-doping as described in brown arrow in **Fig. 5a**. When we consider the vacuum annealing effect on thin (5 and 6 uc) LMO samples, the increased moment is due to the enhanced electronic reconstruction, though the hole-doping induced ferromagnetism is eliminated.

In summary, from the STEM and EELS analysis on the Mn, Ti and O electronic structures, it is conclusively proved that the electronic reconstruction occurs within the first 3 ucs in the LMO film near the interface in the LMO/STO heterostructures. Oxygen non-stoichiometry leads to the suppressed electron transfer in the charge transfer regions and the hole doping in the rest regions of the thin film. The critical thickness of the magnetic transition is reduced to 5 uc once the excess oxygen is removed from the LMO film. The enhanced ferromagnetic insulating properties in the thin LMO films make them suitable for tunnel barriers in spin filter devices.

Experimental Section

Sample fabrication and magnetic properties characterization: The LMO thin films were fabricated by pulsed layer deposition (PLD) with *in situ* RHEED, deposited on TiO₂-terminated 5 (L)×5 (W)×0.5 (H) mm³ STO (001) substrates from a sintered LMO target. The growth temperature and oxygen pressure were 750 °C and 10 mTorr,

respectively, adopted from previous studies.^[28] The laser fluence energy density was kept at 1.8 J/cm². After deposition, all samples were cooled down to room temperature with a cooling rate of 10 °C/min. The oxygen pressure was unchanged during the whole process. One group of the LMO/STO heterostructures was directly used to measure the magnetic properties by a SQUID -VSM system (Quantum Design). The other group was firstly annealed under a vacuum condition, in which the pressure was less than 1×10⁻⁶ Torr, at 700°C for 2 hours. Then the magnetic characterization was carried using same parameters the as-prepared samples. The magnetic moments of all samples were measured from room temperature to 10K with in-plane configuration.

STEM imaging and EELS analysis: The cross-section TEM samples were prepared by a FIB (focused ion beam) system (FEI Versa 3D) with 30 kV Ga ions, followed by a low-voltage (*i.e.* 2 kV) cleaning step. HAADF-STEM imaging was performed by a JEM-ARM200F (JEOL) microscope equipped with an ASCOR aberration corrector, a cold-field emission gun and a Gatan Quantum ER spectrometer, operated at 200 kV. The HAADF-STEM images were acquired using the respective collection inner and outer angles of 68 and 280 mrad, respectively with a beam convergent angle of 30 mrad. The EELS results were recorded using a collection angle of 100 mrad with the energy dispersion of 0.25 and 0.1 eV/channel for the elemental mapping and energy loss near edge structure (ELNES), respectively.

Computational Methods: Theoretical modelling of the orthorhombic *Pbnm* LMO was performed using density functional theory, the projected augmented wave method, and PBEsol pseudopotentials,^[ref] as implemented in the Vienna *ab initio* simulation package.^[ref] Correlation effects beyond generalized gradient approximation (GGA) were treated at a semi-empirical GGA+U level within a rotationally invariant

formalism with $U = 5$ eV on Mn 3d-orbitals.^[ref] We used 340 eV kinetic energy cutoff and 7x7x5 k -points for Brillouin zone integration. Calculations were performed using a $\sqrt{2} \times \sqrt{2} \times 2$ pseudocubic unit cell, which contains 20 atoms. To simulate epitaxial growth of LMO on STO (001) substrate, the in-plane pseudocubic lattice constant was constrained to the theoretical lattice constant of STO, which was found to be $a = b = 3.90$ Å. The out-of-plane lattice constant c and all internal atomic coordinates were fully relaxed for each doping level and magnetic configuration, using the force convergence limit of 1 meV/atom. The constraint of the in-plane lattice constant led to LMO being biaxially compressed by about 2%, resulting in $b/a = 1$ and $c/a = 1.41$, as compared to the bulk values of $b/a = 1.03$ and $c/a = 1.39$. The bipolar doping of LMO was performed by adding electrons/holes to the system and neutralizing the total charge by jellium background.

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References

- [1] M. S. Senn, J. P. Wright, J. P. Attfield, *Nat.* **2011**, *481*, 173.
- [2] M. B. Salamon, M. Jaime, *Rev. Mod. Phys.* **2001**, *73*, 583.
- [3] P. A. Lee, N. Nagaosa, X.-G. Wen, *Rev. Mod. Phys.* **2006**, *78*, 17.
- [4] K. Ueno, S. Nakamura, H. Shimotani, H. T. Yuan, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, M. Kawasaki, *Nat. Nanotechnol.* **2011**, *6*, 408.
- [5] J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, S. S. P. Parkin, *Sci.* **2013**, *339*, 1402.

- [6] J. F. Schooley, W. R. Hosler, M. L. Cohen, *Phys. Rev. Lett.* **1964**, 12, 474.
- [7] M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez, J. M. Triscone, *Nat. Mater.* **2012**, 11, 195.
- [8] M. Gibert, M. Viret, A. Torres-Pardo, C. Piamonteze, P. Zubko, N. Jaouen, J. M. Tonnerre, A. Mougin, J. Fowlie, S. Catalano, A. Gloter, O. Stéphan, J. M. Triscone, *Nano Lett.* **2015**, 15, 7355.
- [9] N. Lu, P. Zhang, Q. Zhang, R. Qiao, Q. He, H.-B. Li, Y. Wang, J. Guo, D. Zhang, Z. Duan, Z. Li, M. Wang, S. Yang, M. Yan, E. Arenholz, S. Zhou, W. Yang, L. Gu, C. W. Nan, J. Wu, Y. Tokura, P. Yu, *Nat.* **2017**, 546, 124.
- [10] Q. Zhang, X. He, J. Shi, N. Lu, H. Li, Q. Yu, Z. Zhang, L. Q. Chen, B. Morris, Q. Xu, P. Yu, L. Gu, K. Jin, C. W. Nan, *Nat. Comm.* **2017**, 8, 104.
- [11] R. J. Sichel-Tissot, R. C. Devlin, P. J. Ryan, J. W. Kim, S. J. May, *Appl. Phys. Lett.* **2013**, 103, 212905.
- [12] J. Shi, S. D. Ha, Y. Zhou, F. Schoofs, S. Ramanathan, *Nat. Comm.* **2013**, 4, 2676.
- [13] M. Huijben, L. W. Martin, Y. H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, R. Ramesh, *Phys. Rev. B* **2008**, 78, 094413.
- [14] N. Biškup, J. Salafranca, V. Mehta, M. P. Oxley, Y. Suzuki, S. J. Pennycook, S. T. Pantelides, M. Varela, *Phys. Rev. Lett.* **2014**, 112, 087202.
- [15] W. A. Harrison, E. A. Kraut, J. R. Waldrop, R. W. Grant, *Phys. Rev. B* **1978**, 18, 4402.
- [16] H. Kroemer, *J. Cryst. Growth* **1987**, 81, 193.
- [17] A. Ohtomo, H. Y. Hwang, *Nat.* **2004**, 427, 423.
- [18] C. F. Chang, Z. Hu, S. Klein, X. H. Liu, R. Sutarto, A. Tanaka, J. C. Cezar, N. B. Brookes, H. J. Lin, H. H. Hsieh, C. T. Chen, A. D. Rata, L. H. Tjeng, *Phys. Rev. X* **2016**, 6, 041011.

- [19] A. Kalabukhov, R. Gunnarsson, J. Börjesson, E. Olsson, T. Claeson, D. Winkler, *Phys. Rev. B* **2007**, *75*, 121404.
- [20] I. C. Tung, G. Luo, J. H. Lee, S. H. Chang, J. Moyer, H. Hong, M. J. Bedzyk, H. Zhou, D. Morgan, D. D. Fong, J. W. Freeland, *Phys. Rev. Mater.* **2017**, *1*, 053404.
- [21] Z. Q. Liu, C. J. Li, W. M. Lü, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, Ariando, *Phys. Rev. X* **2013**, *3*, 021010.
- [22] Y. M. Kim, A. Morozovska, E. Eliseev, M. P. Oxley, R. Mishra, S. M. Selbach, T. Grande, S. T. Pantelides, S. V. Kalinin, A. Y. Borisevich, *Nat. Mater.* **2014**, *13*, 1019.
- [23] F. Y. Bruno, M. N. Grisolia, C. Visani, S. Valencia, M. Varela, R. Abrudan, J. Tornos, A. Rivera-Calzada, A. A. Ünal, S. J. Pennycook, Z. Sefrioui, C. Leon, J. E. Villegas, J. Santamaria, A. Barthélémy, M. Bibes, *Nat. Comm.* **2015**, *6*, 6306.
- [24] J. Rodríguez-Carvajal, M. Hennion, F. Moussa, A. H. Moudden, L. Pinsard, A. Revcolevschi, *Phys. Rev. B* **1998**, *57*, R3189.
- [25] G. Matsumoto, *J. Phys. Soc. Jpn.* **1970**, *29*, 606.
- [26] L. M. Zheng, X. R. Wang, W. M. Lü, C. J. Li, T. R. Paudel, Z. Q. Liu, Z. Huang, S. W. Zeng, K. Han, Z. H. Chen, X. P. Qiu, M. S. Li, S. Yang, B. Yang, M. F. Chisholm, L. W. Martin, S. J. Pennycook, E. Y. Tsymbal, J. M. D. Coey, W. W. Cao, *Nat. Comm.* **2018**, *9*, 1897.
- [27] X. R. Wang, C. J. Li, W. M. Lü, T. R. Paudel, D. P. Leusink, M. Hoek, N. Poccia, A. Vailionis, T. Venkatesan, J. M. D. Coey, E. Y. Tsymbal, Ariando, H. Hilgenkamp, *Sci.* **2015**, *349*, 716.
- [28] K. Nakamura, K. Ogawa, *J. Solid State Chem.* **2002**, *163*, 65.
- [29] J. Töpfer, J. B. Goodenough, *J. Solid State Chem.* **1997**, *130*, 117.
- [30] Z. Marton, S. S. A. Seo, T. Egami, H. N. Lee, *J. Crys. Growth* **2010**, *312*, 2923.

- [31] Y. Anahory, L. Embon, C. J. Li, S. Banerjee, A. Meltzer, H. R. Naren, A. Yakovenko, J. Cuppens, Y. Myasoedov, M. L. Rappaport, M. E. Huber, K. Michaeli, T. Venkatesan, Ariando, E. Zeldov, *Nat. Comm.* **2016**, 7, 12566.
- [32] J. A. Alonso, M. J. Martínez-Lope, M. T. Casáis, A. Muñoz, *Solid State Comm.* **1997**, 102, 7.
- [33] H. Lidbaum, J. Rusz, S. Rubino, A. Liebig, B. Hjörvarsson, P. M. Oppeneer, O. Eriksson, K. Leifer, *Ultramicroscopy* **2010**, 110, 1380.
- [34] Z. L. Wang, J. S. Yin, Y. D. Jiang, J. Zhang, *Applied Physics Letters* **1997**, 70, 3362.
- [35] M. Varela, M. P. Oxley, W. Luo, J. Tao, M. Watanabe, A. R. Lupini, S. T. Pantelides, S. J. Pennycook, *Phys. Rev. B* **2009**, 79, 085117.
- [36] W. J. Son, E. Cho, B. Lee, J. Lee, S. Han, *Phys. Rev. B* **2009**, 79, 245411.
- [37] M. L. Reinle-Schmitt, C. Cancellieri, D. Li, D. Fontaine, M. Medarde, E. Pomjakushina, C. W. Schneider, S. Gariglio, P. Ghosez, J. M. Triscone, P. R. Willmott, *Nat. Comm.* **2012**, 3, 932.
- [38] Z. Chen, Z. Chen, Z. Q. Liu, M. E. Holtz, C. J. Li, X. R. Wang, W. M. Lü, M. Motapothula, L. S. Fan, J. A. Turcaud, L. R. Dedon, C. Frederick, R. J. Xu, R. Gao, A. T. N'Diaye, E. Arenholz, J. A. Mundy, T. Venkatesan, D. A. Muller, L. W. Wang, J. Liu, L. W. Martin, *Phys. Rev. Lett.* **2017**, 119, 156801.
- [39] J. A. Mundy, Y. Hikita, T. Hidaka, T. Yajima, T. Higuchi, H. Y. Hwang, D. A. Muller, L. F. Kourkoutis, *Nat. Comm.* **2014**, 5, 3464.
- [40] R. F. Egerton, *Ultramicroscopy* **2007**, 107, 575.

Figure 1. Fabrication and structural characterization of the LMO/STO heterostructures. a) A RHEED intensity oscillation curve and b) an AFM topography image of a 5 uc LMO film grown on a STO substrate. c) Corresponding cross-sectional HAADF-STEM images and d) Simultaneous acquired HAADF and EELS elemental mappings (Ti, Mn, La and RGB mix) from the green box in Fig. 1c. (e) The line intensity profile for Ti, Mn and La across LMO/STO interface, the dashed line indicate the position of interface. The scale bars in the AFM and HAADF images are 1 μm and 2 nm, respectively.

Figure 2. Magnetic properties of the LMO/STO heterostructures with different LMO thicknesses before and after vacuum annealing. a) Normalized in-plane magnetic moment (measured at 10 K) as a function of the LMO film thickness for the samples before and after vacuum annealing. Multiple data points are presented for 4, 5 and 6 uc samples to near the magnetic phase transition region. The gray shaded area denotes the moment below the threshold of $0.2 \mu_B/\text{Mn}$, which is the canted moment of stoichiometric LMO. b) Temperature dependent magnetic moment of 5 and 24 uc as-deposited (solid lines) and vacuum annealed (dashed lines) samples, respectively. The cooling field is 1 T and measurement field is 0.1 T. c) and d) Magnetic hysteresis loops (measured at 10 K) of 5 and 24 as-deposited and vacuum annealed samples, respectively.

Figure 3. Electronic doping at the LMO/STO interface revealed by STEM-EELS. uc-by-uc Mn- $L_{2,3}$ EEL spectra across the LMO/STO interfaces of 5, 6 and 24 uc samples a), c) and e) before and b), d) and f) after vacuum annealing. Dashed lines are guides to the bulk Mn L_3 peak position.

Figure 4. Quantification analysis of electron and hole doping in the LMO/STO heterostructures. a) and b) uc-by-uc Mn L_3/L_2 area ratios and L_3 peak positions of 5, 6 and 24 uc samples before and after vacuum annealing, respectively. Three dashed lines represent the reference Mn L_3/L_2 area ratios for Mn^{2+} , Mn^{3+} and Mn^{4+} . c) and d) Calculated excess electrons from Mn L_3/L_2 area ratios of 5, 6 and 24 uc samples before and after vacuum annealing, respectively. Green and yellow shaded areas indicate the electron and hole doped regions of the LMO film, respectively.

Figure 5. Stoichiometry and electronic reconstructions as origins of ferromagnetism in LMO/STO heterostructures. (a) Calculated magnetic moments as a function of electron doping in biaxial strained LMO, where it shows an e-doped FM region and a *h*-doped region when the doping concentration is above 0.1 e/uc. Gray arrow represents vacuum annealing reduces hole doping for all thickness films. Orange and brown color arrow represents the change in e-doping for 5 and 6 uc samples. (b) Schematic represents the atomic stacking order of as-deposited and vacuum annealed LMO. Due to the presence of excess oxygen, δ , or equivalent cation vacancies, the formal charge reduces from ± 1 to $\pm 1 - [3\delta/(3+\delta)]$, leading to a smaller driving force for the electronic reconstruction.