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Spin-glass-like behaviour and positive magnetoresistance in oxygen deficient $La_{2/3}Ca_{1/3}MnO_{3-\delta}$ thin films*

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The magnetism and magnetoresistance (MR) in a series of oxygen-deficient $La_{2/3}Ca_{1/3}MnO_{3-\delta}$ (LCMO) thin films have been investigated. Compared with the films with stoichiometric oxygen concentration, the oxygen-deficient LCMO thin films show a spin-glass-like behaviour at low temperatures, and a positive MR effect above the metal–insulator transition temperature. The mechanism of such unusual phenomena is discussed.

Keywords: manganites, oxygen deficiency, spin glass, positive magnetoresistance
PACC: 7530E, 7530V, 7138

1. Introduction

Perovskite manganites $R_{1-x}A_xMnO_3$, with R being the rare-earth element and A the alkaline metal, show the colossal mangnetoresistance (CMR) effect,[1] which is explained mainly by double-exchange (DE) interaction,[2] electron–phonon interaction,[3,4] and electronic phase-separation.[5–8] Similar to high-temperature cuprate superconductors, the CMR manganites also belong to the strongly correlated electron system. The dopants quite effectively influence their properties due to the variation of Mn valence.[9–12] The DE interaction between Mn^{3+} and Mn^{4+} is responsible for the metallic and ferromagnetic properties. So far, the study of CMR materials has been mainly focused on subjects related to the change of alkaline cation concentration rather than that of oxygen as it has been done in high-temperature superconductors. The oxygen deficiency not only suppresses the DE interaction between Mn^{3+} and Mn^{4+} ions and decreases the density of charge carriers, but also leads to the magnetic inhomogeneity in the material.[13–16] Therefore, it is very necessary to study the CMR material by controlling the oxygen concentration. Thin films may be a type of material that can be more easily made with oxygen deficiency compared with others. In this work, we prepare a series of oxygen deficient $La_{2/3}Ca_{1/3}MnO_{3-\delta}$ (LCMO) thin films. In addition to the observation of the spin-glass-like magnetic behaviour as indicated by previous work,[14,15] we have also found the positive MR effect at temperatures above the metal–insulator transition (T_{M-I}).

2. Experiment details

The stoichiometric LCMO thin film S_A and oxygen deficient films S_B, S_C and S_D with a thickness ~150nm were all deposited on (001) single crystal $SrTiO_3$(STO) substrates by the pulsed laser deposition method at 800°C, followed by *in situ* annealing at 850°C for about 40min, then cooled down to room temperature within 30min. Controlling the deposition and annealing oxygen pressure as listed in Table 1, LCMO thin films with different oxygen content were obtained. The phase purity and lattice parameters of the films were examined by x-ray diffraction. Atomic force microscopy (AFM) was used to character the surface morphology. The inductively coupled plasma-atom emission spectrum and energy dispersive x-ray spectrum were used to analyse the ratio of the cations.

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The measurements of temperature dependence of the magnetization $M(T)$ were performed by using a superconducting quantum interference device (SQUID) magnetometer. For transport measurements, the films were patterned into microbridges with a size of 500μm in length and 100 μm in width by using conventional photolithography and argon ion milling. The temperature dependence of the resistivity $\rho(T)$ and the magnetoresistance MR(T) of the microbridges were measured with the SQUID magnetometer using the standard four-point technique. For MR(T) measurements, the magnetic field is applied parallel to the current.

Table 1. Oxygen pressure used in the process of preparation of four LCMO thin films S_A, S_B, S_C and S_D for obtaining oxygen deficiency degree in turn.

Sample	S_A	S_B	S_C	S_D
Deposition oxygen pressure/Pa	100	50	30	3×10^{-3}
Annealing oxygen pressure/Pa	1×10^{5}	50	3×10^{-3}	3×10^{-3}

3. Results and discussion

X-ray analyses show that all the films are single phase with c-axis perpendicular to the film plane. The c-axis unit lengths of S_A, S_B, S_C and S_D are 0.3829, 0.3822, 0.3806 and 0.3795nm, respectively, which seems to be directly associated to the degree of oxygen deficiency. However, it is different from those films grown on $LaAlO_3$(LAO) substrate,[15,16] in which the oxygen deficiency induces the increase of lattice parameter in the c-axis direction. This may be understood as that, in the present case, the film is under tensile stress due to the lattice mismatch with STO substrate (cubic, a=0.3905nm). The oxygen deficiency in Mn-O plane will cause the Mn-O bond strength to be weaker and the lattice parameter to be larger; then, the lattice parameter in the c direction will be contracted from film S_B to S_D. Figure 1 shows the AFM image of the film surface, in which the island-growth mode can be seen quite clearly, and the average roughness of the film surface is about 0.35nm.

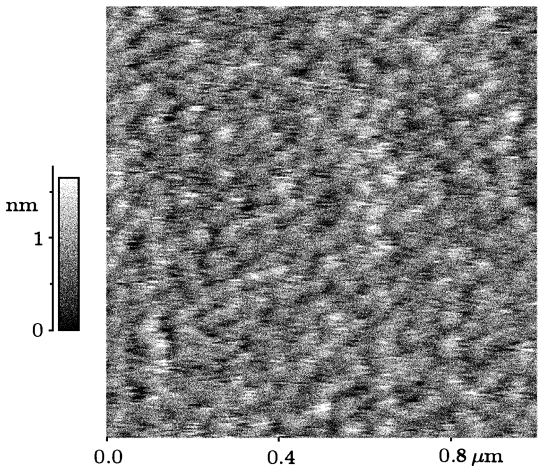


Fig.1. AFM image of a typical oxygen deficient film S_B, showing the flat surface and grain boundary free.

Figures 2(a)–(d) show the $M(T)$ data under zero field cooling (ZFC) and field cooling (FC) conditions. The magnitude of magnetization of the films decreases with increasing oxygen deficiency. For S_A, S_B, S_C and S_D, their T_C, defined as the temperature at which the slope of $|dM/dT|$ shows its maximum, are 270, 270, 260 and 90K, respectively. It is obvious that the $M-T$ relation of the stoichiometric S_A film shows a prefect ferromagnetic state below T_C, similar to the bulk sample, as shown in the inset of Fig.2(a). For the oxygen deficient thin films, however, the magnetization increases in a wide temperature range below T_C, but remarkably deviates from the $M-T$ relation of a ferromagnet. When the temperature is decreased to a certain value, the $M-T$ relations for FC and ZFC samples show a distinct irreversibility, as shown in Figs.2(b)–(d). This is a typical character of the spin-glass-like behaviour. The temperature at which the maximum magnetization is located in ZFC samples may be termed the spin-glass transition temperature T_{SG}. The oxygen deficiency dependence of magnetization magnitude indicates obviously that the development of oxygen deficiency enhances the spin freezing state. Figures 2(e)–(h) show the corresponding $\rho(T)$ and MR(T) for the samples S_A, S_B, S_C and S_D, which also show a quite strong oxygen deficiency dependence. With increasing degree of oxygen deficiency, the resistivity increases remarkably and T_{M-I} decreases from 270K for S_A to below 60K for S_D (below 60K, the resistivity is too large to measure). When the magnetic field (5T) is applied, the magnitude for MR effect, defined as MR=$(R_H\text{-}R_0)/R_H*100\%$, increases from -1.3×10^2 for S_A (Fig.2(e)) to $> -8\times10^5$ for S_D (Fig.2(h)). The maximum values of MR for the four samples lie in a narrow temperature region around T_{M-I}, showing a typical CMR effect.

Figure 2 indicates the intimate relations between the magnetization and transportation of the investigated samples. This can lead us to more insight into the mechanism of the MR effect. With the development of oxygen deficiency, some Mn^{4+} ions will obtain electrons to change into Mn^{3+} ions, which will weaken the DE interaction, and then lead to partial

destruction of the long-range ferromagnetic ordering. Therefore, the oxygen deficient films are magnetically inhomogeneous (phase separation) as in the case of low-level-doped manganites.[14] Then one may suggest that superexchange occurs and the antiferromagnetic state forms in those regions where the number of Mn^{4+} ions becomes less. This case may naturally lead to the competition between ferromagnetic and antiferromagnetic interactions. As has been suggested previously, this is the basic reason for the formation of the spin-glass state.[14,15,17,18] The applied magnetic field has a role to enhance the ferromagnetism and restrict the formation of the spin-glass state. So the direct result can be seen that the spin-glass transition temperature T_{SG} decreases from 50K at 0.1T to 35K at 1T (Fig.2(b)).

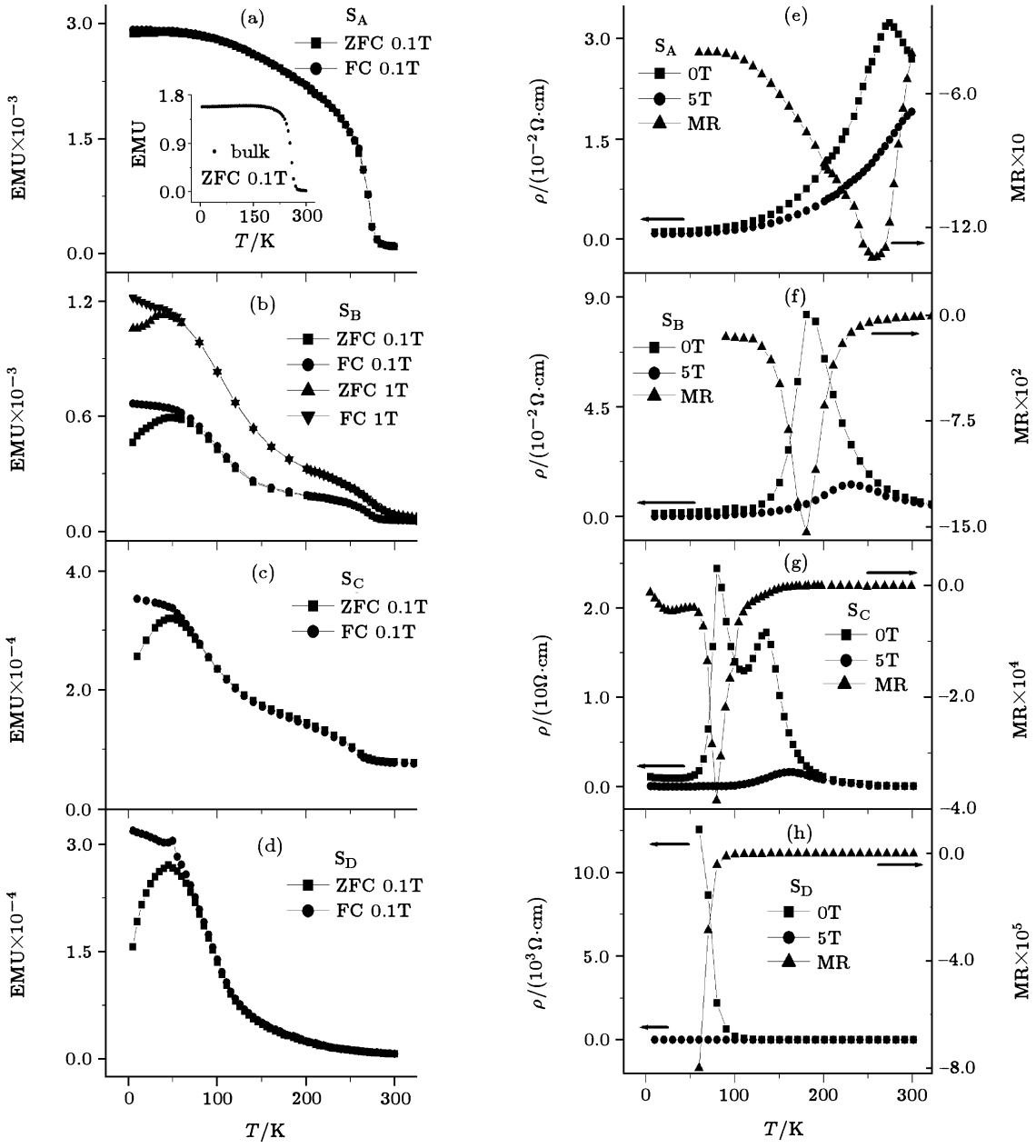


Fig.2. Measured $M(T)$, $\rho(T)$ and MR(T) data for four films. Figs.2(a)–(d) show $M(T)$ from S_A to S_D, Figs.2(e)–(h) show $\rho(T)$ and the corresponding MR(T) from S_A to S_D; for S_D, the resistivity is too large to measure in the zero field case below 60K.

The most unexpected phenomenon in resistivity-magnetic field relation $\rho(H)$ of oxygen deficient LCMO thin films is the positive MR effect observed in a relatively wide magnetic field range at temperatures around and above T_{M-I}, as shown in Fig.3 for sample S_B. For an initial field scan, $\rho(H)$ decreases with increasing magnetic field in the temperature range below T_{M-I} (Figs.3(a) and (b)). When the temperature is increased to that around T_{M-I} (185K), $\rho(H)$ starts to increase with increasing magnetic field in the field range of 0–0.015T (Fig.3(c)), i.e. the unambiguous positive MR effect occurs. The maximal positive MR effect is about 3.8% at 0.015T. In the temperature range above T_{M-I}, the magnetic field range, in which the positive MR effect exists, becomes larger. At 200K, the positive MR of about 16% is kept under the field up to 0.05T (Fig.3(d)). At 250 and 275K (Fig.3(e)), the positive MR being about 10% and $> 17.8\%$ respectively exist at the magnetic field up to 0.5T, even higher than 1T. This kind of effect can also be seen in samples S_C and S_D at temperatures above T_{M-I}. Therefore, it is clearly indicated that oxygen deficiency plays a direct role for the appearance of the positive MR effect.

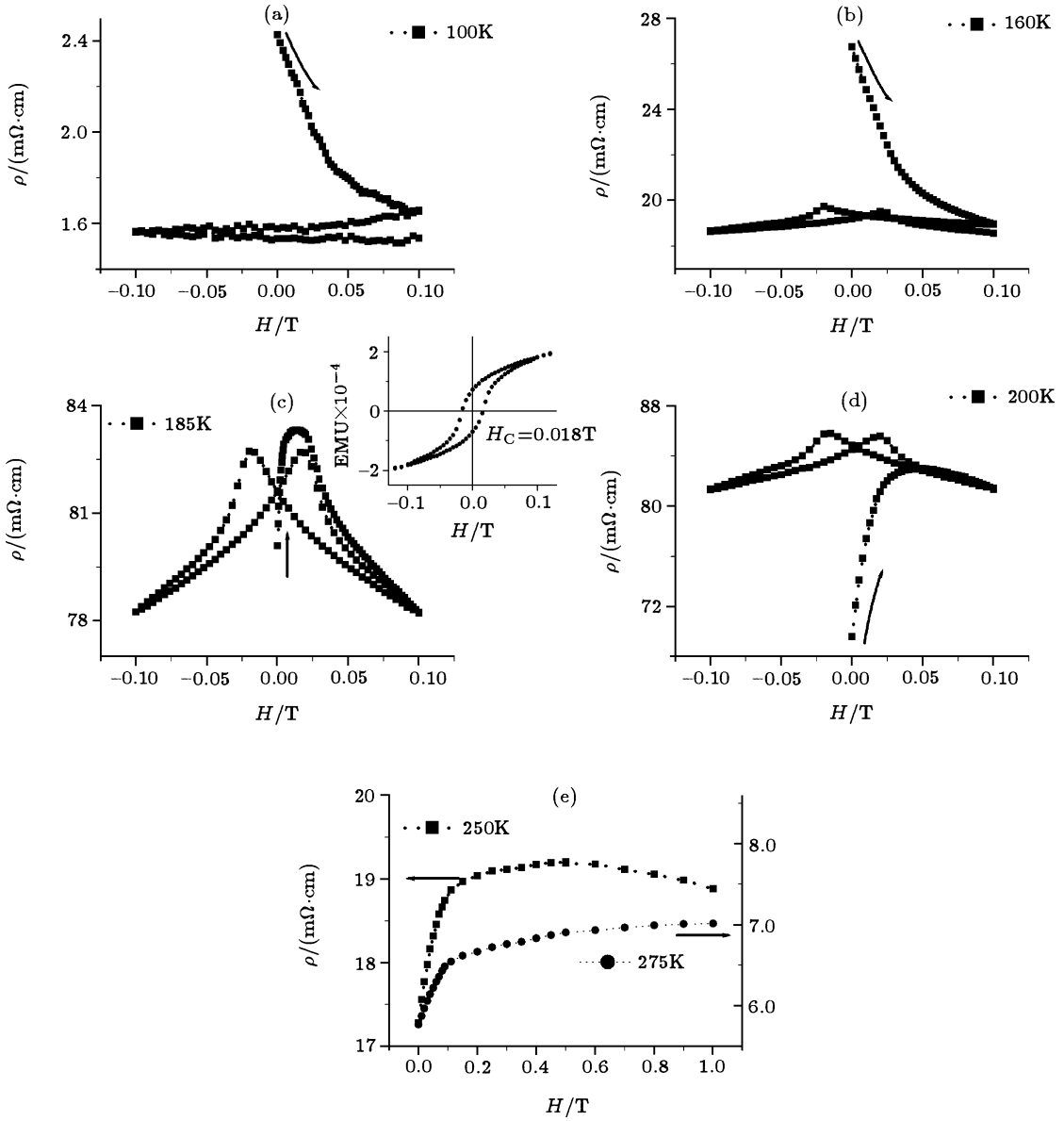


Fig.3. Magnetic field dependence of resistivity $\rho(H)$ of S_B film measured in 100(a), 160(b), 185(c), 200(d), 250 and 275 K(e), respectively.

Now, we attempt a discussion about the origin of the positive MR effect in oxygen deficient LCMO thin films. Previous investigations suggested that the quantum interference effect [19] and grain boundary effect [20,21] can lead to positive MR. The present positive MR is found in the higher temperature region (near and above $T_{\mathrm{M-I}}$). So this could not be attributed to the quantum interference which occurs in the low temperature region only. On the other hand, since the present thin films have a flatness better than 1 nm, the effect of grain boundary induced positive MR seems also impossible. We tend to suggest that the present positive MR effect may be caused by the magnetic polarons which form based on the stress due to oxygen deficiency and contribute to the conductance with hopping mode. It is easily understood that the oxygen deficiency in LCMO films directly induces the local lattice distortions. Then, the charge carriers are very possibly trapped in those lattice distorted regions in LCMO thin films and form magnetic polarons at temperatures higher than $T_{\mathrm{M-I}}$.[4] Therefore, we suggest that the magnetic polaron hopping may be the dominant factor in the conductance of such oxygen deficient LCMO thin films at temperatures above $T_{\mathrm{M-I}}$. According to the model of small polaron hopping, the zero-field resistivity of the oxygen deficient film $\mathrm{S_B}$ can be fitted to an equation of the form $\rho = AT\exp(E/k_{\mathrm{B}}T)$, and we have a hopping energy E=125±3meV. This value, relatively larger than that for the polarons in a high quality film,[22] implies the existence of inhomogeneity in the present oxygen-deficient film. When the magnetic field is applied, the size of magnetic polarons becomes larger (the number of them decreases), and the hopping conductance will be suppressed. This will naturally lead to the positive MR effect. With further increase of magnetic field, the MR effect turns from positive to negative. This may be attributed to the formation of a larger number of ferromagnetic domains near and below T_{C} under the relatively higher magnetic field which contributes to the percolation conductance in thin films.[5,7]

Finally, it should be noted that the ρ(H) curve caused by field scan in the range of 0.1T→ −0.1T→0.1T shows an obvious double-peak in a wide temperature range below T_{C}. The magnetic fields corresponding to the double-peak in $\rho(H)$ are identical to the coercive fields in the hysteresis loop (see the inset of Fig.3(c)). Therefore, such double-peak should reflect the domain wall scattering in the reversal magnetization of the ferromagnetic domains.[23]

4. Conclusions

In summary, oxygen deficient LCMO thin films have been systematically studied on their magnetism and transport properties. Due to the oxygen deficiency, two phenomena appear: (1) the long-range ferromagnetic ordering is partially destroyed and spin-glass behaviour emerges in the low temperature region; (2) the unambiguous positive magnetoresistance appears at and above $T_{\mathrm{M-I}}$ in a relatively low magnetic field range. This may be attributed to the conductance mode of magnetic polarons formed based on the distortion of lattice due to the oxygen deficiency in the film. In order to further understand the properties of the magnetic structure and the mechanism of MR effect in oxygen deficient LCMO films, experiment will be conducted in further work.

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