High-temperature thermopower in $La_{2/3}Ca_{1/3}MnO_3$ films: Evidence for polaronic transport

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Thermoelectric power, electrical resistivity, and magnetization experiments, performed in the paramagnetic phase of $La_{2/3}Ca_{1/3}MnO_3$, provide evidence for polaron-dominated conduction in colossal magnetoresistance materials. At high temperatures, a large, nearly-field-independent difference between the activation energies for resistivity ρ and thermopower S, a characteristic of Holstein polarons, is observed, and $\ln\rho$ ceases to scale with the magnetization. On approaching T_c, both energies become field dependent, indicating that the polarons are magnetically polarized. Below T_c, the thermopower follows a law $S(H)\sim 1/\rho(H)$ as in nonsaturated ferromagnetic metals. [S0163-1829(96)04241-5]

Since Chahara *et al.*[1,2] successfully prepared films showing ferromagnetism and novel magnetoresistance properties, perovskite-based materials of composition $La_{1-x}A_xMnO_3$ (A =Sr,Ca,Ba) have received wide attention from theoretical and experimental researchers, with the consequent proliferation of new models and a rapid improvement in sample quality. A broadening of the magnetization curves, accompanied by a reduction of several orders of magnitude in the electrical resistance, occurs when a magnetic field of the order of 5 T is applied. The effect has been called colossal magnetoresistance (CMR) and attributed to the coherent hopping of electrons between spin-aligned Mn^{3+} and Mn^{4+} ions. In spite of the effort expended, there is still no consensus as to the microscopic mechanisms causing CMR.

Reports of large, negative magnetoresistance (MR) date from 1954 and, because of the potential technological consequences, have attracted considerable attention over several decades.[3,4] The magnetic and transport properties of CMR materials were initially attributed solely to the double exchange (DE) mechanism proposed by Zener.[5] A theoretical consideration of $La_{1-x}Sr_xMnO_3$ predicted[6] band broadening at the ferromagnetic (FM) transition, reducing the gap and leading to increased or metallic conductivity in the FM state and activated conductivity above T_c. However, magnetic interactions alone are insufficient to explain the observed CMR.[7] Recently, we reported low temperature thermopower (S) and resistivity (ρ) data in partially annealed $La_{2/3}Ca_{1/3}MnO_3$ films suggesting that transport via small lattice polarons could be important above T_c.[8] In this paper we present high-temperature results on well-annealed samples, providing strong evidence for magnetic polaron transport in $La_{2/3}Ca_{1/3}MnO_3$.

The formation and transport properties of small lattice polarons in strong electron-phonon (e-ph) coupled systems, in which charge carriers are susceptible to self-localization in energetically favorable lattice distortions, were first discussed in disordered materials[9] and later extended to crystals.[10–12] In a parallel development, Kasuya and Yanase[13] considered the behavior of purely magnetic polarons (MP's), defined as a carrier localized at impurity centers by a polarization cloud, the transport mechanism being thermal hopping between sites. In this picture, the hopping activation energy disappears if the moments are aligned by an external magnetic field; the material transforms from a semiconductor to a dirty metal, exhibiting a large negative MR. On the other hand, Mott[10] argued that the mobility of purely magnetic polarons is diffusive in nature, i.e., has a power law rather than thermally activated temperature dependence. Emin[11] considered the nature of lattice polarons in magnetic semiconductors. In this model, magnetic polarons are carriers self-localized by lattice distortions but also dressed with a magnetic cloud. A transition from large to small polaron occurs as the ferromagnet disorders, successfully explaining the metal-insulator transition observed experimentally in EuO.

If the carrier together with its associated crystalline distortion is comparable in size to the cell parameter, the object is called a small, or *Holstein*, polaron (HP). Because a number of sites in the crystal lattice can be energetically equivalent, a band of localized states can form. These energy bands are extremely narrow (see Fig. 1), and the carrier mobility

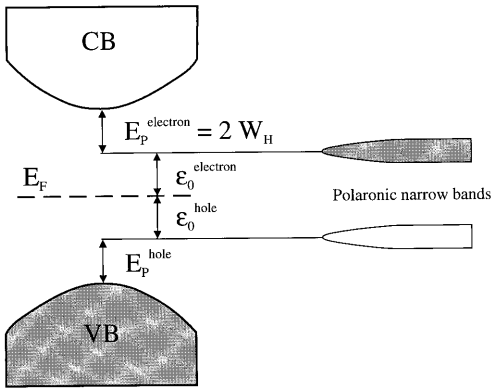

FIG. 1. Band diagram for an electron-phonon coupled system with intrinsic generation of carriers. W_H is the energy required to jump in a given direction, ϵ_0 is the energy required to generate intrinsic carriers, and E_p is the binding energy of a polaron.

associated with them is predominant only at very low temperatures. It is important to note that these are not extended states even at the highest temperatures. Electrical conduction then occurs via either quantum tunneling (QT) or thermal hopping of the HP among sites. Three different temperature regimes can be distinguished. At very low temperatures, where $k_BT \leqslant 10^{-4}$ eV, the only possible mechanism is QT between neighboring distortions. As the temperature is raised, but for $T \leqslant \theta_D/2$, half the Debye temperature, phonon-assisted hopping dominates, producing a conductivity $\sigma \propto \exp(-T^{-1/4})$; this is not, however, associated with variable range hopping. At the highest temperatures the dominant mechanism is thermally activated hopping of carriers, with an activated mobility $\mu_P = [c(1-c)ea^2/\hbar](T_0/T)^s \exp[-(W_H - J^{3-2s})/k_BT]$ where a is the hopping distance, J the transfer integral, c the polaron concentration, and W_H one-half of the polaron formation energy E_p. In the nonadiabatic limit, we have $s = 3/2$ and $k_BT_0 = (\pi J^4/4W_H)^{1/3}$ and, in the adiabatic limit, $s = 1$ and $k_BT_0 = \hbar\omega_0$, where ω_0 is the optical phonon frequency.[14] The criterion for nonadiabatic behavior is that the experimental $k_BT_0 \ll \hbar\omega_0$. Using experimental values for ρ, E_ρ, S, and the cell parameter we find that $k_BT_0/\hbar \simeq 10^{14}$ s^{-1}, comparable to optical phonon frequencies, although it could be considered a marginal case. We will assume the adiabatic limit to hold, in which case the electrical conductivity $\sigma = eN\mu_P$, where N is the equilibrium polaron number at a given temperature, can be expressed as

$$\sigma = \frac{c(1-c)e^2T_0}{\hbar aT}\exp\left(-\frac{\epsilon_0 + W_H - J}{k_BT}\right). \tag{1}$$

Because the carrier hops from one locally distorted site to another that has been thermally activated, it carries only the entropy associated with its chemical potential, leading to a simple expression for the thermopower,

$$S = \frac{k_B}{e}\left[\frac{\epsilon_0}{k_BT} - \ln\left(\frac{5}{4}\right) - \ln\left(\frac{c(1-c)}{(1-2c)^2}\right)\right], \tag{2}$$

where ϵ_0 is the energy difference between identical lattice distortions with and without the hole; the term $-(k_B/e)\ln(5/4) = -19\ \mu$V/K is associated with the spin entropy appropriate for a spin-3/2 hole moving in a spin-2 background; and the last contribution is the mixing entropy term in the case of correlated hopping with weak near-neighbor repulsion.[15] At the nominal doping level $c = x = 1/3$, this last term contributes $-60\ \mu V/K$; without the repulsive interaction, the mixing term contributes $+60\ \mu V/K$ at the same hole concentration.

$La_{2/3}Ca_{1/3}MnO_3$ films were deposited by laser ablation on $LaAlO_3$ substrates to a thickness of 0.6 μm and heat treated as described in Ref. 8. One of the films, annealed at 1000 °C for 48 h in flowing oxygen, was mounted at the end of a stainless steel rod and provided with current and voltage leads, and type-E thermocouples connected in a differential mode. A nonmagnetically wrapped, temperature calibrated 12 μm Pt wire, placed at one end of the sample, served both as a heater to establish a thermal gradient across the sample, and as a thermometer. The rod was placed in a 7 T Quantum Design superconducting quantum interference device (SQUID) magnetometer either with or without an oven option provided by the manufacturer. In this way we were able to apply magnetic fields up to 7 T and to vary the temperature in the range 4 K$< T <$500 K. Following the transport experiments, the magnetization (M) vs temperature and applied field was measured up to 380 K using conventional methods.

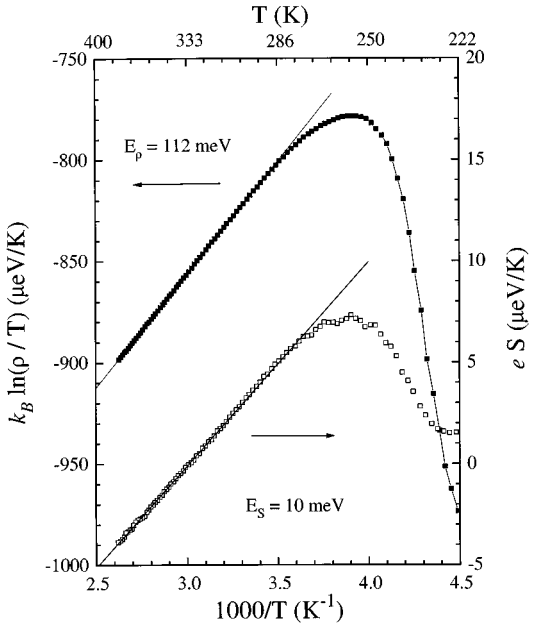

FIG. 2. The resistivity in the adiabatic limit and thermopower vs 1000/temperature. Lines are fits in the high-temperature regime, and $E_\rho \equiv \epsilon_0 + W_H$ and $E_S \equiv \epsilon_0$ are the slopes.

Figure 2 displays ln(ρ/T) and S versus 1000/T in a plot where it is easy to see that both follow a thermal-activated behavior with different activation energies $E_\rho \equiv \epsilon_0 + W_H - J = 112$ meV and $E_s \equiv \epsilon_0 = 10$ meV, respectively. The $T \to \infty$ limit of the thermopower is $\simeq -30\ \mu$ V/K; Eq. (2) suggests that $c = 0.29$ rather than 0.33 which could result from less than nominal Ca doping or, what is more likely, oxygen deficiency. There has been considerable discussion in the literature concerning deviations of the high-temperature extrapolation from the Heikes value, expected to be $+40\ \mu$ V/K at these concentrations.[15] However, in the presence of hole-hole interactions, that value is approached only when k_BT is large enough to overcome polaron repulsion, apparently beyond the accessible experimental range. No $\rho \propto \exp(T^{-1/4})$ regime, expected in the polaron picture for $T \leqslant \theta_D/2$, i.e., $T \sim$ 150–250 K, was observed in the present study as the transition into a metallic state at $T_c = 238$ K occurs above $\theta_D/2$. The activation energies obtained at temperatures $T > T_c$ give $W_H - J = 102$ meV. Assuming, as usual, that $J \ll W_H$ we note that the condition $T < W_H/k_B \approx 1190$ K is satisfied. Use of the nonadiabatic expressions results in activation energies 10% larger, with similar fit quality; we cannot, therefore, distinguish experimentally between the two regimes.

That both ln(ρ/T) and S deviate from linear behavior at $T \simeq 290$ K in zero field provides evidence of identical microscopic mechanisms, i.e., the onset of a long-range order. From the experimental values, the polaron formation energy

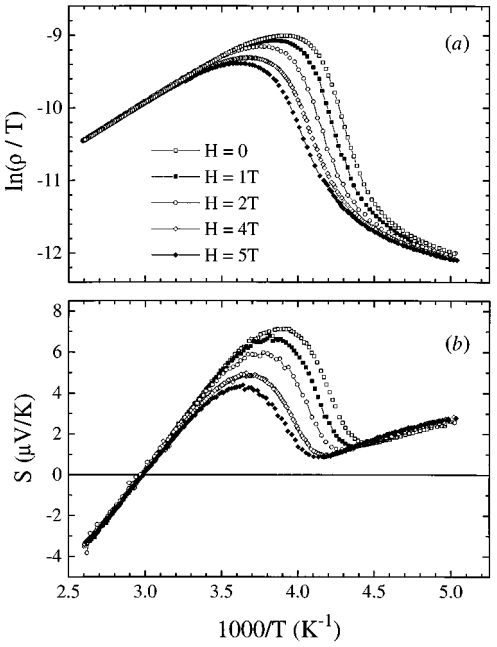

FIG. 3. (a) The resistivity in the adiabatic regime and (b) the thermopower vs the inverse of the temperature for different magnetic fields.

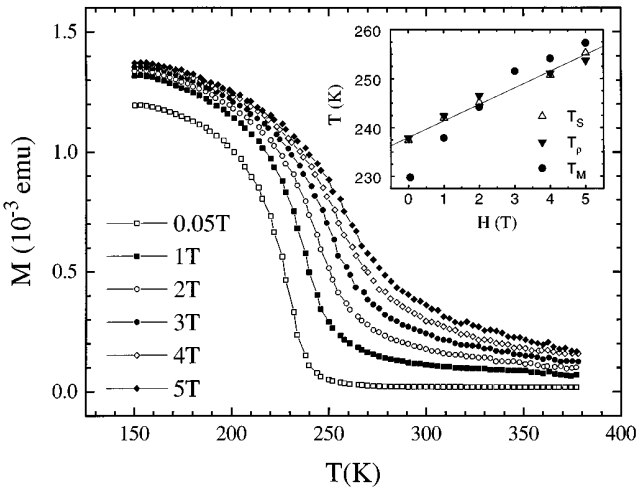

FIG. 4. The magnetization vs temperature for different magnetic fields, after substracting a diamagnetic background. Inset: transition temperatures determined with the resistivity (T_ρ), thermopower (T_S), and magnetization (T_M).

is $E_p = 2W_H \simeq 204$ meV . Combining that value with expressions for E_p in Ref. 12, we obtain the relation $m^*/m_e = Ar_p^{-2}$ between the effective mass of carriers m^* and the polaron radius, with $A = 1.9$ nm^2. This gives, for example, a value $m^*/m \approx 3$ when r_p is of the order of two cell parameters. This value, relatively small for a localized electron in a polaronic system, may reflect the significant role magnetic interactions play in the self-localization process. The mass enhancement is a measure of the e-ph coupling which, in Emin's model,[11] is counterbalanced by spin disorder, thereby causing polaron collapse. Presumably, it is the delicate balance between e-ph coupling and spin disorder that causes T_c to depend sensitively on doping and other factors.

Because we find $E_\rho \neq E_S$, we can exclude the case of a Mott MP. In order to explore the possibility of a Kasuya MP we performed resistivity and thermopower experiments under applied magnetic fields. The results are displayed in Figs. 3(a) and 3(b). In the temperature range where the activation energy can be defined, there is a weak field dependence of E_ρ and E_S. Within experimental resolution, changes in activation energies are different but of the same order of magnitude. An estimation of average experimental values is $\triangle W_H/\triangle H = -0.29$ meV/T or 0.28%/T and $\triangle \epsilon_0/\triangle H = -0.14$ meV/T or -1.4%/T. While ϵ_0 reflects changes in the Fermi energy (see Fig. 1) that can be related to the reported magnetostriction[16] of CMR materials, changes in W_H imply an increase of the radius of the HP with field and consequently some magnetic character of the quasiparticle. This may indicate that thermal entropy limits the magnetic polarization of the HP except in the proximity of T_c, as predicted in Emin's model for polarons in ferromagnetic systems. This small field dependence contrasts sharply with the effect of external pressure,[17] where a strong reduction of E_ρ with pressure was reported, perhaps reflecting the pressure dependence of the transfer integral J in Eq. (1).

In Fig. 4 we show the magnetization vs temperature for several magnetic fields in a similar temperature range. The data can be scaled as $M/(T-T_c)^\beta$ vs $H/(T-T_c)^{\beta\delta}$ with Heisenberg-like exponents $\beta = 0.38$ and $\beta\delta \approx 1.8$. There is considerable similarity between the magnetization and the transport data in the vicinity of T_c. We show this as an inset in Fig. 4, where the temperatures of maximum slope in each quantity are plotted. At higher temperatures, the resistance is much less field dependent than is the magnetization, indicating that the exponential relation between ρ and M observed[4] in CMR ceases at some point, marking perhaps a crossover between regimes where the spin polaron and the HP aspects dominate.

Finally, as can be seen in Fig. 3(b), the thermopower increases with magnetic field at low temperatures. In order to explore the correlation between S and ρ in the FM/metallic

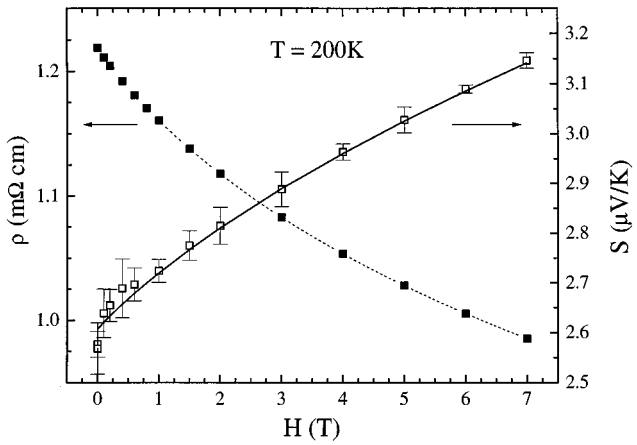

FIG. 5. The resistivity and thermopower at $T = 200$ K vs magnetic field. The solid line is a fit of the form $\alpha + \beta/\rho(H)$ with $\alpha = 0.35\ \mu$VK^{-1} and $\beta = 2.75\ \mu$V mΩ cm K^{-1}. The dashed line is a guide for the eye.

state we measured both as a function of the applied field at a constant temperature $T=200$ K, as shown in Fig. 5. Indeed, both properties change with applied field in the proximity of T_c, even in the metallic state. Below T_c, the absolute value of S increases with field rather than decreasing sharply as observed above T_c. We find that $S(H)\sim 1/\rho(H)$, a result that follows fairly directly from the Nordheim-Gorter rule. If there are two sources of resistance, and they add in series, then the thermopower contributions from each process combine as $S=(\rho_1 S_1+\rho_2 S_2)/(\rho_1+\rho_2)=S_1+\rho_2(S_2-S_1)/\rho$.[18] If we assume that only ρ_1 is field dependent, the observed result follows. A likely explanation is that ρ_1 and S_1 are consequences of spin disorder scattering, which is reduced by an applied magnetic field.

In conclusion, we have presented experimental results showing strong evidence for polaron transport in well-annealed films of $La_{2/3}Ca_{1/3}MnO_3$ at temperatures double the transition temperature $T_c=238$ K, significantly extending our preliminary results in partially annealed samples. Our data allow us to rule out both Kasuya and Mott MP-dominated transport and the formation energy for the HP was found to be $Ep=204$ meV. Although $\rho\sim\exp(-cM)$ behavior is not observed above T_c, indications of a magnetic aspect to the polarons, from the field dependence of their characteristic energies and relatively small mass, suggest that they have both lattice and magnetic character. Even in the FM/metallic state just below T_c, there remain significant indications of spin scattering. Together these conclusions support an intrinsic mechanism for the CMR effect, rather than extrinsic effects due to granularity or other imperfections. Our results indicate that polaronic collapse, such as treated by Emin, is close to the correct picture for conduction in LaCaMnO system. However, unlike the situation in EuO, the collapse of large polarons in the ferromagnetic state reduces the effective exchange coupling via the double-exchange mechanism, causing a ''bootstrap'' destruction of ferromagnetism and a metal-insulator transition. Recent theoretical models[19] that combine Jahn-Teller-driven lattice effects with the double-exchange picture seem to contain the necessary physics.

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[1]K. Chahara *et al.*, Appl. Phys. Lett. **63**, 1990 (1993).
[2]R. von Helmont *et al.*, Phys. Rev. Lett. **71**, 2331 (1993).
[3]J. Volger, Physica **20**, 49 (1954).
[4]S. von Molnár and T. Penney, in *Localization and Metal-Insulator Transitions*, edited by H. Fritzsche and D. Adler (Plenum Press, New York, 1985). See also M. Hundley *et al.*, Appl. Phys. Lett. **67**, 860 (1995).
[5]C. Zener, Phys. Rev. **82**, 403 (1951).
[6]J. Mazaferro, C. A. Balseiro, and B. Alascio, J. Phys. Chem. Solids **46**, 1339 (1985).
[7]A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
[8]M. Jaime *et al.*, Appl. Phys. Lett. **68**, 1576 (1996).
[9]T. Holstein, Ann. Phys. (N.Y.) **8**, 343 (1959).
[10]N. F. Mott and E. A. Davis, in *Electronic Processes in Non-Crystalline Materials (*Clarendon Press, Oxford, 1971).
[11]D. Emin, in *Electronic Structure Properties of Amorphous Semiconductors*, edited by P. G. Le Comber and N. F. Mott (Academic Press, New York, 1973). See also M. S. Hillery, D. Emin, and Nai-li H. Liu, Phys. Rev. B **38**, 9771 (1988).
[12]A. Moliton and B. Lucas, Ann. Phys. (France) **19**, 299 (1994).
[13]T. Kasuya and A. Yanase, Rev. Mod. Phys. **40**, 684 (1968).
[14]R. Raffaelle, H. U. Anderson, D. M. Sparin, and P. E. Parris, Phys. Rev. B **43**, 7991 (1991).
[15]P. M. Chaikin and G. Beni, Phys. Rev. B **13**, 647 (1976); R. Mahendiran *et al.*, *ibid.* **53**, 3348 (1996).
[16]M. R. Ibarra *et al.*, Phys. Rev. Lett. **75**, 3541 (1995).
[17]K. Khazeni *et al.*, Phys. Rev. Lett. **76**, 295 (1996). See also J. J. Neumeier *et al.*, Phys. Rev. B **52**, R7006 (1995).
[18]F. J. Blatt *et al.*, *Thermoelectric Power of Metals* (Plenum Press, New York, 1976), p. 157.
[19]H. Röder, Jun Zang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).