Huge magnetoresistance in ultrathin $La_{0.7}Ca_{0.3}MnO_3$ films: The role of superparamagnetic clusters and domain walls

J. M. Colino
Dept. Física Aplicada Universidad de Castilla la Mancha, Avda. Camilo J. Cela 10, 13071 Ciudad Real, Spain

A. de Andrés[a)]
Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049 Madrid, Spain

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The magnetic behavior of epitaxial $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) films grown on $SrTiO_3$, with thickness down to 2.4 nm, has been analyzed and correlated to the magnetoresistance (MR). Below about 10 nm the canonical ferromagnetic order switches to a distribution of superparamagnetic clusters. These ultrathin films show a huge MR (4000%) at T_c and, at 5 K, the MR is 300 times that of the ferromagnetic films' value. Metallic conductivity is observed below T_c down to the blocking temperature ($T_B \approx 65$ K) but a strong upturn appears below T_B. These findings can be explained by the ordering of uncoupled superparamagnetic clusters and their blocking at lower temperature, together with the collapse of the magnetic domain walls which are substituted by very small Mn magnetic clusters (few Mn) probably localized at the structural domain boundaries. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2081139]

The properties of epitaxial and textured ultrathin films are strongly influenced by the microstructure and nanostructure, the strain induced by the substrate,[1,2] and by confinement effects.[3,4] These aspects are especially important in the magnetism and magnetoresistance (MR) of doped manganese perovskites, where the electron-lattice coupling is a fundamental ingredient in the determination of the stable phases as evidenced by the important role of the strain induced by the intrinsic disorder.[5] Very interesting studies on the effect of the substrate have been carried out for a large variety of doped manganites, demonstrating the possibility of obtaining very different properties compared to bulk compounds or very thick films where strain is relaxed;[6,7] but the very thin-film limit[8] has been much less explored.

In particular, previous studies on $La_{0.7}Ca_{0.3}MnO_3$ epitaxial films revealed that T_c decreases drastically as the layer thickness is reduced [Fig. 1(a)], while no important structural changes are detected and the remanent magnetization is constant. T_c is found to follow the functional dependence of a mean-field approximation for the limitation of the divergence of the spin-spin correlations, estimated to be 5 nm, by the film thickness.[3] The presence of chemical defects, such as oxygen deficiency, or the presence of nonmagnetic ions at Mn sites, produces an increase of the low-field MR around T_c but also a decrease of T_c (Ref. 9). We have investigated the ultrathin limit of 30% Ca-doped LaMnO3 films where the properties are severely influenced by the nanometric scale. In order to understand the origin of the huge increase of the magnetoresistance for the thinnest films, we have carefully analyzed their magnetic behavior.

Epitaxial $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) thin films were grown at room temperature on $SrTiO_3$ by the dc sputtering techniques at growing rates of 3.4 nm/min as described previously.[3] The films thickness ranges between 90 and 2.4 nm as obtained by x-ray reflectivity. The epitaxial growth has been checked by x-ray diffraction. The out-of-plane coherence coincides with the film thickness, and the in-plane domain size has been evaluated[3] to be minimum, about 20 nm, for the 6.5 nm film. The magnetization measurements were performed with a superconducting quantum interference device (SQUID) magnetometer and magnetotransport data were obtained with a PPMS, both from Quantum Design. The applied magnetic field was in the plane of the films and parallel to the current.

Exhaustive magnetic measurements were done in order to have a detailed picture of the magnetism in the thinnest films. At low temperature, upturns of the magnetization M [Fig. 1(b)] and the divergence of their derivatives are indications of the presence of a certain amount of paramagnetic

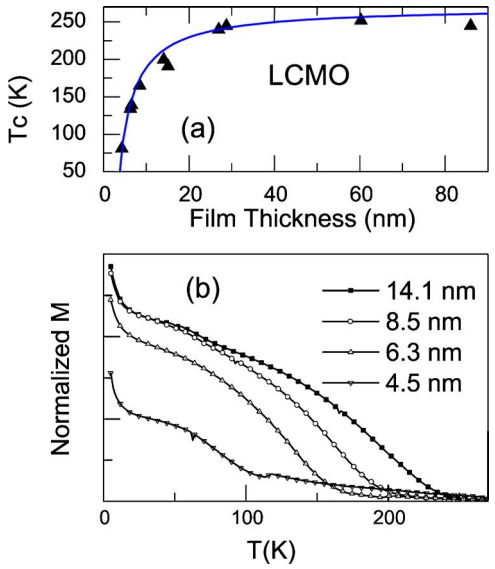

FIG. 1. (a) T_c of LCMO films as a function of their thickness. The line corresponds to a fit to $1/d$. (b) Magnetization, normalized to the weight of the sample and to the thickness of the film, of several films.

[a)]Electronic mail: ada@icmm.csic.es

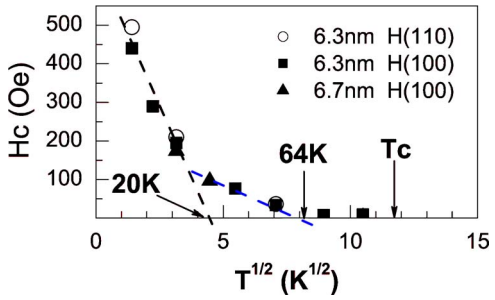

FIG. 2. Dependence of the coercive field of three samples in the 6–7 nm thickness range with the square root of the temperature. Below about 64 K two regimes are observed. The dashed lines are the corresponding linear fits that indicate the blocking temperatures.

Mn. This paramagnetic component is proportional to the volume fraction of the sample in the paramagnetic state and to the square of the effective Bohr magneton number, p. This parameter p is related to the size of possible Mn superparamagnetic (SP) clusters in the unblocked regime. The paramagnetic fraction increases drastically for thicknesses below 10 nm.

The films in the 6–7 nm thickness range show two magnetic components: very small Mn clusters (few Mn), unblocked even at 2 K, generate the paramagnetic tail, and the "ferromagnetic" component that shows an order temperature $T_c=135$ K according to the magnetization derivative. Analyzing in detail the behavior of the magnetization as a function of temperature and magnetic field it is evident that it does not correspond to a canonical ferromagnet but rather to superparamagnetic clusters. In order to check this point we have measured the variation of the coercive field as the temperature increases for films with thicknesses between 6 and 30 nm. The behavior of the three films with thicknesses in the range 6–7 nm is different from that of the thicker films. The coercive field corresponding to the thinner samples (Fig. 2) varies linearly with $T^{1/2}$ and vanishes well below T_c. Both are characteristics of SP clusters. Two blocking temperatures T_B, around 64 and 20 K, can be inferred from the measured data (Fig. 2). According to these values, and taking into account the film thickness, the sizes of the superparamagnetic clusters are estimated to be around 13 and 8 nm. The coercive fields in thicker films vanish at T_c and do not present this functional dependence with the temperature.

The peculiarities of the detailed magnetic structure of these films have drastic effects in the conductivity and magnetoresistance compared to thicker films. Figure 3 shows the resistivity of three films (6.5, 15.5, and 30 nm thick) with and without external applied magnetic field. All films present the metal-insulating transition above and close to T_c, and the room-temperature resistances almost scale with their thickness, but, while no MR (less than 5% with 9 T) is detected for the thickest films, a huge MR is observed in the 6.5-nm films [Fig. 3(b)] related to the drastic upturn of the resistivity below about 60 K. Moreover, these films present colossal MR of 4000% around T_c. In Fig. 3(b) the MR has been defined as $\mathrm{MR}=[R(0)-R(H)/R(H)]\times 100$, necessary to evidence the differences when the standard MR is near 100%.

At low temperatures, epitaxial films (or single crystals) should not present MR since the scattering due to the magnetic domain walls is small as long as these are wide. In the double-exchange mechanism, the transfer integral for the carriers is proportional to $\cos(\theta/2)$ where θ is the angle between the magnetic moments of two consecutive grains, domains, or Mn ions, so that, for $\theta=\pi$ the conductance is zero. An angle $\theta=\pi$ precisely corresponds to two successive domains, but, through a domain wall the conduction is performed by successive steps from one Mn to the other. For a domain-wall thickness, δ, the spin rotation for each step is $\theta=\pi a/\delta$, with a being the Mn–Mn interatomic distance. The magnetoconductance of a single wall (the change in the conductivity when two consecutive magnetic domains are aligned by an external magnetic field) has been estimated to be[10] $\Delta G/G_0=2/3\ (\pi/2k\delta)^3=-\Delta R/R_H$, i.e., very strongly dependent on δ. In the superparamagnetic films, the situation is different. In Fig. 4 a schematic view of the situation at different temperatures has been drawn. Above T_c all the films are identical from the magnetic point of view and therefore their conductivities are also equivalent. Below T_c the magnetic moments of the SP clusters are switching between the

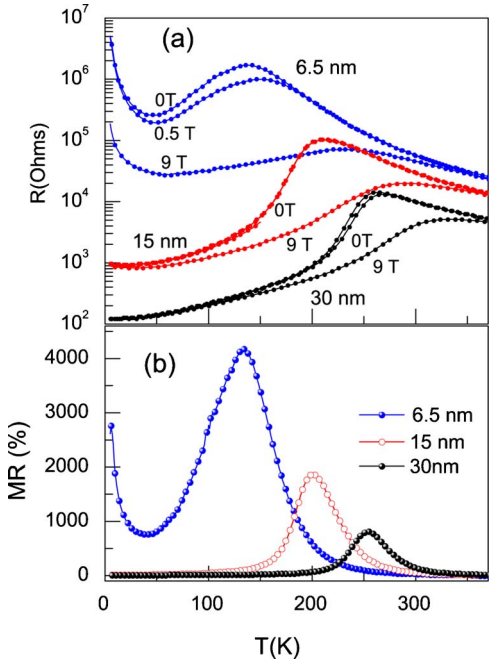

FIG. 3. (Color online) (a) Resistance of three films (30, 15.5, and 6.5 nm thick) with and without applied magnetic field. (b) MR defined as in the text for the three films evidencing the enhancement of the MR around T_c and at low temperatures of the 6.5-nm film.

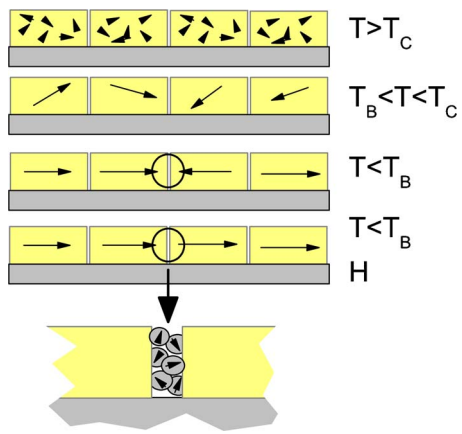

FIG. 4. (Color online) Schematic representation of the magnetic structure of the SP films at different temperatures and applied magnetic fields. The lowest part presents a zoom of the interface between two magnetic clusters.

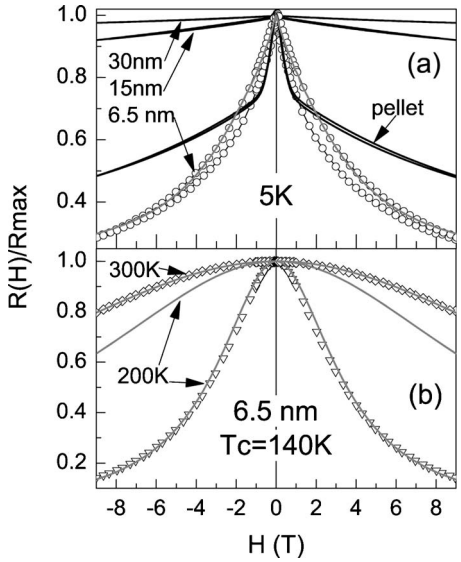

FIG. 5. (a) MR at 5 K of different thin films and a polycrystalline pellet. The gray line is the fit of the 6.5 nm film. (b) MR at 200 and 300 K of the 6.5-nm film. The lines are the fits as explained in the text.

two directions of the easy axis so the carriers have a high probability to tunnel from one cluster to the other. But, below the blocking temperature T_B, most of the paths will be forbidden at some point when the magnetization of two consecutive clusters are opposite ($\theta=\pi$ implies conductance=0) so the resistivity increases as the SP clusters freeze, since, in this case, the magnetic walls are not there to allow an adiabatic flow of the carriers. The effect of the external magnetic field is now important since it aligns all the SP clusters, and a huge MR is in fact observed.

The effect is similar to the low-field MR in polycrystalline systems, but not identical, as shown in Fig. 5(a). The MR of a representative polycrystalline pellet presents the clearly different low- and high-field regimes which are related to different mechanisms. The measured MR for the SP films is continuous and has been fitted using the standard hypothesis that the conductivity increases with the square of the magnetization.[8] The first step was to extrapolate, up to 9 T, the measured magnetization at 5 K using the Brillouin function for the paramagnetic component related to the small Mn clusters and then calculate the MR (the details of the calculation will be presented elsewhere). The measure and fit are shown in Fig. 5(a). One of the conclusions of this procedure is that the alignment of small Mn clusters (formed by few Mn ions) with the external field is controlling the conductivity, indicating that these are, very probably, located between the blocked SP clusters (lower part of Fig. 4). These small Mn clusters are substituting the domain walls but, contrary to them, no correlation exists between successive Mn clusters.

At 200 K, in spite of being well above T_c, the MR curve does not correspond to a paramagnetic regime as it does at 300 K. The parameters obtained with the fit of the 300-K MR, using again the Brillouin function to describe the field dependence of the paramagnetic magnetization, are used to evaluate the MR at 200 K [upper solid lines in Fig. 5(b)] showing total discrepancy with the measured MR. In fact, the substitution of individual Mn ions by small clusters of five Mn gives a good fit of the data as seen in Fig. 5(b). This is the evidence that short-range ferromagnetic order is already present at this temperature more than 60 K above T_c, and an indication of the frustration of the long-range ferromagnetic order occurring in such thin films leading to the decrease of T_c.

In conclusion, the blocking of the SP clusters, together with the disappearance of the magnetic domain walls that are substituted by noncorrelated small Mn clusters (few Mn), is the origin of the huge magnetoresistance values measured in the thin films in the range of 6–7 nm. The canonical ferromagnetic order switches a distribution of superparamagnetic clusters with blocking temperatures of 65 K and below for ultrathin films probably driven by the in-plane nanostructure.

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