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The advertisement for the Lake Shore CRYOTRONICS Model PS-100 Preconfigured Tabletop Probe Station features a photograph of the device. The device is a complex mechanical assembly with various components, including a probe head, a sample stage, and a base. It is set against a blue background. The text 'NEW' is in orange, and 'Model PS-100' is in large, bold, dark blue. Below it, 'Preconfigured Tabletop Probe Station' is in a smaller, dark blue font. The Lake Shore CRYOTRONICS logo is on the right, with 'Lake Shore' in white and 'CRYOTRONICS' in dark blue. Below the logo, the tagline 'An affordable solution for a wide range of research' is written in white, italicized font.

High mobility half-metallicity in the $(\text{LaMnO}_3)_2/(\text{SrTiO}_3)_8$ superlattice

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First principles calculations have been performed to investigate the $\text{LaMnO}_3/\text{SrTiO}_3$ superlattice. Structural relaxation within the generalized gradient approximation results in no significant tiltings or rotations of oxygen octahedra, but in distinct distortions in the SrTiO_3 region. Taking into account the onsite Coulomb interaction, we find that the Mn spins order ferromagnetically, in contrast to the antiferromagnetic state of bulk LaMnO_3 . Most importantly, the interface strain combined with charge transfer across the interface induces half-metallicity within the MnO_2 layers. The superlattice is particularly interesting for spintronics applications because the half-metallic states are characterized by an extraordinary high mobility. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4789506>]

Perovskite-based compounds, including transition metal oxides, have attracted increasing attention in the past decades since the discoveries of high- T_c superconductivity and colossal magnetoresistance. This class of materials can accommodate various electronic and magnetic ground states, ranging from canonical ferromagnetic (FM) metals and half-metallic antiferromagnetic (AF) Mott insulators (for strong onsite Coulomb repulsion) to Fermi liquids (when doping induces screening that prevents the system from localization). Beyond, perovskite heterostructures can accommodate electronic and magnetic properties which are not present in the bulk compounds.¹ For example, a superlattice of the AF materials LaMnO_3 (LMO) and SrMnO_3 has been found to become FM.^{2,3} This behavior can be explained by a leakage of Mn $3d e_g$ charge into the SrMnO_3 region for thin layers of the component materials.

Magnetization can appear at interfaces of non-magnetic bulk compounds, for example, between the polar LaAlO_3 and non-polar SrTiO_3 (STO).⁴ The two-dimensional electron gas formed at this interface has been investigated widely.^{5–7} The different ground state properties of the bulk and interface systems are due to the strain induced by the in-plane lattice mismatch between the component materials as well as possible charge migration across the interface.⁸ Strain can induce a modification of the crystal field and therefore an orbital reconstruction, whereas charge transfer modifies the occupations of the atomic orbitals. In general, it is difficult to predict the structural features of a heterointerface due to strong interplay between the different degrees of freedom (structural, orbital, and magnetic). In addition, this interplay will be affected by oxygen defects. For recent reviews on heterostructures and their properties, see Refs. 9 and 10, for instance.

Apart from understanding the special phenomena encountered in heterostructures, exploiting their properties for applications is a major challenge. Experiments have demonstrated that perovskite heterostructures can be useful in spintronics.¹¹ One property of particular interest is half-metallicity, as it is found for mixed valent Mn compounds such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.2 < x < 0.4$). At heterointerfaces,

the special properties arising from the modified chemical environment usually are restricted to a few atomic layers. A topic that only recently has received attention is the magnetic state of the $(\text{LMO})_n/(\text{STO})_8$ superlattice, with $n = 1, 2, 8$, which is characterized by a higher FM moment than observed in LaMnO_3 films.¹² Different scenarios have been proposed to explain the high magnetization and its dependence on the thickness n . One possibility is that not only the Mn atoms but also the Ti atoms carry a magnetic moment. This idea is supported by experiments on isolated n -type LMO/STO interfaces, which have a higher LMO:STO ratio (17:2 and 3:2, as compared to 2:8).¹³ The authors of Ref. 13 have argued that Ti magnetic moments due to Mn-O-Ti superexchange play a role but that a clear picture is lacking. In particular, spin-orbit interaction seems to induce an orbital moment anti-aligned to the spin.

The aim of the present work is to describe the magnetic ground state and electronic properties of the $(\text{LMO})_2/(\text{STO})_8$ superlattice, with particular emphasis on the interpretation of the experimental findings in Refs. 12 and 13. We will investigate the replacement of the AF state of bulk LMO by a FM state in the superlattice as well as the constitution of high mobility half-metallicity within the MnO_2 layers.

Our $(\text{LMO})_2/(\text{STO})_8$ superlattice is based on a $\sqrt{2} \times \sqrt{2}$ in-plane supercell of the cubic perovskite, in order to account for possible tiltings and rotations of the O octahedra in the vicinity of the interface. While bulk LMO has an orthorhombic structure, the $(\text{LMO})_2/(\text{STO})_8$ superlattice is reported to show tetragonal symmetry,¹² because the STO substrate imposes its structure to the LMO and therefore to the full superlattice. For this reason, we will adopt the tetragonal structure in the following. For the in-plane lattice constant, we employ the average of the two bulk values, weighted by the number of layers of the bulk compounds in the supercell: $2/10 \cdot 3.95 \text{ \AA} + 8/10 \cdot 3.905 \text{ \AA} = 3.914 \text{ \AA}$. Periodic boundary conditions give rise to a superlattice with alternating n -type LaO/TiO_2 and p -type MnO_2/SrO interfaces.

For our calculations, we use the Vienna *ab-initio* simulation package with projected augmented wave pseudopotentials.^{14,15} We employ the generalized gradient approximation in the parametrization of Perdew, Burke, and Ernzerhof.^{16,17} Moreover, the basis set consists of Sr $4s^2$, $4p^6$, $5s^2$, Ti $3p^6$,

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$4s^2$, $3d^2$, O $2s^2$, $2p^4$, Mn $3p^6$, $4s^2$, $3d^5$, and La $4p^6$, $5s^8$, $6d^1$ orbitals. For the structural relaxation, we set the energy tolerance to 10^{-4} eV and use a $4 \times 4 \times 1$ Γ -centered k-mesh, a Methfessel-Paxton¹⁸ first order smearing of 0.1 eV, and an energy cutoff of 500 eV. All calculations are started with a nominal magnetic moment of $4 \mu_B$ on the Mn atoms and no magnetic moment on the other atoms. In order to account for electron correlations, we apply the Dudarev approach¹⁹ using for the difference between the onsite Coulomb interaction U and exchange interaction J values of $U - J = 4$ eV for the Ti $3d$ and $U - J = 3$ eV for the Mn $3d$ states, compare Refs. 20 and 21. To obtain accurate energies and densities of states (DOSs), we adopt an energy tolerance of 10^{-5} eV, a $8 \times 8 \times 1$ k-mesh, a tetrahedron smearing of 0.03 eV with Blöchl corrections,²² and an energy cutoff of 600 eV.

In agreement with Ref. 12, we perform the structural optimization of our superlattice for FM spin ordering. We do not find significant octahedral rotations or tiltings, but rather shifts of the cations off the centers of the O octahedra, see Fig. 1. This distortion pattern is in line with previous findings for other heterostructures such as $\text{LaAlO}_3/\text{STO}$.^{23–25} In the out-of-plane direction, an almost constant 0.08 Å off-centering of the cations affects the STO region, while only the MnO_2 layer next to the p -type interface shows a similar off-centering. Both the Ti and Mn atoms are displaced away from the n -type interface. As a side effect, the distances between the Sr atoms belonging to different layers alternate between short and long, with a typical length difference of 0.11 Å.

The total magnetic moment of the supercell is found to be $15.2 \mu_B$ without and $15.8 \mu_B$ with onsite Coulomb interaction. Under inclusion of the onsite interaction, the magnetic moments within the atomic spheres show that the Mn atoms next to the interfaces are strongly polarized, with magnetic moments of $3.76 \mu_B$, $3.75 \mu_B$ at the n -type and $3.72 \mu_B$, $3.71 \mu_B$ at the p -type interface. These values are similar to the polarization in bulk LMO, for which we obtain for the same computational setup a magnetic moment of $3.70 \mu_B$. The small difference of $0.04 \mu_B$ between the two interfaces reflects valency variations between the two LMO layers. All other atoms carry only minor magnetic moments of magnitude $\leq 0.05 \mu_B$. The almost vanishing polarization of Ti seconds Ref. 12, in which the authors argue that the high magnetic moment in $(\text{LMO})_n/(\text{STO})_8$ ($n = 1, 2, 8$) superlattices is not due to the Ti atoms. As a further support of this conclusion, recent experiments have shown that FM coupling is promoted in nanoscale LMO samples, leading to coexistence of FM and AF domains.²⁶ Such coexistence also explains the fact that the experimental magnetization is too

FIG. 1. Supercell used for the calculations. The lines along the O layers highlight the off-centering of the cations, which is around 0.08 Å throughout the STO region, see the text for details.

low as compared to the magnetic moments obtained in our calculations.

In Fig. 2, we show the total DOS as obtained under inclusion of the onsite Coulomb interaction. The complete closure of the insulating energy gap of LMO in the majority spin channel indicates that the FM state of LMO arises from the in-plane strain due to the tetragonal structure in the superlattice. Closer inspection shows that the DOS is at the verge of half-metallicity, see the magnified inset in Fig. 2. Only some minority spin states, tracing back to O $2p$, Sr $3d$, $5s$, and La $6s$ orbitals prevent a half-metallic nature. We have confirmed that even a strong onsite Coulomb interaction on the Mn $3d$ and O $2p$ orbitals, as used in Refs. 23, 27, and 28, or on the La $4f$ orbitals, as used in Refs. 20 and 21, does not lead to the formation of an energy gap in the minority spin channel, because of the unusual admixture of La $5s$ states.

Figure 3 addresses the Mn $3d$ DOS, together with the O $2p$ DOS, for the whole LMO region. While there are no minority spin states close to the Fermi level, the majority spin t_{2g} and e_g states are fully and partially occupied, respectively. The absence of minority spin states constitutes an ideal half-metallic configuration for the Mn atoms. Further investigation of the DOS shows that the occupation of the e_g states distinguishes the Mn atoms next to the n and p -type interfaces, see Table I, where mainly the occupation of the $d_{x^2-y^2}^\uparrow$ orbital is reduced near the p -type interface. The effect can be attributed to the presence of Sr^{2+} ions (as compared to La^{3+} ions) at this interface. Speaking quantitatively, the Mn valence is reduced from the ideal value $4+$ in LMO to about $3.8+$. Such a mixed valency supports FM ordering, even though it is probably not the driving mechanism behind the replacement of AF (in bulk LMO) by FM ordering (in the superlattice). Interestingly, all four Mn $3d$ e_g DOSs in Fig. 3 reveal a huge band width of about 3 eV. As a consequence, the charge carriers in the LMO region of the superlattice are characterized by a very high mobility,²⁹ which is most useful from the application point of view.

According to Fig. 3, strong hybridization between Mn $3d$ and O $2p$ in-plane states affects both interfaces. In addition, we observe out-of-plane hybridization between the two MnO_2 layers, see, for example, the peaks at -0.4 eV, -0.2 eV, and 0 eV in the Mn $3d$ DOS as well as the peak near 0.2 eV in the O $2p$ DOS. Because there is virtually no

FIG. 2. Total DOS obtained for the $(\text{LaMnO}_3)_2/(\text{SrTiO}_3)_8$ superlattice. The inset shows a zoom of the energy range from -2 to 1 eV, where the DOS range is from -10 to 10 states/eV.

FIG. 3. Left column, first and third row: Mn DOS. Left column, second and fourth row: O DOS for the apical sites. Right column, first and third row: O DOS for the basal sites.

hybridization between Ti 3d and O 2p states from the LMO region, compare Fig. 4, magnetic exchange across the interface is interrupted, which is reflected by the almost vanishing magnetic moments of the Ti atoms. On the other hand, the DOS reveals a significant interaction between the MnO₂ and LaO layers. We find that the small minority spin DOS at the Fermi level is due to hybridized La and O states. Since the Mn 3d states do not contribute here, the MnO₂ layers themselves are perfectly half-metallic.

In Fig. 4, we show the Ti 3d DOS for each atomic layer from the *p*-type (top) to the *n*-type (bottom) interface. The Ti 3d states at both interfaces are shifted to higher energy, which reflects the fact that the workfunction is lower for LMO than for STO. Moreover, we note an orbital ordering between the d_{xy} and $d_{yz,zx}$ states, which is due to the previously discussed shifts of the Ti atoms off the octahedral centers in the STO region.

In conclusion, we have demonstrated a FM spin ordering for the (LMO)₂/(STO)₈ superlattice and have argued that this state is induced by the interface strain that is also responsible for the tetragonal symmetry (while bulk LMO is orthorhombic). In addition, the interface strain and to some extent charge transfer via the interface make the LMO region metallic with charge carriers of exceptionally high mobility. Because of the strong spin polarization, the Mn atoms finally acquire an ideal half-metallic nature. Since the number of occupied minority spin states is small and essentially only

due to hybridized La and O orbitals, already a small modification of the crystal structure (e.g., by O defects) can remove them from the Fermi level. The observed charge transfer agrees with the experimental finding of a slight hole doping of LMO at the *p*-type interface and leads to a mixed valent state of Mn, which in turn supports FM ordering. Concerning

FIG. 4. Ti DOS for atoms from the *p*-type (top) to the *n*-type (bottom) interface. The d_{xy} DOS is shown by an areal representation. The range of the DOS is in each case from -0.5 to 0.5 states/eV.

TABLE I. Occupation of the Mn *d* orbitals (atomic sphere). Only one atom per layer is shown for clarity. The major difference between the two cases concerns the $d_{x^2-y^2}^{\uparrow}$ orbital, whose occupation is higher at the *n*-type interface.

Interface	$d_{xy}^{\uparrow}$	$d_{xy}^{\downarrow}$	$d_{yz}^{\uparrow}$	$d_{yz}^{\downarrow}$	$d_{xz}^{\uparrow}$	$d_{xz}^{\downarrow}$	$d_{x^2-y^2}^{\uparrow}$	$d_{x^2-y^2}^{\downarrow}$	$d_{3z^2-r^2}^{\uparrow}$	$d_{3z^2-r^2}^{\downarrow}$
<i>n</i> -type	0.94	0.05	0.97	0.07	0.99	0.07	0.81	0.17	0.73	0.24
<i>p</i> -type	0.91	0.07	0.94	0.06	0.93	0.06	0.63	0.21	0.77	0.21

the experimental controversy whether Ti develops spin polarization or not, our results clearly point to essentially vanishing magnetic moments. The STO region of the superlattice is found to be entirely insulating, where the onset of the conduction band shifts to higher energy at both interfaces due to the lower workfunction of LMO as compared to STO.

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