Extrinsic magnetoresistance and resistance relaxation in $La_{0.7}Ca_{0.3}MnO_3$ and Fe_3O_4 films and heterostructures

LETTER TO THE EDITOR

Extrinsic magnetoresistance and resistance relaxation in $La_{0.7}Ca_{0.3}MnO_3$ and Fe_3O_4 films and heterostructures

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Abstract. The magnetoresistance and resistance relaxation after a discontinuous field change of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and Fe_3O_4 thin film structures was investigated. We compare the magnetoresistance and resistance relaxation of epitaxial films, polycrystalline films, mechanically induced grain boundaries and heterostructures in current-perpendicular-to-plane geometry. We show that the low-field magnetoresistance of various LCMO structures containing strongly scattering interfaces is significantly larger than the intrinsic magnetoresistance of epitaxial LCMO films. On the other hand, the corresponding structures made from magnetite (Fe_3O_4) show only a small enhancement of the magnetoresistance compared with epitaxial films. The resistance relaxation of the LCMO heterostructures is found to increase with increasing magnetoresistance, whereas no relaxation was observed in the Fe_3O_4 heterostructures. We propose that the extrinsic magnetoresistance in LCMO structures is due to the formation of a spin-glass-like state at highly resistive interfaces.

Recent research activity has focussed on the transport properties of the ferro- and ferrimagnets $La_{0.7}A_{0.3}MnO_3$ (A = Ca, Sr, Ba, Pb), CrO_2 and Fe_3O_4 in view of potential applications. These materials are half-metallic and therefore ideal candidates for an emerging oxide spin-electronics. Whereas the intrinsic magnetoresistance of these compounds is small in moderate magnetic fields of the order of a few hundred Gauss, the extrinsic low-field magnetoresistance of various structures is large. So far the magnetoresistance of tunnel junctions [1–3], ramp-edge junctions [4], single grain boundaries [5–7], mechanically induced grain boundaries [8], step-edge arrays [9], ceramic materials [10, 11], powder compacts [12–14], polycrystalline films [15–18], and metal/ferromagnet/metal structures in current-perpendicular-to-plane (CPP) geometry [19] has been investigated. It is generally believed [1–3, 10, 12–14] that the extrinsic magnetoresistance is due to spin-polarized tunnelling through an insulating, nonmagnetic barrier. However, other explanations involving micromagnetic effects [5] and domain wall scattering [15, 20] have been proposed.

In this letter we show that the extrinsic magnetoresistance of LCMO and Fe_3O_4 structures is quite different in magnitude and is not determined by the half-metallicity alone, but is related to the specific magnetic exchange interactions and the electronic interface states. We observed that the low-field magnetoresistance of LCMO heterostructures is much larger than the magnetoresistance of the corresponding Fe_3O_4 structures. The resistance relaxation of LCMO heterostructures was found to be proportional to the low-field magnetoresistance providing evidence that it is related to interface scattering. No

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resistance relaxation could be detected in the Fe_3O_4 structures. Resistance relaxation in LCMO films was first investigated by von Helmolt *et al* [21]. A large relaxation was observed and discussed in terms of spin-glass properties and magnetic viscosity. However, as demonstrated by the resistance and magnetization transitions, the investigated film was of poor quality and it is unclear whether the resistance relaxation was due to bulk or interface properties.
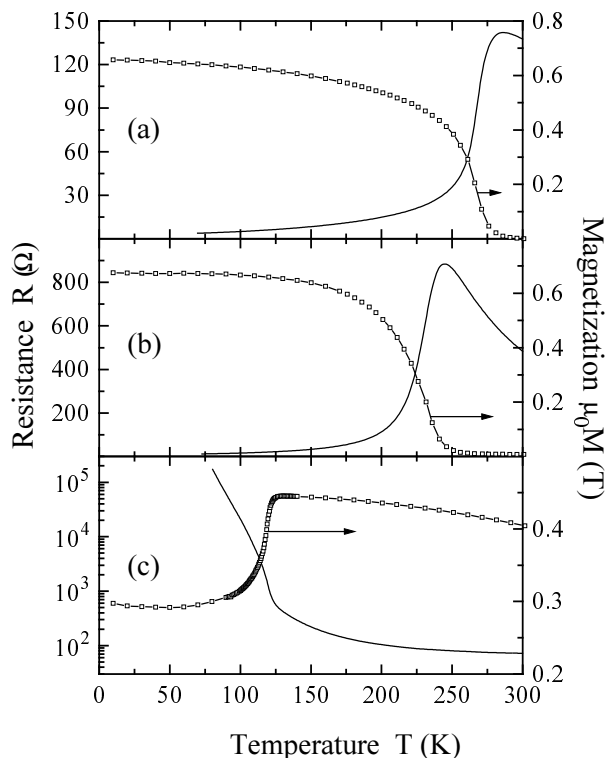

Figure 1. Resistance (left axis) and magnetization (right axis) of (a) a 250 nm thin post-annealed LCMO film on LSAT, (b) a 120 nm thin as-deposited LCMO film on $LaAlO_3$ and (c) a 200 nm thin Fe_3O_4 film on MgO.

The magnetic films were deposited from stoichiometric ceramic targets using pulsed laser ablation at a wavelength of 308 nm (XeCl). During deposition the substrate temperature was held constant at about 650 °C and the oxygen pressure was stabilized at 100 mTorr for the LCMO films. For the magnetite films the substrate temperature was about 400 °C and the chamber pressure was below 2×10^{-5} Torr. Epitaxial LCMO films of various thicknesses have been grown on $LaAlO_3$ (001) and $(LaAlO_3)_{0.3}$–$(Sr_2AlTaO_6)_{0.7}$ (LSAT) (001) [22], and epitaxial Fe_3O_4 films have been grown on MgO (001) [23]. Figure 1 shows the zero field resistance and magnetization in 1 kG of (a) an annealed LCMO film on LSAT, (b) an as-deposited LCMO film on $LaAlO_3$ and (c) a Fe_3O_4 film on MgO. The sharpness of the transition demonstrates the high quality of our samples. As-deposited epitaxial and polycrystalline films show the same magnetization behaviour, but transport characteristics strongly depend on the microstructure. This proves that the differences in the magnetoresistance arise from defect scattering.

[100] grain boundaries in LCMO and Fe_3O_4 films were formed simply by scratching the

substrates prior to deposition with a commercially available diamond needle [8]. The films deposited on the scratched substrates are about 15 nm (LCMO) and 10–25 nm (Fe_3O_4) thin, and the deformed region is about 50 μm wide and about 500 nm deep. Polycrystalline films were deposited on Si(001) substrates. The Ti/LCMO/Ti, Ti/Ni/LCMO/Ti and Cr/Fe_3O_4/Cr CPP-devices were fabricated as described in [19]. The effective contact area of the CPP structures is 37 μm $\times$ 37 μm for the LCMO devices and 100 μm $\times$ 100 μm for the Fe_3O_4 device, respectively. The LCMO and Fe_3O_4 layers in the CPP structures have a thickness of about 100 nm. Resistance measurements were performed in a continuous flow cryostat (Oxford Instruments) using a standard four-point technique for the current-in-plane (CIP) samples and a two-point technique for the CPP devices. Magnetization measurements were carried out in a SQUID magnetometer (Quantum Design, MPMS-5). The magnetic field H was applied parallel to the magnetic films; the mechanically induced grain boundaries were measured with the in-plane field applied perpendicular to the grain boundary. The CIP devices were measured in longitudinal geometry; for the epitaxial films both longitudinal as well as transverse geometry were measured to study the anisotropic magnetoresistance. The CPP devices were measured in transverse geometry.

The magnetoresistance

$$\Delta R/R_0 = \frac{R(H) - R_0}{R_0} \tag{1}$$

of an epitaxial film on $LaAlO_3$, a mechanically induced grain boundary on $LaAlO_3$, a polycrystalline film on Si and a CPP Ti/Ni/LCMO/Ti heterostructure is shown as a function of magnetic field at 100 K in figures 2(a)–(d). R_0 denotes the resistance in zero applied field. The Curie temperatures are 275.2 K for the post-annealed epitaxial film and about 230 K for the other as-deposited LCMO films. Whereas the epitaxial film has only a small magnetoresistance below 0.3% that is clearly due to the anisotropic magnetoresistance [18], the magnetoresistance of the grain boundary as well as the polycrystalline film reaches an appreciable 10% in a field of 1 kG. The magnetoresistance of the CPP device is even larger with a value of 20% in 1 kG.

Figures 2(e)–(h) show the magnetoresistance of the corresponding Fe_3O_4 structures at room temperature: an epitaxial film on MgO, a grain boundary on MgO, a polycrystalline film on Si and a Cr/Fe_3O_4/Cr multilayer in CPP configuration. The Verwey temperatures measured magnetically in a magnetic field of 1 kG are 118.7 K for the epitaxial film on MgO, 122.7 K for the polycrystalline film on Si and 109.2 K for the film on the scratched substrate. These values indicate the high qualities of our films [23]. We do not find any significant effect of the mechanically induced grain boundary on the low-field magnetoresistance for magnetite films 10 nm and 25 nm thin. The polycrystalline film shows an enhanced low-field magnetoresistance, but $\Delta R/R_0$ at 2 kG and temperatures between 100 K and 300 K never exceeds 2.5%. Only a very small magnetoresistance could be detected in the CPP device. The small magnetoresistance values are especially surprising in view of the high Curie temperature, $T_C = 858$ K.

We investigated the time dependence of the resistance after a sudden field change from 1 T to the remanence field of the electromagnet of about 70 G. Figure 3(a) shows the resistive relaxation $\Delta R/R_{(t=15\ s)} - 1$ as a function of time for a post-annealed LCMO film on LSAT, a mechanically induced grain boundary and a Ti/Ni/LCMO/Ti heterostructure at 77 K. The relaxation is approximately logarithmic in time. We determined the relaxation rate

$$S = \frac{1}{R_{(t=15\ s)}} \frac{dR}{d\ln t} \tag{2}$$

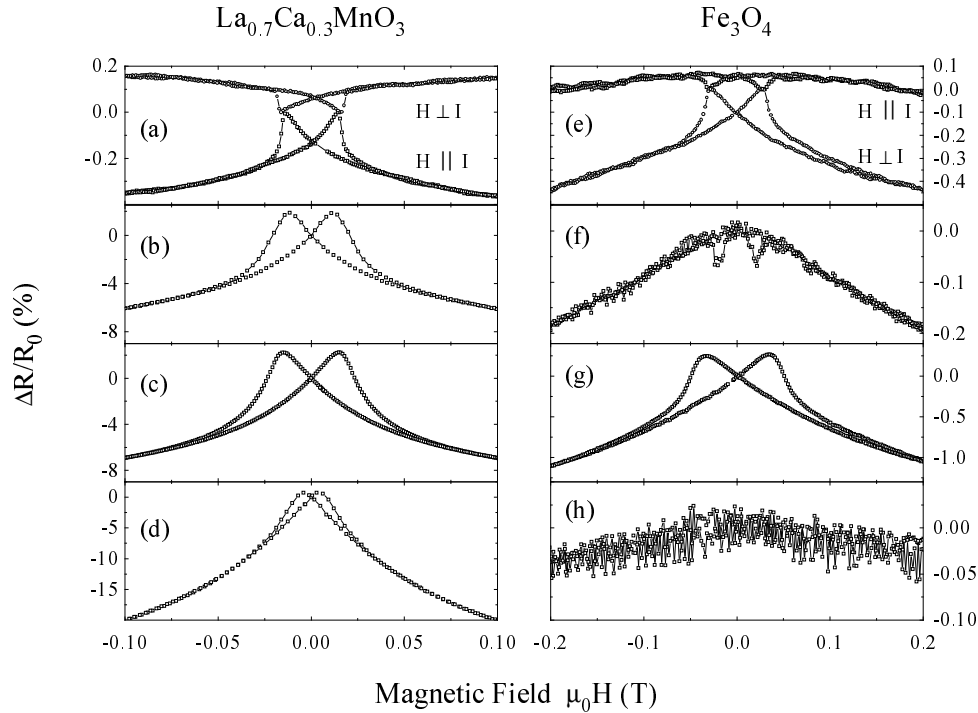$$La_{0.7}Ca_{0.3}MnO_3 \qquad\qquad Fe_3O_4$$

Figure 2. Magnetoresistance ratio $\Delta R/R_0$ at 100 K for (a) an epitaxial LCMO film of thickness 200 nm on $SrTiO_3$, (b) a grain boundary mechanically induced into a 15 nm thin LCMO film on $LaAlO_3$, (c) a polycrystalline LCMO film of thickness 200 nm on Si, and (d) a Ti/Ni/LCMO/Ti multilayer in CPP configuration. The reduced temperatures are $T/T_C \simeq 0.36$ for (a) and $T/T_C \simeq 0.43$ for (b)–(d), respectively. Magnetoresistance ratio $\Delta R/R_0$ at 295 K for (e) an epitaxial Fe_3O_4 film of thickness 200 nm on MgO, (f) a grain boundary mechanically induced into a 25 nm thin Fe_3O_4 film on MgO, (g) a polycrystalline Fe_3O_4 film of thickness 200 nm on Si, and (h) a $Cr/Fe_3O_4/Cr$ multilayer in CPP configuration. The reduced temperature is $T/T_C \simeq 0.34$. For clarity the magnetoresistance of the epitaxial films is normalized by the value at $M = 0$.

and plot it in figure 3(b) versus the low field magnetoresistance $\Delta R_S/R_0$. $\Delta R_S/R_0$ was obtained by extrapolation of the linear high field ($0.5\ \mathrm{T} \leqslant \mu_0 H \leqslant 1\ \mathrm{T}$) magnetoresistance to zero to determine an effective zero-field resistance; $\Delta R_S/R_0$ was then calculated using this effective zero-field resistance, see [6, 14]. S is found to increase linearly with $\Delta R_S/R_0$; see solid line in figure 3(b). Since the magnetic properties of the LCMO films in the heterostructures are largely identical, spin-glass disorder at interfaces is more likely to explain the resistance relaxation than magnetic viscosity.

The resistance relaxation of Fe_3O_4 was measured above the Verwey temperature at 130 K. The average of eleven runs of short duration (about 10 min) yielded a relaxation rate $S = 0.0007 \pm 0.0080\%$ for the polycrystalline Fe_3O_4 film on Si. The low-field magnetoresistance of this sample at 130 K is $\Delta R_S/R_0 = 2.2\%$. From the LCMO results a relaxation rate $S = 0.02\%$ might be expected at that magnetoresistance level. The measured value is below this limit and indicates that the resistance relaxation and therefore the amount of disordered spins at the interfaces might be considerably smaller in Fe_3O_4 structures than in LCMO structures. Resistance relaxation in the epitaxial film and the mechanically
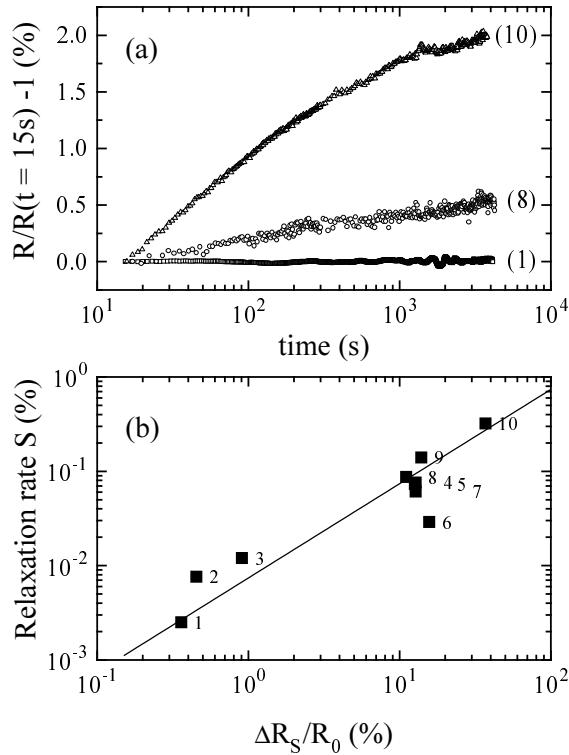
Figure 3. (a) Resistance relaxation after a sudden field change from 1 T to 70 G of (1) a post-annealed LCMO film on LSAT, (8) a mechanically induced grain boundary, and (10) a Ti/Ni/LCMO/Ti heterostructure. (b) Resistance relaxation S versus low-field magnetoresistance $\Delta R_S/R_0$ for various LCMO structures: (1) 250 nm thin post-annealed film on LSAT, (2) 120 nm thin as-deposited film on LaAlO$_3$, (3) 20 nm thin as-deposited film on LaAlO$_3$, (4) post-annealed film on Si, (5) as-deposited film on Si, (6) as-deposited film on MgO, (7) step-edge array, (8) mechanically induced grain boundary, (9) Ti/LCMO/Ti heterostructure, (10) Ti/Ni/LCMO/Ti heterostructure. The solid line is a fit of a linear law $S \propto \Delta R_S/R_0$ to the data.

induced grain boundary was smaller than $S < 0.05\%$; however, this limit is too large to be significant.

The ferromagnet La$_{0.7}$Ca$_{0.3}$MnO$_3$ is obtained from the antiferromagnetic parent compound LaMnO$_3$ by hole doping. In the ferromagnetic state the ferromagnetic double-exchange interaction via Mn–O–Mn bonds dominates the antiferromagnetic superexchange interaction. However, if the double exchange interaction is weakened by straining or bending the Mn–O–Mn bond, the antiferromagnetic superexchange can become locally dominant and might lead to a spin-glass-like state. We suggest that the large low-field magnetoresistance observed in our LCMO structures is mainly due to the suppression of magnetic frustration at interfaces by the application of a magnetic field. Since the transport and magnetic properties of LCMO are intimately connected via the double exchange interaction, a strong decrease of the spin scattering results.

The anomalous magnetic properties of epitaxial Fe$_3$O$_4$ films [24] have been shown to result from disturbed exchange coupling across antiphase boundaries. Whereas the magnetization characteristics can be nicely understood using model calculations, the effect of spin disorder on the transport properties of magnetite is less clear. Our results indicate

that the magnetoresistance of Fe_3O_4 films is less influenced by spin disorder than the low-field magnetoresistance in LCMO structures. However, this issue clearly warrants more study.

In summary, we have studied various structures fabricated with the half-metallic ferromagnet $La_{0.7}Ca_{0.3}MnO_3$ and the half-metallic ferrimagnet Fe_3O_4. Whereas a significant low-field magnetoresistance can easily be induced in LCMO structures, the magnetoresistance of Fe_3O_4 devices at 2 kG in the temperature range $100\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$ does not exceed 2.5%. For LCMO the resistance relaxation rate is found to be proportional to the low-field magnetoresistance. We suggest that the large low-field magnetoresistance in LCMO is due to the suppression of a spin-glass-like state at interfaces by the magnetic field.

References

[1] Sun J Z, Gallagher W J, Duncombe P R, Krusin-Elbaum L, Altman R A, Gupta A, Yu Lu, Gong G Q and Gang Xiao 1998 *Appl. Phys. Lett.* **69** 3266
[2] Yu Lu, Li X W, Gong G Q, Gang Xiao, Gupta A, Lecour P, Sun J Z, Wang Y Y and Dravid V P 1996 *Phys. Rev.* B **54** R8357
[3] Viret M, Drouet M, Nassar J, Contour J, Fermon C and Fert A 1997 *Europhys. Lett.* **39** 545
[4] Kwon C, Jia Q X, Fan Y, Hundley M F, Reagor D W, Coulter J Y and Peterson D E 1998 *Appl. Phys. Lett.* **72** 486
[5] Mathur N D, Burnell G, Isaac S P, Jackson T J, Teo B S, MacManus-Driscoll J L, Cohen L F, Evetts J E, and Blamire M G 1997 *Nature* **387** 266
[6] Steenbeck K, Eick T, Kirsch K, O'Donnell K, and Steinbeiß E 1997 *Appl. Phys. Lett.* **71** 968
[7] Isaac S P, Mathur N D, Evetts J E, and Blamire M G 1998 *Appl. Phys. Lett.* **72** 2038
[8] Srinitiwarawong C and Ziese M 1998 *Appl. Phys. Lett.* **73** 1140
[9] Ziese M, Heydon G, Höhne R, Esquinazi P and Dienelt J 1998 to be published
[10] Hwang H Y, Cheong S-W, Ong N P and Batlogg B 1996 *Phys. Rev. Lett.* **77** 2041
[11] Balcells L L, Fontcuberta J, Martínez B and Obradors X 1998 *J. Phys.: Condens. Matter* **10** 1883
[12] Coey J M D, Berkowitz A E, Balcells L L, Putris F F and Parker F T, 1998 *Appl. Phys. Lett.* **72** 734
[13] Manoharan S S, Elefant D, Reiss G and Goodenough J B 1998 *Appl. Phys. Lett.* **72** 984
[14] Coey J M D, Berkowitz A E, Balcells L L, Putris F F and Barry A 1998 *Phys. Rev. Lett.* **80** 3815
[15] Gupta A, Gong G Q, Gang Xiao, Duncombe P R, Lecoeur P, Trouilloud P, Wang Y Y, Dravid V P and Sun J Z 1996 *Phys. Rev.* B **54** R15629
[16] Li X W, Gupta A, Gang Xiao and Gong G Q 1997 *Appl. Phys. Lett.* **71** 1124
[17] Gu J Y, Ogale S B, Rajeswari M, Venkatesan T, Ramesh R, Radmilovic V, Dahmen U, Thomas G and Noh T W 1998 *Appl. Phys. Lett.* **72** 1113
[18] Ziese M and Sena S P 1998 *J. Phys.: Condens. Matter* **10** 2727
[19] Ziese M, Sena S P, Shearwood C, Blythe H J, Gibbs M R J and Gehring G A 1998 *Phys. Rev.* B **57** 2963
[20] Gehring G A unpublished
[21] von Helmolt R, Wecker J, Lorenz T and Samwer K 1995 *Appl. Phys. Lett.* **67** 2093
[22] Ziese M unpublished
[23] Sena S P, Lindley R A, Blythe H J, Sauer C, Al Kafarji M and Gehring G A 1997 *J. Magn. Magn. Mater.* **176** 111
[24] Margulies D T, Parker F T, Rudee M L, Dpada F E, Chapman J N, Aitchison P R and Berkowitz A E 1997 *Phys. Rev. Lett.* **79** 5162.