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LETTER TO THE EDITOR

Unusual electrical transport mechanism in the ferromagnetic state of the magnetoresistive manganites

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Abstract. We report the precise resistivity data in the ferromagnetic state of high-quality epitaxial thin films of $La_{1-x}Ca_xMnO_3$. The data below 100 K can be perfectly fit by $\rho = \rho_o + BT^{4.5} + C/\sinh^2(\hbar\omega_s/2k_BT)$. Here ρ_o is the residual resistivity, the second term arises from two-magnon scattering, and the third term is associated with small-polaron coherent motion which involves a relaxation due to a soft optical phonon mode. Such a soft mode is related to the tilt/rotation of the oxygen octahedra, and has a low frequency ($\hbar\omega_s/k_B \sim 80$ K). The present result provides an important constraint on the fundamental physics of manganites.

The magnetic properties of the manganite perovskites $Re_{1-x}A_xMnO_3$ (Re = a rare-earth element, and A = a divalent element) have attracted renewed interest because of the observation of colossal magnetoresistance (CMR) in thin films of these materials [1,2]. Despite tremendous experimental efforts [3], the basic physics and the microscopic mechanism for the colossal magnetoresistance in these materials remain controversial [4–6]. A number of experiments have provided strong evidence for the existence of small polaronic charge carriers [8–10] and their hopping conduction in the paramagnetic state of manganites [11,12]. However, the nature of the charge carriers and the electrical transport mechanism in the low-temperature metallic state have not been resolved. At low temperatures, a dominant T^2 contribution in resistivity is generally observed, and has been ascribed to electron–electron scattering [13]. Jaime *et al* [14] have recently shown that the resistivity is essentially temperature independent below 20 K and exhibits a strong T^2 dependence above 50 K. In addition, the coefficient of the T^2 term is about 60 times larger than that expected for electron–electron scattering. They thus ruled out the electron–electron scattering as the conduction mechanism and proposed single magnon scattering with a cutoff at long wavelengths. In their scenario [14], they considered a case where the manganese e_g minority (spin-up) band lies slightly above the Fermi level (in the majority spin-down band) with a small energy gap of about 1 meV. This is in contradition with optical data [15] which show that the manganese e_g minority band is well above the Fermi level. This suggests that the conduction mechanism proposed in [14] is not relevant.

Alternatively, one should consider a contribution from electron–phonon scattering. At low temperatures, the acoustic phonon scattering would give a T^5 dependence, which is not consistent with the data [14]. Recently, Alexandrov and Bratkovsky [6] have proposed a theory for colossal magnetoresistance in doped manganites. Their model predicts that small polaronic transport is the prevalent conduction mechanism even below the ferromagnetic ordering temperature T_C. If this theoretical model is relevant, the resistivity data at low temperatures should be consistent with small polaron conduction mechanism.

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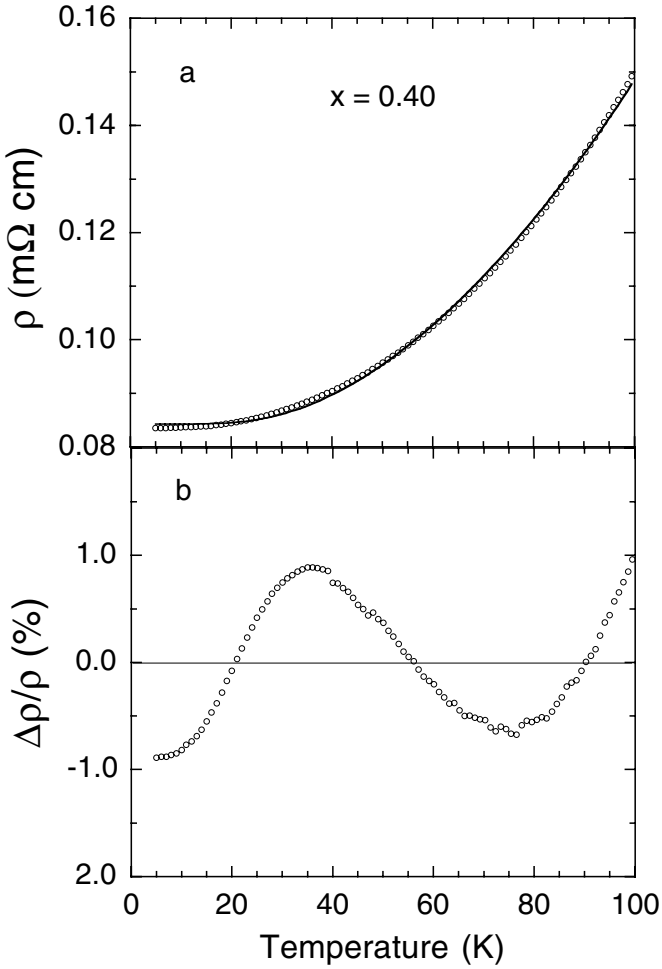

Figure 1. (a) Low-temperature resistivity $\rho(T)$ for a high-quality film of $La_{0.60}Ca_{0.40}MnO_3$. The data can be fitted by equation (3) with $\hbar\omega_s/k_B = 100(2)$ K. The solid line is the fitted curve. (b) The relative deviation $\Delta\rho/\rho$ between the data and the fitted curve in (a). The maximum deviation is about 1%.

Although a theory of small polaron conduction at low temperatures was developed more than 30 years ago [16,17], no experimental data have been used to compare with the theoretical prediction. The theory shows that [16, 17], for $k_BT < 2t_p$, the resistivity is given by

$$\rho(T) = (\hbar^2/ne^2a^2t_p)(1/\tau) \tag{1}$$

where t_p is the effective hopping integral of polarons, n is the carrier density, a is the lattice constant, and $1/\tau$ is the relaxation rate:

$$1/\tau = \sum_\alpha A_\alpha/\sinh^2(\hbar\omega_\alpha/2k_BT) \tag{2}$$

where ω_α is the average frequency of one optical phonon mode, A_α is a constant, depending on the electron–phonon coupling strength. It is worth noting that the above expression for $1/\tau$ has been generalized from one optical phonon mode to multiple modes since complex compounds such as manganites contain several optical phonon modes. From the above equations, one can

see that only the low-lying optical modes with a strong electron–phonon coupling contribute to the resistivity at low temperatures due to the factor of $1/\sinh^2(\hbar\omega_\alpha/2k_BT)$. As discussed below, among the low-lying optical modes, only the softest optical phonon branch that is related to the tilt/rotation of the oxygen octahedra is strongly coupled to the carriers. The high-frequency phonon modes such as the Jahn-Teller modes also have a strong coupling with carriers, but these modes have negligible contributions to the resistivity below 100 K because of an exponentially small factor in equation (2). By inclusion of impurity scattering, the resistivity at low temperatures is

$$\rho(T) = \rho_0 + C/\sinh^2(\hbar\omega_s/2k_BT) \tag{3}$$

where ω_s is the average frequency of the softest optical mode, and C is a constant, being proportional to m^*/n (where m^* is the effective mass of carriers).

Now we consider the contribution from magnon scattering. Kubo and Ohata [7] have studied the magnon scattering for half metals where the spin-up (minority) and spin-down (majority) bands are well separated. In this case, one-magnon scattering is forbidden, and thus the two-magnon process is responsible for the low-temperature resistivity, which gives a contribution that is proportional to $T^{4.5}$ [7]. If we include this contribution, we have

$$\rho(T) = \rho_0 + BT^{4.5} + C/\sinh^2(\hbar\omega_s/2k_BT). \tag{4}$$

In figure 1(a), we show the low-temperature resistivity $\rho(T)$ for a high-quality epitaxial thin film of $La_{1-x}Ca_xMnO_3$ with $x = 0.40$. The films of $La_{1-x}Ca_xMnO_3$ were prepared by pulsed laser deposition using a KrF excimer laser [18]. The films were finally annealed for 10 h at about 940 °C and oxygen pressure of about 1 bar. The resistivity was measured using the van der Pauw technique, and the contacts were made by silver paste. The measurements were carried out in a Quantum Design measuring system. The residual resistivity is 84 $\mu\Omega$cm which is even smaller than that for single-crystalline samples [19]. This indicates that the quality of the film is high, which allows one to study the intrinsic electrical transport properties of this system.

The data can be fitted by equation (3) with $\hbar\omega_s/k_B = 100(2)$ K. It is evident that the fitting is quite good, but still shows a systematic deviation as seen more clearly from figure 1(b) where the relative difference $\Delta\rho/\rho$ between the data and the fitted curve is plotted. This suggests that an additional contribution should be included in the fitting. In figure 2(a), we fit the data with equation (4) which comprises the contribution from two-magnon scattering. It is striking that the fit is nearly perfect with a negligible systematic deviation (see figure 2(b)). The fitting parameter $\hbar\omega_s/k_B = 80.0(8)$ K. In figure 3, we plot the respective contribution to the resistivity from the phonon or magnon scattering. It is apparent that the phonon scattering makes a dominant contribution to the resistivity at low temperatures. This is consistent with the fact that there is a negligible magnetoresistance effect below 100 K [19]. We would like to mention that we have fitted the data only below 100 K. This is because n/m^* is temperature independent below 100 K [20], so that equation (4) is valid only in this temperature range.

Figure 4(a) shows $\rho(T)$ data for another high-quality epitaxial thin film of $La_{1-x}Ca_xMnO_3$ with $x = 0.25$. The data can be perfectly fitted by equation (4) with $\hbar\omega_s/k_B = 74.5(4)$ K. The systematic deviation is very small, as seen from figure 4(b). If we allow the power in the second term of equation (4) to be a fitting parameter, the best fit gives a power of 4.6(4), very close to 4.5 expected from two-magnon scattering [7] or to 5 expected from acoustic phonon scattering.

The excellent agreement between the data and equation (4) implies the presence of small polarons and their metallic conduction in the low temperature ferromagnetic state. The present result thus gives strong support to a theory of colossal magnetoresistance recently proposed

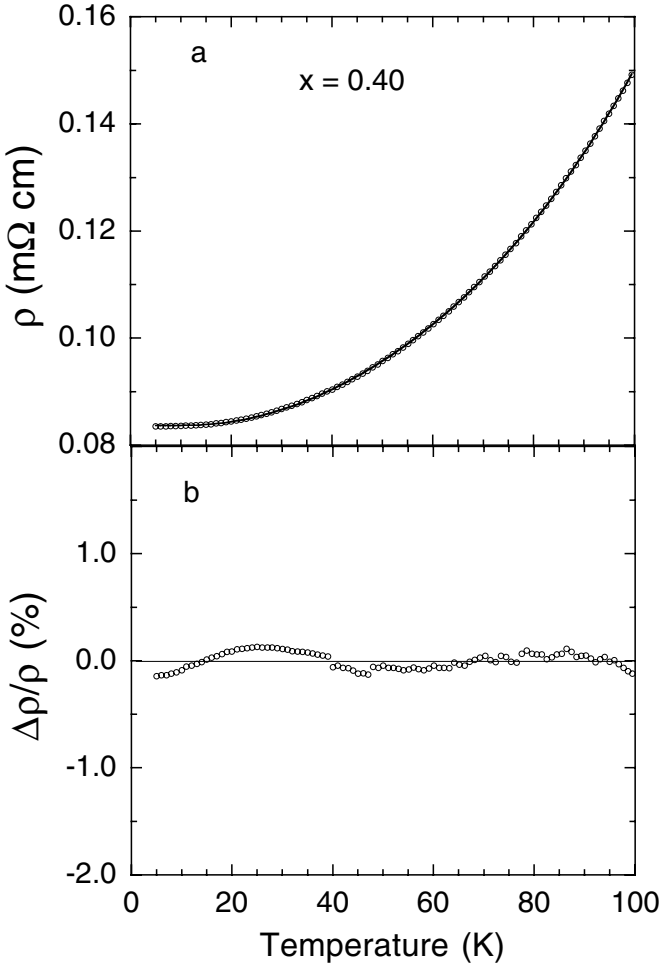

Figure 2. (a) Low-temperature resistivity $\rho(T)$ for a high-quality film of $La_{0.60}Ca_{0.40}MnO_3$. The data are fitted by equation (4) with $\hbar\omega_s/k_B = 80.0(8)$ K. The solid line is the fitted curve. (b) The relative deviation $\Delta\rho/\rho$ between the data and the fitted curve in (a). The maximum deviation is about 0.1%.

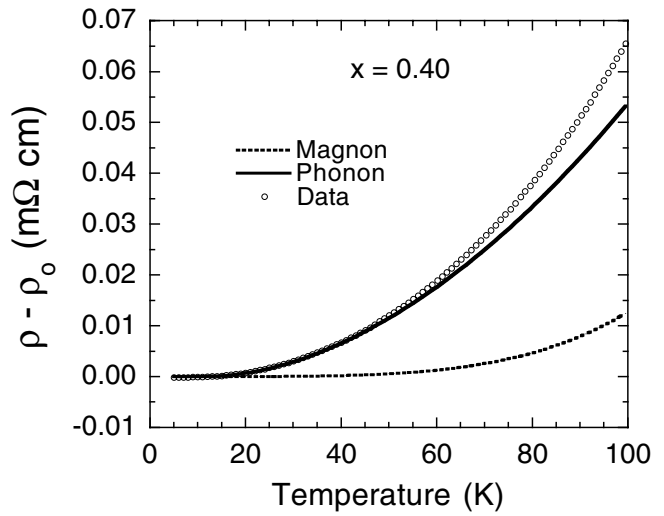

Figure 3. The respective contribution to the resistivity from the phonon or magnon scattering in $La_{0.60}Ca_{0.40}MnO_3$. It is clear that the phonon scattering makes a dominant contribution to the resistivity at low temperatures.

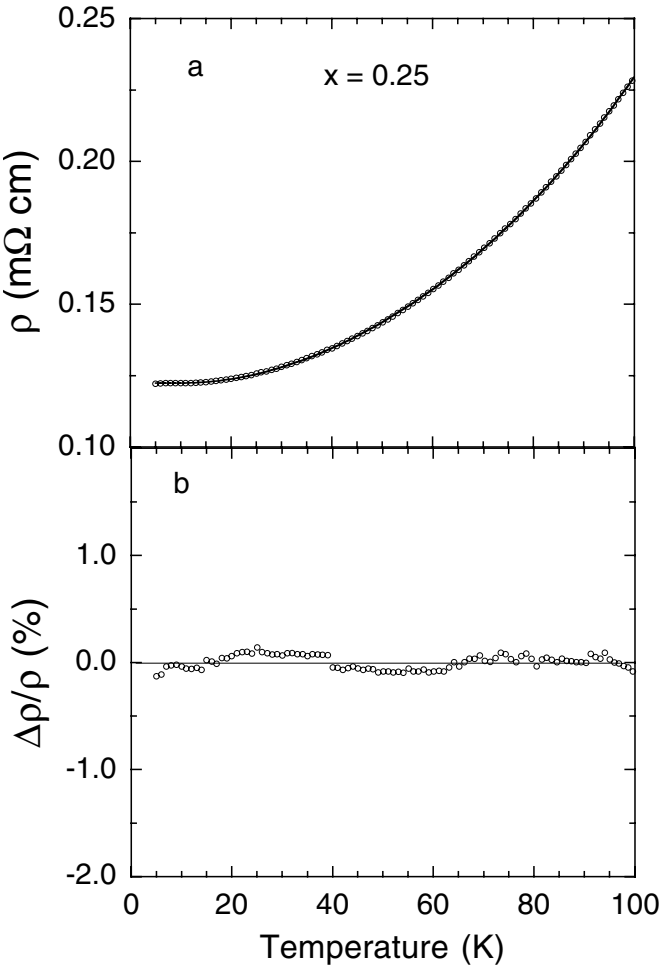

Figure 4. (a) Low-temperature resistivity $\rho(T)$ for a high-quality film of $La_{0.75}Ca_{0.25}MnO_3$. The data are fitted by equation (4) with $\hbar\omega_s/k_B$ = 74.5(4) K. The solid line is the fitted curve. (b) The relative deviation $\Delta\rho/\rho$ between the data and the fitted curve in (a). The maximum deviation is less than 0.1%.

by Alexandrov and Bratkovsky [6]. The result also indicates that the low-lying mode with $\hbar\omega_s/k_B \simeq 80$ K has a strong coupling with the conduction electrons.

Now a question arises: what is the origin of such a soft mode that is strongly coupled to the carriers? We are not aware of any measurements for the phonon dispersions of the manganites by inelastic neutron scattering. However, it is known that the soft mode with $\hbar\omega_s/k_B \simeq 100$ K commonly exists in perovskite oxides, and is associated with the tilt/rotation of the oxygen octahedra [21, 22]. Tunneling experiments on the superconducting $Ba(Pb_{0.75}Bi_{0.25})O_3$ [23] directly reveal a strong electron–phonon coupling at a phonon energy of about 6 meV. Inelastic neutron scattering experiment on the same compound shows a soft mode at 5.9 meV, which is attributed to rotational vibrations of the oxygen octahedra at M point of the cubic Brillouin zone [22]. These results clearly demonstrate that the rotational mode in this perovskite oxide has a strong coupling with the carriers. One should also note that the phonon energy ($\sim$ 6 meV) of the rotational mode observed in $Ba(Pb_{0.75}Bi_{0.25})O_3$ is very close

to that (6.4–6.9 meV) deduced for the manganite films from the resistivity data. Moreover, the theoretical investigations [24, 25] show that a static distortion of the tilting/rotational mode in both cuprates and manganites can open pseudogaps in the conduction bands, implying a strong electron–phonon coupling [24, 25].

Finally, we would like to estimate the mass enhancement factor f_p of the carriers in the low-temperature ferromagnetic state. From the measured screened plasma frequency Ω_p^s, high-frequency dielectric constant ϵ_∞, one can directly obtain the bare plasma frequency Ω_p^b. For $Nd_{0.7}Sr_{0.3}MnO_3$, the screened plasma frequency $\hbar\Omega_p^s$ is about 1.5 eV [26]. Then the bare plasma frequency is given by $\hbar\Omega_p^b = \sqrt{\epsilon_\infty}\hbar\Omega_p^s = 3.35$ eV (we take $\epsilon_\infty = 5.0$ [27, 28]). Using the measured $\hbar\Omega_p^* = 0.57$ eV for $Nd_{0.7}Sr_{0.3}MnO_3$ [26], we find $f_p = (\Omega_p^b/\Omega_p^*)^2 = 35$. Thus the mass enhancement factor is substantial and typical for small polarons [28, 29].

In summary, we report the precise resistivity data in the ferromagnetic state of high-quality epitaxial thin films of $La_{1-x}Ca_xMnO_3$. The data below 100 K can be perfectly fit by $\rho = \rho_o + BT^{4.5} + C/\sinh^2(\hbar\omega_s/2k_BT)$ with $\hbar\omega_s/k_B \sim 80$ K. The present results strongly suggest that the carriers in the metallic ferromagnetic state of the manganites are of small polarons, and thus support a CMR theory recently proposed by Alexandrov and Bratkovsky [6].

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