Effect of magnetic coupling on the magnetoresistive properties in La_{0.67}Sr_{0.33}MnO_{3}/BaFe_{11.3}(ZnSn)_{0.7}O_{19} composites

Q. Huang,a) J. Li, X. J. Huang, and C. K. Ong
Center for Superconducting and Magnetic Materials and Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260

X. S. Gao
Department of Materials Science, National University of Singapore, Lower Kent Ridge Road, Singapore 119260

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The La_{0.67}Sr_{0.33}MnO_{3}/BaFe_{11.3}(ZnSn)_{0.7}O_{19} (LSMO/BaM) composites have been prepared by co-sintering the LSMO and the BaM powders. The microstructural, magnetic, and magnetoresistive (MR) properties of those systems were systematically studied. Due to the magnetic coupling between the LSMO (a soft magnet metal) and BaM (a hard magnet insulator) grains, the low-field MR sensitivity was reduced and the high-field MR slope was enhanced for the composites. In addition, an abnormal MR hysteresis (resistance reaches its maximum before field reversal) was identified for the composite when the field is applied vertical to the sample plane. Its origin was attributed to a coplay of the LSMO/BaM spin coupling and the demagnetization effect. Finally, an anisotropic magnetoresistance (AMR) effect was observed in the composites. The AMR value decreased with increasing the BaM content, which can be explained by the changes of the local effective field on the grain boundaries. © 2001 American Institute of Physics.

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I. INTRODUCTION

Recently, extensive studies have been focused on the extrinsic magnetoresistance (MR) in polycrystalline manganites due to its high sensitivity to a small magnetic field. On application of an external magnetic field, those samples show a sharp decrease in resistivity in the low-field region. Microstructural explorations, such as porous grain-boundary (GB) generation, grain size refining, and two-phase mixed sintering, were carried out in order to enhance the extrinsic MR effects. In these microstructures, the increased structural disorder magnetically decouples the neighboring ferromagnetic grains, resulting in a more random distribution of the grain magnetization at zero field. The enhanced MR response was achieved when the magnetization of grains are aligned in a small magnetic field. Based on those experiments, it is clear that it is crucial to enhance the spin misorientation at virgin states in order to enhance the MR.

Besides the above methods, it is also possible to enhance the spin misorientation by introducing a second magnetic phase into the sample. In this case, it is quite similar to that of a typical giant magnetoresistance (GMR) metal-multilayer structure, where one of the two ferromagnetic (FM) layers is pinned by an antiferromagnetic (AFM) layer to form a pinned layer and the other unpinned layer is called a free layer. A large misorientation angle between the pinned layer and the free layers can be achieved at certain conditions. Along this line, Liu et al. recently reported the enhanced low-field MR in nanosized La_{0.7}Sr_{0.3}MnO_{3}/Pr_{0.5}Sr_{0.5}MnO_{3} (LSMO/PSMO) composites, where LSMO shows FM order and PSMO shows AFM order at low temperature. It is argued that the intergrain coupling layers with AFM order were formed due to the coupling between PSMO/LSMO. The field alignment of the spins in the coupling layers will make an additional contribution to the MR effect, causing the enhanced MR. On the other hand, Yan et al. also briefly reported enhanced low-field MR in a La_{0.67}Sr_{0.33}MnO_{3}/CoFe_{2}O_{4} (LSMO/CF) composite, where LSMO is a soft FM metal and CF a hard FM insulator. However, due to lack of magnetic data, the role of magnetic coupling on MR in this kind of system is still obscure. It is not clear whether the MR enhancement originates solely from the coupling effect between a soft and hard magnet or a certain microstructure is also indispensable. In order to shed some light on this issue and to make clear the effect of magnetic coupling between a soft and a hard magnet on the MR properties, we have prepared a series of La_{0.67}Sr_{0.33}MnO_{3}/BaFe_{11.3}(ZnSn)_{0.7}O_{19} (LSMO/BaM) composites and studied in detail their microstructural, magnetic, and magnetotransport properties.

II. EXPERIMENT

The LSMO/BaM composites, a LSMO_{1-x}BaM_{x} mixture (x is the volume concentration of the hard magnet insulator BaM), were prepared by two steps. First, LSMO and BaM powders were prepared separately. LSMO powders were prepared by standard solid-state reactions. The stoichiometric amount of La_{2}O_{3}, SrO, MnO_{2} powder was repeatedly reacted in air at 1250 °C for several days. Then, the obtained LSMO ceramics were crushed and ball milled for 3 h to form

a)Author to whom correspondence should be addressed; electronic-mail: scip8203@nus.edu.sg
the microsized LSMO powders. The BaM powders were prepared by a chemical coprecipitation method. The stoichiometric aqueous solution of metallic chlorides containing Ba$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, and Sn$^{4+}$ was stirred into an excess of aqueous solution of NaOH and Na$_2$CO$_3$ to form intermediate precipitates. The product of the coprecipitation was filtered off, washed with deionized water and dried. The nanocrystallized BaM particles were obtained after annealed at 750°C for 1 h. More details on the preparation can be found in our previous report.8 Second, the LSMO and BaM powders were mixed together to form LSMO$_{1-x}$BaM$_x$ with different volume fractions $x=0$, 0.3, 0.5, 0.65, 0.8, and 1. The mixtures were cold pressed by a die mold, and subsequently annealed at 680°C for 1 h to obtain the final composites. The measurements were made on the bar-shape samples with a typical size of 10×3×0.5 mm$^3$, if not otherwise indicated. The phases of the samples have been determined by the x-ray diffraction (XRD) and the morphologies were checked by scanning electron microscopy (SEM). The electro- and magnetotransport properties were evaluated using a four-probe method. The magnetoresistance was measured at various field configurations. The magnetic properties were characterized using an Oxford superconducting vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSION

A. Microstructural characterizations

Figure 1 shows the XRD patterns of the as-prepared LSMO$_{1-x}$BaM$_x$ samples. The volume fraction $x$ of BaM for each sample is labeled on the right side. For the pure LSMO sample ($x=0$), only a typical perovskite structure was identified. The reflection lines have been indexed as a pseudocubic structure, which correspond to the LSMO and the BaM reflections, respectively. With increasing BaM volume fraction $x$, the intensity of the (011), (002), (112), and (022) reflections from the LSMO phase clearly decreases, whereas the intensities of the reflections from the BaM phase gradually increase. No extra phase has been detected indicating that interfacial reactions between LSMO and BaM grains are negligible. This can be attributed to the low annealing temperature for the composites. For all the samples, no preferred grain orientation can be identified by XRD. Figure 2 shows the SEM picture of the $x=0.5$ sample, where the microsized LSMO grains are well surrounded by the nanosized BaM grains and the grains are randomly distributed. Those results demonstrate that the LSMO$_{1-x}$BaM$_x$ composites are of an ideal two-phase-mixed microstructure.

B. Magnetoresistive and magnetic properties

The resistivities measured at room temperature was 0.64, 4, and 36 $\Omega$ cm, and 2.2 and 800 k$\Omega$ cm for $x=0$, 0.3, 0.5, 0.65, and 0.8, respectively. With increasing BaM content, the sharp increase in resistivity indicates that the percolation mechanism exists for the LSMO$_{1-x}$BaM$_x$ composites. Figure 3(a) presents the MR hysteresis of the composites at 79 K. Magnetic field $H$ was applied in parallel to current $I$. It is found that the low-field MR sensitivity is reduced but the high-field (HF) MR slope ($d[\rho/\rho_{\text{MAX}}]/dH$) is enhanced with increasing amount of BaM. The low-field MR at 1.2 kOe is 11.5%, 10.5%, 10.1%, and 8.8% for $x=0$, 0.3, 0.5, and 0.65. The corresponding HFMR slope is 4.9×$10^{-3}$, 5.3×$10^{-3}$, 5.7×$10^{-3}$, and 6.4×$10^{-3}$ kOe, respectively. This is in contrast to a previous report in which the low-field MR sensitivity was enhanced in the LSMO/CeO$_2$ composites close to percolation, whereas the high-field MR slope remained unchanged. The discrepancy can be explained by the fact that BaM is magnetic and CeO$_2$ is nonmagnetic. In the LSMO/CeO$_2$ composites, the enhanced low-field MR sensitivity was attributed to the geometric constrains that produce larger misorientation angles between the magnetization of LSMO grains at a zero field; the high-field slope remains unchanged since the magnetic ordering of the grain surface layers are unchanged. In the LSMO/BaM composites, the magnetization of LSMO grains and grain surface layers are strongly coupled to the magnetization of BaM grains, thus resulting in the modified MR response.
However, one is still surprised to find that the MR in the LSMO$_{1-x}$BaM$_x$ composites reported here is reduced but the MR in a LSMO$_{1-x}$CF$_x$ composite in Ref. 7 was enhanced, noting that CF and BaM both are hard magnetic insulators. This clearly indicates that the soft/hard magnetic coupling itself is not enough to cause a MR enhancement. The LSMO/CF composite in Ref. 7 is a mixture of the nanosized LSMO grains and microsized CF grains, whereas the LSMO/BaM composite here is a mixture of the nanosized BaM grains and microsized LSMO grains. In these two cases, the geometric constrains and the magnetic coupling effect might be quite different. Therefore, it seems that the certain microstructure of the LSMO/CF composites also plays a very important role in the MR enhancement. Information on the magnetic properties of LSMO/CF composites will be helpful to further clarify this issue.

C. Abnormal MR hysteresis

Considering that $H_{c,BaM}$> $H_{c,LSMO}$, the demagnetization effect on the BaM and LSMO grains will be different. It is thus of interest to study the MR properties at different magnetic-field configurations. Figure 4(a) shows the MR hysteresis under a sweeping field (1) with the field parallel to the current $H$ (MR$_I$) and (2) with the field perpendicular to the sample plane (MR$_p$). For the pure LSMO ($x = 0$), MR$_i$ differs from MR$_p$ only in magnitude. Both MR$_i$ and MR$_p$ show a normal MR hysteresis and the resistance (R) always reaches its maximum ($R_{MAX}$) after the field reversal. However, for the composites with $x \neq 0$, MR$_i$ differs from MR$_p$ not only in magnitude but also in the sweeping manner. While MR$_i$ shows the normal hysteresis, MR$_p$ shows an abnormal hysteresis, i.e., R reaches $R_{MAX}$ before the field reversal, as indicated by the arrows in Fig. 4(a).

Here, we note that two factors are necessary to induce an abnormal MR hysteresis: (1) A hard magnet (BaM) and a soft magnet (LSMO) were include in the system. (2) The external field is applied in a MR$_i$ configuration, where a large demagnetization field is expected. These suggest that the abnormal MR$_i$ hysteresis originates from a coplay of the magnetic coupling and the demagnetization effect. Figure 5 presents the reduced magnetic hysteresis. For pure LSMO, the demagnetization effect is large and the magnetic easy axis is in plane. For pure BaM, the demagnetization effect is negligible due to the large $H_{c,BaM}$. For the composite, the effect is in between. Based on the magnetic data, the abnormal MR hysteresis can be interpreted as below. Taking $x = 0.5$ as an example, we analyze R sweeping from point A to point D as shown in Fig. 4(a). The corresponding spin states are illustrated in Fig. 4(b). Due to the exchange coupling, part of the LSMO spins are pinned by the neighboring BaM spins. At point A, the external field $H$ is large enough and all pins are aligned. When $H$ decreases from A to B, the free LSMO spins tend to rearrange themselves in plane due to the demagnetization effect. However, the pinned LSMO spins still tend to be out of plane due to the pining of the high coercive BaM spins. Therefore, the angle between the pinned and the free LSMO spins, $\theta_{pf}$, increases with decreasing $H$, resulting in $R$ increasing. At point B, $\theta_{pf}$ reaches its maxi-
mum and a \( R_{\text{MAX}} \) is shown. When \( H \) further decreases from B to C, \( \theta_{\text{pf}} \) and \( R \) decrease again. When \( H \) reversibly increases from C to D, \( \theta_{\text{pf}} \) will be small at all times due to that it is hard to align both the BaM and the LSMO spins in this field configuration. Therefore, \( R \) smoothly decreases as \( H \) aligns the spins inside the grains. Similar things repeat when \( H \) sweep again. Furthermore, since \( \theta_{\text{pf}} \) is responsible for the MR response, it is not surprising that the MR loops for the composites are widened. Since the ferromagnetic spin clusters exist at point B, \( R_{\text{MAX}} \) is lower for the MR\(_{\uparrow}\) loops. It is worth noting that a similar MR\(_{\downarrow}\) hysteresis was also recorded in LSMO thin films on laser-patterned SrTiO\(_3\) substrates.\(^9\) The reason can be attributed to the process producing some magnetic hard phases in the films. In this sense, the observation of the abnormal MR hysteresis might well be an indication of the magnetic inhomogeneity in a manganite system from an application point of view.

To confirm the role of the demagnetization field, we need to prove that the abnormal MR hysteresis cannot be induced by solely a \( \mathbf{H} \parallel \mathbf{I} \) configuration without a large demagnetization field. A short-cylinder-shaped sample 8 mm in diameter and 0.5 mm in thickness was made for \( x = 0.3 \). The electrodes were connected as shown in Fig. 6. Here, the current flows mostly along one direction as indicated by the arrow. A normal MR hysteresis was observed when \( \mathbf{H} \parallel \mathbf{I} \). This confirms that the demagnetization effect is indispensable in inducing the abnormal MR hysteresis. On the other hand, one also notes that MR\(_i\) and MR\(_\downarrow\) are still different even after excluding the demagnetization factors. This clearly indicates that AMR exists for the samples.

**D. Anisotropic magnetoresistance (AMR)**

The angular dependence of \( R \) was measured at different in-plane magnetic fields. For \( x = 0.3 \), the reduced resistivity \( \rho / \rho(\theta = 0) \) is plotted against \( \theta \) as an inset of Fig. 7. Here, \( \theta \) denotes the angle between \( \mathbf{H} \) and \( \mathbf{I} \). It is shown that \( \rho / \rho(\theta = 0) \) varies periodically with \( \theta \), and the variation decreases in magnitude with increasing \( H \). Using the definition
AMR=2[ρ(90)−ρ(0)]/[ρ(90)+ρ(0)],

(1)

de the calculated AMR values are shown in Fig. 7. The AMR value decreases with increasing BaM content, especially when H is small.

According to previous studies, AMR in manganites is composed of an intrinsic part and an extrinsic part. The intrinsic AMR originating from atomic band splitting is normally neglected due to its small value (~0.2%). Therefore, only extrinsic AMR is considered here. For the oriented artificial GBs, Evetts et al. had proposed that the extrinsic AMR originates from the difference in the GB magnetization when the GB spin states when H||I for LSMO, (c) the GB spin states when H||I for LSMO, (d) the GB spin states when H||I for LSMO, (e) the GB spin states when H||I for LSMO.

\[ M_{GB} = \chi_{GB}[H+H_{LEF}(\theta)], \]

(2)

where \( \chi_{GB} \) is the GB spin susceptibility, \( H_{LEF}(\theta) \) represent the local effective field (LEF) on GBs from the neighboring magnetic grains, \( f(\theta) \) is a geometric factor, and \( M_G \) is the saturation magnetization of the grains. The magnitude of the AMR is directly related to the changes in \( H_{LEF} \) for different field configurations, namely,

\[ \text{AMR} \sim \Delta H_{LEF}(\theta). \]

(3)

For a bulk sample, the GBs are randomly distributed. However, the effective GBs are still well oriented because only the GBs that are vertical to the current direction are effective for charge carrier scattering. These effective GBs are comparable to the oriented artificial GBs, as illustrated in Fig. 8(a). Therefore, Eqs. (2) and (3) are still applicable to the samples discussed here. The changes in \( H_{LEF} \) for the samples are illustrated in Figs. 8(b)–8(e). For simplicity, only one representative GB is shown. For pure LSMO, when H||I [Fig. 8(b)], \( H_{LEF}(\theta=0) \) between the magnetic poles of neighboring grains is large, resulting in a good alignment of GB spins and lower resistivity; when H||I [Fig. 8(c)], \( H_{LEF}(\theta=90) \) between the sidewall of the magnetic domains is small, resulting in a bad alignment of the GB spins and higher resistivity. The large AMR effect reflects a large \( \Delta H_{LEF}(\theta) = [H_{LEF}(0) - H_{LEF}(90)] \) in LSMO for the LSMO1_,_,BaM, when H||I [Fig. 8(d)], since the magnetic flux lines are strayed by randomly distributed hard BaM grains, \( H_{LEF}(\theta=0) \) is lowered and the GB spins less aligned; when H||I [Fig. 8(e)], the \( H_{LEF}(\theta=90) \) between the sidewalls remains small. Finally, \( \Delta H_{LEF}(\theta) \) decreases and the AMR effect is reduced for the composites.

IV. CONCLUSIONS

In summary, we have processed a series of two-phase mixed LSMO1_,_,BaM composites and investigated in detail their magnetic and magnetoresistive properties. The significant effects of the magnetic coupling on the MR properties have been identified. The low-field MR sensitivity was reduced and the high-field MR slope was enhanced by adding BaM, which is in contrast to previous reports that the low-
field MR was enhanced in a LSMO$_{1-x}$CF$_x$ composite. This clearly indicates that the soft/hard magnetic coupling itself is not enough to cause a MR enhancement. It seems that a certain microstructure, such as in the reported LSMO$_{1-x}$CF$_x$ composites, where the grain size of the hard magnet insulator is much larger than that of the soft magnet metal, is needed to enhance the low-field MR. On the other hand, an abnormal MR hysteresis was observed for the composite when the field is applied vertical to the sample plane. The origin of this abnormal MR hysteresis can be attributed to a coplay of the LSMO/BaM spin coupling and the demagnetization effect. From an application point of view, this suggests that detection of the abnormal hysteresis might well be an indication of the magnetic inhomogeneity in a manganite system. Finally, an AMR effect was observed for those composites. The AMR value decreased with increasing BaM content, which can be understood by the decreased angular dependence of the local effective field on the GBs. Or, in other words, our results support the argument that the extrinsic AMR in polycrystalline manganites originates from the local effective field on the GBs.