Electrical Transport in the Ferromagnetic State of Manganites: Small-Polaron Metallic Conduction at Low Temperatures

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We report measurements of the resistivity in the ferromagnetic state of epitaxial thin films of $La_{1-x}Ca_xMnO_3$ and the low-temperature specific heat of a polycrystalline $La_{0.8}Ca_{0.2}MnO_3$. The resistivity below 100 K can be well fitted by $\rho - \rho_0 = E\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$ with $\hbar\omega_s/k_B \simeq 80$ K and E being a constant. Such behavior is consistent with small-polaron coherent motion which involves a relaxation due to a soft optical phonon mode that is strongly coupled to the carriers. The specific-heat data also suggest the existence of such a phonon mode. The present results thus provide evidence for small-polaron metallic conduction in the ferromagnetic state of manganites.

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Nearly a half century ago, Volger [1] first observed a large magnetoresistance in a bulk sample of the manganite $La_{0.8}Sr_{0.2}MnO_3$ near room temperature. The recent discovery of "colossal" magnetoresistance (CMR) in thin films of $R_{1-x}A_xMnO_3$ (R = a rare-earth ion, and A = a divalent ion) [2] has attracted renewed interest in these systems. In order to understand the microscopic origin of the CMR effect, extensive studies of magnetic, structural, and transport properties have been carried out on these materials [3]. The physics of manganites has primarily been described by the double-exchange model [4]. Recent calculations [5,6] show that a second mechanism such as a strong polaronic effect should be involved to explain the basic physics. Many recent experiments have provided compelling evidence for the existence of polaronic charge carriers in the paramagnetic state of manganites [7].

However, the electrical transport mechanism below T_C is poorly understood. At low temperatures, a dominant T^2 contribution in resistivity is generally observed, and has been ascribed to electron-electron scattering [8]. Jaime *et al.* [9] 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. Their scenario can qualitatively explain the observed data, but there is no quantitative agreement between the calculated and experimental results.

In this Letter, we report measurements of the resistivity in the ferromagnetic state of epitaxial thin films of $La_{1-x}Ca_xMnO_3$ and the low-temperature specific heat of polycrystalline $La_{0.8}Ca_{0.2}MnO_3$. The resistivity below 100 K obeys a formula $\rho - \rho_0 = E\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$ with $\hbar\omega_s/k_B \simeq 80$ K. Such behavior is consistent with small-polaron coherent motion which involves a relaxation due to a low-lying optical phonon mode.

The epitaxial thin films of $La_{1-x}Ca_xMnO_3$ with x = 0.25 and 0.40 were grown on $\langle 100 \rangle$ $LaAlO_3$ single crystal substrates by pulsed laser deposition using a KrF excimer laser [10]. The deposition frequency is 10 Hz and the laser energy density is about 1.5 J/cm^2. The films were finally annealed for 10 h at about 940 °C and oxygen pressure of about 1 bar. The thickness of the films are about 150 nm. The polycrystalline sample of $La_{0.8}Ca_{0.2}MnO_3$ was prepared by conventional solid state reaction using dried La_2O_3, MnO_2, and $CaCO_3$ [11]. The resistivity was measured using the van der Pauw technique, and the contacts were made by silver paste. The absolute inaccuracy of the resistivity is less than 5%. The measurements were carried out from 5 to 380 K in a quantum design measuring system. The specific heat was measured in a temperature range of 2–16 K by relaxation calorimetry with an absolute inaccuracy of 10%.

Figure 1a shows the zero field resistivity of the thin films $La_{1-x}Ca_xMnO_3$ with $x = 0.25$ and 0.40, respectively. There are metal-insulator transitions at about 240 and 280 K for $x = 0.25$ and 0.40, respectively. The residual resistivity is 123 $\mu\Omega$ cm for $x = 0.25$, and 84 $\mu\Omega$ cm for $x = 0.40$. The values of the residual resistivity in these films are even smaller than that for single crystalline samples [12]. This indicates that the quality of the films is high, which allows one to study the intrinsic electrical transport properties of this system.

In Fig. 1b we plot the low-temperature resistivity of the $x = 0.25$ film in zero and 4 T magnetic field. Basically, there is a negligible magnetoresistance effect below 80 K, in agreement with Ref. [9].

In order to see more clearly whether the low-temperature resistivity has a T^2 contribution, we show, in Fig. 2a, $\rho(T)$ vs T^2 for the $x = 0.25$ film. It is apparent that the resistivity exhibits a dominant quadratic temperature dependence above 60 K, in agreement with Ref. [9]. We try to fit the data below 80 K by $\rho(T) = \rho_0 + FT^2$ and by a power-law $\rho(T) = \rho_0 + FT^n$. Both fits are quite bad as seen

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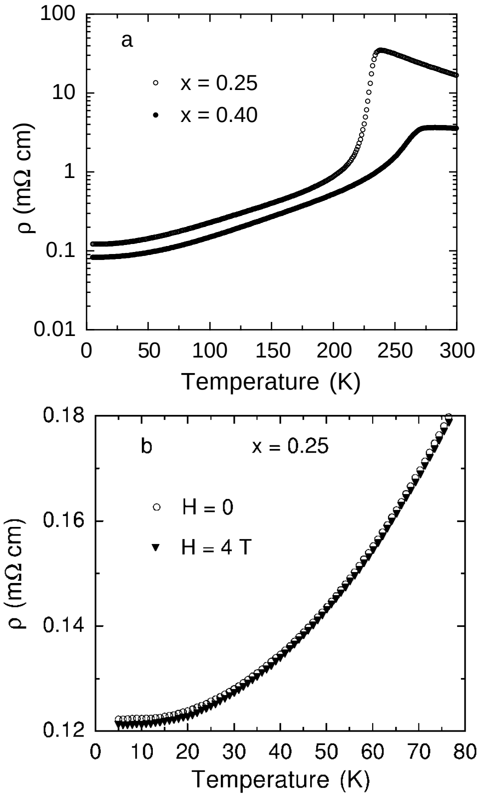

FIG. 1. (a) The zero-field resistivity $\rho(T)$ of the thin films $La_{1-x}Ca_xMnO_3$ with $x = 0.25$ and 0.40. (b) Low-temperature resistivity $\rho(T)$ of the $x = 0.25$ film in zero and 4 T magnetic field.

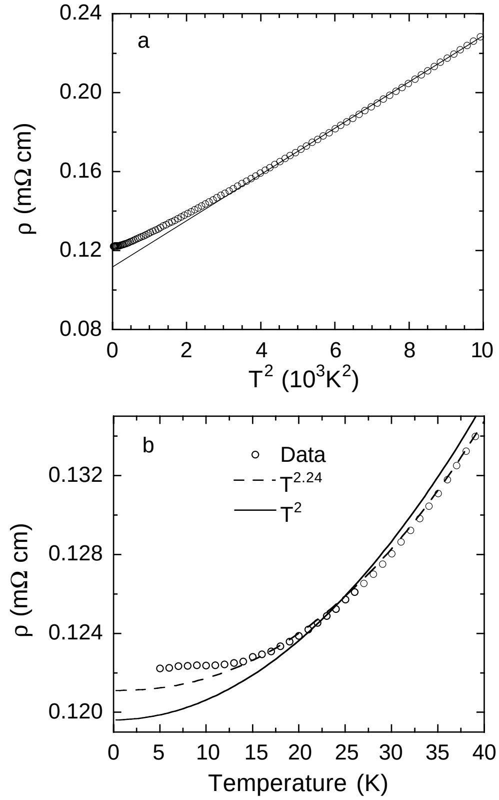

FIG. 2. (a) Resistivity $\rho(T)$ vs T^2 for $x = 0.25$. (b) Resistivity $\rho(T)$ vs T for $x = 0.25$. The solid and dashed lines are the curves for the best T^2 and power-law fits to the data below 80 K, respectively.

clearly from Fig. 2b where only the data below 40 K are shown. Even the best power-law fit with $n = 2.24$ deviates from the data substantially below 20 K where the resistivity is nearly temperature independent.

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. Recently, Alexandrov and Bratkovsky [6] have proposed a theory for colossal magnetoresistance in doped manganites. Their model predicts that polaronic transport is the prevalent conduction mechanism even below T_C. This has been partially supported by the low-temperature optical data which reveal a small coherent Drude weight and a broad incoherent spectral feature [13,14]. If their model is relevant, the temperature dependence of the resistivity at low temperatures should be consistent with small-polaron transport.

Although a theory of small-polaron conduction at low temperatures was worked out more than 30 years ago [15], no experimental data have been used to compare with the theoretical prediction. The theory shows that [15], for $k_B T < 2t_p$, the resistivity is given by

$$\rho(T) = (\hbar^2/ne^2a^2t_p)(1/\tau), \quad (1)$$

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

$$1/\tau = \sum_\alpha A_\alpha \omega_\alpha / \sinh^2(\hbar\omega_\alpha/2k_BT), \quad (2)$$

where ω_α is the average frequency of one optical phonon mode; A_α is a constant, depending on the bare conduction bandwidth and the electron-phonon coupling strength. 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 tilting 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 due to the exponentially small factor in Eq. (2). By inclusion of impurity scattering, the total resistivity at low temperatures is

$$\rho(T) = \rho_0 + E\omega_s/\sinh^2(\hbar\omega_s/2k_BT), \quad (3)$$

where ω_s is the average frequency of the softest optical mode, and E is a constant, being proportional to the effective mass of polarons.

In Fig. 3, we show the low-temperature resistivity $\rho(T)$ for $x = 0.25$ and 0.40 films. The data can be well fitted by Eq. (3) with $\hbar\omega_s/k_B = 86(2)$ K for $x = 0.25$, and 101(2) K for $x = 0.40$. When we include a small $T^{4.5}$ or T^5 term contributed from two-magnon scattering [16] or acoustic-phonon scattering, the fit becomes almost perfect with a negligible systematic deviation, and $\hbar\omega_s/k_B$ is about 80 K for both compositions. This indicates that a soft mode with $\hbar\omega_s/k_B$ of about 80 K has a strong coupling with the carriers and thus contributes to the scattering. The fact that the fit is excellent also implies that other soft modes with $\hbar\omega_s/k_B \sim 200-300$ K [17] are weakly coupled to the carriers.

In order to check whether there exists this soft mode, we measured the low-temperature specific heat of a polycrystalline sample of $La_{0.8}Ca_{0.2}MnO_3$, as shown in Fig. 4a. The specific heat in this temperature region can be expressed as

$$C(T) = BT^{1.5} + \gamma T + \beta T^3 + A/T^2 + \Delta C(T), \quad (4)$$

where the first three terms arise from magnons, charge carriers, and acoustic phonons, respectively, the fourth term is from a Schottky anomaly, and the last term $\Delta C(T) = D(\hbar\omega_s/k_BT)^2 \exp(\hbar\omega_s/k_BT)/[\exp(\hbar\omega_s/k_BT) - 1]^2$, which is contributed from an optical mode. The solid line is the best fit to the data with four fitting parameters, $\gamma = 7.17(6)$ mJ/mole K^2, $\beta = 0.200(2)$ mJ/mole K^4, $D = 3.30(8)$ J/mole K, and $\hbar\omega_s/k_B = 95.9(7)$ K; and with two fixed parameters, $A = 8.0$ mJ K/mole [18] and $B = 0.4$ mJ/mole K$^{2.5}$ [19]. The D value obtained for the manganite is nearly the same as that ($\sim$3.5 J/mole K) for $La_{1.85}Sr_{0.15}CuO_4$ where a similar soft mode was shown by specific-heat and neutron data [20]. In order to see more clearly the contribution due to the optical mode, we plot $\Delta C(T)/T$ vs T^2 in Fig. 4b. It is apparent that the data can be well fitted by an Einstein mode with $\hbar\omega_s/k_B$ of about 100 K.

Neutron scattering of La_2CuO_4 revealed a phonon dispersion of the softest optical branch that is related to the tilting of the oxygen octahedra [21]. The Raman spectra of a $La_{0.7}Ca_{0.3}MnO_3$ thin film [17] show a soft mode with $\hbar\omega_s/k_B = 127$ K, which is nearly the same as the frequency ($\sim$128 K) of the tilting mode at the zone center in La_2CuO_4 [21]. This provides additional evidence that the softest mode observed in the manganites is also associated with the tilting of the oxygen octahedra. Inelastic neutron scattering experiment is essential to further address this issue. In addition, the theoretical investigations [22,23] show that a static distortion of the tilting mode in both cuprates and manganites can open pseudogaps at the middle of the conduction bands, implying a strong electron-phonon coupling [22,23]. Moreover, the charge-ordered phase observed in a manganite compound is accompanied by combined tilting and Jahn-Teller distortions [24]. This indicates that the tilting and Jahn-Teller modes are coupled to each other as a whole, and both are strongly coupled to electrons. We should mention that the average frequency deduced from the resistivity data should be lower than that obtained from the specific-heat data, as observed. This is because the dominant contribution to the scattering comes from the large q phonons, which have much lower frequencies [21], and much stronger coupling to electrons than the zone center phonons [22].

If the charge carriers at low temperatures are indeed of small polarons, the effective mass of the carriers should be substantially enhanced. It is possible to estimate the mass enhancement factor f_p from the measured screened plasma frequency Ω_p^s, high-frequency dielectric constant ϵ_∞, and effective plasma frequency Ω_p^*. For $x = 0.3$ and 0.4, the screened plasma frequencies are nearly the same and equal to 1.5 eV [14,25]. This is consistent with electron-energy-loss spectra which show a maximum pre-O_K peak

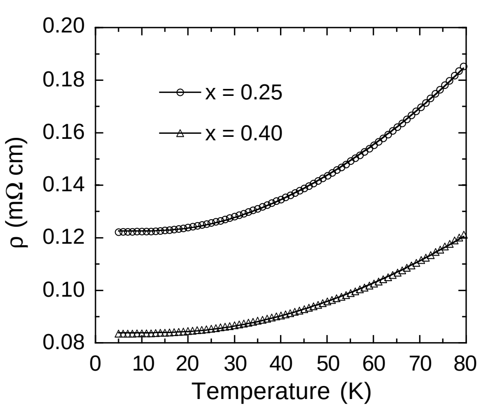

FIG. 3. Low-temperature resistivity $\rho(T)$ for $x = 0.25$ and 0.40 films. The solid lines are fitted curves by Eq. (3) with $\hbar\omega_s/k_B = 86(2)$ K for $x = 0.25$, and 101(2) K for $x = 0.40$.

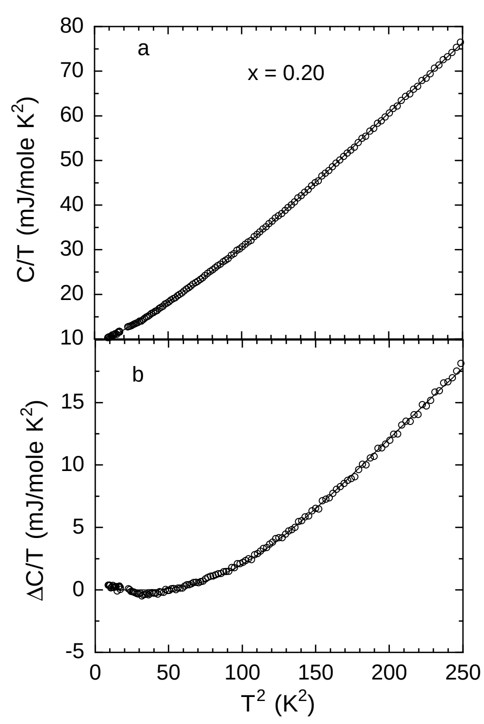

FIG. 4. (a) Low-temperature specific heat of a polycrystalline sample of $La_{0.8}Ca_{0.2}MnO_3$. (b) Specific heat contributed from an optical mode.

intensity (related to doped hole density) around $x = 0.3$ [26]. Then the bare plasma frequency for $x = 0.3$ 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]). The observed $\hbar\Omega_p^b$ is much larger than that (1.3 eV) calculated for a realistic distorted structure using the local density approximation (LDA) [29]. The discrepancy is due to the fact that the LDA calculation does not take into account a strong electron-electron correlation [30]. The large $\hbar\Omega_p^b$ observed is consistent with the fact that doped holes mainly come from the oxygen band with a large bandwidth of about 5 eV [26]. Using the measured $\hbar\Omega_p^* = 1.1$ eV for $La_{0.7}Ca_{0.3}MnO_3$ [13], we obtain $f_p = 9$. For $Nd_{0.7}Sr_{0.3}MnO_3$, $\hbar\Omega_p^* = 0.57$ eV [14], leading to $f_p = 35$. Thus the mass enhancement factor is substantial and typical for small Fröhlich polarons [28,31].

In summary, our low-temperature resistivity data on high-quality epitaxial thin films of $La_{1-x}Ca_xMnO_3$ can be well explained by a theory of small-polaron metallic conduction which involves a relaxation due to a soft optical phonon mode. This optical phonon mode has a frequency of about 100 K, as revealed from both the resistivity and specific-heat data. Our present results provide compelling evidence for the existence of polaronic carriers in the low-temperature ferromagnetic state of manganites, and support a CMR theory recently proposed [6].

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