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Interfacial spin glass state and exchange bias in manganite bilayers with competing magnetic orders

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The magnetic properties of manganite bilayers composed of G-type antiferromagnetic (AFM) SrMnO3 and double-exchange ferromagnetic (FM) La0.7Sr0.3MnO3 are studied. A spin-glass state is observed as a result of competing magnetic orders and spin frustration at the La0.7Sr0.3MnO3/SrMnO3 interface. The dependence of the irreversible temperature on the cooling magnetic field follows the Almeida-Thouless line. Although an ideal G-type AFM SrMnO3 is featured with a compensated spin configuration, the bilayers exhibit exchange bias below the spin glass freezing temperature, which is much lower than the Néel temperature of SMO, indicating that the exchange bias is strongly correlated with the spin glass state. The results indicate that the spin frustration that originates from the competition between the AFM super-exchange and the FM double-exchange interactions can induce a strong magnetic anisotropy at the La0.7Sr0.3MnO3/SrMnO3 interface.

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I. INTRODUCTION

Due to the coexisting spin, charge and orbital degrees of freedom and their reconstruction, interfaces between different oxides in artificially layered heterostructures are expected to exhibit much richer physics than their conventional semiconductor counterparts.1–4 Recent advances in the fabrication of high-quality epitaxial interfaces between perovskite oxides have led to a rapid surge of interest in the study of new interfacial electronic states, and some fascinating phenomena have been revealed.5–8 Heterostructures composed of magnetically active transition metal oxides are especially interesting because of the intricate spin-dependent exchange interaction at the interfaces.9–17 For example, ferromagnetism has been observed at interfaces between two antiferromagnets or between an antiferromagnet and a paramagnet.10,18–22 It is well recognized that epitaxial heterostructures of mixed-valence manganites offer excellent opportunities to exploit such emerging magnetic phenomena and shed light on the competing interactions at the interfaces.

One interfacial phenomenon that has captured lots of attention for several decades is the exchange bias (EB) in heterostructures of ferromagnetic (FM) and antiferromagnetic (AFM) materials. In magnetic hysteresis loop measurements, the EB effect manifests itself as a shift along the field axis, and the additional unidirectional anisotropy is attributed to the exchange interaction between the FM and AFM spins at the interface. Because of its importance in spintronic applications, a large amount of experimental and theoretical work has been undertaken to discern the nature of interfacial AFM/FM exchange coupling. Although several theoretical models have been proposed to explain the EB behavior,23–31 they are challenged by emerging experimental results.

In particular, issues arise when the AFM layer possesses a G-type antiferromagnetic order. In most of the existing models, an uncompensated AFM interface is a prerequisite for the emergence of EB; therefore G-type AFM, where all the nearest-neighboring spins at the AFM/FM interface are compensated by each other, is not expected to pin the FM spins via an exchange coupling. Although some earlier reports considered some extrinsic factors, such as random defects25 and interface roughness,27 which may affect the exchange coupling, there remain open questions regarding the magnetic characteristics of the interface between G-type AFM and FM layers. Recently, EB was observed at epitaxial heterostructures involving G-type AFM layers such as BiFeO332–36 where Dzyaloshinskii-Moriya interaction and ferroelectric polarization were proposed to play important roles.34 Perovskite-structured manganites are well suited to investigate this issue because they boast rich phase diagrams with a myriad of magnetic orders.37–39 Furthermore, epitaxial heterostructures can be routinely achieved as a result of their structural compatibility.

In this paper, we studied the magnetic properties of bilayer heterostructures composed of G-type AFM SrMnO3 (SMO) and FM La0.7Sr0.3MnO3 (LSMO). Since both layers are manganites, a large exchange coupling can be expected at the LSMO/SMO interface due to the direct Mn-O-Mn exchange interaction. Indeed, EB effects have been demonstrated before in all-manganese heterostructures, in particular, in superlattices,40–43 sandwich-type multilayers44 and bilayers15 of La2/3Ca1/3MnO3/La1/3Ca2/3MnO3. In this combination, the La1/3Ca2/3MnO3 layer, which has a noncollinear AFM spin order with a Néel temperature \( T_N \) of about 170 K,46 magnetically couples to the FM La2/3Ca1/3MnO3 layer.

SMO and LaMnO3 (LMO) are the two end members of the La1-xSr_xMnO3 series. Considering that LMO has an A-type AFM order,47 we also explored the magnetic properties of the LSMO/LMO bilayers. However, because the cation vacancies in LMO produce a weak magnetism in the bilayers,47,48 we could not unambiguously determine the interfacial magnetic properties. Therefore we focus on the LSMO/SMO bilayers in this work.

In the simplified scheme of structural and spin orders illustrated in Fig. 1, the two nearest-neighboring spins in the
II. EXPERIMENTAL DETAILS

LSMO/SMO bilayers were grown on atomically flat TiO$_2$-terminated (100)-oriented SrTiO$_3$ (STO) substrates using pulsed laser deposition (PLD). The frequency of the excimer laser was 2 Hz and 10 Hz for the LSMO and SMO layers, respectively. The energy fluence of the laser was $\sim 1.5$ J/cm$^2$. The growth took place at a substrate temperature of 750 $^\circ$C and an oxygen pressure of 20 Pa. After growth, the samples were $\textit{in situ}$ annealed in an O$_2$ atmosphere of 1 bar for one hour before slowly cooling down to room temperature. As reference samples, SMO and LSMO single layers were grown on STO substrates under the same conditions. Magnetic properties of the samples were measured by a superconducting quantum interference device (SQUID, Quantum Design) magnetometer. The applied magnetic field is always parallel to the film plane and along the [010] direction of the STO substrate. For the field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements, the sample was cooled down from 400 K to the desired temperature with and without the magnetic field, respectively. Both the ZFC and FC magnetization versus temperature ($M$-$T$) curves were measured during the warming process. The hysteresis loops were measured after FC from 400 K under a 5000 Oe magnetic field. For the measurement of the relaxation of thermal remnant magnetization, the sample was field cooled under a magnetic field of 0.1 kOe from 400 K to the predetermined temperatures, and then the time dependence of the magnetization was recorded immediately after the magnetic field decreased to zero.

The structural characterization was performed by x-ray diffraction (XRD) and (scanning) transmission electron microscopy [(S)TEM]. The XRD $\theta$-2$\theta$ scan and reflectivity were studied with a high-resolution x-ray diffractometer (Smartlab, Rigaku, Japan). TEM and high-resolution TEM (HRTEM) studies were carried out using a FEI Tecnai G$2$ 30 UT microscope operated at 300 kV. Aberration-corrected high-angle annular dark field scanning TEM (HAADF-STEM) experiments were performed on a Titan “cube” microscope, equipped with an aberration corrector for the probe-forming lens and operated at 300 kV. The convergence semi-angle alpha used for imaging was 21.5 mrad; the inner detection semi-angle beta of the HAADF detector was 50 mrad. Cross-section specimens were prepared by cutting the samples along the (100) STO plane, followed either by mechanical polishing and ion-beam milling in a JEOL Ion Slicer or by focussed ion-beam (FIB) slicing in an FEI Helios FIB-SEM.

III. RESULTS AND DISCUSSION

The reflection high-energy electron diffraction (RHEED) data in Fig. 2(a) suggest that the LSMO layer was grown on the STO substrate with a layer-by-layer mode and the oscillations become weaker as the SMO layer grew thicker. The nominal thicknesses of the LSMO layer and the SMO layer are 4.6 nm (12 unit cells) and 50 nm, respectively. The XRD $\theta$-2$\theta$ scans for the LSMO/SMO bilayer and the reference LSMO and SMO single layers grown on STO(100) substrates. (c) Enlarged view around the (200) diffraction peak of the bilayer. The arrows mark the positions of fringe peaks. (d) Reflectivity data of the LSMO/SMO bilayer. The hollow cycles are the experiment data, and the red line is the fitting to the data.
The reflectivity data are shown in Fig. 2(c), Laue fringes were also observed around the (200) diffraction peak, which suggests a bilayer on the STO substrate. No secondary phase or amorphous layer was observed. The corresponding electron diffraction (ED) pattern shows a single cubic-zone diffraction pattern. No splitting or elongations of the diffraction spots were observed, indicating a perfect interfacial structure based on the experimental Z-contrast image. Figure 3(d) shows the schematic stacking sequence and the interface structure determined by the experimental Z-contrast image. As expected, we observed steps and terrace structures at the interfaces due to the small miscut angle of the STO substrate. Steps and terrace structures at the interfaces, confirming that the bilayer is fully strained.

The low-magnification cross-section TEM image of the SMO/LSMO/STO(100) bilayer film in Fig. 3(a) confirms the layer thicknesses. No secondary phase or amorphous layer was observed. The corresponding electron diffraction (ED) pattern shows a single cubic-zone diffraction pattern. No splitting or elongations of the diffraction spots were observed, indicating a perfect interfacial structure based on the experimental Z-contrast image. As expected, we observed steps and terrace structures at the interfaces due to the small miscut angle of the STO substrate. Steps and terrace structures at the interfaces, confirming that the bilayer is fully strained. The high-resolution HAADF-STEM (Z-contrast) image in Fig. 3(c) provides direct evidence of the sharp interface between the layers. As the contrast in this technique is related to the atomic number $Z$, the interface structure can be unraveled as the superposition of patterns produced by the STO substrate, LSMO and SMO layers. The STO substrate is TiO$_2$ terminated, the interface structure can be represented as -TiO$_2$-SrO-TiO$_2$-La(Sr)O-MnO$_2$-, and the LSMO/SMO interface as -La(Sr)O-MnO$_2$-SrO-MnO$_2$-.

The magnetization versus temperature ($M$-$T$) data measured under 0.1 kOe for the bilayer LSMO/SMO and the single layer LSMO and SMO reference films are shown in Fig. 4. The ferromagnetic transition temperature $T_c$ determined by the differential of the $M$-$T$ curves are 288 and 271 K for the bilayer and the LSMO single layer, respectively. The origin of the slightly higher $T_c$ observed in the bilayer is not clear at the moment. The magnetic signal of the reference SMO layer is weak because of its AFM nature. To determine the Néel temperature $T_N$, we grew a thick SMO film of 300 nm and the measured temperature dependence of magnetization suggests a $T_N$ of 227 K, which is close to the reported bulk value of ~240 K.$^{49}$ Nevertheless, the fact that the contribution of the SMO layer to the overall magnetic signal is negligible facilitates the interpretation of magnetization data.

There are two prominent features in the bilayer data in Fig. 4: a peak in both ZFC and FC $M$-$T$ curves, and a bifurcation between the two curves below the irreversibility temperature $T_{irr}$. These features have been reported for several commonly known magnetic systems such as spin glass,$^{50,51}$ cluster glass,$^{52-54}$ and superparamagnet.$^{51,55}$ But the characteristics of the curves have subtle differences from superparamagnets, which often exhibit monotonously increasing FC...
magnetization on decreasing temperature.\textsuperscript{51} We can also exclude cluster glass systems because their peak temperature in the $M$-$T$ curves is usually lower than $T_{\text{irr}}$, whereas in our case the two temperatures are very close to each other.\textsuperscript{53} Thus the temperature dependence of the magnetization in Fig. 4 most likely suggests a spin glass state in the LSMO/SMO bilayer. On the other hand, for the LSMO single layer with the same thickness of 4.7 nm, the ZFC magnetization data overlap well with the FC one, which suggests that the spin glass state in the LSMO/SMO bilayer cannot be attributed to the “bulk” parts of the films, instead it must be related to the magnetic coupling at the LSMO/SMO interface. Moreover, the weaker magnetization of the bilayer compared with that of the LSMO single layer at low temperatures suggests that the spin glass state occurs at least partially in the LSMO layer and disturbs the FM spin order; otherwise, the overall magnetization would stay roughly the same since the SMO layer contributes very little to the overall magnetization.

We also measured the $M$-$T$ curves of the samples under a larger field of 5 kOe as shown in the inset of Fig. 4. For ideal ferromagnetic La$_{1-x}$Sr$_x$MnO$_3$ with all the spins parallel to each other, the low-temperature saturation moment as expected from the 3$d$ electrons present in manganese ions should be\textsuperscript{56}

$$M_S = xMn^{3+}(S = 4/2) + (1-x)Mn^{4+}(S = 3/2) = 4x\mu_B + 3(1-x)\mu_B.$$ \hspace{1cm} (1)

For $x = 0.3$, $M_S$ should be 3.3$\mu_B$, which agrees well with the LSMO data shown in the inset of Fig. 4. Under a magnetic field of 5 kOe, the magnetization of the LSMO/SMO bilayer approaches that of the single LSMO layer, suggesting that the magnetic frustration is suppressed to a certain degree by the strong magnetic field, but at low temperatures, the magnetization of the LSMO/SMO bilayer remains lower than that of the reference LSMO layer.

Figure 5(a) shows the $M$-$T$ curves for the LSMO/SMO bilayer measured under different magnetic fields, and it can clearly be observed that the irreversibility temperature decreases with the increasing field. As shown in Fig. 5(b), the field dependence of the $T_{\text{irr}}$ follows the Almeida-Thouless (AT) line:\textsuperscript{57}

$$H(T_{\text{irr}})/\Delta J \propto (1 - T_{\text{irr}}/T_F)^{3/2},$$ \hspace{1cm} (2)

where $T_F$ is the zero-field spin-glass freezing temperature and $\Delta J$ is the width of the distribution of the exchange interaction. Although the critical line is predicted for ideal Ising spin systems, the collapse of the experimental data to the AT line in Fig. 5(b) supports the existence of spin-glass behavior in LSMO/SMO bilayer.\textsuperscript{50,58,59} The fitting gives a freezing temperature $T_F = 178$ K. To further demonstrate the spin-glass behavior in the LSMO/SMO bilayer, we studied the magnetic relaxation and the data are show in Fig. 5(c).

The relaxation of the thermal remnant magnetization was measured at three temperatures: 100 K where the spins are frozen, 160 K, which is just below the spin-glass freezing temperature $T_F$, and 230 K, which is above $T_F$. The decay curves can be fitted by a stretched-exponential function:

$$M(t) = M_0 \exp[-C(\omega t)^{1-n}/(1 - n)],$$ \hspace{1cm} (3)

where $C$ is the exponential factor and $\omega$ is the relaxation frequency.\textsuperscript{60} The fitting parameter $n$ was determined to be 0.8727 at 160 K and 0.6977 at 100 K, which are similar to the values reported for other spin glass systems such as AgMn, i.e., $n \sim 0.87$ at $T_F$ and --0.67 in the temperature region far below $T_F$.\textsuperscript{60} For the temperature 230 K, the thermal remnant magnetization is quite small, and no clear relaxation was observed. These data clearly suggest that the magnetic relaxation and glassy behavior are most prominent near the spin freezing temperature $T_F$. We also tried to study the spin-glass state in the bilayer using ac susceptibility;\textsuperscript{53,59,61} however, the signal of the thin film was too weak to achieve reliable measurements.

In the LSMO/SMO bilayer, the spin glass state as a result of magnetic frustration can be linked to the competition between the AFM super-exchange and the FM double-exchange interactions at the interface. In fact, such a competition has been reported in previous studies on manganite superlattices.\textsuperscript{21,22,62,63} As illustrated in Fig. 1, at the interface of G-type AFM and FM layers, the nearest neighboring FM spins will always be influenced by an opposite pinning force from the AFM layer regardless whether the interface exchange coupling is FM or AFM type. As a result, the FM spin shows a frustrated behavior when the interface coupling is strong enough. The spin frustration could appear in both the AFM and FM layers, and the characteristics of the frustrated regions are determined.
by the stability of AFM and FM exchange interactions and the coupling strength between the layers.

Figure 6 shows the hysteresis loops of the LSMO/SMO bilayer and the reference single layers measured at 50 K after field cooling from 400 K. An obvious shift of the hysteresis loop, a signature of the exchange bias, was observed in the LSMO/SMO bilayer. The EB field $H_{EB} = |H_+ + H_-|/2$ is 80 Oe at 50 K, where $H_+$ and $H_-$ denote the right and left coercivity fields, respectively. Meanwhile, the coercivity defined as $H_C = |H_+ - H_-|/2$ significantly increases from 30 Oe for the LSMO single layer to 230 Oe for the bilayer. For the SMO single layer, the magnetization is negligible. Moreover, we did not observe any EB in the LSMO single layer, thus the EB in LSMO/SMO bilayer unambiguously originates from the interface coupling. We note here that the G-type AFM order in the SMO layer is not expected to pin the FM spins of the LSMO layer since the nearest-neighboring spins are compensated by each other. However, the spin order of the SMO at the interface could be modified and different from that of the ideal bulk form. It was reported that in LaMnO$_3$/SrMnO$_3$ superlattices with thin layer thicknesses (up to four unit cells), the entire superlattices exhibit A-type AFM order, i.e., the spins of the SMO layer does not possess a G-type order any more. In our LSMO/SMO bilayers, the strong magnetic coupling and frustration may modify the interfacial spin orders, and the detailed spin configuration at the interface clearly warrants future investigation.

The hysteresis loops in Fig. 7(a) measured at different temperatures for the LSMO/SMO bilayer show that both $H_{EB}$ and $H_C$ increase with decreasing temperature. The temperature-dependent trend is illustrated in Fig. 7(b), and the Néel temperature $T_N$ of bulk SMO and the spin-glass freezing temperature $T_F$ of LSMO/SMO bilayer are also marked. One can see that the EB appears below a blocking temperature $T_B$ of about 130 K, which is much lower than $T_N$. Therefore it is clear that above $T_B$ the AFM order in the SMO layer is not stable enough to provide the unidirectional anisotropy, which depends on the ratio of the average interfacial coupling energy to the domain wall energy.$^{65}$ On the other hand, $T_B$ is quite close to the freezing temperature $T_F$ of the interfacial spin glass state, suggesting that the competition of the magnetic orders and the emergence of the spin glass state play important roles in the EB effect at the LSMO/SMO interface.

Furthermore, the existence of spin frustration due to the competing magnetic interactions is known to lead to an exponential temperature-dependent decay of $H_{EB}$ and $H_C$, which has previously been observed in a range of diverse materials such as Ni/Ni$_{76}$Mn$_{24}$ bilayers,$^{66}$ La$_{1-x}$Ca$_x$MnO$_3$ ferromagnetic/antiferromagnetic superlattices,$^{67}$ and La$_{0.25}$Ca$_{0.75}$MnO$_3$ nanopaticles.$^{68}$ Indeed, the temperature dependencies of $H_{EB}$ and $H_C$ of LSMO/SMO bilayer in Fig. 7(b) can be fitted by the phenomenological formula

$$H_{EB}(T) = H_{EB}^0 \exp(-T/T_1)$$

$$H_C(T) = H_C^0 \exp(-T/T_2),$$

(4)

where $H_{EB}^0$ and $H_C^0$ are the extrapolations of $H_{EB}$ and $H_C$ to the absolute zero temperature; $T_1$ and $T_2$ are constants. The fitting results in Fig. 7(b) give further support to the scenario that the EB in the LSMO/SMO bilayer can be attributed to the interface spin glass state originated from the competition between the AF superexchange and the FM double-exchange interactions. However, we should note that the $H_C$ data appear to deviate from the exponential behavior.

FIG. 6. (Color online) $M$-$H$ loops measured on the LSMO/SMO bilayer and the reference single layers at 50 K after field cooling from 400 K. The measurement range is between $-5$ and 5 kOe. For clarity, only the data between $-1.5$ and 1.5 kOe are shown. The arrows and numbers show the scanning sequence of the magnetic field.

FIG. 7. (Color online) (a) $M$-$H$ loops for the LSMO/SMO bilayer measured at different temperatures. For clarity, only the data between $-1$ and 1 kOe are shown in the figures, while the actual measurements took place between $-5$ and 5 kOe. (b) Temperature dependence of $H_{EB}$ and $H_C$ for the LSMO/SMO bilayer. Also shown are the $H_C$ data measured for the LSMO single layer. The solid and dashed lines are the fittings to Eq. (3). The two arrows mark the Néel temperature $T_N$ of bulk SMO and the freezing temperature $T_F$, respectively.
in the high-temperature regime, suggesting the increasingly important role of thermal excitation at high temperatures.

IV. CONCLUSIONS

The magnetic properties of the LSMO/SMO bilayer appear to be quite rich, and the emergence of the spin glass state can be attributed to the competition of the AFM superexchange interaction in SMO and the FM double-exchange interaction in LSMO through the interfacial exchange coupling. This spin glass state at the FM/AFM interface further contributes to the EB effect; although the G-type AFM order in the SMO layer presents compensated spins at the interface, a uniaxial glass state at the FM/AFM interface contributes to the EB effect. The AFM superexchange interaction in SMO and the FM double-exchange interaction in LSMO through the interfacial exchange coupling. Future experiments involving tools like soft x-ray and polarized neutron reflectometry are needed to explore the depth-dependent magnetic profiles in the heterostructures.

In a broad perspective, the variation of spin configuration at the manganite interfaces offers opportunities to examine the outcome of competing exchange interactions and to achieve functionalities in heterostructures which are absent in individual components.

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