Exchange biasing and low-field magnetoresistance in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ bilayers

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Exchange biasing and magnetoresistance (MR) behaviors have been investigated in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ bilayers with specially designed interfacial structures. The exchange coupling is found to be strongly related to interfacial structures. Exchange field H_E decreases as the cooling field H_{fc} increases at high H_{fc} region. Especially, the coercivity H_C is enhanced by exchange coupling for bilayers with rough interface, while it is reduced for relatively smooth interface. Also, large low-field MR has been achieved by introducing regular in-plane grain boundaries, and a biasing of R - H loop has been observed.

Recently, intensive studies have been focused on perovskite manganites due to their colossal magnetoresistance (MR).¹ However, the intrinsic MR of manganites requires a high magnetic field and only occurs in a narrow temperature range, which limit their practical application. Therefore there is growing interest on the extrinsic low-field MR of various structures,²⁻⁸ which exploit the half metallic nature of manganites. Analogs to metal multilayers and granular films hold promise in improving the low-field MR in manganite films. Such attempts include the trilayer tunnel junction.² However, compared to the complicated fabrication process for trilayer junction, it is more attractive to introduce in-plane grain boundaries for the enhancement of low-field MR.⁸

Exchange biasing, which refers to the shift of the hysteresis loop when a ferromagnet (FM)/antiferromagnet (AF) bilayer is cooled in a magnetic field through the Néel temperature T_N of the AF,⁹ is a result of interfacial FM/AF exchange coupling. Main features of the exchange coupling include a shift of the FM loop away from $H=0$ by an amount known as the exchange field H_E , and usually an enhanced coercivity H_C . Recently, it attracted much attention¹⁰⁻¹⁴ due to its application in spin-valve-based devices.¹⁵ However, the understanding of the exchange coupling is still not well established. The exchange biasing is different in different FM/AF systems.

Especially, in Fe- FeF_2 bilayer, positive exchange bias was observed.¹¹ Hence it posts questions on the mechanism for exchange coupling with fully compensated interfacial AF

spins, and perpendicular coupling between AF spin and FM spin has been suggested.^{12,14,16} To date, only a little work has been done on the exchange coupling in manganites systems.¹⁷ $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, which shows different ground state as AF or FM with change of x ,^{18,19} provides a good candidate for study of FM/AF coupling, and it may shed light on the nature of exchange coupling due to its special spin structure.

$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ first becomes a FM during cooling, and then becomes an AF as further cooled, while the ground state of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ is FM. In this work, we fabricated $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (FM)/ $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (AF) bilayers with different interfacial structures in order to study the exchange coupling as well as improve the low-field MR by introducing in-plane grain boundaries in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ layer. We investigated the exchange bias and its dependence on cooling field and interfacial structures. In the films with in-plane grain boundaries, large low-field MR is obtained. Also, the influence of exchange anisotropy on the resistance behavior has been discussed, and a biasing of resistance loop was observed.

Bilayers were grown on (100) SrTiO_3 substrates by pulsed-laser deposition. At first, a $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ layer about 1800 Å was deposited, followed by the deposition of a $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ layer about 1100 Å. The AF layers were deposited with special surface structures described previously.^{8,20} In Fig. 1, we show the atomic force microscopic images of three samples with different interfacial structures. In sample L1 [Fig. 1(a)], there are many rectan-

FIG. 1. AFM images of the surface of samples (a) L1, (c) L2, (d) L3, and (b) the surface of the bottom AF layer for sample L2 before the FM layer was deposited.

gular crystals on the surface of the FM layer, which is due to the inherence of the surface of the AF layer. The height of some crystals is even larger than the average thickness of the FM layer. This bilayer has the roughest interface, which is induced by the strongly ordered surface structure of the bottom AF layer. For sample L2, we show both the surface morphology before [Fig. 1(b)] and after [Fig. 1(c)] the FM layer was deposited. In the surface of the AF layer of L2, arrays of orthogonal cracks are observed. Such arrays introduce grain boundaries in the FM layer, although it is much weaker compared with L1. For sample L3, there are no orthogonal cracks in the AF layer, and thus no regular in-plane grain boundaries are introduced in the FM layer [Fig. 1(d)].

X-ray diffraction data showed that both FM and AF layers were (001) oriented. The magnetization was measured by a superconducting quantum interference device magnetometer. For all the measurements mentioned in this paper, the magnetic field was applied parallel to the film surface.

From Figs. 2(a)–2(c), we show the magnetization (M) as a function of temperature (T) measured with zero-field cooled (ZFC) and field cooled (FC). For all the bilayers, there is a blocking temperature (T_B) in ZFC curves, which suggests the existence of FM clusters.

Although the FC M - T curves are similar and they all show a beginning of FM transition at about 270 K, there are different fine magnetic structures for the films with different interface. Note that the magnetization of a single AF layer of the same thickness is an order smaller than the bilayer. Hence the above fine magnetic structures are mainly due to the coupling between AF layer and FM layer. ZFC M - H loops show that at the same temperature, H_c of sample L1 is the largest and that of sample L3 is the smallest, which implies the pinning of FM domains by the interfacial structures.

To measure the exchange field H_E , samples were cooled

from 300 K in a magnetic field H_{fc} . In Fig. 3(a), we give the dependence of H_E and H_c on H_{fc} for sample L1 at 5 K. The inset of Fig. 3(a) shows the ZFC M - H loops at 5 K and that for $H_{fc}=1$ T. It is clear that in the field-cooled case, the loop shifts negatively with an enhanced H_c . The interfacial exchange energy per unit area is given by

$$\delta E = M_{FM} t_{FM} H_E, \quad (1)$$

where M_{FM} and t_{FM} are the magnetization per unit volume and thickness of the FM layer, respectively. We estimate that δE is about 0.2 erg/cm² for sample L1 with $H_{fc}=1$ T. As temperature increases, H_E decreases and vanishes at 30 K. Due to the size effect of the thin film, the Néel temperature is much lower than the bulk value of La_{0.5}Ca_{0.5}MnO₃.

For the roughest sample L1, H_E rises first as H_{fc} increases, and reaches a maximum of about 50 Oe at 1 T, and then slightly decreases. As for H_c , it shows a rapid increase at low H_{fc} , and then rises much more slightly. However, for sample L2, H_E shows a larger drop from 50 Oe at $H_{fc}=1$ T to 20 Oe at $H_{fc}=5$ T, accompanied by a decrease of H_c from 275 to 248 Oe. Especially for a bilayer with similar interface as sample L2 except for denser arrays of cracks in the AF layer, this trend is most clear [Fig. 3(b)]. For this bilayer with denser cracks array, H_E sharply increases in a small H_{fc} of 500 Oe, and then decreases as H_{fc} increases. It is important to note that H_c becomes much smaller in high H_{fc} , and it is reduced compared with the ZFC H_c , which is different with the usual case in other systems that H_c enhanced by exchange coupling.^{9,11,21}

The inset of Fig. 3(b) shows the M - H loops at 5 K for $H_{fc}=1$ and 5 T, respectively. The left part of the loop shrinks from -331 Oe at $H_{fc}=1$ T to -263 Oe at $H_{fc}=5$ T, while the right part of the loop remains unchanged.

FIG. 2. ZFC and FC M - T curves for samples (a) L1, (b) L2, (c) L3, respectively. Resistance (R) versus temperature (T) at zero field, at 5000 Oe, and the MR for samples (d) L1, (e) L2, (f) L3, respectively.

For the sample with smooth interface (sample L3), the exchange field at 5 K is smaller (H_E is about 20 Oe at $H_{fc} = 1$ T), and at $H_{fc} = 5$ T, H_E is decreased to near zero with a reduced H_c .

In conclusion, the main features of exchange coupling for the above bilayers include: (i) The strength of exchange biasing depends on the interfacial structure. Obviously, with introducing the ordered surface structure in the bottom AF layer, the exchange coupling is enhanced. Although the influence of the ordered interfacial structure on the exchange coupling is not clearly understood, the density of the orthogonal pattern seems crucial in determining the strength of the exchange biasing. For the bilayer without ordered interfacial structure and with the smallest interface roughness (sample L3), the exchange coupling is much weaker.

(ii) The dependence of H_E and H_c on H_{fc} is strongly related to interfacial roughness. For the bilayers with the roughest interface (induced by the pattern of large rectangular crystals), H_E first rises then slightly decreases as H_{fc} increases, while H_c is enhanced with larger H_{fc} . On the contrary, for samples with a relatively smoother interface, the exchange bias is sensitive to lower cooling field (a $H_{fc} \sim 20$ Oe can cause a notable loop shift), and a larger cooling field weakens the exchange bias, accompanied by a much reduced H_c , in contrast to a usual observation of enhanced H_c in other FM/AF systems. The above features must be due to the spin structure of the AF layer. For (001) oriented $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, the interface spins are fully compensated.²²

The dependence of H_E on H_{fc} reminds us of that in FeF_2 -Fe bilayers,¹¹ although we did not observe a positive exchange bias in the bilayers we studied. It is possible that FM spin and AF spin may also couple perpendicularly in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ bilayer.^{14,16} The sharp increase of H_E at low field may be due to the formation of larger FM domains in the FM layer. Once the FM layer is saturated, H_E essentially reaches a maximum value. And the further decrease of H_E at higher H_{fc} may be ascribed to the interaction between the AF layer and the applied field.¹¹ Also, it is important to note the possible melt of AF state by high field in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.²² However, the different trend in H_c - H_{fc} curves for samples with different interfacial structures still remains a question.

In Figs. 2(d)–2(f), we show the temperature dependence of the resistance at zero field, 5000 Oe, and $MR = (R_H - R_0)/R_0$, for samples L1, L2, and L3, respectively. For sample L3 without introduced regular in-plane grain boundaries, the resistance is the smallest, and the resistance peak (R_p) occurs near T_c [Fig. 2(f)]. For sample L2 with in-plane grain boundaries, the resistance is much larger, and R_p shift to about 210 K. While for the roughest sample L1, the resistance is the largest due to the contribution of grain boundaries (most obviously at the low-temperature range), accompanied by a lower R_p at about 175 K. In all the samples, MR can be clearly separated into an intrinsic part and an extrinsic part induced by the grain boundaries. The intrinsic MR is

FIG. 3. The dependence of H_E and H_c on cooling field H_{fc} at 5 K (a) for bilayer L1 (with the roughest interface); (b) for a bilayer with dense array of cracks in the bottom AF layer. The insets show the hysteresis loops with different cooling field.

near T_c . It is quite notable for sample L3, while negligible for samples L1 and L2. For sample L3 without arrays of grain boundaries, the low-temperature extrinsic MR is small. On the contrary, the extrinsic MR is quite large at a wide temperature range (from 5 K to about 220 K) for samples L1 and L2. Also, MR drops around 220 K, and it can even become positive. We found that the temperature variance in the measurement is impossible to cause such a positive MR. Note that the MR drops occur near the temperature where ZFC and FC MT curves fall apart. One possible explanation is: when passed over that temperature range, the long-range correlation between the FM clusters corrupts and thermal disturbance induces a metastable high-resistance state (it may be higher than the resistance at zero field and cause the positive MR); after the high-resistance state is relaxed, negative MR appears again.

Figure 4(a) shows the field dependence of resistance at 50 K. The low-field MR in samples L1 and L2 is much larger than L3. The MR first undergoes a drop after H_c , which may be due to the alignment of the body magnetic moments of different grains. Then there is moderate, nearly linear MR as H increases, which may be due to the further suppression of magnetic frustration in the boundary region. Previously, intergrain spin polarized tunneling^{6,7} or spin-dependent scattering at the grain boundaries³ have been proposed for the low-field MR. However, we did not find that the MR is proportional to $(M/M_s)^2$ as predicated by spin-dependent scattering or traditional spin polarized tunneling. In the

FIG. 4. (a) The field (H) dependence of normalized resistance (R/R_{max}) at 50 K for samples L1, L2, and L3, respectively. (b) $R-H$ loops measured at 5 K with field cooled at 1 T from 300 K for bilayer L1; the triangle curve is measured from 1 T to -2500 Oe, and then back to 1 T again, and the circle curve is measured from 1 to -1 T, and then back to 1 T again.

present case, it is most likely that the grain boundaries region is a spin-glass-like insulator, and the low-field MR may be due to the tunneling through such a magnetic insulator.⁶

By back extrapolating the high field $R(H)/R_{max}$ to find the zero-field intercept R_z/R_{max} , and getting a MR* associated with the magnetic domain rotation by $MR^* = 1 - (R_z/R_{max})$, we find that MR* is increased as temperature decreases.

Also, similar to the work of Ziese *et al.*,⁶ by current-voltage curves, we find that the conductance is nonlinear, and the dynamic conductance $G = dI/dV$ can be fit quite well with

$$G/G_0 = 1 + g_x V^x, \quad (2)$$

which is suggested by investigation of inelastic tunneling.²³ Here G_0 is the low-voltage dynamic conductance, and g_x is the nonlinear term coefficient. The conductance exponent x depends on the temperature (at 5 K, it is about 0.6).

Furthermore, to study the influence of exchange coupling on the MR behavior, we also measured the $R-H$ loops with the field cooled from 300 K. Figure 4(b) shows the $R-H$ loops for sample L1 (with the roughest interface) at $H_{fc} = 1$ T. Compared with the ZFC $R-H$ loops, in addition to a reduced resistance due to the suppression of magnetic frustration by field cooling, a $R-H$ loop shift associated with the exchange bias is clearly observed. Note that the left peak is

broad than the right peak. It shows the pinning effect of the exchange anisotropy on the resistance behavior. Moreover, asymmetry appears if the R - H measurement is ended at -2500 Oe and then back again: the final state at -2500 Oe seems to be memorized, and results in a higher resistance peak at right part. The asymmetry disappears if we measure the R - H loops in the range 1 T to -1 T. Such an asymmetry occurs if the measuring field range is lower than H_{fc} . For samples L2 and L3 with smoother interface, no R - H loop shift can be observed. Because the exchange coupling is an interfacial effect, for bilayer with relatively smoother interface, the contribution of the interface resistance to the total resistance is small and cannot induce the R - H shift. While for bilayer L1, the roughness is larger than the average thickness of FM layer, thus the interfacial resistance becomes dominant and the influence of exchange biasing can be clearly observed.

In summary, magnetic and transport properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ bilayers with different in-

terfacial structures have been studied. Exchange biasing is observed and the dependence of H_E and H_c on cooling field H_{fc} is investigated, which is found to be closely related to the interfacial structure. Especially with relatively smooth interface, H_c with FC can be reduced much compared with the ZFC H_c , which is different to other systems with a usually enhanced H_c . Also, by introducing regular in-plane grain boundaries in the FM layer, large low-field MR over a wide temperature range is obtained. Moreover, the influence of exchange coupling on the transport behavior is discussed, and with much rough interface, the exchange coupling can also induce a R - H loop shift. Such work is interesting in understanding the mechanism of exchange coupling, as well as promising in improving the low-field MR in manganites films.

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