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$_x$MnO$_3$ 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 $\rho - \rho_o = E\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$ with $\hbar\omega_s/k_BT \simeq 100$ 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. 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.

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 Re$_{1-x}$A$_x$MnO$_3$ (Re = 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$_x$MnO$_3$ and the low temperature specific heat of polycrystalline La$_{0.8}$Ca$_{0.2}$MnO$_3$. The resistivity below 100 K obeys a formula $\rho - \rho_o = E\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$ with $\hbar\omega_s/k_BT \simeq 100$ K. Such behavior is consistent with small-polaron coherent motion which involves a relaxation due to a low-lying optical phonon mode.

FIG. 1. (a) The zero-field resistivity $\rho(T)$ of the thin films La$_{1-x}$Ca$_x$MnO$_3$ with $x = 0.25$ and 0.40; (b) Low-temperature resistivity $\rho(T)$ of the $x = 0.25$ film in zero and 4 Tesla magnetic field.

The epitaxial thin films of La$_{1-x}$Ca$_x$MnO$_3$ with $x = 0.25$ and 0.40 were grown on $<100>$ 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$_2$O$_3$, MnO$_2$ and CaCO$_3$. 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%.

Fig. 1a shows the zero field resistivity of the thin films La$_{1-x}$Ca$_x$MnO$_3$ with $x=0.25$ and 0.40, respectively. There are metal-insulator transitions at about 240 K and 280 K for $x=0.25$ and 0.40, respectively. The residual resistivity is $123 \pm 280$ K for $x=0.25$ and 84 $\mu$Ωcm 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.

![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 dash lines are the curves for the best $T^2$ and power-law fits to the data below 80 K, respectively.](image)

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

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. [1]. We try to fit the data below 80 K by $\rho(T) = \rho_0 + FT^2$ and by a power-law $\rho(T) = \rho_o + F T^n$. Both fits are quite bad as seen 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 $T^3$ dependence, which is not consistent with the data. Recently, Alexandrov and Bratkovsky [1] 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].

![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 dash lines are the curves for the best $T^2$ and power-law fits to the data below 80 K, respectively.](image)

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

$$\rho(T) = (h^2/e^2a^2t_p)(1/\tau),$$  \hspace{1cm} (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:

$$1/\tau = \sum_\alpha A_\alpha \omega_\alpha / \sinh^2(h\omega_\alpha/2k_B T),$$  \hspace{1cm} (2)

where $\omega_\alpha$ is the average frequency of one optical phonon mode, $A_\alpha$ is a constant, depending on the bare conduction bandwidth and 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 soft modes may contribute to the resistivity at low temperatures due to the factor of $1/\sinh^2(h\omega_\alpha/2k_B T)$. By inclusion of impurity scattering, the total resistivity at low temperatures is

$$\rho(T) = \rho_0 + E\omega_s / \sinh^2(h\omega_s/2k_B T),$$  \hspace{1cm} (3)

where $\omega_s$ is the average frequency of the softest optical mode, and $E$ is a constant, being proportional to the effective mass of polarons. Eq. 3 is valid only if all other optical modes that are strongly coupled to the carriers have much higher frequencies than the softest mode. Otherwise, one has to use a more general formula that includes the contributions from all the modes.
In Fig. 3, we show the low temperature resistivity $\rho(T)$ for $x = 0.25$ and 0.40 films. The data can be fitted by Eq. 3 with $h\omega_s/k_B = 86(2)$ K for $x = 0.25$, and 101(2) K for $x = 0.40$. This indicates that a soft mode with $h\omega_s/k_B$ of about 100 K has a strong coupling with the carriers and thus contributes to the scattering. Such a soft mode is commonly present in perovskite oxides such as cuprates and nickelates. For La$_{1.85}$Sr$_{0.15}$CuO$_4$, a soft mode with $h\omega_s/k_B$ of about 115 K has been observed from both neutron scattering and specific heat measurements [16].

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

$$C(T) = BT^{1.5} + \gamma T + \beta T^3 + A/T^2 + \Delta C(T), \hspace{1cm} (4)$$

where the first three terms arise from magnons, charge carriers, and acoustic phonons, respectively, the fourth term is from a Schottky anomaly, the last term $\Delta C(T) = D(h\omega_s/k_BT)^2 \exp(h\omega_s/k_BT)/[\exp(h\omega_s/k_BT) - 1]^2$, which is contributed from an optical mode. The solid line is the best fit to the data with four fitting parameters: $\gamma = 7.16(7)$ mJ/mole K$^2$, $\beta = 0.200(2)$ mJ/mole K$^3$, $D = 3.30(8)$ J/mole K and $h\omega_s/k_B = 95.9(7)$ K, and with two fixed parameters: $A = 8.0$ mJ/K/mole [17] and $B = 0.4$ mJ/mole K$^{2.5}$ [17]. 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$_4$ [16]. This implies that the soft mode in the manganite is similar to that in the cuprate. If we fix $D = R/2 = 4.15$ J/mole K, the quality of the fit remains unchanged, and the value of $h\omega_s/k_B$ increases to 104 K. 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 $h\omega_s/k_B$ of about 100 K. This justifies the above explanation to the low temperature resistivity data.

![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 $h\omega_s/k_B = 86(2)$ K for $x = 0.25$, and 101(2) K for $x = 0.40$.

Such a soft mode should also be observed by other experimental techniques such as Raman scattering. Raman spectra of a La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin film [16] reveals a phonon mode with a frequency $h\omega_s/k_B = 127$ K, which is close to that (101 K) deduced from the resistivity data of La$_{0.6}$Ca$_{0.4}$MnO$_3$. This is reasonable since the frequencies of the zone-center (Raman active) optical modes are normally higher than the average ones. The other modes with $h\omega/k_B = 599$ K, 686 K, and 964 K, respectively, should have a negligible contribution to the scattering rate below 100 K due to the factor of $1/\sinh^2(h\omega/2k_BT)$ in Eq. 2. But the mode with $h\omega/k_B = 212$ K may contribute a little to the scattering rate above 50 K if the mode is strongly coupled to the carriers. The fact that an excellent fit has been achieved without including this mode implies that the mode may have a weak coupling to the carriers.

![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.

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 $\Omega_p^s$, high-frequency dielectric constant $\epsilon_\infty$, and effective plasma frequency $\Omega_p$. For $x = 0.3$ and 0.4, the screened plasma frequencies are nearly the same and equal to 1.5 eV [19,20]. This is consistent with electron-energy-loss spectra (EELS) which show a maximum pre-O$_K$ peak intensity (related to doped hole density) around $x = 0.3$ [21]. Then the bare plasma frequency for $x = 0.3$ is given by $\Omega_p^0 = \sqrt{\epsilon_\infty}\Omega_p^s = 3.35$ eV (we take $\epsilon_\infty = 5.0$ [22,23]). So we obtain $f_p = 9$ using
the measured $\hbar \Omega_p^b = 1.1$ eV [13]. The observed $\hbar \Omega_p^b$ is much larger than that (1.9 eV) calculated from the local density approximation (LDA) [24]. This is quite reasonable since the LDA calculation does not take into account a large onsite $U$ on Mn sites [21]. We can also estimate the mass enhancement factor from the specific heat data. Since the manganites are doped charge-transfer insulators [21,22], the carrier concentration for a doped manganite should be equal to $x$ per cell when $x \leq 0.3$ (see the argument of Ref. [2]). Then, the bare mass of the carriers is estimated to be 0.61 $m_e$ for $x = 0.3$, where $m_e$ is the mass of an electron. This leads to the bare electronic specific heat coefficient $\gamma_b = 0.52$ mJ/mole K$^2$ for $x = 0.2$. So $f_p = \gamma / \gamma_b = 14$ for $x = 0.20$ where $\gamma = 7.17(6)$ mJ/mole K$^2$. Thus the mass enhancement factor is substantial and typical for small Fröhlich polarons [23,24]. The small Fröhlich polarons are not very heavy because such polarons have a small size of the wavefunction but a large size of lattice deformation [26].

In summary, our low-temperature resistivity data on high-quality epitaxial thin films of La$_{1-x}$Ca$_x$MnO$_3$ can be well explained by a theory of small polaron metal-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 [26].

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