Anomalous exchange bias at collinear/noncollinear spin interface

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We report on the interfacial magnetic coupling in manganite bilayers of collinear ferromagnetic La₀.₇Sr₀.₃MnO₃ and noncollinear multiferroic TbMnO₃. Exchange bias is observed at the Neéel temperature of TbMnO₃ (~41 K) due to the onset of long-range antiferromagnetic ordering in the Mn spin sublattice. Interestingly, an anomalous plateau of exchange bias emerges at the ordering temperature of Tb spins (~10 K), and we ascribe this unique feature to the strong coupling between Tb and Mn spin sublattices in TbMnO₃, which in turn influences the magnetic coupling across the interface. On the other hand, the enhancement of coercivity in La₀.₇Sr₀.₃MnO₃/TbMnO₃ shows monotonous temperature dependence. Our results illustrate a strong interfacial magnetic interaction at the La₀.₇Sr₀.₃MnO₃/TbMnO₃ interface, highlighting the roles of competing spin orders, magnetic frustration, and coupling between multiple spin sublattices in artificial collinear/noncollinear spin heterostructures.
hybridized. In such noncollinear multiferroics, the complex spin orders and the exchange interactions are important for not only the multiferroic ground states but also potentially provide novel electronic paths towards controlling the magnetic degree of freedom in heterostructures\(^{47-49}\).

So far, most works on TMO have focused on the properties of bulks and thin films\(^{39,50,51}\), and the properties of TMO-based heterostructures were seldom studied. Recently, it was demonstrated that rectifying junctions can be formed by growing TMO thin films on conducting Nb-doped SrTiO\(_3\) substrates\(^{52,53}\), but the study was limited to transport properties. In general, there is a lack of effort on incorporating multiferroics with noncollinear spin orders like TMO into functional thin film heterostructures. It has been proposed that the magnetic frustration and the noncollinear spin structure in the AFM layer contribute to the EB effect at the AFM/FM interface\(^{32,54}\). Multiferroic TMO exhibits unique and complex spin orders, thus offering new perspectives to exploit the exchange coupling in multiferroic heterostructures. In the LSMO/TMO bilayer illustrated in Fig. 1(a), both Mn and Tb spin sublattices in TMO may couple, either directly or indirectly, with the Mn spin lattice in LSMO. In such a case, we expect to observe not only the onset of EB below the Néel temperature of TMO (Fig. 1(a)), but also additional features in the interfacial magnetic coupling at the ordering temperature of Tb spins (Fig. 1(b)). Such an exchange coupling at the oxide interface highlights the intricate interactions between the multiple spin sublattices, enriching the magnetic properties of multiferroic heterostructures.

Results

Figure 2(a) shows the oscillation of the in-site RHEED specular intensity recorded during the growth of bilayer. A layer-by-layer growth mode can be observed for the eight unit cells of LSMO and the first several unit cells of TMO. In addition, as shown in Figure 2(b), the atomic force microscopy (AFM) image measured on the LSMO layer shows a clear step-and-terrace surface with the height of steps being around one unit cell, which is consist with the layer-by-layer growth mode of LSMO. As shown in the XRD \(\theta-2\theta\) scan (Fig. 2(c)), only reflections corresponding to the substrates and the TMO (001) planes were observed, indicating that the films were...
Figure 3(a) shows the zero field cooling (ZFC) and field cooling (FC) data of magnetization versus temperature measured on the reference single layer TMO sample. The magnetization shows an upturn at low temperature as a result of the ordering of Mn spins. In the plot of inverse susceptibility ($\chi^{-1}$) vs. temperature, a deviation from the paramagnetic linear behavior occurs at $T_N \approx 41$ K. On decreasing temperature, the cusp feature at $-10$ K can be related to the long range Tb spin ordering ($T_{\text{Tb}}$).

Furthermore, we measured the thermal remanent magnetization after ZFC (RM-ZFC) and FC (RM-FC), which often gives valuable information regarding the irreversible magnetization in disordered systems. During the RM-ZFC (RM-FC) measurements, sample was first cooled down under zero field (6 Tesla) from 300 K, then a 6 Tesla field is applied and removed, which was followed by magnetization measurements under zero field on increasing temperature. As shown in Fig. 3(b), in addition to the magnetic transitions mentioned above, there is a weak anomalous feature at $-26$ K in the difference of the ZFC and FC data, which is close to the Mn spiral spin ordering temperature observed in bulk TMO ($T_{\text{lock}}$) at $-28$ K, but it is much less pronounced than the bulk result.

Figure 4 shows the ZFC and FC curves and the $M-H$ loops measured on the LSMO/TMO bilayer and reference samples. The bifurcation between the ZFC and FC curves which was already observed in the TMO single layer (Fig. 3(a)) becomes stronger in the bilayer (Fig. 4(a)), which likely indicates the magnetic frustration at the LSMO/TMO interface. It was previously proposed that the strain effect can induce a weak ferromagnetic signal at low temperatures, which was observed in the TMO reference single layer. This weak ferromagnetism of TMO may contribute to the overall magnetism of the LSMO/TMO bilayer. Regarding to the LSMO component, as shown in Fig. 4(a), the Curie temperature of the reference LSMO single layer is $\sim 220$ K, which is much lower than the bulk value $\sim 369$ K. The strong suppression of magnetic properties is likely the result of strain which is known to induce distortion of MnO$_6$ octahedra in the Jahn-Teller systems. In the bilayer, the Curie temperature of LSMO is further suppressed to $\sim 165$ K, which indicates that the magnetism of the 8 unit cell LSMO is significantly affected by the presence of the TMO overlayer. We note that the possible intermixing at the LSMO/TMO interface must be limited to one or two unit cells because the Curie temperature of five unit cell LSMO was reported to dramatically decrease to $\sim 100$ K. However, the exact origin of the Curie temperature reduction in the bilayer and the detailed structure of the interface clearly warrant further studies.

The definite evidence of magnetic coupling at the LSMO/TMO interface is the enhancement of coercivity in the bilayer. As shown in Fig. 4(b), at 50 K, $H_C$ of the bilayer is enhanced to 178 Oe, which is much larger than the value of the reference LSMO single layer (44 Oe). Further enhancement was observed at lower temperatures: at 10 K $H_C$ of the bilayer reaches as high as 960 Oe (Fig. 4(c)). Furthermore, we observed the EB effect in the bilayer as evidenced by the shift of the hysteresis loop towards the opposite direction of the cooling field (Fig. 4(d)); $H_E$ at 5 K under a cooling field of 4 Tesla is 42 Oe. The observed exchange coupling and bias unambiguously suggest the existence of interfacial magnetic coupling between LSMO and TMO.

The temperature dependence of $H_C$ and $H_E$ shown in Fig. 5 sheds more light on the magnetic coupling at LSMO/TMO interface. As the temperature goes down, the EB emerges at the Néel temperature $T_N$ of TMO (Fig. 5(a)), which is expected because the AFM order in the TMO layer needs to develop and pin the FM domains of the LSMO layer. However, the magnetic order in TMO is quite complex: besides the A-type and G-type modulated structures, a neutron diffraction study revealed the coexistence of C-type and F-type orderings below $T_N$. On further decreasing temperature, $H_E$ shows an anomalous plateau around $T_{\text{Tb}}$ and then it increases by almost four fold to a value of 128 Oe. This non-monotonous temperature dependence of $H_E$ reflects the complex magnetic interactions between various spin sublattices. It was proposed that the competing exchange interactions, i.e., magnetic couplings between nearest ($J_1$) and next nearest ($J_2$) Mn spin sublattices, along with the clamping magnetic interaction between Tb and Mn ($J_{\text{Tb-Mn}}$) spin sublattices, collectively determine the Mn–O–Mn bound angles and modulate the strength of the exchange interaction between Mn ions in TMO. As a result of the strong coupling between Tb and Mn spin sublattices of TMO, the formation of long-range Tb$^{3+}$ spin ordering could lead to a significant canting of the neighboring Mn spin order. Consequently, the spin frustration within the AFM TMO layer affects the coupling strength across the interface between the Mn sublattices of TMO and LSMO, resulting in the nontrivial temperature-dependent variation of $H_E$. 
However, it is noteworthy that the schematic in Fig. 1(b) apparently over-simplifies the spin configuration at the LSMO/TMO interface. There remain open questions regarding the magnetic ordering of Tb spins in TMO at low temperatures as well as the exchange interactions between the Tb and Mn sublattices. Furthermore, although in the schematics of Fig. 1(a) and (b) the MnO$_2$ layer at the LSMO/TMO interface adopts the spin order of TMO, it is apparently shared by both layers, and spin-flop coupling may develop at the interface. The detailed elucidation may require neutron and synchrotron experiments. As far as we know, there has been no theory so far on elucidating the magnetic order/disorder at such an interface between a spiral multiferroic and a ferromagnet.

The anomalous temperature dependence of $H_E$ at $T_{TB}$ invites future theoretical efforts to shed light on the ground-state spin configuration and exchange coupling at such strongly frustrated interfaces.

As shown in Fig. 5(b), the temperature dependence of $H_C$ shows a monotonous behavior, which is different from the trend of $H_E$, suggesting that $H_E$ and $H_C$ perhaps have different origins. As reported previously, the enhancement of $H_C$ may occur without the onset of $H_E$, which depends on not only the spin structure in the AFM layer (e.g., collinear or noncollinear) but also the detailed domain structures. The frustration of interfacial spins and the spin-flop coupling between FM and AFM layers have been proposed to be responsible for a large uniaxial anisotropy and enhanced $H_C$, whereas additional effects like interfacial defects are needed to explain the EB. Moreover, because $H_C$ is not an intrinsic property of material, it is sensitively dependent on sample morphology and other factors.

The coercivity is supposed to have a power law dependence on the thickness of FM layer, i.e., $H_c \sim 1/t_{FM}^\alpha$, when the random interaction at the AFM/FM interface is assumed. We measured bilayers with the thickness of LSMO layer varying from 8 to 13 unit cells while keeping the thickness of TMO layer fixed. Indeed, as shown in Fig. 6, both $H_C$ and $H_E$ decrease with increasing LSMO thickness. The enhancement of $H_C$ is quite significant within the range of LSMO layer thickness. In a phenomenological model, the exchange bias field is expressed as $H_E = \Delta \sigma / M_{FM}$, where $\Delta \sigma$ is the interfacial exchange energy density, which represents the strength of interfacial exchange coupling, $M_{FM}$ and $t_{FM}$ are the magnetization and thickness of the FM layer, respectively. As shown in Fig. 6, $H_E$ appears to follow the trend of $1/t_{FM}$, which is consistent with the interfacial nature of the EB effect.
TMO is very limited. Further studies focused on controlling the in situ SCIENTIFIC

We prepared thin film bilayers of LSMO/TMO on TiO$_2$-terminated SrTiO$_3$ (001)

Methods

lots of attention$^{4,21,27}$. In the previously reported bilayers composed of

Figure 6 | The dependence of $H_E$ and $H_C$ on the thickness of LSMO, while

netic properties of such collinear/noncollinear magnetic heterostruc-

H$_{\text{e}}$ at $T_B$. These data put constraints on future

Discussion

As mentioned previously, EB has also been reported in heterostructures

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