PRAMANA
— journal of
physics

Vol. 58, Nos 5 & 6
May & June 2002
pp. 1079–1083

Electrical transport in $La_{1-x}Ca_xMnO_3$ thin films at low temperatures

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Abstract. We report here the low-temperature resistivity of the chemical solution deposited $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.3 and 0.33) thin films on $LaAlO_3$ substrates. The films were post-annealed in atmosphere at 850°C. The low-temperature resistivity data has been studied in order to understand the nature of low-temperature conduction processes. The data showed T^2 dependence from 60 K to 120 K consistent with the single magnon scattering process. The deviation from this quadratic temperature dependence at low temperatures is attributed to the collapse of the minority spin band. The two-magnon and electron–phonon processes contribute to scattering of carriers in the temperature range above 120 K.

Keywords. $La_{1-x}Ca_xMnO_3$ thin films; electrical transport; low temperature resistivity; colossal magnetoresistance.

PACS No. 75.30.Vn

1. Introduction

Colossal magnetoresistance property of alkaline earth (Ca, Sr, Ba, etc.) doped rare earth (La, Nd, Pr, etc.) manganites rekindled the interest of the researchers to understand the origin of the conduction mechanisms in these compounds [1]. The low-temperature resistivity of these manganites is believed to be dominated by electron–electron, electron–magnon and electron–phonon conduction processes [2]. The transport properties of the device-worthy and epitaxial thin films, prepared by the simple and inexpensive chemical solution deposition method, need to be studied completely in order to utilize them in device applications. We report here the low-temperature transport properties of the chemical solution deposited $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.3, 0.33) thin films.

2. Experiment

Thin films of $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.3, 0.33) were coated on $LaAlO_3$ substrates by chemical solution deposition. A precursor solution consisting of lanthanum, calcium and manganese propionates in stoichiometric proportion was used for this purpose. The films were post-annealed in atmosphere at 850°C for 1 h. The detailed preparation method has

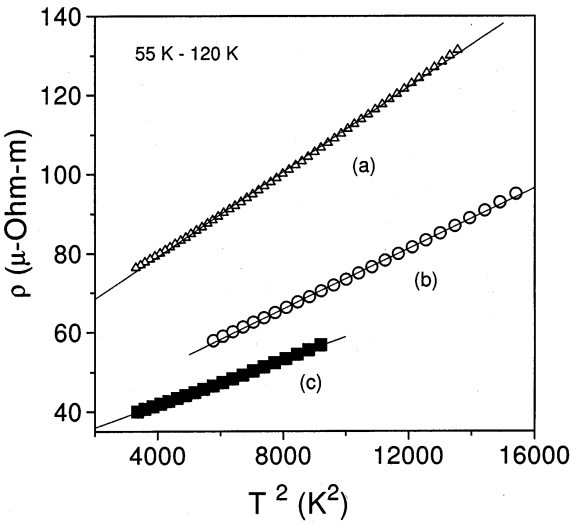

Figure 1. Resistivity vs. T^2 plots of $La_{1-x}Ca_xMnO_3$ thin films. (**a**) $x=0.2$, (**b**) $x=0.3$, (**c**) $x = 0.33$.

been published elsewhere [3]. X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies showed that the films are of good quality and epitaxial in nature. The films are of thickness about 1 μm. The electrical resistivity of the films was measured by linear four-probe method down to 20 K.

3. Results and discussion

The resistivity vs. temperature plots of all the films show an insulator to metal (I–M) transition. The maximum value of the resistivity (ρ_{max}) lies between 2.0×10^5 $\mu\Omega$-cm and 4.0×10^5 $\mu\Omega$-cm. The resistivity data between 60 K and 120 K was fitted to an expression $\rho_0 + \rho_2 T^2$. Figure 1 shows the resistivity vs. T^2 plot for the films. The slope (ρ_2) of the straight lines was found to decrease with the composition from $x = 0.2$ to 0.33. At higher temperatures the resistivity data was found to be proportional to T^n, where $n = 4.5$ or 5. Figures 2 and 3 show the resistivity vs. $T^{4.5}$ and T^5 plots, respectively in the temperature range 155–230 K for all the samples.

Many investigators attributed the T^2 dependence to the electron–electron (e–e) scattering process [4]. Kadowaki and Woods [5] derived an empirical relation between the coefficient ρ_2 and the coefficient γ of the electronic specific heat for materials exhibiting electron–electron scattering. It was found that, ρ_2/γ^2 has a material-independent value of $\approx 1 \times 10^{-5}$ $\mu\Omega$-cm (mol K/mJ)^2. Thus in the manganites if e–e scattering occurs at low temperatures this calculated ratio should be close to the above value for the Kadowaki–Woods parameter. We have calculated this parameter for our films using ρ_2 and γ of the specific heat data reported for single crystal samples [6] and found a value of about 1000 times the Kadowaki–Woods parameter. This rules out e–e scattering process in our films.

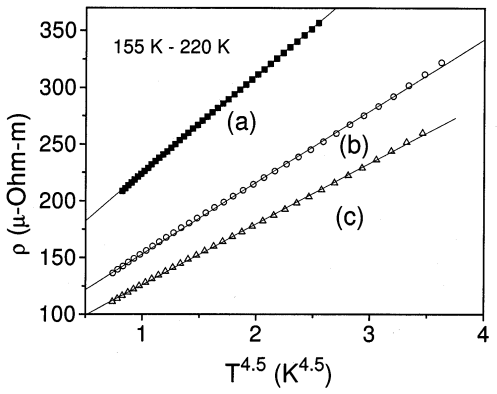

Figure 2. Resistivity vs. $T^{4.5}$ plots of $La_{1-x}Ca_xMnO_3$ thin films. (**a**) $x = 0.2$, (**b**) $x = 0.3$, (**c**) $x = 0.33$.

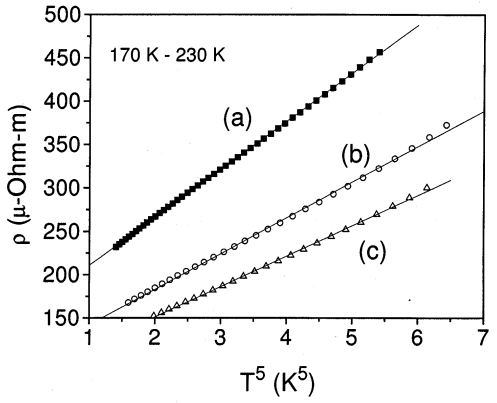

Figure 3. Resistivity vs. T^5 plots of $La_{1-x}Ca_xMnO_3$ thin films. (**a**) x=0.2, (**b**) x=0.3, (**c**) $x = 0.33$.

Jaime *et al* [7] argued that the T^2 contribution reflects the reappearance of minority spin states that are accessible to thermally excited magnons. Mannari's [8] calculation of electron–magnon resistivity has been extended to the calculation of energy bandwidth of minority spin sub-band [7]:

$$\rho_2 = \frac{9\pi^3 N^2 J^2 \hbar^5}{8e^2 E_F^4 k_F} \left(\frac{k_B}{m^* D}\right)^2 I(\varepsilon)\,, \tag{1}$$

where NJ is the electron–magnon coupling energy, which is equal to $W - E_F$ in the double exchange Hamiltonian. $2W$ is the bandwidth and the magnon energy is given by Dq^2.

$I(\varepsilon)$ was defined by

$$I(\varepsilon) = \int_{\varepsilon}^{\infty} \frac{x^2}{\sinh^2 x}\,\mathrm{d}x\,. \tag{2}$$

Table 1. Fit parameters of low temperature resistivity data.

$La_{1-x}Ca_xMnO_3$	$\rho_2(\times 10^{-1}$ $\mu\Omega$-cm/K^2)	γ (mJ/mol K^2)	$N(\varepsilon_F)$ ($\times 10^{28}$/eV m^3)	ε_F (eV)	m^*/m	$2W$ (eV)
$x = 0.2$	5.39	7.17	1.06	0.49	1.7	1.64
$x = 0.3$	3.84	5.2	1.15	0.68	1.6	5.18
$x = 0.33$	2.86	4.7	1.14	0.75	1.58	5.70
$Nd_{0.67}Sr_{0.33}MnO_3$ thin film [10]	0.39	25	6.4	0.13	8.8	0.55

The lower limit is $\varepsilon = Dq^2_{\min}/2k_BT$, where $Dq^2_{\min}$ is the minimum magnon energy that connects spin-up and spin-down bands. The value of $I(\varepsilon) \approx 1.2$ between 60 K and 120 K where T^2 dependence is observed. D is the stiffness constant, which is determined by neutron scattering and muon spin resonance [9]. The density of states $N(\varepsilon_F)$ was calculated from the γ value. Fermi energy (ε_F), effective mass (m^*) and Fermi wave vector (k_F) were calculated from n, the number of states per unit volume. (n is assumed to be equal to the concentration per unit cell volume per mole). Table 1 shows the calculated values of the parameters. The Fermi energy, E_F and the bandwidth of the thermally excited magnons, $2W$ were found to increase with x from 0.49 eV to 0.75 eV and from 1.6 eV to 5.7 eV, respectively. The calculated parameters are compared with the corresponding values reported earlier for $Nd_{0.67}Sr_{0.33}MnO_3$ pulsed laser deposited thin films in table 1 [10].

The $T^{4.5}$ dependence of the resistivity may be attributed to the two magnon process in the double exchange ferromagnets at low temperatures whereas the T^5 behavior would arise from electron–phonon interaction [11]. The overlap in the temperature range of the two fits in our films proved that either one or both of these processes might contribute to the resistivity in the temperature range from 120 K to 220 K.

4. Conclusion

Low-temperature resistivity data of the chemical solution deposited $La_{1-x}Ca_x$-MnO_3 ($x = 0.2, 0.3, 0.33$) thin films showed a dominant T^2 temperature dependence from 60 K to 120 K, which is consistent with the one-magnon scattering process. The disappearance of T^2 behavior below 60 K is attributed to the collapse of the magnon (minority) sub-band as each local spin-down axis aligns with the magnetization. The minority spin bandwidth is found to increase with the concentration of Mn^{4+} ions. The large value of Kadowaki–Wood's parameter appears to rule out an electron–electron scattering mechanism. The resistivity data above 120 K up to 220 K was fitted to $T^{4.5}$ as well as a T^5 dependence which may be consistent with the double magnon and the electron–phonon scattering processes respectively.

Acknowledgements

The authors thank M Pattabiraman for useful discussions.

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