Bulk experimental evidence of half-metallic ferromagnetism in doped manganites

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We report measurements and quantitative data analysis on the low-temperature resistivity of several ferromagnetic manganites. We clearly show that there exists a $T^{4.5}$ term in low-temperature resistivity, and that this term is in quantitative agreement with the quantum theory of two-magnon scattering for half-metallic ferromagnets. Our present results provide bulk experimental evidence of half-metallic ferromagnetism in doped manganites.

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The concept of half-metallic ferromagnets was first introduced by de Groot *et al.* in 1983.[1] Half-metallic ferromagnets are characterized by completely spin-polarized electronic density of states at the Fermi level, that is, the majority spin channel is metallic while the Fermi energy falls in a band gap in the minority spin density of states. Such a novel physical property makes the materials very promising in technological applications such as single-spin electron sources and high-efficiency magnetic sensors. The half-metallic feature has been predicted for CrO_2.[2] However, spin-resolved photoemission measurement on the material has not confirmed this prediction.[3] On the other hand, the local density approximation (LDA) band-structure calculation on $La_{2/3}Ca_{1/3}MnO_3$ (Ref. 4) has shown an electronic structure of a nearly half-metallic ferromagnet (i.e., the majority spin channel is metallic while the Fermi energy lies within a band edge of the minority spin channel). Spin-resolved photoemission study on a $La_{0.7}Sr_{0.3}MnO_3$ film has demonstrated an electronic structure with spin polarization of nearly 100% at Fermi level, which possibly manifests the half-metallic feature.[5] Scanning tunneling spectroscopy on ferromagnetic $La_{0.7}Ca_{0.3}MnO_3$ also provides evidence for the half-metallic electronic density of states.[6] However, the spin-resolved tunneling measurements showed 54% (Ref. 7) and 81% (Ref. 8) polarization of conduction electrons in $La_{0.67}Sr_{0.33}MnO_3$. Since both photoemission and tunneling experiments are rather surface sensitive, the controversial conclusions drawn from these experiments are not so surprising. One needs to look for bulk sensitive experiments to unambiguously demonstrate whether the doped manganites are truly half-metallic ferromagnets or not. The clarification of this issue can place an essential constraint on the future prospect of this material in technological applications.

Since the Fermi level only crosses the majority spin bands in half-metallic ferromagnets, the emission or absorption of single magnon is forbidden, because the carriers have no conducting minority states at low energy to spin-flip scatter into. Therefore, the T^2 temperature-dependent term in the low-temperature resistivity due to single-magnon scatter[9] should be absent. Instead, two-magnon scattering is allowed, and leads to a $T^{4.5}$ temperature dependence in resistivity, as predicted by Kubo and Ohata.[10] Since this $T^{4.5}$ term should be rather small, it is difficult to identify this term if the other contributions to the resistivity are dominant. Nevertheless, if one can unambiguously identify the $T^{4.5}$ term, one provides bulk experimental evidence for the half-metallic nature. In this letter we not only show that there indeed exists the $T^{4.5}$ term in several manganite ferromagnets, but also demonstrate that the coefficient of the $T^{4.5}$ term is in quantitative agreement with the quantum theory of two-magnon scattering.[10]

In half-metallic ferromagnets, the low-temperature resistivity due to two-magnon scattering was found to be $\rho_{KO} = AT^{4.5}$ (Ref. 10). The coefficient A has an analytical expression in the case of a simple parabolic conduction band (occupied by single-spin holes).[10] In terms of the hole density per cell n, the spin stiffness D_s^R, and the effective hopping integral t^*, the coefficient A can be written as[10]

$$A=\left(\frac{3a\hbar}{32\pi e^2}\right)(2-n/2)^{-2}(6\pi^2 n)^{5/3}\left(2.52+0.0017\frac{D_s^R}{a^2 t^*}\right)\times\left\{\frac{a^2 k_B}{D_s^R(6\pi^2)^{2/3}(0.5^{2/3}-n^{2/3})}\right\}^{9/2}. \quad (1)$$

Here we have used the relations $ak_F=(6\pi^2 n)^{1/3}$ (where $\hbar k_F$ is the Fermi momentum, and a is the lattice constant); $E_F = t^*(6\pi^2)^{2/3}(0.5^{2/3}-n^{2/3})$ (where the Fermi energy E_F is measured from the band center); the effective spin $S^*=2-n/2$. The value of t^* can be estimated to be about 40 meV from the measured effective plasma frequency $\hbar\Omega_p^* = 1.1$ eV and $n\sim 0.3$ in $La_{0.7}Ca_{0.3}MnO_3$.[11] In ferromagnetic manganites, D_s^R is about 100 meV Å^2 (see below), so the term $0.0017D_s^R/a^2t^* \ll 2.52$, and can be dropped out in Eq. 1. Then there are two parameters n and D_s^R that determine the

magnitude of A. In doped manganites, n should be approximately equal to the doping level x.

From Eq. (1), one can see that the coefficient A is inversely proportional to $(D_s^R)^{4.5}$ for a fixed carrier concentration. Furthermore, T_C should be proportional to D_s^R. This is indeed the case, as recently shown by specific heat measurements.[12] Since both specific heat and low-temperature resistivity reflect the dispersion of the low energy spin-wave that is thermally excited, the magnitude of the spin stiffness D_s^R determined by resistivity should be similar to that of the spin stiffness D_s^C deduced from specific heat. Therefore, for a fixed n, one should expect

$$A \propto (1/T_C)^{4.5}. \tag{2}$$

It has recently been shown[13] that the dominant contribution to the low-temperature resistivity in doped manganites is due to scattering from a soft optical phonon mode, which gives a term proportional to $\omega_s/\sinh^2(\hbar\omega_s/2k_BT)$, where ω_s is the frequency of a soft optical mode. If we include a possible contribution from two-magnon scattering,[10] or from acoustic-phonon scattering,[9] the temperature dependent part of the resistivity can be generally expressed as

$$\rho(T)-\rho_o = AT^{\alpha} + B\omega_s/\sinh^2(\hbar\omega_s/2k_BT), \tag{3}$$

where ρ_o is the residual resistivity; A and B are temperature independent coefficients. The power $\alpha=4.5$ if the first term in Eq. (3) is due to two-magnon scattering, while $\alpha=5$ if it is due to acoustic phonon scattering. The coefficient A for acoustic phonon scattering is proportional to $(m^*/n)^2(\theta_D)^{-5}$ (θ_D is the Debye temperature).[9] This implies that A should decrease rapidly with increasing θ_D. We would like to mention that in the case of two-magnon scattering, Eq. (3) should be applied below $T_C/3$ where linear spin-wave theory or the Bloch law for the magnetization [i.e., $M(T)/M(0)=1-bT^{1.5}$] is valid.[14]

Epitaxial thin films of $La_{1-x}Ca_xMnO_3$ were grown on $\langle 100\rangle LaAlO_3$ (LAO) or $NdGaO_3$ (NGO) single crystal substrates by pulsed laser deposition using a KrF excimer laser.[15] The thickness of the films is between 1500–1900 Å. The films were post annealed in 1 bar oxygen at 940°C for 10 h. The oxygen-isotope exchanged $La_{0.75}Ca_{0.25}MnO_3$ films are the same as those in Ref. 16. 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.

Figure 1 shows the temperature dependence of the resistivity for the films of $La_{1-x}Ca_xMnO_3$ over 100–300 K. The Curie temperature T_C is defined as a temperature where $d\ln\rho/dT$ exhibits a maximum. The T_C values with this definition are listed in Table I. The fact that the T_C values of these films are nearly the same as those for the bulk samples[17] suggests that the strains in these films are negligible. This is reasonable since the films are rather thick and were post annealed at a high temperature (940°C) for 10 h.

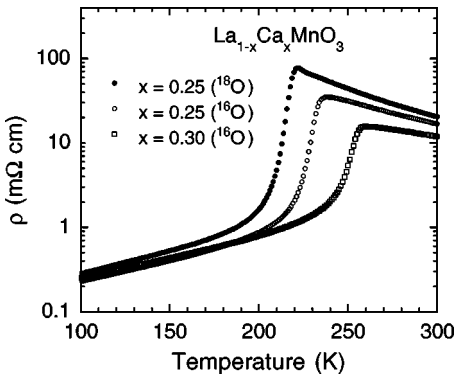

FIG. 1. The resistivity of the $La_{1-x}Ca_xMnO_3$ films over 100-300 K. The Curie temperature T_C is defined as a temperature where $d\ln\rho/dT$ exhibits a maximum.

In Fig. 2, we show the temperature-dependent part of the resistivity at low temperatures (below $T_C/3$) for the oxygen-isotope exchanged $La_{0.75}Ca_{0.25}MnO_3$ films. We fit the data by Eq. (3) using four fitting parameters α, A, B, and ω_s. As discussed above, the theory of two-magnon scattering is applicable below $T_C/3$, so we fit the data below 75 K ($\simeq T_C/3$). The best fits lead to $\alpha=4.0\pm0.3$ for the ^{16}O sample and $\alpha=4.0\pm0.4$ for the ^{18}O sample. These values are very close to 4.5, as expected from two-magnon scattering in half-metallic ferromagnets. We would like to point out that the fitted values of α are systematically lower than 4.5. This might be due to small contributions from electron-electron scattering ($\propto T^2$) and/or from unconventional one-magnon scattering ($\propto T^3$).[18]

In order to check whether the first term in Eq. (3) is due to acoustic phonon scattering, we plot the temperature-dependent part of the resistivity at low temperatures for the ^{16}O films of $La_{0.75}Ca_{0.25}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ in Fig. 3. We fit the data by Eq. (3) using three fitting parameters A, B, and ω_s, and with a fixed $\alpha=5$. From the best fits, we find $A=1.69(5)\times10^{-12}$ mΩ cm/K^5 for $x=0.25$, and $A=2.5(1)\times10^{-12}$ mΩ cm/K^5 for $x=0.3$. Since θ_D for $x=0.3$ is larger than for $x=0.25$ by about 3%,[12] one should

TABLE I. The summary of the fitting parameter A, the measured T_C, the calculated spin stiffness D_s^R for $La_{0.75}Ca_{0.25}MnO_3$ (LCMO25), $La_{0.70}Ca_{0.30}MnO_3$ (LCMO30), and $La_{0.67}Ba_{0.33}MnO_3$ (LBCO33). The uncertainty in T_C is ±1 K. The values of D_s^C deduced from specific heat (Ref. 12) are included in the last column.

Compounds	T_C (K)	A(mΩ cm/K$^{4.5}$)	D_s^R (meV Å^2)	D_s^C (meV Å^2)
LCMO25 (^{18}O)	216	$2.20(7)\times10^{-11}$	129	
LCMO25 (^{16}O)	232	$1.70(4)\times10^{-11}$	137	130
LCMO30	253	$2.04(9)\times10^{-11}$	155	160
LBMO33	337	$2.2(7)\times10^{-12}$	202	

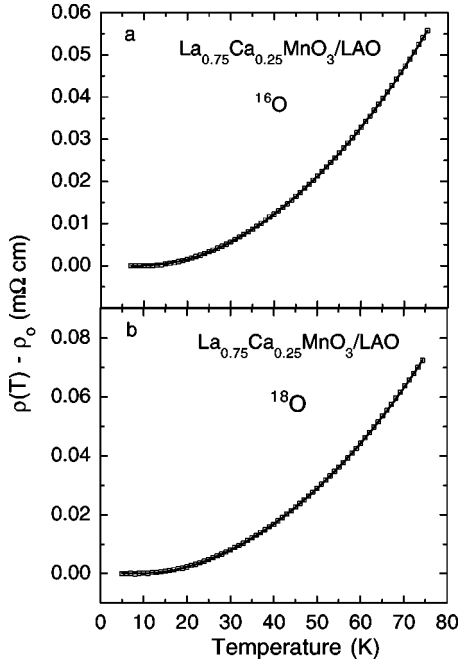

FIG. 2. The temperature-dependent part of the resistivity at low temperatures (below $T_C/3$) for the ^{16}O and ^{18}O films of $La_{0.75}Ca_{0.25}MnO_3$. The solid lines are the fitted curves by Eq. (3) using four fitting parameters α, A, B, and ω_s. The best fits lead to $\alpha=4.0\pm0.3$ for the ^{16}O sample and $\alpha=4.0\pm0.4$ for the ^{18}O sample.

expect that the A value for the former should be at least 15% lower than for the latter (the value of m^*/n for $x=0.3$ should be smaller). This is in contradiction with the fact that the A value for $x=0.3$ is larger than for $x=0.25$ by a factor of

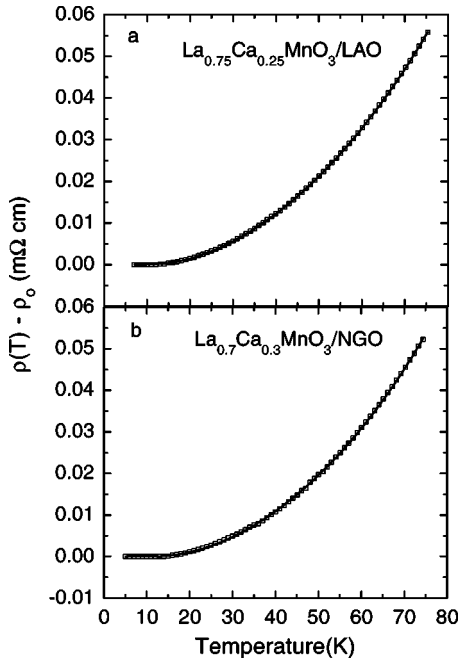

FIG. 3. The temperature-dependent part of the resistivity at low temperatures for the $La_{1-x}Ca_xMnO_3$ ^{16}O films with $x=0.25$ and 0.30. The solid lines are fitted curves by Eq. (3) with a fixed $\alpha=5$.

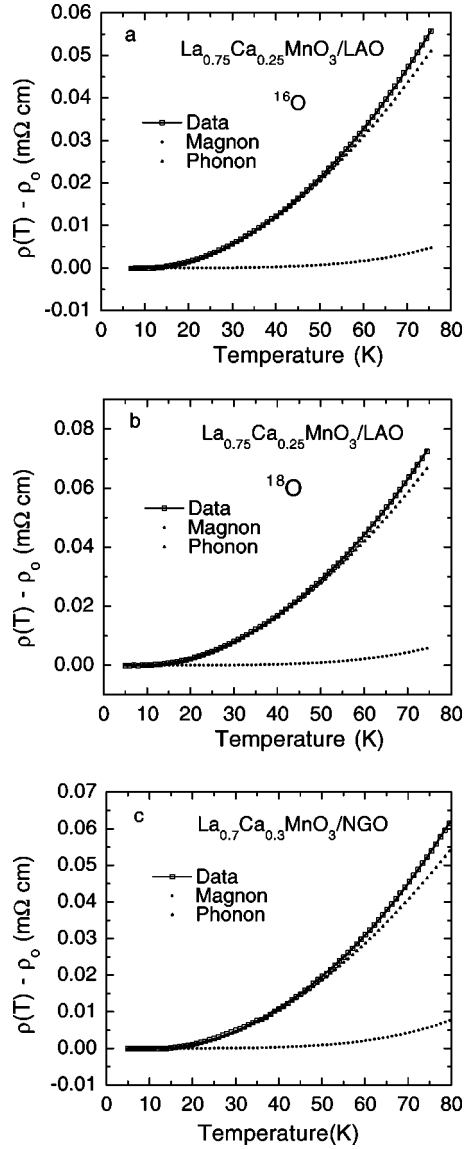

FIG. 4. The temperature-dependent part of the resistivity at low temperatures (below $T_C/3$) for the $La_{1-x}Ca_xMnO_3$ films. The solid lines are fitted curves by Eq. (3) with a fixed $\alpha=4.5$. Plotted is also the respective contribution from the two-magnon scattering (solid circle) or from the soft optical phonon scattering (solid triangle).

about 1.5. Therefore, it seems unlikely that acoustic phonon scattering contributes the first term in Eq. (3).

In Fig. 4, we fit the data by Eq. (3) using three fitting parameters A, B, and ω_s, and with a fixed $\alpha=4.5$. The values of the fitting parameter A are listed in Table I. We also plot in Fig. 4 the respective contribution from the two-magnon scattering or from the soft optical phonon scattering. It is clear that the former contribution is rather small in these compounds. From Table I, one can easily check that Eq. (2) is satisfied for the two isotope samples with the same carrier concentration (also see Fig. 5). This provides strong evidence for the existence of the $AT^{4.5}$ term arising from two-magnon scattering. Furthermore, the absolute values of $\hbar\omega_s$ are very close to the phonon energy (6 meV) of the rotational vibrations of the oxygen octahedra in a similar perovskite

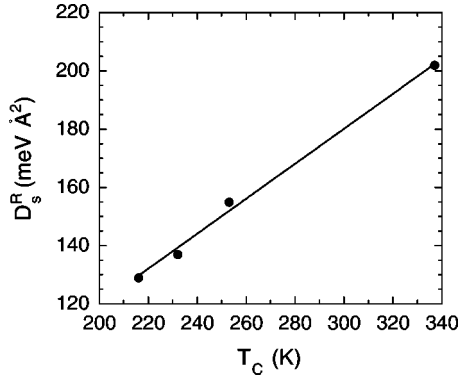

FIG. 5. The T_C dependence of the calculated spin stiffness D_s^R. The solid line is the linear fit with $D_s^R/k_BT_C=6.96(5)$ Å^2.

oxide $Ba(Pb_{0.75}Bi_{0.25})O_3$.[19] Such a rotational mode has a large anharmonicity,[20,21] and is strongly coupled to conduction electrons as shown by tunneling experiment.[19] The magnitude of $\hbar\omega_s$ for the ^{18}O sample is $7.6\pm2.4\%$ lower than for the ^{16}O sample, as expected for the oxygen-related rotational mode with a significant anharmonicity.

In order to give further confirmation that the $T^{4.5}$ term indeed originates from two-magnon scattering, it is necessary to show that the values of the coefficient A in Table I should be in quantitative agreement with Eq. (1). We can calculate the spin stiffness D_s^R using Eq. (1), $n\simeq x$, and the A values listed in Table I. The calculated D_s^R values for four manganite compounds are summarized in Table I. It is remarkable that the D_s^R values deduced from the resistivity data are very close to those determined from specific heat data.[12] Moreover, the D_s^R is proportional to T_C with $D_s^R/k_BT_C=6.96(5)$ Å^2, as shown in Fig. 5. This provides a quantitative confirmation for the quantum theory of two-magnon scattering.[10]

Since the quantum theory of two-magnon scattering is valid only for half-metallic ferromagnets, the quantitative proof for the theory in the doped manganites gives bulk experimental evidence that the ferromagnetic manganites are indeed half-metallic materials. We are not aware of any other materials which have been confirmed to be half-metallic ferromagnets by bulk-sensitive experiments. The unique half-metallic nature only found in these doped manganites makes them one of the most important and useful materials in future technological applications.

In summary, we report measurements and quantitative data analysis on the low-temperature resistivity of several ferromagnetic manganite films. We show that there exists a $T^{4.5}$ term in low-temperature resistivity, and that this term is in quantitative agreement with the quantum theory of two-magnon scattering for half metallic ferromagnets. Our present results provide bulk experimental evidence of half-metallic ferromagnetism in doped manganites, and strongly support spin-resolved photoemission and sanning tunneling spectroscopic studies.[5,6]

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