Strain and interface effects on the magnetic and transport properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$/CaO multilayers

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Abstract. La$_{0.7}$Ca$_{0.3}$MnO$_3$/CaO (LCMO/CaO) multilayers were deposited on (100) LaAlO$_3$ substrates by pulsed injection metal organic chemical vapour deposition. The samples were characterised by X-ray diffraction, transport and magnetization measurements. An anomalous behaviour of the electrical resistance under applied magnetic field and an exchange bias effect for the magnetization are observed for the multilayers with thinner LCMO layers. These results suggest the existence of a short range antiferromagnetic coupling at the layer interfaces.

1. Introduction

The discovery of colossal magnetoresistance (CMR) in the manganite compounds [1,2] generated an enormous interest on their fundamental properties and on their potential applications in the spintronics industry. In particular, much attention has been devoted to the magnetic and magnetotransport properties of thin film and heterostructures, in view of their relevance for device fabrication. In these materials, the lattice mismatches with the substrate induce tensile or compressive strains that strongly influence magnetic and transport properties such as the metal to insulator transition temperature or the magnetoresistance. As an example, it is now well established that the metal to insulator transition temperature decreases with increasing biaxial distortions, since these distortions increase the Jahn-Teller effect and, therefore, increase electron localization [3,4].
Several types of heterostructures and superlattices have been fabricated, conjugating the ferromagnetic manganese oxides with different kinds of spacers: magnetic conductors, non magnetic conductors or non magnetic insulators [5,6]. A large enhancement of the magnetoresistance at low temperatures was found, for instance, in La$_{0.67}$Ca$_{0.33}$MnO$_3$/SrTiO$_3$ multilayers [5] and La$_{0.67}$Ca$_{0.33}$MnO$_3$/SrRuO$_3$ multilayers [6]. A possible explanation for this interesting effect is the creation of magnetic nonuniformities near the interfaces due to disorder, functioning as additional spin-dependent scattering centres.

The manganite perovskite La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and the insulator CaO coexist naturally in the Ruddlesden-Popper (RP) phases. RP phases (AO)(ABO$_3$)$_n$ consist of perovskite slabs of $n$ layers of corner-sharing BO$_6$ octahedra separated from neighbouring blocks by an AO rock-salt layer. Thus, LCMO and CaO are good candidates for the engineering of multilayers and other heterostructures, keeping in mind, nevertheless, that the rather large ($\approx$20%) lattice mismatch between LCMO and CaO is likely to impose strong strains on the LCMO layers.

In this work we present magnetization and magnetoresistance measurements performed on a La$_{0.7}$Ca$_{0.3}$MnO$_3$ film, on a La$_{0.7}$Ca$_{0.3}$MnO$_3$/CaO/La$_{0.7}$Ca$_{0.3}$MnO$_3$ trilayer and on [(La$_{0.7}$Ca$_{0.3}$MnO$_3$)/(CaO)]$_N$ multilayers.

![Figure 1. X-ray 0-2θ diffraction scan around the substrate (LAO) (002) peak for the 20/20 sample: the small height of the satellite peaks adjacent to the main peak (SL0) indicates a heterostructure growth with significant interface roughness.](image)

**Table 1. Sample description.**

| Type      | Designation | Layer thicknesses                           | $T_p$ (K) | $T_c$ (K) |
|-----------|-------------|---------------------------------------------|-----------|-----------|
| film      | —           | LAO/LCMO(120 nm)                            | 257       | 240       |
| trilayer  | —           | LAO/LCMO(120nm)/CaO(30nm)/LCMO(40 nm)      | 225       | 205       |
| multilayer| 10/10       | LAO/[LCMO(10nm)/CaO(10nm)]$\times$12/LCMO(20 nm) | <55       | —         |
| multilayer| 20/20       | LAO/[LCMO(20nm)/CaO(20nm)]$\times$12/LCMO(20 nm) | 58        | —         |
| multilayer| 30/30       | LAO/[LCMO(50nm)/CaO(50nm)]$\times$2/LCMO(20 nm) | 63        | —         |
The samples were grown by pulsed injection metal organic chemical vapour deposition on (100) single crystalline LaAlO$_3$ (LAO) substrates. In this technique, the metalorganic precursors are injected to the reactor in a liquid solution and the number of droplets for each deposition is accurately controlled. Substrate temperature was kept at 700$^\circ$C and the droplets were evaporated at a temperature of 200$^\circ$C. The injection rate was 2 Hz and the injector opening time was 2 ms. The reactor pressure was kept at a constant pressure of 5 torr with Ar flow rate of 900 ml/min and O$_2$ flow rate of 600 ml/min. All the samples were slowly cooled down to room temperature in situ in 1 bar of O$_2$ after deposition. In the multilayers, an additional LCMO thin layer (20 nm thick) was deposited on top, to avoid the degradation of the last CaO layer. To control the layers’ thickness, the deposition rate was established by Rutherford Backscattering Spectroscopy: for LCMO a deposition rate of 0.1 nm per droplet was obtained.

The structural characterization of the samples was performed by X-ray diffraction with a Bruker diffractometer using the Cu K$_{\alpha 1}$ line. Symmetric (002) 2$\theta$ scans were collected with a point detector positioned 290 mm away from the sample and operating with an acquiring time of 2 s per 2$\theta$ step (0.001º). Magnetization measurements were performed on a 5 T Quantum Design SQUID magnetometer with the field applied parallel to the samples surface. The electrical resistance was determined by the standard dc four-probe method, with indium contacts directly attached to the sample surface. The measurements were performed inside an OXFORD cryostat, in magnetic fields up to 16 T, with the field parallel to the current. Sample properties are summarized in Table 1, where $T_p$ refers to the zero field peak temperature in the resistance curves and $T_c$ is the Curie temperature.

Figure 2. (a) Temperature dependence of the resistance for applied magnetic fields up to 16 T for the LCMO film. (b) Temperature dependence of the magnetization for the same LCMO film: zero field cooled (ZFC) and field cooled under a 100 Oe field (FC).

2. Experimental
3. Results and discussion

Figure 1 shows a $2\theta$-ω scan for sample 20/20 around the LAO substrate (002) reciprocal lattice point. The main peak is centered at $2\theta \approx 47.45^\circ$ which is the experimental Bragg angle obtained for the LAO (002) substrate. Keissig fringes can be observed but the small height of the satellite peaks and the fact that the $2\theta$ angular separation between SL0 and SL-1 is slightly different from the separation between SL-1 and SL-2, implies the existence of a small thickness period fluctuation or intermixing and, consequently, reveals a significant interface roughness.

The temperature dependence of the electrical resistance at several magnetic fields for the LCMO film is shown in figure 2a: the film presents the usual behaviour found in good quality La$_{1-x}$Ca$_x$MnO$_3$ films at optimal doping ($x \approx 0.3$), with the peak temperature ($T_p$) at zero field equal to 257 K; as the applied magnetic field is increased, the peak in the resistance shifts to higher temperatures, as a result of the increased alignment of the Mn$^{3+}$ and Mn$^{4+}$ ion moments that reduces the electron scattering. Figure 2b shows the temperature dependence of the magnetization for the same LCMO film, in agreement with the expected behaviour and indicating a Curie temperature of 240 K.

Figure 3a shows the temperature dependence of the electrical resistance at several magnetic fields for the LCMO/CaO/LCMO trilayer: the curves present essentially the same behaviour of the film but with the peaks appearing at lower temperatures: the zero field peak ($T_p$) occurs at 225 K. This temperature is close to the Curie temperature $T_c = 205$ K derived from magnetization curves, a value that is smaller than that obtained for the single layer. The difference between the values of $T_p$ and $T_c$, indicates some degree of structural disorder in the LCMO layers [7]. The shift of the metal to insulator transition temperature to lower temperatures can be ascribed to the additional tensile strain at the LCMO/CaO interfaces due to the lattice mismatch between CaO and LCMO: the larger unit cell parameters of CaO induce an in-plane tensile stress leading to a smaller $c$ lattice parameter in the LCMO layers. It is known that tensile strain in LCMO [4] has the same effect of compressive strain: it increases the Jahn-Teller (JT) lattice distortion, with the consequent increase in the $e_g$ levels splitting and enhancement of electron localization; consequently the metal to insulator transition temperature decreases. Furthermore we should consider the possibility of Ca diffusion into...
the ferromagnetic layers, giving rise to non-optimal hole doping and a lowering of the critical temperature \[T_c\] in a volume fraction of the ferromagnetic layers.

In figure 4, the temperature dependence of the electrical resistance is plotted for several magnetic fields for the three multilayers, hereby designated according to their LCMO/CaO thicknesses by (10/10), (20/20) and (50/50) as shown in table 1. For the 10/10 sample, the resistance at zero field is extremely large below 100 K and can not be measured with our experimental setup. Nevertheless, we can estimate that \(T_p(0T)\) is below 55 K, since the magnetoresistance curve obtained at this temperature displays a \(H^2\) dependence, usually observed above the metal-insulator transition in these compounds [9]. For samples 20/20 and 50/50, the zero field resistance peak occurs at 58 K and 63 K, respectively. The overall reduction of the metal to insulator transition temperature can be the result of several combined effects: the strain effects, already discussed for the trilayer; a reduction in the \(e_g\) band width due to the reduced dimensionality and the existence of phases with suppressed ferromagnetism (or with antiferromagnetic ordering). As to the high resistance values, particularly high for the 10/10 and 20/20 multilayers, they can indicate magnetic barriers between misaligned ferromagnetic regions resulting in increased spin dependent scattering [10]. The most striking feature in the curves of figure 4 is the odd magnetic field dependence exhibited by the resistance peak for the samples 10/10 and

![Figure 4](image-url)

Figure 4. Temperature dependence of the resistance under various applied magnetic fields: (a) for the 10/10 multilayer; (b) for the 20/20 multilayer and (c) for the 50/50 multilayer. (d) Resistance peak temperature as a function of the magnetic field for the three samples: for the 10/10 and 20/20 samples, the peaks presents an odd magnetic field dependence, shifting to lower temperatures as the field increases.
20/20: as the field increases, the height of the peak decreases as expected, but the peak temperature ($T_p$) decreases. This unusual magnetic field dependence of $T_p$ has never been observed, to our knowledge, in manganite systems and cannot be understood in the framework of a simple double exchange mechanism. For the multilayer with the thicker layers (50/50), the resistance peak temperature exhibits the usual behaviour, shifting to higher temperatures with increasing field (cf. figure 4d).

In order to clarify these observations, the resistance of samples 10/10 and 20/20 was measured as a function of the magnetic field at several fixed temperatures. Figure 5a shows that, for sample 10/10, at a constant temperature of 30 K the resistance at first increases with applied magnetic field, up to a field of about 6 T and then decreases consistently up to the maximum scanned field of 16 T. Figure 5b shows that for sample 20/20, at $T = 10$ K and after the initial curve, a hysteretic resistance develops with a resistance maximum between 3 T and 6 T. For a temperature of 55 K, near the zero field resistance peak, the hysteresis is no longer observable and the resistance decreases monotonically with applied field (cf. inset to figure 5). The main features exhibited by the $R(H)$ curves in our samples are similar to those found in Gd/Co multilayers, which were interpreted in the framework of a field induced spin-flop transition [11], as a consequence of the existence of an antiferromagnetic coupling in the interface region between alternating Co and Gd$_{0.7}$Co$_{0.3}$ layers. Furthermore, strong hysteretic effects on the magnetoresistance were observed in systems where a canted antiferromagnetic state is transformed into a metastable ferromagnetic state by application of large magnetic fields [8].

In order to get further insight on the samples’ properties, we performed magnetization measurements of the multilayers. The magnetization curves as a function of temperature displayed in figure 6 for the samples 10/10 and 20/20 are reminiscent of those for systems with some type of magnetic frustration such as spin glasses or cluster glasses. Figure 7a shows the magnetization hysteresis loops for sample 10/10 at 5 K, obtained after field cooling in a 10 kOe field: the loop presents an evident shift towards the negative values of applied field. This shift is the so-called exchange bias effect and can be evaluated through the exchange bias field $H_{EB} = -\frac{(H_1+H_2)}{2}$, $H_1$ and $H_2$ being, respectively, the negative and positive coercive fields (cf. figure 7a). This effect has also been observed in sample

**Figure 5.** (a) Magnetic field dependence of the resistance for the 10/10 multilayer at $T = 30$ K, showing a maximum at a 6 T field. (b) Magnetic field dependence of the resistance for the 20/20 multilayer at $T = 10$ K, evidencing hysteretic behaviour; the arrows indicate the field sweep sequence (0 T → 14 T → -14 T → 0 T). Inset: at $T = 55$ K, no hysteresis is observed.
20/20, whereas it is negligible for sample 50/50. Figure 7b shows the temperature dependence of the exchange field $H_{EB}$ for the three samples (all data obtained after field cooling in a 10kOe field). Two features are evident from the plot: the exchange bias increases in magnitude and persists to higher temperatures with decreasing layer thickness. These features point to the existence of a strong interfacial effect that becomes less significant as the volume of the ferromagnetic layers increases. This result correlates with the unusual resistance behaviour under applied magnetic field observed for the 10/10 and 20/20 samples. The exchange bias effect is usually attributed to the existence of adjacent ferromagnetic and antiferromagnetic layers, with $T_N < T_C$: if the ferromagnetic and the antiferromagnetic layers are cooled in an applied field, the exchange coupling between the layers makes it energetically favourable for the ferromagnetic layer to maintain the magnetization direction acquired while cooling; for temperatures well below the Néel temperature ($T_N$) a shift in the hysteresis loop will occur. The exchange bias effect has also been observed in samples with a spin glass phase surrounding a ferromagnetic region [12,13], when the freezing temperature is $T_f < T_C$. In order to investigate the spin glass hypothesis we measured the time dependence of the resistance under zero applied field for sample 20/20, at 10 K and 5 K after zero field cooling from room temperature for both measurements. No relaxation of the resistance is observable for a time scan of 50000 s; therefore, in the absence of any other direct evidence, we must rule out the spin glass scenario.

In the multilayers considered in the present work the relative importance of the exchange bias effect on the overall sample properties increases as the thickness of the LCMO layers decreases. As suggested by the X-ray analysis, the interfaces in the multilayers may present considerable roughness, and thus, we expect an important degree of mixing between the two materials. This could result in the formation of Ca rich phases of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compound ($x > 0.5$) that are antiferromagnetic [8]. The possibility of formation of antiferromagnetic Ruddlesden-Popper phases may also be considered; several authors have shown that RP phases can appear at the interface between different perovskite structures as way of accommodating lattice mismatches through the formation of planar defects [14]. These considerations are schematically illustrated on figure 8.

Figure 6. Temperature dependence of the magnetization for samples: (a) 10/10 and (b) 20/20.
Addressing now the field dependence of the resistance displayed in figure 5, we propose a preliminary interpretation: at a fixed temperature, by applying a magnetic field the ferromagnetic metallic state associated with the LCMO phases is promoted. However, on the adjacent antiferromagnetic phases, whose existence is inferred from the exchange bias effect, the antiferromagnetic order starts to be disrupted as the field increases and so, the magnetic disorder increases in the percolation path of the conducting electrons, resulting in an electrical resistance enhancement. At a large enough field, the canted antiferromagnetic state is transformed into a metastable ferromagnetic state, with the magnetic moments aligned with the applied field; with the application of even larger fields, more magnetic moments align with the applied field and the resistance of the sample decreases. This explanation is in agreement with the magnetic field dependence of the resistance for sample 10/10 shown in figure 5a, where a change in behaviour is observed for a 6 T field, which we ascribe to a spin-flop transition as the one observed in the Co/Gd multilayers [11]. A transition from an antiferromagnetic to a ferrimagnetic state and then to a ferromagnetic state has also been theoretically proposed by Rößler and Bogdanov [15], in antiferromagnetic multilayers with uniaxial anisotropy. The possible existence of Ruddlesden-Popper (RP) phases in our multilayers could provide the strong anisotropy required to observe a transition similar to the one predicted. At this moment, it is not clear if such a mechanism can account for the odd temperature dependence of the resistance peak in samples 10/10 and 20/20, but it is clear that such behaviour is correlated to the predominance of interfacial effects associated with the exchange bias mechanism. Further experimental and theoretical work is necessary in these and similar systems in order to clarify these issues.

4. Conclusions

We have grown a La$_{0.7}$Ca$_{0.3}$MnO$_3$ film, a La$_{0.7}$Ca$_{0.3}$MnO$_3$/CaO/La$_{0.7}$Ca$_{0.3}$MnO$_3$ trilayer and [(La$_{0.7}$Ca$_{0.3}$MnO$_3$)/CaO]$_N$ multilayers by pulsed injection metal organic chemical vapour deposition on LaAlO$_3$ substrates. The film presents magnetic and transport properties in agreement with those found in the literature. The trilayer exhibits a Curie temperature and a metal to insulator transition temperature lower than the single layer, a behaviour ascribed both to strain effects and to possible Ca diffusion into the ferromagnetic layers. The multilayers show very large electrical resistance values and metal to insulator transition temperatures close to 60 K; under applied magnetic field the resistance presents an anomalous behaviour for the multilayers with the thinner layers, suggesting interfacial effects and not readily understood in the framework of the double exchange mechanism.
The multilayers also exhibit an exchange bias effect for the magnetization that increases in magnitude and persists to higher temperatures with decreasing layer thickness, again suggesting a link to interfacial features. We interpret these results as a consequence of the interfaces’ roughness, where antiferromagnetic Ca rich or Ruddlesden-Popper phases may have formed. The coexistence of ferromagnetic and antiferromagnetic phases can account for the observed large resistance values resulting from the increased spin dependent scattering. We also propose that the existence of a field induced spin-flop transition from a canted antiferromagnetic state into a metastable ferromagnetic state may account for the isothermal field dependence of the resistance.

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