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Magnetoresistive anisotropy and strain relaxation in oxygen deficient $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ films near the metal-insulator transition

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The magnetoresistance (MR) and the "out-of-plane" magnetoresitive anisotropy (AMR^{out}) peaks were measured in vacuum annealed $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ films across the metal-insulator transition. The measurements were performed for a very small increase in oxygen deficiency δ, which leads not only to an increase of resistivity but also to a decrease of the magnitude of both the AMR^{out} and MR peaks. The decrease of the MR and AMR^{out} peaks is attributed to the epitaxial strain relaxation resulting from thermal treatment. These properties could originate from the lattice strain in agreement with a recent model of strain-induced metal-insulator phase coexistence in manganites. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2199594]

The manganites $La_{1-x}Ca_xMnO_3$ have been considered as potential candidates for applications such as magnetic sensors and detectors because they exhibit colossal magnetoresistance (MR) close to the Curie temperature T_C. Studies of $La_{1-x}Ca_xMnO_3$ films of compositions within the range of $x = 0.30-0.35$ revealed that the "in-plane" anisotropic magnetoresistance (AMR) of these films show a maximum at temperatures near the metal-insulator transition, just below the MR peak.[1–4] The AMR is defined as $AMR = (\rho_\parallel - \rho_\perp)/\rho_0$, where $\rho_\parallel$ and $\rho_\perp$ are the resistivities of the film for a magnetic field in the plane of the film but oriented parallel and perpendicular to the current, respectively, and ρ_0 is the resistivity in zero field. The temperature dependence of the AMR in $La_{2/3}Ca_{1/3}MnO_3$ films is very different from that reported for the AMR in metallic ferromagnetic alloys. In the alloys, no maximum is observed; instead, the AMR decreases gradually and roughly linearly with increasing temperature, reaching zero at T_C.[5] The AMR effect observed in ferromagnetic alloys has been used in magnetoresistive read heads and nonvolatile magnetic random access memory. Implementation of similar applications based on colossal MR thin films requires, however, a better understanding of their anisotropic magnetoresistance at temperatures close to the metal-insulator transition (MIT). It has been well established that the AMR in ferromagnetic alloys originates from the spin-orbit interaction.[5] The origin of the anomalous AMR in $La_{2/3}Ca_{1/3}MnO_3$ films is, however, still not clear. It has been suggested by O'Donnell *et al.*[4] that the anomalous AMR peak could be caused by a local, spin-orbit induced, orbital deformation of the Mn *d* orbitals and O *p* orbitals during rotation of the magnetization. This orbital deformation influences the local hopping conduction process characteristic of manganites near MIT. Ziese[6] has pointed out that there is a correlation in these films between the AMR peak and the anomalous negative Hall resistivity (NHR) peak at temperatures close to MIT. Bibes *et al.*[7] studied these effects in more detail in a (110)-oriented thin film of $La_{2/3}Ca_{1/3}MnO_3$ by performing AMR and NHR measurements with the current along the $[001]$ and $[1\bar{1}0]$ directions. The amplitude of these two effects was found to be larger when the current was applied along the $[1\bar{1}0]$ direction. The authors of this work have suggested that this could be caused by an anisotropy in the spin-orbit interaction, due to Jahn-Teller distortion effects, either of intrinsic nature or related to residual anisotropic strains. Recent work by Ahn *et al.*[8] suggested that the metal insulator phase coexistence in manganites is strain-induced. In their model the phase with lattice distortions is insulating and that without lattice distortions is metallic. This implies that physical properties of manganites near the MIT could be lattice strain and phase separation dependent and raises questions regarding the true nature of the AMR and MR peaks in manganite films.

In $La_{1-x}Ca_xMnO_{3-\delta}$ films the main source of long-range lattice strains is the elastic misfit between the film and the substrate. These strains can be reduced by thermal treatment. Long-range lattice strains can be also induced in the film by oxygen deficiency. Oxygen outdiffusion produces vacancies and consequently a lattice distortion (expansion) due to the variation of the valence of Mn ions.[9] In addition, the resultant changes in Mn^{+3}/Mn^{+4} ratio cause a decrease of both T_C and the metal-insulator transition temperature T_p. Studies of the magnetoresistive anisotropy and magnetoresistance in oxygen deficient films could therefore be essential in revealing the effect of lattice strain on these properties.

In view of the recent theoretical work on strain-induced metal-insulator phase coexistence in manganites near the MIT mentioned above,[8] we carried out studies to address the following questions about the nature of the AMR and MR peaks in $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ films: (a) What is the effect of an increase in the oxygen deficiency δ on the magnitude and the temperature dependence of the AMR peak? (b) Is there any correlation between the AMR and MR peaks? (c) What is the mechanism responsible for the AMR peak at T_p and what is the role of the lattice strain in the formation of the AMR peak?

The magnetoresistive anisotropy peak at the MIT in $La_{2/3}Ca_{1/3}MnO_3$ films has also been observed for the "out-of-plane" configuration. Here, the AMR is defined as $AMR^{out} = (\rho_\parallel^{in} - \rho_\perp^{out})/\rho_0$, where $\rho_\parallel^{in}$ was measured for a magnetic field in the film plane and parallel to the transport current but $\rho_\perp^{out}$ was determined for a magnetic field perpendicular to both the film plane and the transport current direction.[10] Measurements of the out-of-plane anisotropy

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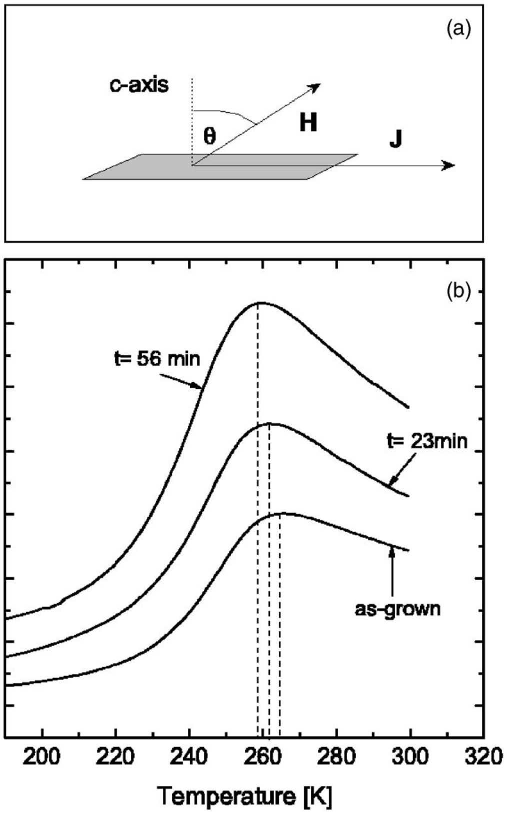

FIG. 1. (Color online) (a) Schematic of the experimental configuration used in this work. (b) Temperature dependence of resistivity at the metal-insulator transition measured in a zero magnetic field for $La_{0.65}Ca_{0.35}MnO_3$ film, as grown (optimally doped) and the same oxygen deficient film measured after annealing in vacuum for 23 and 56 min, respectively (see Table I). Vertical dashed lines mark the positions of the resistivity maxima.

could be more useful in some experiments than that of the in-plane one, since the former is almost independent of the crystallographic directions of the current flow. The measurements of the AMR in our letter are of AMR^{out}.

According to some authors[11] a clear AMR peak at T_p can only be found in high-quality epitaxial films. In our experiments epitaxial thin films of *c*-axis oriented $La_{0.65}Ca_{0.35}MnO_3$ (LCMO) were deposited by dc magnetron sputtering in an argon-oxygen mixture (of partial pressures 100 mTorr of oxygen and 20 mTorr of argon) at 750 °C on $LaAlO_3$ substrates which provide good lattice matching with the film. The films, which have a thickness of 100 nm, were subsequently annealed at 650 °C for 2 h in an oxygen at atmospheric pressure in order to ensure that the samples gained the optimum oxygen content and hence the maximum T_C. The *c*-axis orientation of the films was confirmed by x-ray diffraction. The films were patterned using standard lithography in the form of 60 μm wide bridges for four-probe resistivity measurements.

The resistivity ρ of the LCMO film was measured as a function of temperature and the angle θ between an applied magnetic field H and the c-axis direction. The experimental configuration is shown in Fig. 1(a). The magnetic field was rotated from $\theta=0°$ (out-of-plane magnetic field, where $H \| c$, $H \perp J$) to $\theta=90°$ (in-plane magnetic field, where $H \perp c$, $H \| J$). Using this arrangement, $\rho_\perp$, $\rho_\|$, and ρ_0 were measured for various films with different oxygen contents, and the AMR^{out} was calculated. Only small amounts of oxygen (δ up to 0.003) were removed from the film by vacuum annealing at temperatures up to 345 °C according to the annealing procedure listed in Table I.

Figure 1(b) shows the temperature dependence of the resistivity of $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ films measured in a zero magnetic field for different oxygen contents. The resistivity increases and the peak position shifts to lower temperatures as the oxygen content in the films decreases. The dependence of resistivity ρ on the angle θ between the magnetic field and the c-axis direction follows $\sin^2 \theta$ over the whole temperature range studied, which is similar to $\rho(\theta)$ measured previously by O'Donnell *et al.*[4] for a magnetic field rotated in the plane of the film.

The magnetoresistance $MR=(\rho_B-\rho_0)/\rho_0$, where ρ_B and ρ_0 are resistivities in a magnetic field of 0.68 T parallel to the film and in a zero field, respectively, is plotted in Fig. 2(a) as a function of temperature for as-grown and oxygen deficient $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ films. Note that the magnitude of the MR peak decreases and its position shifts to lower temperatures with an increasing δ. The temperature dependence of the AMR^{out} displayed in Fig. 2(b) shows similar behavior. Note, however, that the maximum of the AMR peak does not coincide with that of the MR peak but is instead located on the low temperature side of the MR peak. It also shifts to lower temperatures as the oxygen deficiency in the films increases.

Let us discuss the possible origins of the AMR^{out} peak at the metal-insulator transition and the reasons for its suppression in oxygen deficient films. One should first consider the possibility that geometric demagnetization effects (due to the sample shape) contribute to the AMR^{out} peak. The largest changes in the AMR^{out} due to a reduction in the oxygen content were detected at temperatures close to the MIT. At lower temperatures (below 210 K) the AMR^{out} is independent of δ [see Fig. 2(b)], excluding geometric demagnetization effects as a possible cause of a reduction in the magnitude of the AMR^{out} peak.

Previous studies have shown that lattice strain resulting from oxygen removal leads to the tetragonal distortion in

TABLE I. Parameters that describe as-grown and oxygen deficient $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ thin films used in the current studies. T_p and T_{max}^{MR} are the MIT temperature and the MR peak temperature, respectively. T_{max}^{anneal} is the annealing temperature in vacuum. t_{rise}, t_{anneal}, and t_{cool} correspond to the rise, annealing, and cooling times of the sample during deoxygenation at the background pressure P_b.

LCMO film	T_p (K)	T_{max}^{MR} (K)	T_{max}^{anneal} (°C)	t_{rise} (min)	t_{anneal} (min)	t_{cool} (min)	P_b (mTorr)	δ
As grown	265.4	248.6	⋯	⋯	⋯	⋯	⋯	0
Vacuum anneal 1	262.1	245.7	320	5	0	18	0.1	0.002[a]
Vacuum anneal 2	260.1	241.0	345	7	8	18	0.005	0.003[a]

[a] Reference 14.

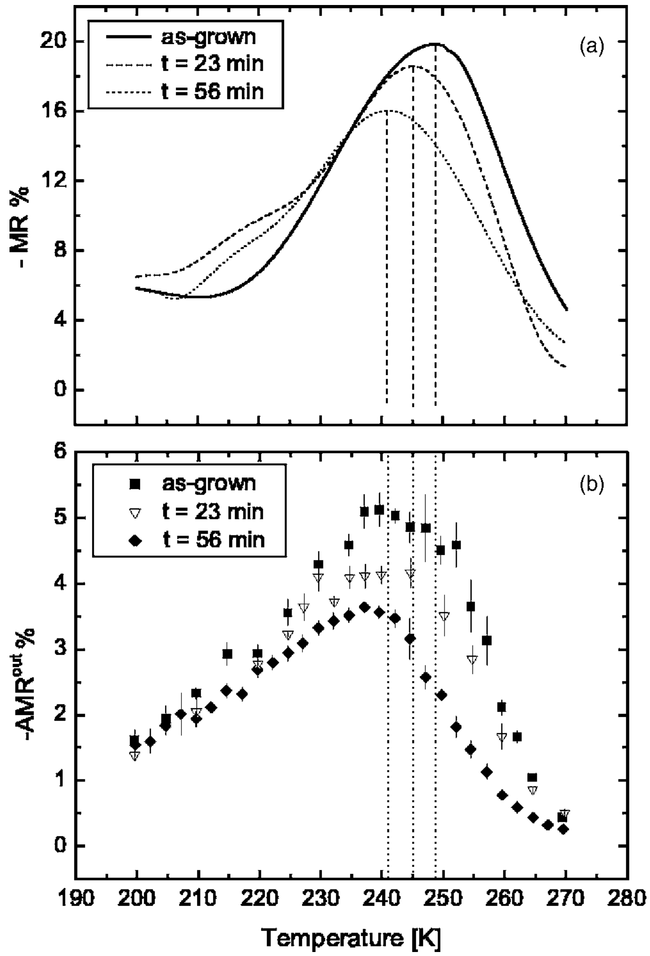

FIG. 2. (Color online) (a) Temperature dependence of the MR at MIT, induced by a magnetic field of 0.68 T applied in the film plane for $La_{0.65}Ca_{0.35}MnO_{3-\delta}$ film, as grown (optimally doped) and the same oxygen deficient film measured after annealing in vacuum for 23 and 56 min, respectively (see Table I). Vertical dashed lines mark the positions of the MR maxima. (b) The corresponding temperature dependence of the AMR^{out}. Vertical dotted lines mark the positions of the MR maxima shown in (a).

LCMO films.[12] In the absence of stress relaxation, oxygen deficiency tends to increase the volume of the unit cell in these films, while the in-plane lattice constants are fixed due to the presence of the substrate. The tetragonal distortion, as the Mn–O distance is increased in a direction perpendicular to the oxygen deficient film, weakens the ferromagnetic double exchange,[13] leading to an increase in resistivity. The magnitude of the MR peak at the MIT (Ref. 12) in oxygen deficient LCMO films (of $\delta=0.02$ or higher) is found to increase in LCMO films. These results are different from our observation, implying that another mechanism is dominant.

Thermal treatment of the film in vacuum can lead to the increase of the internal strain due to oxygen loss (increase of MR at MIT) or the decrease of strain due to epitaxial stress relaxation (decrease of MR at MIT). Within this model, whether an increase or a decrease is observed in the MR or AMR^{out} depends on the relative importance of these two competing factors. As discussed above, and as shown in Fig. 2, we observe a reduction in both the MR and AMR^{out} peaks at the MIT. Our samples were annealed at relatively low temperatures of 345 °C, implying that oxygen loss is very small, and hence that the epitaxial stress relaxation is the dominant effect. The result of this work also implies that it is possible to manipulate the magnitudes of the magnetoresistance and the magnetoresistive anisotropy in LCMO films by careful thermal treatment in vacuum at relatively low temperatures or by using suitably applied external stress.

In summary, it appears that a decrease of both the MR and AMR^{out} peaks in LCMO films due to vacuum annealing is due to epitaxial strain relaxation. This also suggests that these two properties could be strain induced, in agreement with a recent model of the strain-induced metal-insulator phase coexistence in perovskite manganites developed by Ahn *et al.*[8]

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[1] M. Ziese and S. P. Sena, J. Phys.: Condens. Matter **10**, 2727 (1998).
[2] V. S. Amaral, A. A. C. S. Lourenco, J. P. Araujo, A. M. Pereira, J. B. Sousa, P. B. Tavares, J. M. Vieira, E. Alves, M. F. da Silva, and J. C. Soares, J. Appl. Phys. **87**, 5570 (2000).
[3] B. I. Belevtsev, V. B. Krasovitsky, D. G. Naugle, K. D. D. Rathnayaka, A. Parasiris, S. R. Surthi, R. K. Pandey, and M. A. Rom, Phys. Status Solidi A **188**, 1187 (2001).
[4] J. O'Donnell, J. N. Eckstein, and M. S. Rzchowski, Appl. Phys. Lett. **76**, 218 (2000).
[5] P. A. Stampe, H. P. Kunkel, Z. Wang, and G. Williams, Phys. Rev. B **52**, 335 (1995).
[6] M. Ziese, Phys. Status Solidi B **228**, R1 (2001).
[7] M. Bibes, V. Laukhin, S. Valencia, B. Martinez, J. Fontcuberta, O. Yu Gorbenko, A. R. Kaul, and J. L. Martinez, J. Phys.: Condens. Matter **17**, 2733 (2005).
[8] K. H. Ahn, T. Lookman, and A. R. Bishop, Nature (London) **428**, 401 (2004).
[9] J. R. Sun, C. F. Yeung, K. Zhao, L. Z. Zhou, C. H. Leung, H. K. Wong, and B. G. Shen, Appl. Phys. Lett. **76**, 1164 (2000).
[10] M. Ziese, Phys. Rev. B **62**, 1044 (2000).
[11] M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).
[12] K. Dorr, J. M. De Teresa, K.-H. Muller, D. Eckert, T. Walter, E. Vlakhov, K. Nenkov, and L. Schultz, J. Phys.: Condens. Matter **12**, 7099 (2000).
[13] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
[14] Oxygen content was estimated using the equation: $\delta=(0.03)\{[265.4\ \mathrm{K}-T_p(\mathrm{K})]/(50\ \mathrm{K})\}$ which was derived from the modified dependence of δ on T_p shown in Fig. 3 of Ref. 9 for $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ thin films.