Unusual resistivity hysteresis in a bulk magnetoresistive ferromagnetic/ferrimagnetic composite ($La_{0.7}Ca_{0.3}MnO_3/Mn_3O_4$): Role of demagnetization effects

B. Vertruyen,[a] R. Cloots, M. Ausloos, J.-F. Fagnard, and Ph. Vanderbemden
SUPRATECS, University of Liege, Sart-Tilman, B-4000 Liege, Belgium

(Received 10 May 2007; accepted 16 July 2007; published online 8 August 2007)

The authors report an intriguing resistivity versus magnetic field dependence in polycrystalline composite samples containing a magnetoresistive manganite (ferromagnetic/conducting $La_{0.7}Ca_{0.3}MnO_3$) and a magnetic manganese oxide (ferrimagnetic/insulating Mn_3O_4). At 10 K, when the magnetic field is scanned from positive to negative values, the resistance peak occurs at positive magnetic field, instead of zero or negative field as usually observed in polycrystalline manganite samples. The position of the resistance peak agrees well with the cancellation of the internal magnetic field, suggesting that the demagnetization effects are responsible for this behavior. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768883]

Due to the numerous applications of magnetoresistance properties, the magnetic field dependence of the electrical resistivity of magnetoresistive manganites has been scrutinized by many researchers.[1–5] The double exchange mechanism[3] predicts that the resistivity should be maximum when the magnetic disorder is maximum, i.e., when the magnetization is zero, either at zero applied magnetic field (material with reversible magnetic properties) or at the coercive field (material with hysteretic magnetic properties). In the case of *polycrystalline* manganites, the main source of magnetic disorder is located at the grain boundaries, whose resistance depends strongly on the angle between the magnetization of the neighboring grains.[3] The resulting "low-field magnetoresistance" has attracted much interest[1–5] and several groups[6–8] have shown that it is possible to enhance this effect by preparing composites of a magnetoresistive manganite phase and an insulating secondary phase, where the insulating phase acts as an additional barrier to the conduction at the grain boundaries and lengthens the percolating conduction path.

In this letter, we report an intriguing resistivity versus magnetic field dependence in a composite sample containing a mixture of conducting $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and insulating Mn_3O_4. Below ~42 K, LCMO is a soft ferromagnet whereas Mn_3O_4 is a hard ferrimagnet due to a strong magnetocrystalline anisotropy.[9] When the magnetic field is scanned from positive to negative values, the resistance peak of the composite occurs at positive magnetic field, instead of zero or negative field as usually observed in single phase polycrystalline manganite samples.[10,11] It is important to stress that the behavior described here concerns *polycrystalline* materials, whose magnetoresistance at low temperature stems from grain boundary effects. Therefore the considerations discussed here do not apply to *single-crystalline* epitaxial thin films,[12,13] where resistivity maxima at $H \neq 0$ may occur due to tensile/compressive strain and anisotropic magnetoresistance.

The synthesis and characterization of $La_{0.7}Ca_{0.3}MnO_3/Mn_3O_4$ composites have been reported elsewhere.[14] The one-step spray drying synthesis followed by a long heat treatment at 1300 °C leads to the formation of dense samples containing Mn_3O_4 and a LCMO manganite phase, whose stoichiometry is close to $La_{0.7}Ca_{0.3}MnO_3$. The data reported here are for a $1.1 \times 1.1 \times 5.5$ mm^3 prism containing 20 vol % LCMO, 60 vol % Mn_3O_4, and 20 vol % porosity. The LCMO content is just above the percolation threshold Φ_c ($\Phi_c \sim 19$ vol % LCMO).[14] Composites containing smaller amounts of Mn_3O_4 display less marked but qualitatively similar results (not shown).

The magnetic moment and the electrical resistance were measured in a physical property measurement system (PPMS) from Quantum Design. The electrical resistance was measured by the conventional four-point technique. Unless otherwise stated, the magnetic field was perpendicular to the largest face of the sample and increased by 5 mT steps in "persistent, no overshoot" mode. Before each measuring sequence the remnant field of the superconducting magnet was eliminated by applying a succession of decreasing fields in alternate directions and the sample was demagnetized by heating it above its Curie temperature ($T_C \sim 245$ K). The sample was then cooled in zero field. The reliability of the magnetic field measurement by the PPMS was ascertained by measuring the voltage across a Hall probe through a magnetic field cycle: a strictly anhysteretic linear dependence was observed.

Figure 1(a) shows the behavior of the 10 K resistivity when the applied field $\mu_0 H_a$ is cycled between +2 and −2 T. Data corresponding to scans from $+H$ to $-H$ ($-H$ to $+H$) are plotted as lines with full (empty) symbols. Data corresponding to the first magnetization curve (0 to $+H$) are not shown. Starting from the low-resistance state at positive magnetic field, the resistance increases when the magnetic field decreases and reaches a maximum value for a slightly positive field (68 mT). When the field is scanned from negative to positive values, a similar dependence is observed, with a resistance peak occurring for a slightly negative magnetic field (−68 mT). The resistivity follows the same hysteresis curve under further cycling. Figure 1(b) presents the corresponding magnetization versus $\mu_0 H_a$ curve at 10 K. The $M(H)$ plot exhibits a large hysteresis ($\mu_0 H_c \sim 0.15$ T) with some wasp-waist character, as expected[15] for a mixture of a

[a]Electronic mail: b.vertruyen@ulg.ac.be

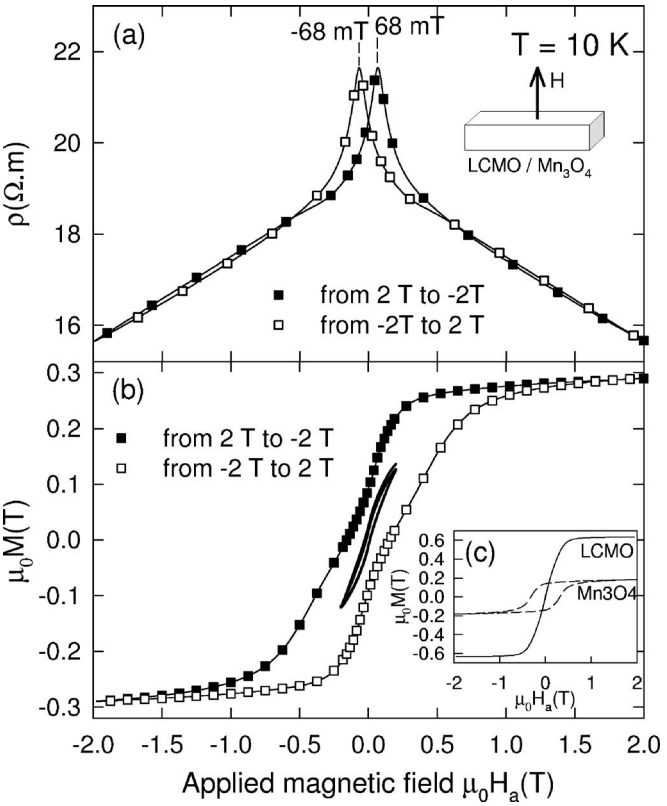

FIG. 1. (a) Magnetic field dependence of the resistivity of the composite sample at 10 K when $\mu_0 H_a$ is cycled between 2 and −2 T. (b) Magnetic field dependence of the magnetization at 10 K when $\mu_0 H_a$ is cycled between 2 and −2 T (line with symbols) or between 0.2 and −0.2 T (thick line). (c) Magnetic field dependence of the magnetization at 10 K for pure LCMO and pure Mn_3O_4.

magnetic hard phase (Mn_3O_4) and a magnetic soft phase (LCMO). For comparison, the $M(H)$ data for pure LCMO and pure Mn_3O_4 are shown in Fig. 1(c).

Similar experiments (not shown) were carried out (i) at 10 K for several values of maximum applied magnetic field ($H_{a,\max}$) and (ii) at several temperatures with $\mu_0 H_{a,\max}=2$ T. Up to the ferrimagnetic transition temperature (T_C) of the Mn_3O_4 phase (~42 K),[9] the results are qualitatively similar to those of Fig. 1(a). However, just below $T_C(Mn_3O_4)$ or for $\mu_0 H_{a,\max} \leqslant 0.5$ T, the first $+H \rightarrow -H$ scan differs noticeably from the following scans. Above $T_C(Mn_3O_4)$, the "usual" hysteresis behavior (i.e., maximum resistivity occurring at a negative magnetic field for the $+H$ to $-H$ scan) is recovered.

Figure 2 shows that the position of the resistivity maximum is shifted to smaller magnetic fields when $H_{a,\max}$ is decreased at 10 K. The agreement with the dependence of the magnetization at the resistivity maximum versus $H_{a,\max}$ (dotted line) is very good, except for the lowest $\mu_0 H_{a,\max}$ (0.2 T), i.e., when the sample is cycled well below magnetic saturation [see bold line in Fig. 1(b)]. Figure 3 shows that the position of the resistivity maximum is shifted to smaller magnetic fields when the temperature approaches $T_C(Mn_3O_4)$. Again the agreement with the dependence of the magnetization at the resistivity maximum versus temperature (dotted line) is rather good.

All data reported above are for an applied magnetic field perpendicular to the long axis of the sample. When the magnetic field is applied along the long axis of the sample, the $\rho(H)$ curve (not shown) is similar to the behavior depicted in

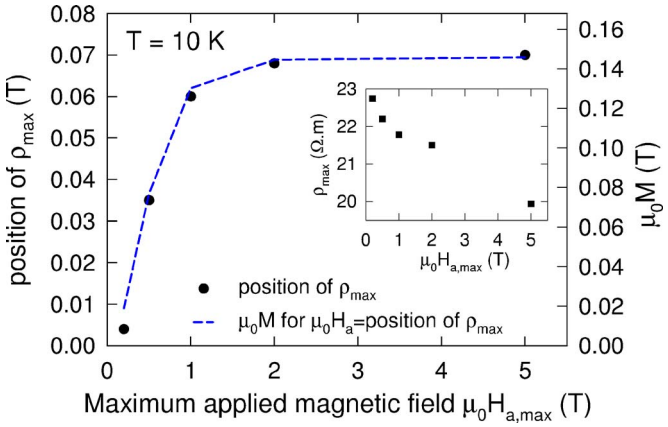

FIG. 2. (Color online) Position of the resistivity maximum (symbols) and corresponding magnetization value (dotted line) as a function of the maximum applied magnetic field at 10 K when the applied magnetic field is scanned from $+H_{a,\max}$ to $-H_{a,\max}$. Inset: resistivity at the resistivity maximum as a function of $H_{a,\max}$ at 10 K.

Fig. 1, but the resistivity maxima occur at smaller applied fields (e.g., ~5 mT instead of ~68 mT at 10 K and $\mu_0 H_{a,\max}=2$ T). This points to the demagnetization effects resulting from the shape anisotropy of the sample.[6,10] Figure 4(a) compares the demagnetizing field DM with the applied field H_a. The average demagnetizing factor $D \sim 0.46$ has been taken from the work of Aharoni for rectangular prisms.[16] The intersection of the two curves [labeled $\mu_0 H^*$ in Fig. 4(a)] corresponds to the cancellation of the internal magnetic field H_i (where $H_i=H_a-DM$). Figure 4(b) shows that $\mu_0 H^*$ is very close to the position of the resistivity maximum, except for the highest temperature (40 K) and lowest $\mu_0 H_{a,\max}$ (0.2 T).

These results suggest that the resistivity maxima occur for zero internal magnetic field. It is possible to propose an explanation that reconciles this observation with the usual idea that the resistivity maximum in $\rho(H)$ occurs for zero magnetization of the manganite phase. Contrary to the magnetization, which results from both ferromagnetic LCMO and ferrimagnetic Mn_3O_4 contributions, the electrical current percolates through the conducting LCMO phase only and avoids the highly insulating Mn_3O_4 phase.[14] Therefore the electrical resistance can be viewed as a probe of the magnetic order in the LCMO phase. If we assume that, at the resistivity maximum, the magnetization of the composite is due to

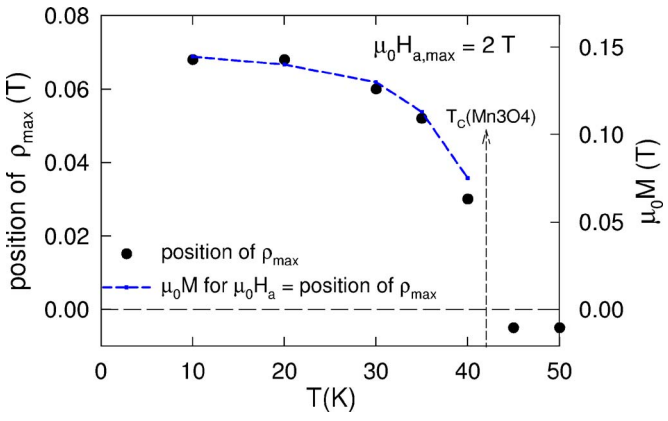

FIG. 3. (Color online) Position of the resistivity maximum (symbols) and corresponding magnetization value (dotted line) as a function of temperature when $\mu_0 H_a$ is scanned from 2 to −2 T.

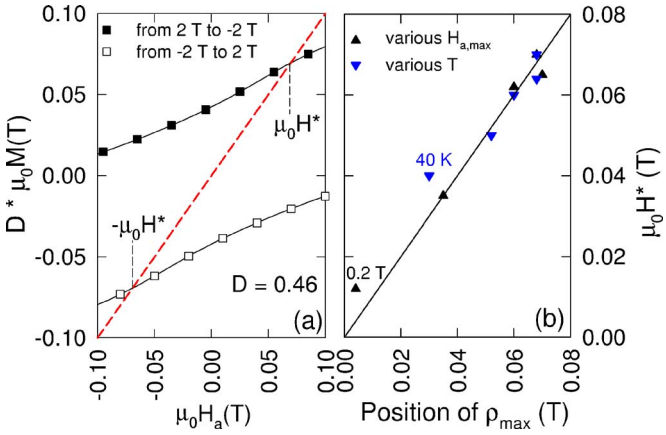

FIG. 4. (Color online) (a) Magnetization multiplied by the bulk demagnetization factor (D=0.46) as a function of $\mu_0 H_a$ (lines with symbols). $\mu_0 H_a$ is presented in the same scale (dashed line). Intersections occur at $+\mu_0 H^*$ and $-\mu_0 H^*$. (b) $\mu_0 H^*$ vs position of the resistivity maximum for various maximum applied magnetic fields at 10 K (▲) or for various temperatures with 2 T maximum applied magnetic field (▼). The straight line corresponds to $\mu_0 H^*$=position of the resistivity maximum.

the Mn_3O_4 phase only [because Mn_3O_4 is a magnetic hard phase, see Fig. 1(c)], then the demagnetizing field of the Mn_3O_4 phase cancels the applied field in the LCMO phase and the magnetization of the LCMO phase is zero at the resistivity maximum.

It is astonishing that such a simple model of the composite works so well, considering that the demagnetizing field in nonellipsoidal samples is not uniform, i.e., the D value results from an averaging of the local fields.[16] The actual magnetic field distribution is even more complex in the case of the present composite sample, which contains two phases with quite different magnetic properties. Therefore it is probably more realistic to rephrase the above statement to say that the resistivity maximum occurs when the applied magnetic field and the demagnetizing field are of the same order of magnitude, resulting in a maximum magnetic disorder in the manganite phase. As can be seen in the inset of Fig. 2, the peak resistivity value decreases when $\mu_0 H_{a,\max}$ increases. This suggests that the domain distribution in the LCMO phase at the resistivity peak is less fragmented after the composite has been subjected to a large applied field.[17] This phenomenon can be due to the microscopic distribution of domains in each phase: a large maximum applied field leads to a large remnant magnetization of the Mn_3O_4 phase, and therefore to a large average domain size of Mn_3O_4.

In conclusion, we have shown that an unusual resistivity behavior occurs in composites containing both a ferromagnetic magnetoresistive phase and a ferrimagnetic hard phase (Mn_3O_4). This phenomenon appears to be related to local demagnetization effects, although some influence of other mechanisms (such as magnetostriction[18,19]) cannot be ruled out. We believe that these observations concerning polycrystalline LCMO/Mn_3O_4 composites may have wider application in the case of other systems containing a mixture of magnetic phases. Finally, we would like to emphasize the importance of explicitly identifying the field scan directions when reporting hysteresis curves, in order to allow easier comparison between data sets if unusual results are subsequently obtained.

One of the authors (B.V.) thanks the FNRS (Belgium) for a postdoctoral researcher fellowship. Part of this work was supported by the European Network of Excellence FAME.

[1] Ph. Vanderbemden, B. Vertruyen, A. Rulmont, R. Cloots, G. Dhalenne, and M. Ausloos, Phys. Rev. B **68**, 224418 (2003).
[2] B. Vertruyen, R. Cloots, A. Rulmont, G. Dhalenne, M. Ausloos, and Ph. Vanderbemden, J. Appl. Phys. **90**, 5692 (2001).
[3] J. M. D. Coey, M. Viret, and S. von Molnar, Adv. Phys. **48**, 167 (1999).
[4] M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).
[5] A. Gupta and J. Z. Sun, J. Magn. Magn. Mater. **200**, 24 (1999).
[6] S. Valencia, O. Castaño, J. Fontcuberta, B. Martínez, and Ll. Balcells, J. Appl. Phys. **94**, 2524 (2003).
[7] L. E. Hueso, J. Rivas, F. Rivadulla, and M. A. Lopez-Quintela, J. Appl. Phys. **89**, 1746 (2001).
[8] D. K. Petrov, L. Krusin-Elbaum, J. Z. Sun, C. Feild, and P. R. Duncombe, Appl. Phys. Lett. **75**, 995 (1999).
[9] K. Dwight and N. Menyuk, Phys. Rev. **119**, 1470 (1960).
[10] B. Vertruyen, A. Rulmont, R. Cloots, J.-F. Fagnard, M. Ausloos, I. Vandriessche, and S. Hoste, J. Mater. Sci. **40**, 117 (2005).
[11] X. W. Li, A. Gupta, G. Xiao, and G. Q. Gong, Appl. Phys. Lett. **71**, 1124 (1997).
[12] J. N. Eckstein, I. Bozovic, J. O'Donnell, M. Onellion, and M. S. Rzchowski, Appl. Phys. Lett. **69**, 1312 (1996).
[13] H. S. Wang, Q. Li, K. Liu, and C. L. Chien, Appl. Phys. Lett. **74**, 2212 (1999).
[14] B. Vertruyen, R. Cloots, M. Ausloos, J.-F. Fagnard, and Ph. Vanderbemden, Phys. Rev. B **75**, 165112 (2007).
[15] J. D. Livingtson, A. E. Berkowitz, and J. L. Walter, IEEE Trans. Magn. **15**, 1295 (1979).
[16] A. Aharoni, J. Appl. Phys. **83**, 3432 (1998).
[17] J. E. Evetts, M. G. Blamire, N. D. Mathur, S. P. Isaac, B. S. Teo, L. F. Cohen, and J. L. MacManus-Driscoll, Philos. Trans. R. Soc. London, Ser. A **356**, 1593 (1998).
[18] T. Suzuki, K. Adachi, and T. Katsufuji, J. Magn. Magn. Mater. **310**, 780 (2007).
[19] H. Szymczak, J. Magn. Magn. Mater. **210**, 186 (2000).