



Magnetism, conductivity, and orbital order in $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$ superlattices

Shuai Dong,^{1,2,3} Rong Yu,^{1,2} Seiji Yunoki,^{4,5} Gonzalo Alvarez,⁶ J.-M. Liu,³ and Elbio Dagotto^{1,2}

¹Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA

²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 32831, USA

³Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

⁴Computational Condensed Matter Physics Laboratory, RIKEN, Wako, Saitama 351-0198, Japan

⁵CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

⁶Computer Science and Mathematics Division and Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

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The modulation of charge density and spin order in $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$ ($n=1-4$) superlattices is studied via Monte Carlo simulations of the double-exchange model. G -type antiferromagnetic barriers in the SrMnO_3 regions with low charge density are found to separate ferromagnetic LaMnO_3 layers with high charge density. A metal-insulator transition with increasing n is observed in the direction perpendicular to the interfaces. Our simulations provide insight into how disorder-induced localization may cause the metal-insulator transition occurring at $n=3$ in experiments.

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Transition-metal oxide heterostructures provide a new avenue to utilize the complex properties of strongly correlated electronic materials to produce multifunctional devices. Several exotic phenomena emerge in these heterostructures due to the reconstruction at the interfaces, such as the existence of a conducting state between two insulators in $\text{LaAlO}_3/\text{SrTiO}_3$ (STO) and $\text{LaTiO}_3/\text{SrTiO}_3$.¹ As one of the most representative families of strongly correlated oxide materials, the manganites can also be prepared into heterostructures with other oxides, such as cuprates, and they exhibit interesting behavior, such as orbital reconstruction.²

Even without involving other oxides, manganite heterostructures can be prepared utilizing manganites with different doping, e.g., LaMnO_3 (LMO) and SrMnO_3 (SMO).³⁻⁸ At low temperature (T), bulk LaMnO_3 is an A -type antiferromagnetic (A -AFM) insulator, while SrMnO_3 is a G -type antiferromagnetic (G -AFM) insulator.⁹ The alloy-mixed $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) is a ferromagnetic (FM) metal at low T and $0.17 < x < 0.5$. However, the LMO-SMO superlattices can behave differently from bulk LSMO even with the same average charge density: (i) the ordered A -site cations in the superlattices remove the A -site disorder, which is important in alloy manganites and (ii) the artificially modulated A -site cations also modulate the physical properties, such as charge density, magnetism, and conductivity. In fact, recent experiments on $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices highlighted the existence of an exotic metal-insulator transition (MIT) at $n=3$.⁵⁻⁸ Moreover, LMO thin films on a STO substrate were found to be FM instead of A -AFM.^{7,8}

Theoretically, in addition to *ab initio* calculations,¹⁰ most previous model Hamiltonian investigations on manganite heterostructures were based on the one-orbital model,¹¹ missing the important orbital degree of freedom. Although more realistic two-orbital models were used very recently,^{12,13} several properties of the $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices are still not understood particularly the explanation for the $n=3$ MIT.

The two-orbital double-exchange (DE) model is used here to study $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices via Monte Carlo

(MC) simulations. This model Hamiltonian has been extensively studied before and it is successful to reproduce the several complex phases in manganites.¹⁴ Details about the Hamiltonian and MC technique can be found in previous publications.¹⁵ Schematically, the Hamiltonian reads as

$$H = H_{\text{DE}}(t_0) + H_{\text{SE}}(J_{\text{AF}}) + H_{\text{EP}}(\lambda) + \sum_i (\epsilon_i - \mu)n_i, \quad (1)$$

where H_{DE} , H_{SE} , and H_{EP} are the standard two-orbital large-Hund-coupling DE, superexchange (SE), and electron-phonon (EP) interactions, respectively.¹⁴ n_i is the e_g charge density at site i . μ is the uniform chemical potential, and ϵ_i is the on-site effective potential generated by long-range Coulomb interactions that cannot be neglected in superlattices involving different electronic compositions. There are four main input parameters: the SE coupling J_{AF} , the EP coupling λ , μ , and ϵ_i . All these parameters are in units of t_0 , which is the DE hopping between nearest-neighbor (NN) $d_{3z^2-r^2}$ orbitals along the z direction.^{14,15} The constant-density phase diagram is determined by J_{AF} and λ . The expected e_g charge density is obtained by tuning μ . Due to the valence difference between La^{3+} and Sr^{2+} , the on-site Coulomb potential ϵ_i is inhomogeneous for the Mn sites. In almost all previous model investigations, the Coulomb interaction is treated using the Hartree-Fock (HF) approximation.¹¹⁻¹³ However, this HF approximation is rather difficult to converge for the three-dimensional (3D) two-orbital model when both t_{2g} classical spins and lattice distortions are also MC-time evolving. For this reason, here we adopt another strategy. Each ϵ_i will be determined by its eight NN A -site cation neighbors.¹⁶ More specifically, in the LMO-SMO superlattices, ϵ_i is 0 for those Mn between two LaO planes (LMO region), it becomes $V/2$ for those between LaO and SrO planes, and finally it is V for those between two SrO planes (SMO region) [Figs. 1(a) and 1(b)]. Therefore, this (positive) constant V is the only parameter to regulate the Coulomb potential and it is related with the dielectric constant in the

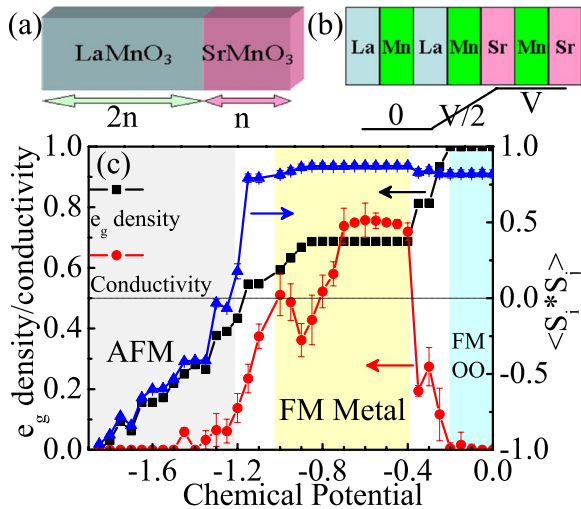


FIG. 1. (Color online) (a) Superlattice unit studied here. (b) On-site potential used in our simulation. (c) The e_g charge density, NN spin correlation, and conductivity (see Ref. 17 for its units) of a $4 \times 4 \times 4$ lattice vs μ at $T=0.01$. All ϵ_i are set to zero to simulate bulk clean-limit LSMO.

HF approach. Our approximation is expected to capture the main physics in the LMO-SMO superlattices since the effective Coulomb potential is mainly caused by the modulation of A-site cations, and we believe that our qualitatively simple results shown below do not depend on these assumptions. The Coulomb screening by the e_g electron redistribution is also taken into account in part by regulating the value of V . In our simulation, four sets of V : 0.3, 0.6, 0.9, and 1.2 are used, covering the realistic potential drop range between LMO and SMO. The important practical fact is that this approximation enables the MC simulation on large enough lattices.

For our studies, we use 3D ($L_x \times L_y \times L_z$) clusters with periodic boundary conditions (PBCs). Both L_x and L_y are set to 4, while L_z equals $3n$ ($1 \leq n \leq 4$). Thus, the superlattices are grown along the z direction ([001]) [Figs. 1(a) and 1(b)]. The MC simulation on the $4 \times 4 \times 12$ lattice is already at the cutting edge of current computational resources. To characterize physical properties, the charge density, spin structure factors, and conductivity are calculated.^{15,17}

Before the simulation of superlattices, it is essential to understand why the LMO thin films on STO are experimentally found to be ferromagnetic, instead of A-AFM. For most RMnO_3 ($R=\text{La, Pr, Nd, Sm, and Eu}$), the A-AFM phase is the ground state.¹⁸ However, in the previously obtained theoretical phase diagram for the two-orbital DE model, the A-AFM regime was found to be rather narrow in parameter space, while the FM orbital-ordered (OO) phase was clearly more robust.¹⁹ Thus, to understand the FM nature of LMO thin films, we should consider lattice distortions in real manganites. In the bulk, the LMO lattice transits from a cubic perovskite to an orthorhombic one at $T \sim 800$ K, below which the lattice constant along the c axis shortens compared with those along the a and b axes.²⁰ For instance, at $T = 300$ K, l_c is only $\sim 0.964l_{ab}$, where l_c (l_{ab}) is the NN Mn-Mn distance along the c axis (within the a - b plane).

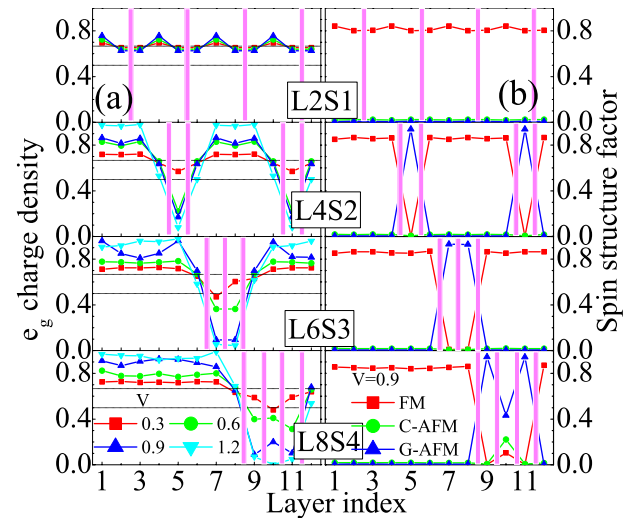


FIG. 2. (Color online) (a) Charge modulation in the superlattices with different V 's (the case of L2S1 with $V=1.2$ cannot be obtained due to phase separation). The two horizontal lines denote 0.5 and $2/3$. (b) In-plane spin structure factor for $V=0.9$. In (a) and (b), pink bars denote SrO layers in the $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattice, while LaO layers are not highlighted. The lattices are simply repeated along the z direction if their periods are shorter than 12.

Using an empirical formula by Zhou and Goodenough,²¹ the AFM exchange intensity along c becomes about 1.3 times that on the a - b plane. Thus, this stronger AFM coupling along c will favor the A-AFM state. However, for LMO thin films on STO, the LMO lattice is compressed in the a - b plane but it is elongated along the c axis, leading to an almost cubic crystal structure.⁴ Therefore, the theoretical phase diagram,¹⁹ derived assuming lattice isotropy, should be applicable to the LMO thin films that prefer the FM OO phase instead of the A-AFM one.

Following the theoretical phase diagram,¹⁹ here we choose a particular set of parameters ($J_{\text{AF}}=0.09$, $\lambda=1.2$) for the simulation below. To justify this choice, first we perform a MC calculation on a $4 \times 4 \times 4$ lattice (PBCs) with all $\epsilon_i = 0$ to examine whether the above parameters are suitable for LSMO. The e_g charge density n_i , NN spin correlation ($\langle S_i \cdot S_j \rangle$), and conductivity are calculated at low T ($T=0.01$) (~ 60 K if $t_0 \sim 0.5$ eV), as shown in Fig. 1(c). For $n_i \sim 1$, the phase is found to be FM but insulating, in agreement with the results found for experimental LMO thin films. The energy gap at the Fermi level is 0.3 (~ 150 meV), which is compatible with the experimental excitation energy (≈ 125 meV).⁷ The insulating character of the state is caused by orbital ordering driven by Jahn-Teller distortions.²² In the density range $0.5 < n_i < 0.8$, the system is FM and conducting, also in agreement with the LSMO properties at the corresponding dopings. For $n_i < 0.5$, the NN spin correlations turn out to be negative, suggesting an AFM phase. The conductivity becomes poor with decreasing n_i until it reaches an insulating state. This $n_i < 0.5$ behavior is also compatible with LSMO at the corresponding doping. Then, as a conclusion, the set $J_{\text{AF}}=0.09$ and $\lambda=1.2$ should be a proper parameter set to describe (cubic) LSMO. Below, we will use this set to study the $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices.

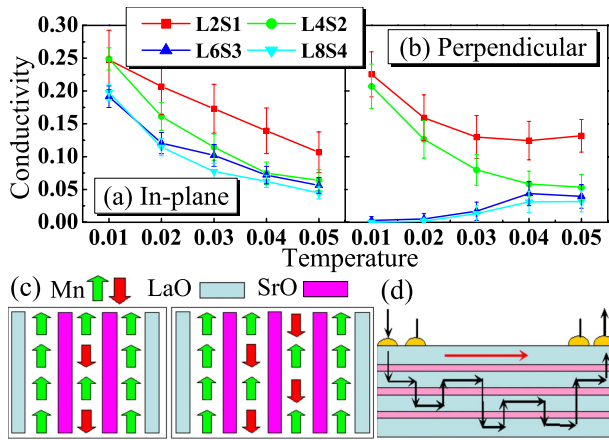


FIG. 3. (Color online) (a) In-plane conductivity for the superlattices studied here. (b) Perpendicular conductivity. (c) Sketch of the spin order at interfaces for L4S2 (left) and L6S3 (right). (d) Sketch of experimental setup for resistance measurements. Pink bars are SMO regions. Typical conducting paths via the DE process (black curves) connect NN interfaces, but they will be broken when $n \geq 3$.

We will focus first on the low- T ($=0.01$) MC results which can shed light on the ground-state properties. The local e_g charge densities of each layer vs layer index are shown in Fig. 2(a). For $(\text{LMO})_2/(\text{SMO})_1$ (L2S1), the charge distribution is fairly uniform despite the use of substantial values for V (0.3–0.9); namely, the local charge density fluctuates weakly around the average of $2/3$. This is easy to understand since there is no SMO region in the L2S1 superlattice and, thus, the potential fall here is only $V/2$. For other superlattices, and usually ($V > 0.3$), the densities in the SMO regions are lower than 0.5. The $V=1.2$ case already restricts most of the e_g electrons to be in the LMO regions, while $V=0.3$ is low enough that it spreads e_g electrons to the SMO regions. Therefore, it is reasonable to conclude that the potential amplitude range used in our model is the proper one to cover the potential drop in real manganites. In the following, we will focus on the case $V=0.9$, for which the results are similar to the experimental data.

Figure 2(b) shows the x - y plane spin structure factors vs layer index for $V=0.9$ and $T=0.01$. There are only two main components: FM and G -AFM. The latter exists only in the SMO regions, while FM dominates in the LMO regions, and at the LMO/SMO interfaces. This spin arrangement agrees with experiments.^{6,7} Our calculated spin order supports the idea that the local phases in superlattices are mainly determined by the local densities n_{local} .¹³ If $n_{\text{local}} > 0.5$, the spin order is FM, and it is G -AFM when $n_{\text{local}} \approx 0$. Therefore, other spin orders, e.g., A -AFM or C -AFM, may emerge once the n_{local} is slightly lower than 0.5. In fact, we observed the coexistence of several complex spin orders at, e.g., the SMO region ($n_{\text{local}} \approx 0.15$) for L8S4 with $V=0.9$ [Fig. 2(b)].

One of the most important experimental discoveries in the $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices is the MIT with increasing n . To try to understand this phenomenon, here two conductivities (only from the DE process) are calculated vs T : the in-plane one (along the x or y direction) and the perpendicular one (along the z direction), as shown in Figs. 3(a) and 3(b).

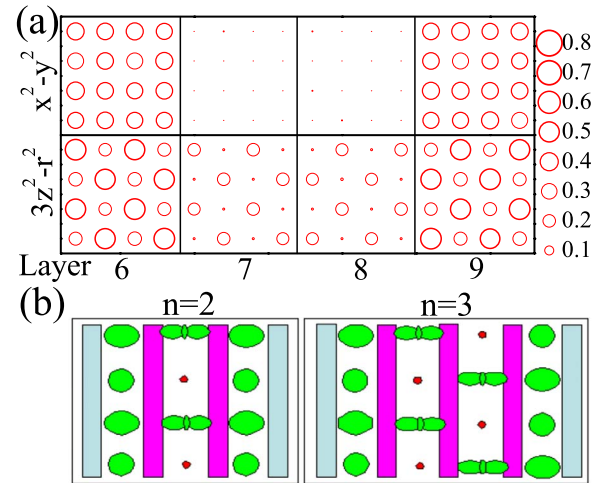


FIG. 4. (Color online) (a) Orbital occupation of the sixth to ninth layers for L6S3 when $V=0.9$ and $T=0.01$. The sixth and ninth are interface layers between the LaO and SrO layers, while the seventh and eighth are within the SMO region. Here the circle's area is proportional to the local e_g charge density. (b) Sketch of orbital ordering at the interface for $n=2$ and 3.

All in-plane conductivities are robust and increase with decreasing T , suggesting metallicity. Our result agrees with previous studies showing that the charge transfer at interfaces between Mott and band insulators can generate conducting interfaces.^{1,11} In contrast, the perpendicular conductivities show metallic behavior when $n \leq 2$, but insulating behavior when $n \geq 3$. To understand this MIT, the spin arrangement at the FM/ G -AFM interface should be considered. The intralayer NN spin correlations (not shown here) confirm that spins at the FM/ G -AFM interfaces are almost collinear at low T , namely, the NN spins are parallel or antiparallel, as shown in Fig. 3(c). Therefore, when there is only one G -AFM layer in each superlattice unit ($n=2$), the spin-up channels of the G -AFM layer link the NN FM layers, allowing for a good conductance. However, once the SrO layers thickness is 3, the two G -AFM layers cut off the same-spin channels, giving rise to an insulating behavior along the z direction. Therefore, it is natural to expect that $n=3$ must be the MIT critical point in $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices.

However, it should be noted that the experimental resistance measurements were performed using the four-point method [Fig. 3(d)].^{6,7} Thus, to understand the experimental MIT, Anderson localization effects should also be considered. When $n \geq 3$, as mentioned before, the DE conducting process becomes exclusively two-dimensional-like (within the x - y plane). In this case, insulating behavior may be induced by interface disorder, such as roughness, and Anderson localization, as discussed in the experimental literature.⁷ But a 3D metallicity in the $n \leq 2$ superlattices, avoiding the Anderson localization mechanism, can be achieved by the DE process perpendicular to the interfaces, as shown schematically in Fig. 3(d). In short, although the in-plane conductivity is metallic in our small lattices without disorder, the critical n for the real superlattices MIT may still correspond to the same value found in our simulations via studies of the perpendicular conductivity.

The spin configuration in Fig. 3(c) can also induce orbital order near the interfaces. It should be pointed out that the strain or stress due to the lattice mismatch between substrates and LMO/SMO can induce orbital order, even without charge transfer.¹⁰ However, here we propose that the parallel spin channels can provide another driving force for orbital order in manganite superlattices. Our simulations in the $n = 2, 3$, and 4 cases show that the e_g electrons have more tendency to occupy the $d_{3z^2-r^2}$ orbital than the $d_{x^2-y^2}$ one around the interfaces. One example is shown in Fig. 4. This orbital order optimizes the DE process between the FM regions via the G -AFM layers. But in real superlattices the combined effect of this spin-driven tendency to orbital order and that induced by strain or stress may compete and more quantitative calculations will be needed to decide which orbital order dominates.

We have studied the two-orbital double-exchange model for the $(\text{LMO})_{2n}/(\text{SMO})_n$ superlattices. First, we have explained why the LMO thin films on STO are FM instead of

A -AFM. Then, our simulations showed that the spin order in the SMO regions is G -AFM, while it is FM elsewhere. The spin arrangement between the FM and G -AFM layers causes a metal-insulator transition, with $n=3$ as the critical value, which may explain the experimental results.

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