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Transport and magnetic properties of *in situ* grown thin-film La–Y–Ca–Mn–O

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We report a large magnetoresistance in *in situ* grown $La_{0.60}Y_{0.07}Ca_{0.33}MnO_x$ thin films made at a low substrate temperature of 600 °C without postdeposition annealing. The zero-field resistivity peaks around 120 K. The resistivity peak is reduced by two orders of magnitude by a 6 T field. Comparison of transport and magnetization data reveals a correlation of conductivity versus magnetization below the ferromagnetic transition temperature, which may suggest a double-exchange-based conduction mechanism. Above the ferromagnetic transition at low fields, a quadratic dependence of conductivity on magnetization is found, consistent with a spin-scattering-limited conductivity. © *1995 American Institute of Physics.*

The recent discovery of colossal magnetoresistance[1–3] (CMR) in La–Ca–Mn–O has spurred much interest in its mechanism and the potential use of this class of materials in magnetic sensors and read-head applications. However, for such applications the low-field room-temperature magnetoresistance (MR) needs to be significantly improved. Work on CMR thin-film materials to date uses a delicate high-temperature annealing process which most times involves temperatures as high as 900 °C.[1–3]

In this letter we present studies of the CMR effect in low-temperature deposited thin films of La–Y–Ca–Mn–O (LYCMO). We show that for this material, films with large (20 000%) CMR effect can be produced with a processing temperature not exceeding 600 °C, significantly lower than previous reports. Low growth temperature is important for synthesis of layered structures of the CMR perovskite and other materials because it reduces interface diffusion. The material LYCMO was chosen because it is the first system reported to have a large MR effect in its bulk form,[4] whereas most other CMR perovskites require a thin-film form with a well-tuned high-temperature annealing procedure to produce a large MR. This is presumably due to a smaller lattice constant ($a/2=3.859$ Å) of LYCMO,[4] which is induced by partial substitution of lanthanum with yttrium that has a smaller ionic radius.

Thin films of LYCMO were grown *in situ* using laser ablation with a Continuum Nd-YAG laser operating in frequency-tripled mode ($\lambda=355$ nm). A sintered ceramic target of the composition $La_{0.6}Y_{0.07}Ca_{0.33}MnO_x$ was used. A typical deposition was made with an oxygen pressure of 300 mTorr, a substrate temperature of 600 °C, and a laser power density around 3 J/cm^2. Single-crystal (100) $SrTiO_3$ substrates were used, on which about 100-nm-thick films are deposited. The deposition rate was about 0.5 Å/pulse. X-ray diffraction scans show a predominant (001) oriented growth with a lattice constant of $a/2=3.872$ Å, which is smaller than the value of 3.89 Å for a $La_{0.67}Ca_{0.33}MnO_x$ thin film,[1,2] but is still a bit larger than the bulk value[4] of 3.859 Å. This is probably due to stress from the lattice mismatch with $SrTiO_3$ substrate, which has a lattice constant of 3.90 Å.

The temperature-dependent resistivity is shown in Fig. 1. The zero-field resistivity peaks at a temperature which we will call T_p, corresponding to the ferromagnetic ordering, as observed in magnetization measurements described below. A magnetic field was applied perpendicular to the measurement current but parallel to the film surface. The field suppresses the broad resistance peak, and a relative MR ratio of 20 000% is obtained around 120 K in 6 T. This value is comparable with that obtained in La–Ca–Mn–O film after annealing at 900 °C.[2]

Figure 2 shows the temperature dependence of the magnetization for several values of magnetic field applied parallel to the film surface. To have an estimate of the size of the

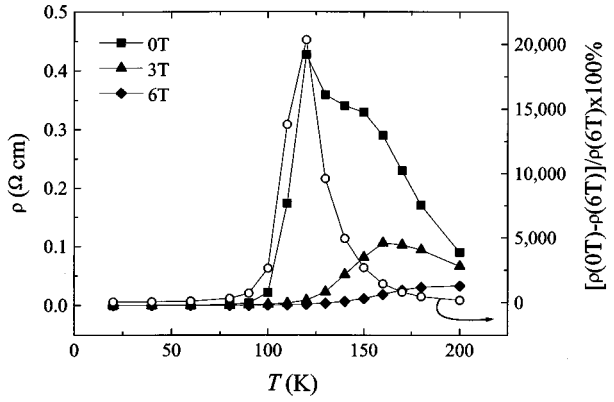

FIG. 1. Temperature dependence of resistivity (solid symbols) and magnetoresistance (open circles). Magnetic field is parallel to film but perpendicular to measurement current. Film has a dimension of around 0.2 cm×1.0 cm×100 nm. Current transport is along the long axis. The measurement current is 10 μA.

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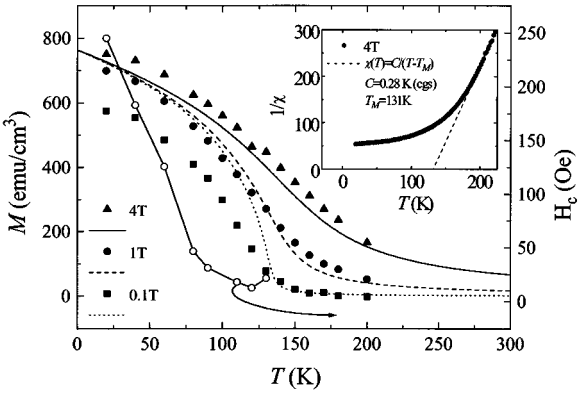

FIG. 2. Temperature dependence of magnetization. Points are data, lines are calculations based on mean-field model. Calculation parameters are: $T_M=131$ K, $C=0.28$ K (cgs), $M_s=765$ emu/cm^3. T_M and C are estimated from the high-temperature, high-field Curie-Weiss slope as shown in the inset. M_s is taken as the low-temperature saturation moment. Open circles show the magnetic coercivity as a function of temperature as determined from hysteresis loop measurements.

magnetic moment, a simple classical mean-field model is used to parameterize the observed data. In this model the mean-field magnetization is written as[5] $M/M_s=L(\alpha)$, where $L(\alpha)=\coth\alpha-1/\alpha$, and $\alpha=\mu H/kT+3(T_M/T)(M/M_s)$, where T_M is the mean-field ordering temperature, k is the Boltzman constant, M_s is the saturation moment, and μ is the magnetic moment of the basic magnetic cluster whose internal degree of freedom is frozen in the energy range of concern. The model assumes a uniform magnetic cluster size.

The high-field, high-temperature data were used to obtain an estimate on the mean-field Curie temperature T_M and Curie constant $C=\mu M_s/3k$, as shown in the inset of Fig. 2. Combining this with the low-temperature, high-field magnetization, which we assume to be M_s, we obtain $\mu=3kC/M_s\approx16.6\mu_B$, where μ_B is a Bohr magneton. Magnetization curves calculated using this set of parameters are shown as lines in Fig. 2. The general shape of the temperature and field dependence of the data is well reproduced, although in low fields such as 0.1 T, the measured magnetization falls below model prediction. A spin-freeze process related to the anisotropy energy of individual clusters may play a role in this field range. This is consistent with a low-temperature magnetic coercivity of around 0.25 T as shown in open circles in Fig. 2.

A ferromagnetically ordered Mn^{3+}/Mn^{4+} mixture has an effective magnetic moment between $3.8\mu_B$ for the $3d^3$ state of Mn^{4+}, and $4.9\mu_B$ for the $3d^4$ state of Mn^{3+} (spin only, calculated values). With a measured M_s around 765 emu/cm^3 and a pseudocubic cell volume of (3.872 Å),[3] one gets around $4.79\mu_B$/Mn site. Thus the magnetic cluster of $16.6\mu_B$ involved here appears to contain only three or four Mn ions. The volume density of such magnetic clusters coincides roughly with the Ca concentration. Whether this implies a ferromagnetic cluster centered around each Ca^{2+} dopant is not yet clear, but it is an intriguing thought.

It is known that in these perovskite manganates below their ferromagnetic transition, the increase of electrical conductivity is accompanied by the development of a ferromagnetic moment.[6] This is explained by the double-exchange model,[7] in which the doping of conduction carriers also causes a deformation of the Mn^{3+}-O-Mn^{4+} spin alignment between the neighboring Mn-O sites, creating a change in net ferromagnetic moment. Since the conductivity depends on carrier concentration also, a definite correlation between conductivity σ and magnetization M is expected. Above T_p, the Mn spins are disordered, and for conduction carriers strong spin-dependent scattering is present which reduces conductivity, possibly resulting a quadratic dependence of conductivity on magnetization in the low-field limit. For the rest of this letter, we will focus on the experimental investigation of the relationship between conductivity σ and magnetization M.

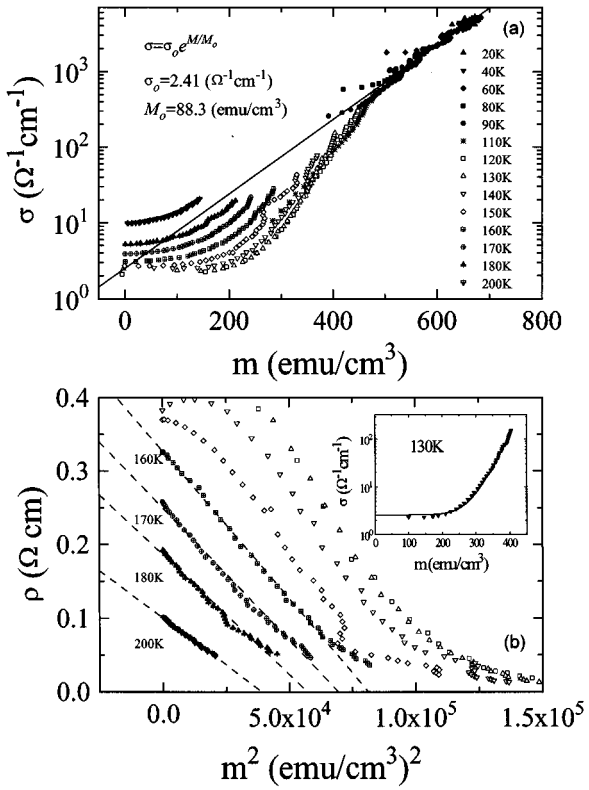

FIG. 3. (a) Relationship between conductivity and magnetization. Data taken below T_p appear to follow a correlation $\sigma=\sigma_0\exp(M/M_0)$. Data above T_p do not. (b) Above T_p and at low fields, resistivity shows a quadratic dependence on magnetization, as shown here by the dashed lines. Inset: a fit of Eq. (2) to data at 130 K.

Figure 3(a) shows the relationship between electrical conductivity $\sigma(H,T)$ and magnetization $M(H,T)$. For temperatures below T_p, a universal correlation is seen for σ vs M, in the form of $\sigma=\sigma_0\exp(M/M_0)$, regardless of the values of H and T. Similar behavior has also been observed in the La-Ca-Mn-O thin films.[8] The appearance of the σ-M correlation in Fig. 3(a) depends on the handling of background substraction in the measurement of $M(H,T)$. For data presented in this letter, a linear susceptibility as measured from the 20 K high-field M-H curve is used as background correction. Separate measurements on blank substrates between 5 and 300 K show that the background correlation is temperature independent.

The simple correlation between σ and M breaks down

for temperatures above T_p, and conductivity data fall below the correlation line, plausibly due to the presence of strong spin-dependent scattering. Data in this temperature region are replotted in Fig. 3(b), where in low-field, small M limit, a different dependence, namely, $\rho=\rho_0-\rho_1 M^2$ is found, in which ρ_0 is the zero-field resistivity, and ρ_1 appears to be rather insensitive to temperature variations.

The correlation $\sigma=\sigma_0 \exp(M/M_0)$ is taken by Hundley *et al.*[8] as evidence for polaronic hopping. However, it is not clear how this could be reconciled with the observation of a rather temperature insensitive M_0, as seen in Fig. 3(a). A thermal activation picture would result in $M_0 \propto T$. On the other hand, one may wonder if it is possible that such correlation may result from a bandlike conduction of small magnetic polarons.

The M^2 dependence of resistivity is commonly seen in dilute magnetic systems with exchange scattering.[9] Although in such cases it is often the band splitting, rather than the alignment of localized spins in field, that is the dominant cause for a negative magnetoresistance. Searle and Wang[10] have explored the relationship between σ and M with a simple spin-scattering model for a double-exchange-coupled system, and obtained a relation of

$$\sigma(T,H)=\sigma_0 \frac{1+(M/M_s)^2}{1-(M/M_s)^2}, \tag{1}$$

which at small M limit also leads to a quadratically dependent conductivity. Good agreement was obtained for Eq. (1) in perovskite $La_{0.69}Pb_{0.31}MnO_3$ single crystals.[10] For us, however, while Eq. (1) describes data well above T_p, it fails to account for the correlation near or below T_p. Even above T_p, a strongly temperature-dependent saturation moment M_s must be used, which makes the model somewhat unphysical.

In reviewing the data, we found that an empirical relation

$$\sigma(T,H)=\sigma_0 \exp(-E/kT)+\sigma_1(T) \exp(M/M_0)\left(\frac{M}{M_s}\right)^2 \tag{2}$$

describes the behavior of data well both above and below T_p. Two parallel conduction channels are considered in arriving at Eq. (2). The first term is the hopping conductivity that is apparently present at high temperatures, the second term is a spin-dependent conduction term, where the $\exp(M/M_0)$ factor describes the low-temperature correlation, and the $(M/M_s)^2$ factor accounts for the high-temperature magnetic scattering. The second term in Eq. (2) is more like a band-conduction term with strong spin-scattering present at high temperature which may cause significant localization effects, and a bandlike conduction at low temperature with parameters that may depend on the spin canting angle. An example of Eq. (2)'s fit to measured data is shown in the inset of Fig. 3(b).

In conclusion, we have observed a large magnetoresistance effect in *in situ* grown films of La–Y–Ca–Mn–O. The growth of such film was accomplished at a low substrate temperature of 600 °C, which is potentially important for fabrication of multilayer structures. Studies of the correlation between transport and magnetization reveals two temperature regions, one below and one above the ferromagnetic ordering temperature T_p, where two different limits of conductivity are obtained. For temperatures below T_p, conductivity shows a universal correlation with magnetization M. Above T_p a quadratic dependence of resistivity on M is seen at low fields.

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