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Magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$:x glass composites

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The effects of interfacial states on the temperature dependence of the magnetoresistance (MR) of $\text{Sr}_2\text{FeMoO}_6$ -glass composites have been studied. X-ray diffraction analyses show that the glass is most likely located at the grain boundary without causing a change of the crystal structure of $\text{Sr}_2\text{FeMoO}_6$. The variation of the resistance with temperature and magnetic field indicates that the added glass layer has profound influence on the MR properties. At low temperature, the MR in low fields is enhanced notably because the insulating barrier for the intergranular tunneling is improved by adding the glass layer at the grain surface. However, at high temperature, the MR decreases rapidly with the increase of temperature due to, in addition to the enhancement of spin-independent hopping of electrons through the localized states, the fast decay of spin polarization at the surfaces of the grains. This decay is induced by the separation of the ferromagnetic grains with the nonmagnetic glass layer at the grain boundaries. © 2007 American Institute of Physics.

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I. INTRODUCTION

Half-metallic ferromagnets with fully spin-polarized carrier have attracted a great deal of attention recently since large tunneling magnetoresistance (MR) dominated by spin-polarized tunneling through grain boundaries can be obtained at low fields in such materials,^{1,2} which makes the half-metallic ferromagnets potential candidates for spintronic device applications.^{3,4} However, the magnitude of the MR effect usually falls off rapidly with increasing temperature and only a small MR can be observed at room temperature, which seriously limits their practical applications.

Several mechanisms have been proposed to explain the temperature dependence of the MR of half-metallic ferromagnets. Dai and Tang pointed out that the spin-independent hopping conductance through the localized states at grain boundary begins to dominate the total conductance at high temperature, thus reducing the MR with increasing temperature.⁵ Shang *et al.* proposed that, in addition to the contribution of spin-independent hopping channel, the MR could also be reduced by the suppression of spin polarization with increasing temperature due to thermally excited spin

wave.⁶ In this model, spin polarization P has the same $T^{3/2}$ behavior as that of magnetization in the temperature range far below T_C . However, the low field MR (LFMR) reported in perovskite manganites decreases drastically with increasing temperature, exhibiting temperature dependence very different from that of magnetization. Park *et al.*, on the basis of spin-resolved photoemission experiment, suggested that the rapid decrease of the intergranular MR with increasing temperature is caused by the much stronger temperature dependence of spin polarization at the surface than that in the bulk.⁷ Furthermore, the theoretical results of Ju and Li showed that the spin polarization at the grain surface has a temperature dependence of exponential form and plays an important role in determining the reduction of MR in CrO_2 cold pressed compacts.⁸ But detailed analysis of the relation between the temperature dependence of the MR and spin polarization in half-metallic ferromagnets is still lacking so far.

Double perovskite $\text{Sr}_2\text{FeMoO}_6$ (SFMO) is usually considered a half-metallic ferromagnet according to the band structure calculation.^{9,10} Among most known half-metallic oxides, SFMO has a relatively weak temperature dependence of MR, which largely follows its magnetization.¹¹ Therefore, SFMO is an ideal system to investigate the influence of the interface states on the temperature dependence of MR. We

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FIG. 1. Room-temperature XRD patterns of (a) pure SFMO annealed at 430 °C in 36% H_2/N_2 and (b) 20 wt % glass added samples. The inset shows the scanning electron micrograph of the 30 wt % glass added sample.

have investigated the temperature dependence of the MR of SFMO composites in this article, where the interface states was controlled such that the original grain boundary is replaced with non-magnetic insulating glass that separates the ferromagnetic half-metallic grains. We aim to clarify the effects of interfacial modulation on the temperature dependence of surface spin polarization and thus on the MR.

II. EXPERIMENTS

The SFMO: x glass composites (weight ratio $x=20, 30, 40$, and 50 wt %, respectively) were prepared by the following steps. First, pure SFMO powders were synthesized by conventional solid-state reaction described in Ref. 12. Second, the samples were ground by ball milling and then mixed with appropriate proportions of Pb-Si-B glass, which has a soft temperature of about 400 °C, in pure Ar (3 bar) for 1 h. Finally, the mixed powders were compacted into thin pellets under 450 MPa pressure and then annealed at 430 °C for 20 min in 36% H_2/N_2 .

X-ray diffraction (XRD) powder patterns were collected using a Bede D^1 XRD spectrometer with Ni-filtered Cu $K\alpha$ radiation. The morphology of the SFMO: x glass composites were carried out by using the HITACHI S-4700 field emission scanning electron microscope. The resistivity measurements in different magnetic fields with standard direct current four-probe method were carried out using a physical properties measurement system of Quantum Design.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the glass added sample ($x=20$ wt %) and the pure SFMO sample annealed at 430 °C in 36% H_2/N_2 . It is obvious that both samples are of single phase double perovskite structure, except for a broad peak of glass in the XRD pattern of the glass added sample. The XRD patterns of other samples have the same characteristics. The scanning electron micrograph of 30 wt % glass added sample is also shown in Fig. 1. The grain size of SFMO is about 1 μm , and the SFMO grains are surrounded by bright regions, which is the insulated glass confirmed by the energy dispersive x-ray analysis, similar as that of $La_{0.7}Sr_{0.3}MnO_3$ -glass composites.¹³ It can be seen from Fig. 2 that, with increasing glass content, the resistivity

FIG. 2. The variation of the room temperature resistivity and saturation magnetization at 10 K and 5 T with glass concentration. The solid line is the linear fitting to the saturation magnetization data.

(ρ) at room temperature of SFMO: x glass composites increases drastically while the saturation magnetization value (M_S) at 10 K and 5 T decreases proportionally. The linear dependence of M_S on the glass content gave us the strong proof that the nonmagnetic glass on the grain boundary has no reaction with the SFMO grains.¹⁴ The variation of ρ indicates that the glass layer is most likely located at the surface of SFMO grain and, therefore, has strongly influence on the spin-dependent tunneling through grain boundaries.

Figure 3 displays the LFMR of the glass added samples ($x=30$ and 50 wt %) as a function of magnetic field up to 1 T at 10 K. Here, the MR is defined as $MR(\%) = 100\% \times [\rho(H) - \rho(0)] / \rho(H)$. For comparison, the MR data of the pure SFMO polycrystalline sample annealed under the same condition as that of glass added sample is also shown in Fig. 3 and labeled as $x=0$ wt %. The very small MR of this sample indicates that the intergranular tunneling barrier and so the spin-dependent tunneling in it were weakened strongly by the annealing. However, it is clear from the inset of Fig. 3 that the LFMR is remarkably enhanced with increasing glass content and reaches 39% for sample $x=50$ wt % at 1 T. This means that adding glass at the grain boundaries can notably improve the spin-dependent carrier tunneling across the grain boundaries.

As shown in Fig. 4, the logarithms of normalized conductance of all SFMO-glass composites show linear dependence on $T^{-1/2}$ at low temperatures, which is characteristic of

FIG. 3. The magnetic field dependence of MR at 10 K for the pure SFMO sample annealed at 430 °C in 36% H_2/N_2 and glass added samples ($x=30$ and 50 wt %). The inset shows the variation of MR at 1 T and 10 K with glass concentrations.

FIG. 4. The $\ln G$ vs $T^{-1/2}$ curves of samples with different glass contents.

spin-dependent intergranular tunneling. The spin-dependent tunneling conductance as a function of temperature is usually described as,^{15,16} $G = G_0(1 + P^2 m^2) \exp[-(\Delta/T)^{1/2}]$, where P is the spin polarization, $m = M/M_S$ is the relative magnetization, and Δ is proportional to the Coulomb charging energy and the tunnel barrier thickness. It can be found from Table I that, the value of Δ calculated from the slope of the linear part of $\ln G$ vs $T^{-1/2}$ curves at low temperature increases notably with increasing glass content, demonstrating that the added glass is located at the grain boundaries and improves the barrier layer quality for spin-dependent tunneling. However, different from that of pure SFMO polycrystalline sample,¹² the MR of glass added samples decreases rapidly with the increase of temperature, as shown in Fig. 6. This difference should derive from the change of the interfacial state by adding glass at the grain boundary.

Based on the model proposed by Dai and Tang for CrO_2 powder compacts,⁵ the reduction of MR with increasing temperature was attributed to the suppression of spin-dependent contribution to the total conductance when a spin-independent hopping conductance through the defects or localized states in the grain boundaries becomes dominant at high temperature. According to this model, the conductance of SFMO-glass system in the whole temperature range can be described as

$$G = G_{SD} + G_{SI} = C_1(1 + P^2 m^2) \exp[-(\Delta/T)^{1/2}] + C_2 T^{1.33} + C_3 T^{2.5} + \dots + C_N T^{N-[2/(N-1)]}, \quad (1)$$

where G_{SD} is the intergranular spin-dependent conductance, $G_{SI} = \sum_{N=2} C_N T^{N-[2/(N-1)]}$ is the spin-independent hopping conductance, and the parameters C_N represent the contributions from hopping channels of different orders, respectively. It can be seen from Fig. 5 that this model works well in describing the variation of conductance with temperature though only two or three orders of hopping are considered.

TABLE I. Fitting parameters of Figs. 4–6 for pure SFMO and glass added samples ($x=20, 30, 40$, and 50 wt %).

Glass content (wt %)	Δ (K)	C_1	C_2	C_3	P_0	β
Pure SFMO	0.08	1.11	5.46×10^{-5}	...	0.28	...
20	3.24	1.54	1.49×10^{-3}	...	0.41	1.98×10^{-3}
30	5.29	1.86	1.71×10^{-3}	8.76×10^{-12}	0.50	2.54×10^{-3}
40	13.32	2.69	2.83×10^{-3}	3.53×10^{-7}	0.61	3.07×10^{-3}
50	30.57	5.08	2.02×10^{-3}	5.89×10^{-6}	0.65	3.52×10^{-3}

FIG. 5. Illustration of the fits of G as a function of T obtained from Eq. (1) for the pure SFMO sample and glass added samples ($x=20, 30, 40$, and 50 wt %).

The parameters C_2 and C_3 increase with increasing glass content, as shown in Table I, reflecting the importance of the higher-order hopping conductance due to the introduction of more defects or localized states in the barriers by adding the glass, which leads to the suppression of MR at high temperature.

According to Eq. (1), the MR in the SFMO-glass system can be given as

$$\begin{aligned} \text{MR} &= \frac{G_{(H=0)} - G_H}{G_{(H=0)}} = \frac{-C_1 P^2 m^2 \exp[-(\Delta/T)^{0.5}]}{C_1 \exp[-(\Delta/T)^{0.5}] + G_{SI}} \\ &= -\frac{P^2 m^2}{1 + G_{SI}/G_{SD(H=0)}}. \end{aligned} \quad (2)$$

For half-metallic SFMO, the spin polarization P has been predicted to be 100% by band structure calculation. If we assume that P is invariant in the whole temperature range, the MR can be expressed by the following expression when the external field is high enough to saturate the magnetization ($m=1$):

$$\text{MR} = -\frac{1}{1 + G_{SI}/G_{SD(H=0)}}. \quad (3)$$

However, the calculated results based on the earlier equation deviate significantly the experiment data for all samples. As an example, the calculated result for sample $x=50$ wt % is shown in Fig. 6.

In most cases, ideal half-metallic behavior of ferromagnet is expected only at low temperature far below T_C and the value of spin polarization P usually decreases with increasing temperature. This variation of P must be taken into account in order to obtain a comprehensive understanding of the temperature dependence of MR. It has been pointed out that the MR can be reduced by the suppression of spin polarization P at high temperature due to the thermally excited spin waves.⁶ Conventionally, spin polarization is taken as having the same temperature dependence as the magnetization in ferromagnetic materials at temperatures far below T_C , $P(T) = P_0(1 - \alpha T^{3/2})$. So, Eq. (2) is changed to

FIG. 6. Temperature dependence of the MR at 1 T for the 50 wt % glass added sample, the sample ball milled for 2 h, and the pure SFMO polycrystalline. The scattered symbol indicates the experiment data, while the lines are the fitted results. The dashed-dotted line indicates the fitted result for the 50 wt % glass added sample with Eq. (3); the dotted line is the fitted result for the pure SFMO sample with Eq. (4); the dashed line is the calculated result for the 50 wt % glass added sample with Eq. (4); and the solid line represents the fitted results for the 50 wt % glass added sample and ball milled SFMO power with Eq. (5).

$$\text{MR} = -\frac{P_0^2(1 - \alpha T^{3/2})^2 m^2}{1 + G_{\text{SI}}/G_{\text{SD}(H=0)}}, \quad (4)$$

where P_0 is the full effective spin polarization at $T=0$ K and α is a material-dependent constant. The MR at 1 T of the pure SFMO, which shows weak temperature dependence, can be fitted well by using Eq. (4) with $m=1$, as shown in Fig. 6. The slow temperature decay of MR in pure SFMO has been attributed to the ferromagnetic nature of insulating grain boundaries¹¹ and Garcia *et al.* also found a smooth decay of spin polarization when the magnetism was preserved in the vicinity of interface.¹⁷ But the MR of glass added samples decreases much more rapidly with increasing temperature than that of pure SFMO. Since the spin-dependent tunneling mainly reflects the properties of the electrode/barrier interface,¹⁸ the fast reduction of MR in glass added samples should be ascribed to the abnormal decay of spin polarization at grain boundaries, which has been postulated as an intrinsic property of the surfaces of half-metallic oxides.¹⁸ We also tried to use Eq. (4) to calculate the temperature dependence of MR of glass added samples, but the obvious deviation of this model from the experimental data, as shown in Fig. 6 for the $x=50$ wt % sample, indicates that the spin polarization at the grain boundary of the glass added sample would obey a law with the temperature different from that of bulk SFMO. Spin-polarized photoemission also showed that the spin polarization of the free surface of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ decreases much more rapidly with the temperature than the magnetization of the bulk material.⁷ In addition, the temperature dependence of the surface magnetization in Fe_2O_3 nanoparticles exhibits an exponential form very different from that of the bulk.¹⁹ So we can assume the spin polarization in our SFMO-glass samples also has the temperature dependence with an exponential form: $P = P_0 \exp(-\beta T)$, where P_0 is the full effective spin polarization at $T=0$ K and β is a constant associated with the grain surface.⁸ Therefore, the temperature dependence of the MR of the SFMO-glass composites should be described as

$$\text{MR} = -\frac{[P_0 \exp(-\beta T)m]^2}{1 + G_{\text{SI}}/G_{\text{SD}(H=0)}}, \quad (5)$$

where $m=1$. It can be seen from Fig. 6 that Eq. (5) can excellently fit the temperature dependence of the MR of the sample with 50 wt % glass. Other glass added samples gave the same results. It suggests that the fast decay of spin polarization at the grain boundary plays an important role in determining the reduction of MR at high temperature. In the SFMO-glass composites, the glass phase that situates in the grain boundaries has a strong influence on the interface magnetic states. Compared to the pure SFMO, the superexchange interaction through Fe-O-Mo chain at the grain boundaries in the composites are broken by the added glass layer. So the magnetization at the surface decreases more rapidly than in the bulk as the temperature increases, which leads to the rapid drop of the spin polarization. From Table I, the fitting parameter β increases with the concentration of glass, indicating that the decay of spin polarization P originating from surface spin-wave excitation is accelerated by adding the nonmagnetic glass at the grain boundaries. Though its half-metallic nature should have given 100% spin polarization, only a small value of 28% was observed for the fitting parameter P_0 in the pure SFMO sample due to the poor quality of the natural grain boundary tunnel barrier. With increasing glass content, P_0 increases and reaches 65% for $x=50$ wt % as the added glass layer drastically improves the tunnel barrier quality. Our experimental results clearly show that, in addition to the enhancement of the inelastic spin-independent hopping of electrons through the localized states, the fast decay of MR with increasing temperature in glass added samples is also attributed to the fast decay of spin polarization at the grain surface.

Moreover, we have also investigated the influence of ball milling on the magnetoresistance of SFMO powders in order to verify the relation between the MR and interfacial states. Although the crystal structure of the SFMO polycrystalline sample was not changed in the process of ball milling, its interfacial state was modulated by introducing paramagnetic insulating SrMoO_4 at the grain boundaries, and the MR decreased rapidly with increasing temperature.²⁰ It can be seen from Fig. 6 that Eq. (5) can perfectly reproduce the change in the MR with temperature in ball milled SFMO, too. As the concentration of SrMoO_4 increases from 3.0 wt % to 7.5 wt %, the parameter β increases from 2.55×10^{-3} to 3.45×10^{-3} . Since the SrMoO_4 is not magnetically ordered, the mechanism for the reduction of MR in this system should be similar to that in SFMO-glass composites.

IV. CONCLUSIONS

In the SFMO-glass composites, the added glass layer at the grain boundary can improve the insulating barrier for the spin-dependent intergranular tunneling and thus enhance the low field MR remarkably at low temperatures. However, adding nonmagnetic glass on the grain surface leads to a rapid reduction of MR of SFMO-glass composites with increasing temperature because this glass layer breaks down the superexchange interaction across the grain boundary,

which causes fast decay of spin polarization on the grain surface and then the rapid reduction of MR. Our results suggest that, not only the enhancement of spin-independent hopping of carriers, but also the fast decay of spin polarization at the grain boundary should be taken into account in order to obtain a comprehensive understanding of the rapid decrease of the MR with temperature in the polycrystalline half-metallic materials.

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