Origin of an enhanced colossal magnetoresistance effect in epitaxial Nd_{0.52}Sr_{0.48}MnO_{3} thin films

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I. INTRODUCTION

Hole-doped manganites L_{1-x}A_{x}MnO_{3}, where L and A are trivalent lanthanide ions and divalent alkaline-earth ions, respectively, have attracted considerable attention due to their interesting properties, especially colossal magnetoresistance (CMR), and potential for applications. The CMR phenomenon is traditionally interpreted in terms of a competition between the double-exchange (DE) ordering, which leads to a ferromagnetic (FM) metal state, and the cooperative Jahn-Teller effect, resulting in polaron localization at temperatures above the Curie point (T_C). However, it has been shown recently that incorporation of the antiferromagnetic (AFM) interaction can be drastically enhanced the CMR effect, increasing the magnetoresistance (MR) ratio to as high as 30 000%. In that case the CMR is associated with the development of short-range correlations among polarons above T_C, which resemble the charge configuration in the charge-ordered (CO) state, which is stabilized by the AFM interactions. Therefore, experimental observation of an enhanced CMR effect is more to be expected in the manganites with T_N > T_C, where T_N is the Néel temperature. A Nd_{0.52}Sr_{0.48}MnO_{3} thin film is a more suitable object for a test of this theoretical approach, because FM and AFM phases are present and the transition temperature can be controlled by the deposition mode. It has also been shown that both phases are formed from the paramagnetic state and exist separately from one other.

In this paper we report experimental results for Nd_{0.52}Sr_{0.48}MnO_{3} films deposited on single crystal LaAlO_{3} (001) substrates. The origin of the observed enhanced CMR is discussed in detail.

II. EXPERIMENTAL TECHNIQUES

The films were prepared by dc magnetron sputtering at a substrate temperature of 650 °C. Under these conditions the Nd_{0.52}Sr_{0.48}MnO_{3} (NSMO) films with a thickness of d ≈ 50, 110 and 160 nm were deposited on single crystal LaAlO_{3} (001) (LAO) substrates. θ-2θ x-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer in Cu Kα radiation. The lattice parameters evaluated directly from the XRD data were plotted against cos^2θ/\sin θ. From the intercept of the extrapolated straight line to cosθ/\sin θ = 0, a more precise lattice parameter was obtained. High-resolution electron microscopy (HREM) was carried out using a Philips CM300UT-FEG microscope with a field emission gun operated at 300 kV. The point resolution of the microscope was in the order of 0.12 nm. The cross-sectional specimens were prepared by the standard techniques using mechanical polishing followed by ion-beam milling at grazing incidence. All the microstructure measurements were carried out at room temperature. The resistance measurements were made by the four-probe method at temperatures of 4.2–300 K and in magnetic fields up to 5 T. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves were taken with a Quantum Design SQUID magnetometer with an in-plane magnetic field orientation. The magnetization curves for the bare substrates were extracted from the raw experimental data.

III. MICROSTRUCTURE

Figure 1(a) shows θ-2θ XRD scans for NSMO films with d ≈ 50 and 160 nm. Only the fundamental Bragg peaks of high intensity for the film (F) and the substrate (S) were observed, indicating that the deposition yields a highly c-oriented...
crystal structure. This is confirmed by analysis of the transmission contrast of the HREM images. Figure 1(b) shows the cross-sectional HREM image for a thick NSMO film ($d = 160$ nm). Inset A in Fig. 1(b) is a high-magnification view of the same image taken along the [010] zone axis, including the film/substrate interface. It can be seen that the film has an atomically clean and sharp interface without an amorphous intermediate layer or precipitations. The epitaxial relationship for film and substrate was determined to be $[001]_{\text{NSMO}}\parallel [001]_{\text{LAO}}$. This is confirmed by the corresponding fast Fourier transform (FFT) for the HREM image, shown in inset B of Fig. 1(b), which reveals the almost rectangular pattern of only basic Bragg spots. Microstructure analysis showed that these films have an orthorhombic crystal structure with lattice parameters $a \approx 0.387$, $0.383$ and $0.379$ nm, and $c \approx 0.388$, $0.39$ and $0.394$ nm for $d \approx 160$, $110$ and $50$ nm, respectively, or very close to published data.\(^5,6\)

Thus, all the deposited films have a homogeneous microstructure without an intermediate layer\(^7\) and column-like texture.\(^8,10\) On the other hand, the lattice mismatch between the film and the substrate ($\approx 2\%$) leads to biaxial compressive in—plane and tensile out-of-plane strains.

IV. EXPERIMENTAL RESULTS OF MAGNETIC AND TRANSPORT PROPERTIES

Figure 2 shows the in-plane FC temperature variations in the magnetic moment, $M(T)$, for NSMO films with thickness $d \approx 50, 110$ and $160$ nm for magnetic fields of $100$ Oe and $1$ T. The low-field FC $M(T)$ curves reveal a significant thickness dependence of the Curie temperature: $T_C \approx 220$, $180$ and $115$ K for $d \approx 160$, $110$ and $50$ nm, respectively. The Néel temperature $T_N$ was extracted from the reduced temperature dependence of the magnetic moment, $M_{\text{FC}}/M_{\text{ZFC}}(T)$, at $H = 100$ Oe (shown as the inset in Fig. 2(a)) and essentially the same for all the films, $T_N \approx 125$ K. The peak position for the thinner film or the well-defined kink for the thicker ones in the $M_{\text{FC}}/M_{\text{ZFC}}(T)$ curve was associated with the onset of the AFM transition (indicated by an arrow). Therefore, the Curie temperature decreases rapidly with decreasing thickness of the NSMO film and falls to below the Néel point for $d \approx 50$ nm.

The effect of lattice-strain on the Curie temperature of these films has been discussed in detail\(^10\) on the basis of the Mills model.\(^11\) It was found that the change in the crystal lattice parameters with decreasing thickness can lead to the observed suppression of spin ordering in these films.

Figure 2(b) shows the FC $M(T)$ curves for the same films, taken at $H = 1$ T, which can be treated as the temperature variations in the saturated magnetic moment. This is...
confirmed by the magnetic hysteresis loops for the same films, shown in the inset to Fig. 2(b), which manifests a saturation of the magnetic moment even in an applied magnetic field of 1 T and at a low temperature (10 K).

Figure 3 is the temperature-dependent resistance $R(T)$ for the NSMO films with $d \approx 160, 110$ and 50 nm without and with an applied magnetic field of 5 T. It can be seen that the thicker and thinner films undergo a complete metal-insulator (MI) transition with decreasing temperature: $T_{MI} \approx 175$ and 95 K for $d \approx 160$ and 50 nm, respectively. At the same time, the film with $d \approx 110$ nm manifests two MI transitions at 160 and 85 K, which are sensitive to the applied magnetic field. This effect can not be explained by the existence of an additional FM phase with a different Curie point, because the FM $M(T)$ dependence for this film has only a single FM transition (see Fig. 2).

Figure 4 shows the temperature dependence of the magnetoresistance ratio for the same films. MR is defined as $100\% \times \frac{R(0) - R(H)}{R(0)}$, where $R(0)$ and $R(H)$ are the resistances with and without, respectively, an applied magnetic field of 5 T. The main peculiarity of the films studied here is an enormous increase in the CMR effect with decreasing thickness. Thus, MR $\approx 60\%$ for a thin film ($d \approx 50$ nm) while it does not exceed 400% for a thick one ($d \approx 160$ nm).

V. DISCUSSION

The following intriguing results require discussion: (i) the appearance of a second MI transition with decreasing temperature in the intermediate thickness film ($d \approx 110$ nm) and (ii) an enormous increase in the MR ratio in the thinnest film ($d \approx 50$ nm).

An explanation for the observed peculiarities in $R(T)$ must account for the following experimental facts. First, because the FC $M(T)$ behavior is the same at the Néel temperature for all the films (see Fig. 2), one can conclude that the AFM phase arises from a precursor paramagnetic state rather than from the existing FM phase. Therefore, both the FM and AFM phases co-exist separately from one other in the film at low temperature ($T < T_{C1}$) and can be treated as a percolating net of metallic (FM) and insulating (AFM) resistors. This is the principal difference between the samples and the bulk materials or half-doped films. Second, using the magnetic hysteresis loops and the FC $M(T)$ curves for $H = 1$ T shown in Fig. 2(b), one can estimate the concentration of the FM (metal) phase in our films at different temperatures as $M_s(T)/M_{s,bulk}$, where $M_{s,bulk} \approx 3.5 \mu_B/M_n$ is the magnetic moment for the bulk NSMO in the fully FM state. At low temperatures $M_s(T)/M_{s,bulk} \approx 0.49, 0.77$, and 0.91, while at the Néel point $M_s(T)/M_{s,bulk} \approx 0.154, 0.371$, and 0.591 for $d \approx 50, 110$ and 160 nm, respectively. At the same time the percolation threshold for the 3-dimensional magnetic percolating system is $p_c \approx 0.395$. Consequently, two kinds of resistor circuit can be realized in the film depending on the concentration of the FM metal phase: a parallel-resistor circuit for $M_s(T)/M_{s,bulk} \geq p_c$, and a series-connected resistor for $M_s(T)/M_{s,bulk} \leq p_c$, where the FM and AFM phases play the roles of separated resistors with a different temperature behaviors.

Given the above, we suggest the following explanation for the unusual behavior of $R(T)$ in the NSMO films. Thick films ($d \approx 160$ nm) undergo a classical MI transition at $T_{MI}^{FM} \approx 175$ K through the regular DE mechanism, because

![Figure 3](image3.png)

**Figure 3.** Temperature dependence of the resistance for NSMO with $d = 50$ (1), 110 (2), and 160 (3) nm without (solid symbols) and with (open symbols) an applied magnetic field of 5 T. The MI transition temperature is indicated by the arrows. $T_N$ indicates the Néel point. The curves are only guides for the eye.

![Figure 4](image4.png)

**Figure 4.** Temperature dependence of the MR ratio for NSMO with $d = 50$ (1), 110 (2), and 160 (3) nm. The curves are only guides for the eye.
\[ \frac{M_s(T)}{M_s^{\text{bulk}}} \geq p_r \] over the entire temperature range and the parallel-resistor circuit, alone, is realized. Therefore, the low-resistance FM metal-like phase shunts the high-resistance AFM phase, which exists for \( T_N < T_C \), and the corresponding \( R(T) \) rise with decreasing temperature associated with the CO AFM state, does not show up in the experimental curve. A similar transition occurs in the intermediate film with \( d \approx 110 \text{ nm} \) at high temperature, \( T_{MI}^{AFM} \approx 160 \text{ K} \) above \( T_N \) and not very far from the Curie point, \( T_C \approx 180 \text{ K} \). At the same time, the concentration of the FM phase (\( \approx 0.371 \)) does not exceed the percolation threshold at the Neel point, thereby providing the series-resistor circuit between the FM and AFM phases. Figure 3 shows that the resistance sharply increases for \( T \leq T_N \), as is typical for this compound and explained by electron localization in the CO AFM state.\(^{5,12} \)

However, in our case, the expected increase in \( R(T) \) with decreasing temperature does not extend to low temperatures and the resistance begins to fall off below a certain temperature, thereby forming the additional peak in \( R(T) \) \( T_{AFMI} \approx 85 \text{ K} \). At this temperature the concentration of the FM phase (\( \approx 0.57 \)) exceeds the percolation threshold and forms an infinitely conducting cluster which shunts the CO AFM resistance. In contrast to the thicker films, a thin NSMO film (\( d \approx 50 \text{ nm} \)) undergoes an AFM transition above the FM transition. Therefore, the observed rise in resistance for \( T \leq T_N \) with decreasing temperature only results from formation of the CO AFM state. On further cooling the FM phase appears in the film and completely shunts the AFM phase at a low temperature, \( T \leq T_{AFMI} \approx 95 \text{ K} \), thereby yielding the metal-like behavior of \( R(T) \).

The observed large difference in the MR ratio between thick and thin films is related to different mechanisms for the MI transition. In the first case, the FM-metal-like state develops from the paramagnetic (PM) insulating phase by the DE mechanism. An applied magnetic field increases the Curie point and shifts the MI transition to higher temperatures, causing a CMR effect. In the second case, a PM \( \rightarrow \) AFM transition takes place in the film and the FM phase acts as a shunt-resistor. In this case the MI transition has a percolation origin and is caused by a competition between the FM metal-like and the AFM insulating phase concentrations. A similar mechanism for CMR has been proposed recently, which includes stabilization of the CO AFM state among correlated polaron clusters owing to AFM coupling.\(^2 \) The huge drop of the resistance in an applied magnetic field, in that case, is governed by a collapse (melting) of the CO state, which leads to an enhanced CMR effect.\(^{13} \)

VI. CONCLUSIONS

We have shown that the magnetic- and electron-phase states are controlled by the thickness of Nd\(_{0.52}\)Sr\(_{0.48}\)MnO\(_3\) films. The thickest film in these experiments manifests almost complete FM ordering and the MI transition is realized through the regular DE mechanism. The film with an intermediate thickness manifests an additional MI transition with decreasing temperature, which is provided by competition between the increasing FM phase and the AFM ordering, and has a percolation origin. The thinnest film has an MR ratio of up to \( \approx 60 \text{ 000\%} \) for an applied magnetic field of 5 T. The observed enhanced CMR effect in the thinnest film is explained by formation of a CO AFM state at a temperature above the Curie point and the collapse of the CO state in the high magnetic field. Thus, the deposition technique enables us to control the mechanism of the CMR effect in thin Nd\(_{0.52}\)Sr\(_{0.48}\)MnO\(_3\) films. This is a first step toward strongly correlated electron devices.

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