ELECTRONIC TRANSPORT IN La-Ca MANGANITES

Marcelo Jaime
Los Alamos National Laboratory
Los Alamos, NM 87545

Myron B. Salamon
Department of Physics and Materials Research Laboratory.
University of Illinois at Urbana-Champaign.
Urbana, IL 61801

Plenum Press, to be published.

INTRODUCTION

So called colossal magnetoresistance (CMR) manganites of composition $A^{3+}_{1-x}B^{2+}_{x}MnO_3$ ($A$: La, Nd; $B$: Ca, Sr, Pb) have been subject of intense research during the last years, especially after their re-discovery [1], in part due to their potential use as device applications in the magnetic storage industry, and in part because of the complexity of the mechanisms responsible for unusual, interdependent electric, magnetic and structural properties. The materials and some of their transport properties, however, have been known since the early experiments by Jonker and van Santen [2], and Volger [3] in the early fifties. Somewhat later, resistivity, magnetoresistance, specific heat and magnetization were studied as functions of temperature in $La_{1-x}Sr_xMnO_3$ polycrystalline samples. The transport data show clearly most of the relevant physics that we know today, including a surprising disagreement between the thermoelectric and Hall effects regarding the sign of the charge carriers, accompanied by a quite small Hall mobility. Volger interpreted the simultaneous metal-insulator and ferromagnetic phase transitions observed in his samples in terms of the double exchange theory (DE) for metallic ferromagnets first suggested by Zener [4] and, perhaps worried about specimen quality issues, intergrain-barrier effects, neglected the clues that his data provided in support of some lattice involvement. This trend persisted over the ensuing years, inspiring both theoretical models [5-13] and the interpretation of experimental results [14-17].

We revisit the transport properties of CMR in detail below, since they have been confirmed in a number of CMR-exhibiting materials, and present new data considered the
hallmark of an unusually high electron-phonon coupling responsible for charge localization and small polaron transport. The discussion is organized in four different sections. In the first place we briefly review materials and phase diagrams, as well as general properties, with remarks on differences between intrinsic and extrinsic properties. Second, the high temperature properties are analyzed, emphasizing those which more clearly show the role of the coupling to the lattice. Next, the very low temperature limit is considered, were the double exchange physics is believed to rule. Finally, in the fourth section, an statistical model for the phase transitions of manganites is presented, in an attempt to bridge the far less well understood region of intermediate temperatures with a reasonable extrapolation of what we know and understand in the extremes. We will see that transport experiments give us again an important insight into the dominant physics, that of localized charge carriers that reinforce the tendency toward magnetic order when they gain mobility through the ferromagnetic transition. Most of the discussion is restricted to the doping region $x \approx 1/3$, where the low temperature metallic properties are optimized.

GENERAL PROPERTIES

LaMnO$_3$ is a cubic antiferromagnetic (AFM) semiconductor perovskite, with Neel temperature $T_N \approx 140$ K, where magnetic moments at Mn sites are ferromagnetically (FM) coupled in planes that alternate spin orientations in what is known as A-phase, as displayed in Fig. 1a. In this structure Mn$^{3+}$, surrounded by six oxygen atoms, is a Jahn-Teller (JT) atom. The $d$-shell electronic energy levels $t_{2g}$ (triplet) and $e_g$ (doublet), in consequence, split under a distortion of the octahedrally coordinated Mn-O bonds. The JT splitting reduces the electronic energy as schematically shown in Fig. 1c. Three strongly coupled and localized ($t_{2g}$) electrons, occupy the bottom-most levels and form the core spin $S = 3/2$. The fourth electron, occupying the first $e_g$ level, is coupled to the core spin through the intra-atomic Hund’s coupling constant $J > 0$, estimated on the scale of $\approx 1$ eV.

This apparently simple system is by itself a materials-science challenge. In first place pure and ideal LaMnO$_3$ crystals are in principle semiconductors, while real laboratory samples are often good conductors that show a variety of magnetic structure and ordering. This behavior originates in unavoidable cationic (La$^{3+}$) vacancies that naturally occur during sample preparation and introduce charge carriers, magnetic frustration and lattice stress in the system. Cationic vacancies in particular and deviations from ideal stoichiometry in general are the most common causes for discrepancy among experimental results reported in the literature. Associated with cationic vacancies it is not unusual to observe also oxygen deficiency.

Band calculations using density-functional methods (LDA) predicted a metallic ground state for an hypothetical cubic/undistorted version LaMnO$_3$, a finding that is at odds with the experimental results. Satpathy et al. have investigated and identified the physical reason for this behavior by introducing different distortions into the oxygen octahedrons. They have studied three different distortions, i.e. the breathing mode (Q1), the basal-plane distortion mode (Q2) displayed in Fig. 1b, and a stretching mode (Q3) in addition to a small rotation of the octahedron. They claim that “for LaMnO$_3$ a Jahn-Teller distortion of the
Q2 type, with the basal-plane oxygen atoms displaced by at least the amount \( \approx 0.1 \) Å from their ideal positions, is necessary for an insulating band structure within the LDA and that the Q1 or the Q3 distortions are not effective in opening up the gap.” They also argue that Jahn-Teller (JT) like distortions favor antiferromagnetic rather than ferromagnetic order. The implications of these findings are quite relevant. Even though they only discuss static distortions, its clear that the electronic band structure is extremely sensitive to particular phonon modes and that a large enough distortion of the Mn-O bonds can drive the system through a metal-insulator phase transition.

Another surprising, and has turned out to be, important characteristic of LaMnO\(_3\) is that hole doping by means of chemical substitution of La\(^{3+}\) with Ca\(^{2+}\) or Sr\(^{2+}\), while increasing the electrical conductivity, does not always produce metallic samples. Again, a rich spectrum of magnetic ordering and/or charge localization has been found experimentally. In particular, as much as 30% content of B\(^{2+}\) is required to observe a metallic behavior at room temperature, as it can be seen in the phase diagram in Fig 2.

When a divalent atom replaces La in the structure, electrical neutrality is granted by the mixed valence nature of Mn. Indeed, Mn\(^{3+}\) gives up one electron per dopant atom in order to keep oxygen happy, resulting in \( x \) Mn\(^{4+}\) atoms per formula. As a result, a random elastic strain field is introduced in the lattice. Because \( e_g \) levels are empty in Mn\(^{4+}\) ions, they cannot profit from the JT effect; there is no energy gain obtained in the \( e_g \) level and the distortion is no longer favored. In consequence the lattice long-range periodic distortion is now frustrated by a non-JT atom, as schematically displayed in Fig. 3. Holes are likely to stay localized at those Mn\(^{4+}\) sites, since some elastic energy must be paid to move them into a Mn\(^{3+}\) site, and eventually they reach some kind of periodic distribution, generating charge ordering in the system as the density of holes increases. This would likely be the scenario in the case of spin-less charge carriers. In the case of the manganites, however, the spin-1/2 holes move in a spin-2 environment resulting in a remarkable enrichment of the physics and phenomenology. Indeed, for a critical concentration of holes experimentally found to be close to \( x = 1/3 \), and temperatures low enough to keep the spin fluctuations small, holes improve their jump probability, reducing their kinetic energy, while moving between Mn sites with core \( t_2g \) moments that point toward the same direction. This is direct consequence of a very strong Hund’s rule at Mn atoms, and is the essence of the double exchange mechanism. When these clusters of magnetically aligned Mn are large enough to overlap the same holes that benefited form local magnetic order, delocalize acting as the driving force for global ferromagnetism and a phase transition into a FM metallic state.

A large electron-phonon coupling is evidenced by an overwhelming amount of experimental data. Outstanding unambiguous evidence of coupling to Jahn-Teller lattice distortions include large pressure effects [22, 24], magnetostriction effects associated with the metal-insulator transition [23, 25], a discrepancy between the chemical potential estimation by means of thermoelectric effects and thermally activated behavior of the electrical conductivity [26, 35], the sign anomaly of the Hall effect, and the Arrhenius behavior of the drift and Hall mobilities [36]. Further, optical properties [37], charge ordering observed in the low doping limit [38], local atomic structure studies [39], neutron diffraction studies [40, 41], isotope effect [42, 44], X-ray absorption fine-structure measurements that indicate delocalization of charge carriers at the Curie temperature (\( T_C \)) as well as coupling between distortions, charge distribution and magnetism [45, 46], electron paramagnetic resonance [47], thermal
transport [18], and muon spin relaxation (µSR) [19] add to the list.

The transport properties can be discussed qualitatively with the help of a resistivity vs. temperature curve. We will use the simple diagram in Fig. 4 to illustrate them. The temperature range is divided in three regions, e.g. much lower than $T_C$ (I), much higher than $T_C$ (II), and around to $T_C$ (III). The most important energy scale in this diagram is obviously $T_C$, which is determined by (i) bandwidth, (ii) band filling, (iii) local disorder, and (iv) effective electron-phonon coupling. The bandwidth is fundamentally fixed once the structure of the system is fixed, e.g. atomic radii determine the structure and an average Mn-O-Mn bond angle for a particular composition (A, B, x). A clever way to characterize the structure is to use the so called "tolerance factor" $tf = \frac{A-O}{\sqrt{2}Mn-O}$ where $A-O$ and Mn-O are equilibrium metal-oxygen bond lengths for, respectively, twelve-fold and sixfold oxygen coordination and its physical meaning is quite clear. The more colinear the three atoms are, the larger the transfer integral for charge carriers between them. This is a static, average property of the system. Temperature-$tf$ phase diagrams as well as bandwidth effects have been discussed with detail in the bibliography [50–52], although Hwang et al. seem to have used incorrect (ninefold) coordination numbers. Band filling is determined by the doping level in the system (x), also quite relevant. Because of the Coulomb repulsion in the paramagnetic state, there is a strong tendency of the system towards charge order as x increases. There is always in the system an underlying competition between charge order and metallicity, and band filling is what inclines the scale towards one or the other. Finally, local disorder effects produced mainly by difference in atomic radii between A$^{3+}$ and B$^{2+}$ ions but also by cationic vacancies and oxygen defects play a very important role. These random defects introduce elastic stress in the lattice that interferes with the relaxation of the JT effect described in Fig. 3 affecting the lattice dynamics as well as the hopping process at high temperatures. The disorder is quantified by means of the variance of the A-cation radius distribution ($\sigma^2$) defined as $\sum y_i r_i^2 - \langle r_A \rangle^2$, where $y_i$ are the fractional occupancies of the species [53,54]. Rodriguez-Martinez and Attfield find that the temperature at which the resistivity peaks ($T_p$) and $T_C$ are monotonically decreasing functions of $\sigma^2$. At constant $\langle r_A \rangle$ (corresponding to the maximum $T_C$ in Fig. 5) they report $d(Tp)/d(\sigma^2) = 20600$ K/Å$^2$ for a series of six samples.

The physical properties of interest for this review are $T_C$, $T_p$, and lattice transition temperature $T_{latt}$, all determined by the bandwidth, band filling and local disorder but with different intensity. As a consequence, while the physical properties are coupled to each other, in general $T_C \neq T_p \neq T_{latt}$ [53]. It has been reported, on the other hand, that A-Mn transference is also important, but the experimental situation is still far from clear [56]. Regarding the extrinsic transport properties of CMR manganites, they are most likely dominated by grainsize effects, grain boundary scattering and/or spin-flip, irreversible disorder produced by partial annealing of polycrystalline and film samples, mechanical strain induced by the substrates [57], and very importantly deviations from nominal stoichiometry. Extrinsic effects are quite important, they are evidently responsible for the largest magnetoresistance values reported in the literature [1] and are critical for the many prospective technological applications of the materials. They have been identified as the cause of large low-temperature magnetoresistance by spin polarized tunneling through intergrain barriers, as well as anisotropic magnetic effects.
The transport properties have been, for more than forty years, the easier and more straightforward characterization and study method for CMR manganites. However, not until very recently have the clues in favor of lattice involvement in the electronic properties been discussed. Fig. 6a and 6b display typical results obtained in polycrystalline samples of composition La$_{2/3}$Ca$_{1/3}$MnO$_3$ prepared by standard solid state reaction techniques. The resistance in zero field peaks at $T_p \approx 267$ K, somewhat above $T_C (H < 10$ Oe) $\approx 261$ K. The magnetoresistance peaks at $T_p$, but does not vanish at low temperatures as a consequence of the granular nature of the specimen. The granular behavior is not relevant in the high temperature region because the mean free path for charge carriers much smaller that the grain size; an external magnetic field then has little effect on the transport properties. A large (intra-grain) mean free path in the metallic phase below $T_C$, on the other hand, makes the transport extremely sensitive to intergrain barriers caused by magnetic misalignment between weakly coupled grains. An external magnetic field reduces those barriers by aligning neighboring grains. At high temperatures, the thermoelectric power or Seebeck effect $S(T)$ is also sensitive to the metal-insulator phase transition. A sharp change from semiconductor-like absolute values $|S| \approx 10 \, \mu$V/K toward metallic values $|S| \approx 1 \, \mu$V/K is found coincident with $T_C$, in Fig 6b). That the Seebeck coefficient approaches a negative value at high temperatures has been attributed in part to the reduction in spin entropy produced when a hole converts a Mn$^{3+}$ ion to Mn$^{4+}$ and is not in disagreement with hole doping in the system. The Seebeck effect, a zero current experiment, shows no indication of grain boundary effects in the proximity or above $T_C$. These effects are present at much lower temperatures, where the phonon mean free path approaches the grain size, as a large spike centered at 30-50 K.

In the case of band semiconductors $E_S = E_\sigma$ is the semiconductor gap defined from the temperature dependence of the conductivity by $\sigma(T) \propto \exp(-E_\sigma/k_BT)$. This is clearly not the case in manganites, where it has been found that $E_\sigma (\sim 100$ meV) $> E_S (\sim 4$ meV). The relatively large activation energy in the electrical conductivity has to be interpreted in a different way. $E_\sigma$ is, then, not just the semiconducting gap but the gap added to the “hopping energy” $W_H$, a consequence of a thermally activated mobility of localized carriers jumping between neighboring sites.

The formation and transport properties of small lattice polarons in strong electron-phonon coupled systems, in which charge carriers are susceptible to self-localization in energetically favorable lattice distortions, were first discussed in disordered materials and later extended to crystals. Emin considered the nature of lattice polarons in magnetic semiconductors, where 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, and the carrier mobility 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, where the dominant mechanism is thermally activated hopping, with an activated mobility
\[
\mu_p = \frac{\epsilon (x-1) e a^2 / h}{(T_0/T)^s} \exp\left(-\frac{W_H - J^{3-2x}}{k_B T}\right)
\]
where \(a\) is the hopping distance, \(J\) the transfer integral, \(x\) the polaron concentration, and \(W_H\) one-half of the polaron formation energy. In the non-adiabatic limit, we have \(s = 3/2\) and \(k_B T_0 = (pJ^4/4W_H)^{1/3}\) and, in the adiabatic limit, \(s = 1\) and \(k_B T_0 = h \omega_0\), where \(\omega_0\) is the optical phonon frequency. The criterion for non-adiabatic behavior is that the experimental \(k_B T_0 \ll h \omega_0\). Using experimental values for \(\sigma, E_\sigma, S\) and cell parameter we find that \(k_B T_0/h \approx 10^{14} \text{s}^{-1}\), 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

\[
\sigma = \frac{x(1-x)e^2T_0}{\hbar a T} \exp\left(-\frac{\epsilon_0 + W_H - J}{k_B T}\right)
\]

Figure 7 shows the same resistance data of figure 6a displayed in two different charge localization scenarios, i.e. adiabatic small polaron-like: \(\log(R/T)\) vs \(T^{-1/4}\). While the data mimics VRH behavior at temperatures close enough to \(T_C\), the adiabatic small polaron (Eq. 2) describes the system well in the entire temperature range. \(R(T)\) data obtained up to \(T \approx 5T_C\) show excellent agreement with this model [39,41], and we can assume that the localization of holes persists up to the material’s melting point.

The field dependence of the activation energies \(E_S\) and \(E_\sigma\) has been discussed for film samples of similar nominal composition [26]. Within experimental resolution, changes in activation energies are different but of the same order of magnitude. An estimation of average experimental values is \(\Delta W_H/\Delta H = -2.9 \times 10^{-5} \text{meV/Oe}\) or \(2.8 \times 10^{-5} \text{%/Oe}\) and \(\Delta E_S/\Delta H = \Delta \varepsilon_0/\Delta H = -1.4 \times 10^{-5} \text{meV/Oe}\) or \(-1.4 \times 10^{-4} \text{%/Oe}\). While \(\varepsilon_0\) reflects changes in the Fermi energy that can be related to the reported magnetostriction of CMR materials [25], changes in \(W_H\) imply an increase of the radius of the small polaron with field and consequently some magnetic character of the quasiparticle. Because of this double character of the localized holes, elastic as well as magnetic at temperatures up to \(2T_C\), they are named magnetoelastic polarons in an attempt to emphasize differences with purely magnetic polarons [4,50] and HP.

In Eq. 1, the temperature independent term \(B < 0\) is given by two contributions, namely
\[
-(k_B/e) \ln\{[2x(3/2) + 1]/[2x^2 + 1]\} = -(k_B/e) \ln(4/5) = -19 \text{µV/K}
\]
associated with the spin entropy appropriate for a spin-1/2 hole moving in a spin-2 background [44]; and a mixing entropy term that counts in how many different ways \(x\) holes can be distributed between \(n\) Mn sites. In the case of correlated hopping with weak near-neighbor repulsion [63] this term is \(\ln[x(1-x)/(1-2x)^2]\) and at the nominal doping level \(x = 1/3\) contributes \(-60 \text{µV/K}\); without the repulsive interaction, the mixing term contributes \(+60 \text{mV/K}\) at the
same hole concentration. In either case the prediction is unable to reproduce the experimental value $S_\infty \approx -25 \, \mu V/K$, see Fig. 6b. Attempts to understand the high temperature limit of the thermopower $B = S_\infty$ following its changes with hole concentration via Ca concentration changes have been frustrating so far. An alternative way to modify the doping level is via control of the concentration of oxygen vacancies, which can be accomplished with thermogravimetric methods. As part of a cooperative program with the group at the Centro Atómico Bariloche, Argentina polycrystalline samples were placed in an oven equipped with atmosphere control capabilities where the isotherm displayed in Fig. 8 was obtained. The maximum concentration of vacancies observed without mass instability effects characteristic of phase segregation was $d = 0.051$, enough to depress $T_C$ from 265 K to 221 K. Figure 9a shows $S(T)$ vs $1000/T$ for three polycrystalline samples of composition La$_{0.67}$Ca$_{0.33}$MnO$_3$, La$_{0.67}$Ca$_{0.33}$MnO$_{2.49}$, and La$_{0.75}$Ca$_{0.25}$MnO$_3$. Indeed, the variation in $S_\infty$ confirms changes in the doping level. The overall changes however, are not as large as they would be expected. Fig. 9b show data by Mahendiran et al. as well as our samples and different model predictions. Besides the Chaikin-Beni (Ch-B) model discussed above, alternative models considered in the bibliography are the correlated and uncorrelated limits by Heikes:

$$S_{ME}^{H_{corr}} = \ln \left( \frac{1 + x}{1 - x} \right); \quad S_{ME}^{H_{uncorr}} = \ln \left( \frac{x}{1 - x} \right)$$

and the D-dimensional extension of Ch-B formula:

$$S_{ME}^D = \ln \left\{ \frac{x(1 - Dx)^D}{2[1 - x(D + 1)]^{D+1}} \right\}$$

These predictions are in general unable to reproduce results, except perhaps in the case of Heikes uncorrelated limit. There are three possible explanations for this behavior. A disproportionation theory, where two Mn$^{2+}$ atoms generate Mn$^{2+}$ and Mn$^{4+}$ sites with the transference of one electron. The disproportionation density is related to oxygen non-stoichiometry. In an alternative explanation by Emin, the small polarons are proposed to be correlated with divalent atoms in real space due to the elastic stress introduced in the lattice by atomic size mismatch. In this kind of “impurity” conduction, the number of available sites for localized states increases with doping and as a consequence the mixing entropy remains unchanged. Finally, the Heikes uncorrelated limit suggest that multiple occupancy or collective behavior could be possible for small polarons. This possibility, unlikely in principle, finds some support in recent neutron diffraction data where spin clusters (charge droplets) of a few holes localized in regions of $\sim$20Å were identified.

Perhaps the most distinctive property of steady-state small-polaronic transport is its Hall mobility $\mu_H$. The activation energy of the Hall mobility is calculated to be always less than that for drift mobility $E_d$. The simplest model predicts $\approx E_d/3$, and this has been observed before in, for example, oxygen-deficient LiNbO$_3$. The sign of the Hall effect for small polaron hopping can be “anomalous.” A small polaron based on an electron can be deflected in a magnetic field as if it were positively charged and, conversely, a hole-based polaron can be deflected in the sense of a free electron. As first pointed out by Friedman and Holstein, the Hall effect in hopping conduction arises from interference effects of nearest neighbor hops along paths that define an Aharonov-Bohm loop. Sign anomalies arise when
the loops involve an odd number of sites. The first successful measurement of the high-
temperature Hall coefficient in manganite samples was reported by Jaime et al. [36], finding
that it exhibits Arrhenius behavior and a sign anomaly relative to both the nominal doping
and the thermoelectric power. The results are discussed in terms of an extension of the
Emin-Holstein (EH) theory of the Hall mobility in the adiabatic limit.

The authors exploit the sensitivity of CMR materials to rare-earth substitutions to lower
the transition temperature in \((\text{La}_{1-y}\text{R}_y)_{0.67}\text{Ca}_{0.33}\text{MnO}_3\) from \(\sim 260\) K at \(y = 0\) to \(\sim 130\) K,
thereby extending the accessible temperature range to \(\approx 4T_C\). The samples used in
this study were laser ablated from ceramic targets and deposited on \(\text{LaAlO}_3\) substrates, as
described previously [30], showing a temperature dependence in resistivity and thermopower
data qualitatively similar to Fig. 6.

Sections of these specimens were patterned by conventional lithographic methods into a
five-terminal Hall geometry. Hall experiments were carried out in a high-temperature insert
constructed for use at the 20 Tesla superconducting magnet at the National High Magnetic
Field Laboratory (Los Alamos, NM). The transverse voltage data taken while sweeping the
field from -16 Tesla to +16 Tesla, and that taken while sweeping back to -16 Tesla, were each
fit to a second-order polynomial with the term linear in field attributed to the Hall effect.
We verified in each case that the longitudinal magnetoresistance is completely symmetric
in field. Figure 10 shows the Hall coefficient derived from the linear term. Several points
for the \(y = 0\) film are included. Due to the much higher \(T_C\) of that sample, extraction of
the Hall contribution leads to greater uncertainty. The data are, however, consistent with
the Gd-substituted film. The line through the data points is an Arrhenius fit, giving the
expression \(R_H = -(3.8 \times 10^{-11} \text{ m}^3/\text{C}) \exp(91 \text{ meV}/k_B T)\). Note that the sign is negative,
even though divalent dopants should introduce holes. This is shown more clearly in an
Arrhenius-like plot (inset b). Inset a, displays \(1/R_H\) vs \(T\). If the observed linear term in the
Hall data is due to the well known skew scattering, then \(R_H\) is expected to be proportional
to the magnetization and in consequence the data should extrapolate to \(T_C\). Our data
extrapolates to 245 K, more than a hundred degrees above \(T_C\). Skew scattering is then
unlikely to explain the negative sign of the Hall data in these samples.

Detailed expressions for the Hall effect in the adiabatic limit have been calculated by EH
[70] for the hopping of electrons with positive transfer integral \(J_H\) on a triangular lattice,
and results in a normal (electron-like) Hall coefficient. However, the sign of both the carrier
and the transfer integral changes for hole conduction, leaving the sign of the Hall coefficient
electron-like, and therefore anomalous. However, no anomaly would arise if the hopping
involves 4-sided loops with vertices on nearest-neighbor Mn atoms. A sign anomaly, then,
implies that hopping involves odd-membered Aharonov-Bohm loops. Such processes arise
when next-nearest neighbor (nnn) transfer processes across cell face diagonals are permitted.
If the Mn-O-Mn bonds were strictly colinear, the former processes would be disallowed by
symmetry. However, the bond angles are substantially less than 180°, implying the presence
of \(p\)-bond admixture, and opening a channel for diagonal hops. The triangular-lattice
calculation of EH is extended to the situation in which a hole on a Mn ion can hop to any
of its four nearest neighbors in the plane normal to the applied field with transfer matrix
element \(J < 0\) and to its four \(nnn\) with a reduced transfer energy \(\gamma J\). The effect of these
diagonal hops (plus those in the plane containing both electric and magnetic fields) has
also to be considered on the conductivity prefactor. The Hall coefficient can be written as
\[ R_H = R_H^0(T) \exp(2E_\sigma/3k_B T) \], with

\[ R_H^0 = -\frac{g_H}{g_d} \frac{F(|J_H|/k_B T)}{ne} \exp\left\{ -\varepsilon_0 + (4|J_H| - E_S)/3/k_B T \right\} \] (5)

EH found that the factor \( g_H = 1/2 \) for three-site hopping on a triangular lattice. In Eq. 7 the carrier-density is included as \( n \exp(-E_S/k_B T) \), where \( E_S \) is estimated to be 8 meV from the thermopower data. The quantity \( \varepsilon_0 \) is the \( J_H \)-dependent portion of a carrier’s energy achieved when the local electronic energies of the three sites involved in an Aharonov-Bohm loop are equal. For the problem considered by EH, an electron hopping within a lattice composed of equilateral triangles, \( \varepsilon_0 = -2|J_H| \), and \( g_H/g_d = 1/3 \). Within the domain of validity of EH, the temperature dependence of \( R_H \) arises primarily from the factor \( \exp(2E_\sigma/3k_B T) \) when \( E_\sigma >> E_S \). For holes hopping within a cubic lattice in which three-legged Aharonov-Bohm loops include \( \varepsilon_0 \) varies from \(-\sqrt{2}|J_H|\) to \(-|J_H|\) as \( \gamma \) increases from zero to unity, and the temperature dependence of \( R_H \) remains dominated by the factor \( \exp(2E_\sigma/3k_B T) \). Indeed, the energy characterizing the exponential rise of the Hall coefficient that we observe, \( E_H = 91 \pm 5 \) meV, is about 2/3 the measured conductivity activation energy, \( E_H/E_\sigma = 0.64 \pm 0.03 \), in excellent agreement with theory.

The geometrical factor \( g_d \) depends on the ratio of the probability \( \text{P}_{nnn} \) of \( nnn \) hops to \( \text{P}_{nn} \), that of \( nn \) hops, through \( g_d = (1 + 4\text{P}_{nnn}/\text{P}_{nn}) \). If these probabilities are comparable (\( \gamma \approx 1 \)) \( g_d = 5 \), \( g_H = 2/5 \) and the exponential factor in Eq. 7 becomes \( \exp((E_S - |J_H|)/3k_B T) \approx 1 \). In the regime \( |J_H| \geq k_B T \), the function \( F(|J_H|/k_B T) \) is relatively constant with a value \( \approx 0.2 \), and we find \( R_H^0 \approx -0.02/ne = -3.8 \times 10^{-11} \text{ m}^3/\text{C} \). This yields an estimated carrier density \( n = 3.3 \times 10^{27} \text{ m}^{-3} \), quite close to the nominal level of \( 5.6 \times 10^{27} \text{ m}^{-3} \).

Before moving over to the low temperature transport properties the following conclusions can be reached. The high-temperature Hall coefficient in manganite films is consistent with small-polaron charge carriers that move by hopping. The magnitude of the conductivity prefactor indicates that the carrier motion is adiabatic. The sign anomaly in the Hall effect implies that small polarons hop not only among near-neighbor sites (making Aharonov-Bohm loops with an even number of legs) but must have a significant probability of traversing Hall-effect loops with odd numbers of legs. As such, the results indicate the occurrence of significant \( nnn \) transfer across face diagonals, and therefore a crucial role for deviations of the Mn-O-Mn bond angle from 180°. In other words, the sign anomaly its a simple consequence of the geometry of the sublattice where the small polarons move and the fact that it is triangular and not square indicate an interesting possibility, that may also relate to unusual high-temperature values observed for the Seebeck coefficient [30,32]. That is that transport is a type of impurity conduction in which carriers remain adjacent to divalent cation dopants (i.e. Ca ions). The local distortions associated with the presence of the impurity may also increase the admixture of \( \pi \)-bonds, and enhance diagonal hopping.

In a recent paper, Worledge et al. [71] discuss the temperature and doping dependence of the resistivity in \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) laser ablated films measured up to \( T = 1200 \) K for \( 0 > x > 1 \). They conclude that the results can be unambiguously explained by adiabatic small polaron hopping, which is limited by on-site Coulomb repulsion. The magnitude of the conductivity prefactor, however, is too large to be accounted by the classical theory by Emin and Holstein [70] and the authors claim that a proper description should consider hopping
beyond nearest neighbors, in good agreement with high temperature Hall effect results. A few other reports on the Hall effect of manganites are now available \cite{72,73}, they are restricted however to the relatively low temperature side of the diagram in Fig.4, i.e. regions I and III. The low temperature Hall effect is not less intriguing than the high temperature counterpart, and is not yet understood. The Hall resistance in the metallic regime imply carrier concentrations up to $3 \times$ the nominal values suggesting some compensation effects and/or two-band conduction, the spontaneous Hall contribution is opposite in sign from the normal Hall effect with the overall effect exhibiting a sign change around $T_C$ from hole-like in the ferromagnetic phase to electron-like in the paramagnetic phase. In order to clarify the subject, more experiments in the very high temperature limit ($T \geq 2T_C$) are desirable.

LOW TEMPERATURE TRANSPORT

The low temperature region I, in Fig. 4 in optimally doped cubic manganites is perhaps the most interesting one since it corresponds to a ground state that is the closest to half metallic systems ever synthesized. Unfortunately, the transport properties of polycrystalline samples in this regime are dominated, or at best highly influenced, by grain boundary scattering, and close attention has to be paid to sample quality issues. These problems have led in the past to misunderstanding about the most basic transport properties, like resistivity and Seebeck effect for example. One common problem in the resistivity of polycrystalline specimens is the presence of a minimum at $T \approx 10-20$ K that has been attributed to localization effects. In the same temperature range, the Seebeck effect shows large anomalies (as big as $-40 \mu$V/K) by no means compatible with a metallic state. None of these features have been reproduced in carefully prepared ($x \sim 1/3$) single crystals and are thus considered non-intrinsic. One of the simplest methods of characterization seems to be the magnetoresistance (MR), since granular samples show large ratios in small applied magnetic fields down to the lowest temperatures. On the other hand, MR rapidly vanishes below $T_C$ in long time annealed films \cite{30} and single crystals.

The double exchange mechanism is generally agreed to provide a good description of the ferromagnetic ground state. In that model, strong Hund’s Rule coupling enhances the hopping of $e_g$ electrons between neighboring Mn$^{3+}$ and Mn$^{4+}$ ions by a factor $\cos(\theta/2)$, where $\theta$ is the angle between the spin of their respective $t_{2g}$ cores, thereby producing a ferromagnetic interaction. In KO’s treatment of the problem \cite{3}, occupied sites are assumed to have total spin $S = 2$, the combination of the spin-$3/2$ $t_{2g}$ core and spin-$1/2$ $e_g$ electron demanded by strong Hund’s rule exchange. Holes are then assumed to couple antiparallel to each localized spin. In the ferromagnetic ground state, with all local spins aligned, only spin-down holes can move to form a band. However, once the system begins to disorder, a locally down-spin hole is the appropriate combination of majority and minority carriers, referred to the global magnetization axis. Therefore, the minority-spin hole band reappears as the system disorders, even though the local moments retain their Hund’s rule value. Furukawa has treated this explicitly in a many-body context, demonstrating that both minority and majority bands are split by Hund’s rule exchange in the paramagnetic state. As the system magnetizes, the lower majority-spin band gradually gains spectral weight at the expense of...
the lower minority-spin band. Both treatments predict that the ground state is half-metallic; that is, that the carriers are fully spin-polarized. We can leave aside here electron-phonon coupling which dominates near and above $T_C$.

At low temperature, there are no propagating minority-spin hole states in the $S = 2$ manifold; they only exist on sites at which the $t_{2g}$ core is not ferromagnetically aligned. As a consequence, single-magnon scattering processes, which cause the resistivity of conventional ferromagnets to vary as $T^2$, are suppressed. KO extended the standard perturbation calculation of Mannari [6] to consider two-magnon processes, predicting a leading $T^{9/2}$ temperature dependence of the resistivity. However, a dominant $T^2$ contribution is universally observed in the manganites, and has usually been ascribed to electron-electron scattering. [75,76,30] New resistivity data on single crystals is discussed below, demonstrating that the quadratic temperature dependence is strongly suppressed as the temperature is reduced. The constancy of the low-temperature resistivity has been noted elsewhere, but not explained. [77] It is argued that the observed $T^2$ contribution reflects the reappearance of minority spin states that are accessible to thermally excited magnons. Quite recently, spin-polarized photoemission data, taken on films exhibiting square hysteresis loops, indicate 100% spin polarization at low temperatures, decreasing as the temperature is increased. [78] Single crystals, which have essentially no hysteresis, would be expected to depolarize more rapidly. To explore the consequences, Mannari’s calculation is extended to the situation in which a minimum magnon energy is required to induce spin-flip transitions. At temperatures well below that energy, single magnon scattering is suppressed exponentially as predicted by KO. The treatment discussed by Jaime et al. [74] is in the context of the relaxation time approximation while a proper theory would consider lifetime effects from magnon scattering using Furukawa’s many-body approach. Nonetheless, the results are in qualitative agreement with the data. Band structure calculations also indicate that minority spin states persist at $E_F$, even at $T = 0$ K. [74]

High quality single crystals of nominal composition La$_{0.66}$(Pb$_{0.67}$Ca$_{0.33}$)$_{0.34}$MnO$_3$, determined by inductively coupled plasma spectroscopy on samples from the same batch, were grown from a 50/50 PbF$_2$/PbO flux and used to study the low temperature properties. X-ray diffractometry shows a single pseudo-orthorhombic structure with lattice parameters $a = 5.472(4)$ Å, $b = 5.526(6)$ Å, and $c = 7.794(8)$ Å. Gold pads were evaporated onto both oriented and unoriented crystals using both standard four-terminal and Montgomery eight-corner contact arrangements as described elsewhere [74]. Fig. 11 shows the resistivity of sample sc3, a single crystal of dimensions $1.04 \times 1.24 \times 0.3$ mm$^3$ with $T_C = 300$ K, vs the square of the temperature in fields up to 70 kOe. The data show a dominant $T^2$ temperature dependence with evidence of a small $T^5$ contribution (10 $\mu$Ωcm at 100 K). A calculation of the $T^{9/2}$ contribution predicted by KO for two-magnon processes predicts only 0.5 $\mu$Ωcm at 100 K with appropriate parameters. It is likely, then, that this is the usual $T^5$ contribution from electron-phonon processes. Within the spin-wave approximation, the low temperature magnetization is given by $M(T) = M(0) - BT^{3/2} - \ldots$, where $B = 0.0587g\mu_B(k_B/D)^{3/2}$. The stiffness constant $D$ has been determined by neutron scattering [80] and muon spin resonance [19] to be $D \approx 135 - 170$ meV Å$^2$. The right side of Fig. 11 shows the magnetization for this sample, from which we extract $B(10$ kOe) and the value $D = 165$ meV Å$^2$, in good agreement with other results.

The plot in the right on Fig. 12 shows that the data do not follow a $T^2$ dependence to
the lowest temperatures. Rather, they deviate gradually from the curve \( \rho_0 + \alpha(H)T^2 \), fit over the range \( 60 \leq T \leq 160 \) K, saturating at an experimental residual resistivity \( \rho_0^{\text{exp}} = 91.4 \ \mu\Omega\text{cm} \), comparable to values observed by Urushibara et al. \[23\], but \( \approx 7\% \) larger than \( \rho_0 \). This conclusion is not changed by including the \( T^5 \) contribution. Fits to data taken in various fields show that \( \alpha(H) \) decreases with increasing field and is the source of the small negative magnetoresistance at low temperatures. To quantify the disappearance of the \( T^2 \) contribution, the authors calculate \( \frac{(\rho - \rho_0^{\text{exp}})}{\alpha(H)T^2} \) and display it in Fig. 13a. The \( T^5 \) contribution which gives a slight upward curvature to the data at higher temperatures has not been subtracted. Should the \( T^2 \) description be valid in the low temperature range, we should have \( (\rho - \rho_0^{\text{exp}})/\alpha(H)T^2 = 1 \). Note that this description of the data is extremely sensitive to the value of \( \rho_0^{\text{exp}} \), and it must be determined very carefully. An alternative description is possible by means of a numerical derivative, as discussed elsewhere \[4\], similar conclusions are arrived at.

Previous investigators have attributed the \( T^2 \) term in the resistivity to electron-electron scattering. An empirical relationship has been found between the coefficient \( \alpha \) and the coefficient \( \gamma_{\text{he}} \) of the electronic specific heat by Kadowaki and Woods \[22\]: \( \alpha/\gamma^2 = 1 \times 10^{-5} \ \mu\Omega\text{cm(mole K/mJ)}^2 \). Using our experimental value and \( \gamma \sim 4 \) \( mJ/\text{mol K}^2 \) from ref. \[24\], we find a value \( \approx 60 \times \) the Kadowaki-Woods parameter which argues against \( e-e \) scattering. With an electron density at the nominal doping level \( n = 5.7 \times 10^{27} \text{ m}^{-3} \), the effective mass that follows from \( \gamma_{\text{he}} \) is \( m^*/m = 2.5 \) and the Fermi energy is \( E_F = 0.5 \) eV and the \( e-e \) relaxation rate of the order of \( 2 \times 10^{11} \text{ s}^{-1} \) at 100 K. The experimentally observed \( T^2 \) contribution at that temperature is 100 \( \mu\Omega \) which with the same parameters correspond to a relaxation rate of \( 6 \times 10^{13} \text{ s}^{-1} \) more that two orders of magnitude larger. This disagreement is not fixed by using low temperature Hall-deduced effective concentration of carriers \[7\]. Rather than vanishing, what is more, \( e-e \) scattering should become more apparent as the temperature is reduced. We conclude that \( e-e \) scattering is an unlikely explanation for the observed quadratic dependence on temperature.

When the usual calculation of the electron-magnon resistivity \[3\] is extended to allow the minority-spin sub-band to be shifted upward in energy such that its Fermi momentum differs by an amount \( q_{\text{min}} \) from that of the majority sub-band, the one-magnon contribution can be written as \( \rho_e = \alpha_e T^2 \), where \( \alpha_e = (9\pi^3 N^2 J^2 h^5/8 e^2 E_F^4 k_F)(k_B/m^* D)^2 I(\epsilon) \). Here \( N J \) is the electron-magnon coupling energy which is large and equal to \( \mu = W - E_F \) in the DE Hamiltonian of KO; \( 2W \) is the bandwidth.. The magnon energy is given by \( Dq^2 \), and

\[
I(\epsilon) = \int_{\epsilon}^{\infty} \frac{x^2}{\sinh^2 x} dx \quad (6)
\]

The lower limit is \( \epsilon = Dq_{\text{min}}^2/2k_BT \), where \( Dq_{\text{min}}^2 \) is the minimum magnon energy that connects up- and down-spin bands; result that reproduces Mannari’s calculation in the limit \( \epsilon \rightarrow 0 \), and KO’s exponential cut-off for large \( \epsilon \). At high temperatures, the lower limit of the integral in Eq. 6 can be set equal to zero, leaving only the coupling energy \( N J = W - E_F \) as a parameter. Equating the calculated value to the experimental \( \alpha \) fixes the coupling to be \( W - E_F \approx 1.0 \) eV or \( W \approx 1.5 \) eV, in good agreement with a virtual crystal estimate of the band width. \[79\] In Fig. 12 we have plotted \( I(\epsilon, T) \) assuming \( D(0)q_{\text{min}}^2 = 4 \) meV and including the temperature dependence observed experimentally, \( D(T)/D(0) = (1-T/T_C)^{0.38} \)
which is important only at higher temperatures. While the curve follows the data qualitatively, it is clear that the minimum magnon energy is substantially larger than 4 meV at low temperatures, and decreases rapidly with increasing temperature.

Fig. 13 shows the Seebeck coefficient $S(T)$, measured on the same unoriented sample. Below 20 K, $S(T)$ is positive as expected for hole conduction, linear in temperature, and extrapolates to zero as $T \to 0$. If we take the scattering to be independent of energy, which is the case below 20 K, Seebeck coefficient can be expressed as $S(T) = (\pi^2 / 2e)(k^2 T / E_F)$.

Using the simplistic approximation of parabolic band $E_F = \hbar^2 k_F^2 / 2m^*$, and spherical Fermi surface $k_F^3 = 3n\pi^2$, the effective mass results to be $m^* / m \approx 3.7$, comparable to the value obtained from specific heat measurements. The sharp deviation from linear behavior in the temperature range $20 - 40$ K correlates with the onset of electron-magnon scattering which, being a spin flip process, must involve the minority spin band, and which therefore has a different dependence on energy near $E_F$.

In conclusion, the low temperature transport data cannot be explained by electron-electron scattering as proposed before \cite{30,75–77} and, while oversimplified, the extension of the standard calculation of one-magnon resistivity to describe spin-split bands gives a qualitative account of the half metallic suppression of the spin-wave scattering at very low temperatures.

**INTERMEDIATE TEMPERATURES, $T \approx T_C$**

As Millis and coworkers \cite{85–88} have emphasized, the Jahn-Teller effect in Mn$^{3+}$, if strong enough, can lead to polaron formation and the possibility of self-trapping. The effective JT coupling constant $\lambda_{\text{eff}}$, in this picture, must be determined self-consistently, both because it depends inversely on the bandwidth and because the effective transition temperature increases with decreasing $\lambda_{\text{eff}}$. If $\lambda_{\text{eff}}$ is larger than a critical value $\lambda_c$, the system consists of polarons in the paramagnetic phase. As the temperature is lowered to the Curie temperature $T_C$, the onset of ferromagnetism increases the effective bandwidth, which reduces $\lambda_{\text{eff}}$, thereby increasing the effective transition temperature. As a result, the polarons may dissolve into band electrons if $\lambda_{\text{eff}}$ drops below $\lambda_c$ and the material reverts to a half-metallic, double exchange ferromagnet at low temperatures. The tendency toward polaron formation is monitored by a local displacement coordinate $r$, which is zero for $\lambda_{\text{eff}} < \lambda_c$, and grows continuously as $\lambda_{\text{eff}}$ increases beyond that value. However, polarons are typically \cite{70} bimodal–large or small–so that we should consider $r$ to be a measure of the relative proportion of large polarons (band electrons for which $r \approx 0$) and small polarons (for which $r$ is an atomic scale length).

Indeed, there is growing experimental evidence \cite{41,92,93,39} that polaronic distortions, evident in the paramagnetic state, persist over some temperature range in the ferromagnetic phase, as displayed in Fig 2 as a coexistence zone. This possibility can be explored by considering the observed electrical resistivity to arise from the parallel conduction of a field- and temperature-dependent polaronic fraction (with activated electrical conductivity) and band-electron fraction (with metallic conductivity). The validity of this model is tested by
applying it to the thermoelectric coefficient using an extension of the well-known Nordheim-Gorter rule for parallel conducting channels. The La\(_{2/3}\)Ca\(_{1/3}\)MnO\(_3\) film samples used in this study were prepared by pulsed laser deposition onto LaAlO\(_3\) substrates to a thickness of 0.6 µm. As described previously [32], they were annealed at 1000 °C for 48 hr. in flowing oxygen. Measurements were carried out in a 7T Quantum Design Magnetic Property Measurement System with and without an oven option provided by the manufacturer. A modified sample rod brought electrical leads and type-E thermocouples to the sample stage. A bifilar coil of 12 µm Pt wire was calibrated to serve both as a thermometer and to provide a small heat input for the thermopower measurements. Measurements in fields up to 70 kOe could be carried out over the temperature range 4 K ≤ T ≤ 500 K. Following the transport measurements, magnetization data \(M(H, T)\) were acquired up to 380 K by conventional methods.

Figure 14a shows the resistivity data in zero field over the full temperature range. The data below 200 K exhibit metallic behavior, and are well fit by a power law, \(\rho(T) = [0.22 + 2 \times 10^{-5} K^{-2}T^2 + 1.2 \times 10^{-12} K^{-5}T^5] m\Omega cm\). Above 260 K, the resistivity is exponential, given \([31]\) by the form expected for the adiabatic hopping of small polarons, \(\rho_{ht} = (1.4\mu\Omega cm K^{-1})T \exp(1276 K/T)\). These are shown as broken lines. The assumption is that these represent the resistivity of band electrons and polarons, irrespectively, and that the transition region can be represented by a parallel combination characterized by a mixing factor \(c(H, T)\) which is envisaged to be the fraction of the carriers that are in the metallic state; that is

\[
\rho(H, T) = \left[ \frac{c(H, T)}{\rho_{ht}(T)} + \frac{1 - c(H, T)}{\rho_{lt}(T)} \right]^{-1} \tag{7}
\]

As a first approximation \(c(0, T) = M(0, T)/M_{sat}\) is chosen, using the data in the inset of Fig. 14a. The solid curve through the data shows the result of this process with no further adjustable parameters. As a second test of this approach, the Seebeck coefficient \(S(H, T)\) is considered, measured over the same temperature range and plotted in Fig. 14b. We fit the low temperature thermopower arbitrarily to a power law, \(S_{lt}(T) = [(0.051 K^{-1})T - (1.3 \times 10^{-4} K^{-2})T^2 - (3.2 \times 10^{-7} K^{-3})T^3]\) µV/K, and the high temperature data [32] to the form expected for small polarons, \(S_{ht}(T) = [(9730 K)^{-1} - 29] \mu V/K\). Broken lines in Fig. 14b show the extrapolation of these fits into the transition region. The Nordheim-Gorter rule [34] can now be applied to compute the thermopower for parallel conduction,

\[
S(H, T) = \rho_{exp}(H, T) \left[ \frac{c(H, T)S_{lt}(T)}{\rho_{lt}(T)} + \frac{(1 - c(H, T))S_{ht}(T)}{\rho_{ht}(T)} \right] \tag{8}
\]

The result is shown as a solid line in Fig. 14b, again using the reduced magnetization as a measure of the relative concentration of band electrons and polarons.

The association of \(c(H, T)\) with \(m(H, T) ≡ M(H, T)/M_{sat}\) does not hold in applied fields. Fig 15a shows the magnetization in fields up to 50 kOe. In Fig. 15b, the dashed curve shows the calculated \(\rho(10 kOe, T)\) along with the experimental data. Clearly, \(m(H, T)\) significantly overestimates the mixing factor \(c(H, T)\). In order to explore this two-fluid approach further, the mixing coefficient is computed from the field-independent low and high temperature resistivities, and its validity tested by calculating from it the field-dependent Seebeck coefficient. Explicitly, \(c(H, T)\) is defined through the expression
\[ c(H, T) = \frac{\rho_{ht}(T)/\rho_{exp}(H, T) - 1}{\rho_{ht}(T)/\rho_{lt}(T) - 1} \]  

which clearly approaches zero and unity in the high and low temperature limits respectively.

Fig. 16a shows the mixing factor at various applied fields extracted from the data of Fig. 15b. In Fig. 16b, these experimental mixing factors are used in Eq. 8 to generate curves for the field dependent Seebeck coefficient. These give an excellent account of the data, providing an independent check on the validity of this two-fluid approach. The main effect of the magnetic field is to shift the onset of the band-electron phase without broadening the transition. However, as we shall see, the vanishing of \( c(H, T) \) does not represent a shifted critical point for the material.

The essential feature of the Millis et al. model is that the effective Jahn-Teller coupling constant is very near its critical value in the paramagnetic phase. In this case, coupling to the magnetization via the associated band-broadening of the double exchange model, reduces \( \lambda_{eff} \) through its critical value \( \lambda_c \), inducing the expansion of small polarons into band electrons. A simple mean-field model is proposed here, that reproduces the essential features of the microscopic model and provides a comparison with experiment. The assumed ferromagnetic free-energy functional is of conventional form

\[ F_{mag} = \frac{1}{2} \left( \frac{T}{T_C} - 1 \right) m^2 + \frac{1}{4} bm^4 - mh \]  

where the free energy is written in units of \( 3S k_B T_C / (S + 1) = 1.94k_B T_C \) for \( S = 2(1 - x) + 3x/2 = 1.83 \) and \( x = 1/3 \), and \( h = g\mu_B(S+1)H/3k_B T_C = H/2360 \) kOe. The dependence of \( \lambda_{eff} \) on the magnetization can be approximated by writing \( \lambda_{eff} - \lambda_c \propto \alpha - \gamma m^2 + ... \), where \( \alpha \) is small and positive. The electronic free energy can then be written, in the same dimensionless units as Eq.10, as

\[ F_{el} = \frac{1}{2} \left( \alpha - \gamma m^2 \right) c^2 + \frac{1}{4} \beta c^4 \]  

Here \( c(H, T) \) is a nearly-critical secondary order parameter, driven by the difference \( \lambda_{eff} - \lambda_c \). Minimizing the total free energy two coupled equations are obtained, \((T/T_C - 1 - \gamma c^2)m + bm^3 - h = 0 \) and \((\alpha - \gamma m^2)c + \beta c^3 = 0 \). From the later it is obvious that the concentration of metallic electrons is zero until the magnetization reaches the value \( m = \sqrt{\alpha/\gamma} \), beyond which point \( c \) increases. In the limit \( \alpha \to 0 \), \( c \) is proportional to \( m \), with the result that \( b \to b - \gamma^2/\beta \), signalling a tendency for the system to approach a tricritical point and first order transitions as the coupling constant is increased. Note that the existence of a non-zero concentration \( \bar{c} \) can be considered to increase the critical point to \( (1 + \gamma \bar{c}^2)T_C \), causing the magnetization to increase more rapidly than would be the case without coupling to the metallic electron concentration. Solutions to the coupled equations are,

\[ m = B_S \left( \frac{3ST_C}{(S+1)T} \left[ (1 + \gamma \bar{c}^2)m + h \right] \right) \]  

and

\[ c = \tanh \left[ (1 - \alpha + \gamma m^2)c \right] \]
In Fig. 17 the simultaneous solutions of Eqs. 12 & 13 for $\alpha = 0.02$ and $\gamma = 0.3$ at $H = 0$, 24 kOe, and 48 kOe is found. Application of the magnetic field increases the temperature at which $c$ becomes non-zero by 7% or 20 K, consistent with the experimental data in Fig. 16a, but does not produce a high-temperature tail. As no thermal factors are included in the definition of $c$, the concentration of free carriers does not approach unity, and therefore differs slightly from the experimentally defined $c(H, T)$ in Eq. 9. The abrupt appearance of band electrons in this model produces a kink in the zero field magnetization curve at the onset temperature $T_D$, seen as a deviation from the $H = 0$, $\gamma = 0$ curve.

In non-zero field, the kink persists as seen in Fig. 18a where we plot $\chi^{-1} \equiv H/m$ at several magnetic fields. These results show clearly how the delocalization of charge carriers produces a rise in the effective $T_C$, in good agreement with experimental data [96] for La$_{0.79}$Ca$_{0.21}$MnO$_3$. The magnitude of the kink present in the experimental $\chi^{-1}(T)$ is larger and more evident in samples that show broader ferromagnetic transitions at constant doping, [97] and are consequently considered of "lower quality". This deserve a further analysis. Fig. 18b shows the resistivity curves determined using the mean-field $c(H, T)$. Clearly, the model must be extended to include critical fluctuations and associated rounding.

The proposed model differs from a percolation-like picture in which more or less static regions of high conductivity are weakly connected by surrounding insulating material. If that were the case, the standard Nordheim-Gorter rule for series connection would emphasize the increasing Seebeck coefficient of the resistive polaronic contribution, rather than the small thermopower of the more conductive component. There is ample experimental evidence, from studies of spin waves for example, that the ordered phase emerges with its full three-dimensional properties —albeit with strong evidence of slow, diffusive contributions— in materials in the composition regime discussed here. This mean-field model ignores a number of features that should be included in a complete treatment. In particular a term $m^2c$ is missing, because it leads to a first-order transition for all values of the parameters; it cannot be ruled out on symmetry grounds. Similarly, there should be a mixing entropy in the electronic free energy which, at sufficiently high temperatures, will lead to thermal dissociation of the polarons. Finally, no gradient terms were included and therefore ignore inhomogeneous thermal fluctuations that are certain to be significant in a system such as this where there are competing order parameters. Nonetheless, this phenomenological approach provides a qualitative understanding of the field and temperature dependence of the transport properties while correctly predicting the existence of kinks in the magnetization curves.

In summary, we have discussed the transport properties of optimally doped manganite materials and showed how they play a key role in the understanding of their ground state, as well as their different magnetic phases. Transport properties allow us to distinguish different temperature regimes and also to identify the relevant physics ruling them. As indicated in Fig. 4, DE physics dominates the very low temperature region. Additional theoretical work is needed however to describe the details of the gradual changes in the band structure with temperature, from 100% spin-polarized to partial polarization just bellow $T_C$. Such a model should allow us to properly calculate the temperature dependence of the electrical resistivity at very low temperature. JT and localization of charge dominates at high temperatures, but more experimental work is needed to improve the understanding of the Seebeck and Hall effects. One of the hardest experimental problems is related to sample quality issues. As
discussed before, the physical properties of manganites are strongly dependent on bandwidth, doping, and local defects. Most of the experimental work done until now has concentrated on samples where these three parameters are changed simultaneously. For example, studies of $T_C$ vs doping do not usually take into account the concentration of local defects nor the tolerance factor. It would be useful for the understanding of the high temperature Seebeck effect to be able to prepare samples with different doping levels and different concentration of local defects, keeping the tolerance factor $t_f$ a constant. Samples like these were prepared at Urbana, to test the impurity conduction model proposed by Emin, however discrepancy between nominal and measured chemical compositions make the experimental results hard to analyze [8]. At intermediate temperatures, both DE and JT mechanisms are required to understand the details of the phase transition between a paramagnetic insulator and a highly polarized ferromagnetic metal. The gradual delocalization of charge carriers is driven by a temperature dependent effective coupling between charge and lattice, which at the same time is determined by a DE controlled bandwidth. While the coexistence of itinerant and localized charges explain some experimental properties the situation is still unclear as respects the origins and mechanisms of very slow spin dynamics and cluster formation just above $T_C$. More careful measurements in this regime as well as a theoretical description that includes both double exchange, strong electron-phonon coupling, and spin fluctuations, should help.

We would like to thank A. Caneiro and F. Prado, Centro Atómico Bariloche; M. Rubin-stein, U.S. Naval Research Laboratory; D. Emin, University of New Mexico, Albuquerque, N.M.; P. Han, P. Lin, and S.-H. Chun, University of Illinois at Urbana. This work was possible thanks to the support from U.S. Department of Energy at Los Alamos National Laboratory, NM, USA. MBS acknowledges support by the Department of Energy, Office of Basic Energy Sciences through Grant No. DEFG0291ER45439 at the University of Illinois and by National Science Foundation Grant No. DMR-9120000 through the Science and Technology Center for Superconductivity.
REFERENCES

[1] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. 63: 1990 (1993). R. von Helmolt, J. Wecker, B. Holzapfel, L. Shultz, and K. Samwer, Phys. Rev. Lett. 71: 2331 (1993). S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, Science 64: 413 (1994). M. McCormack, S. Jin, T.H. Tiefel, R.M. Fleming, J. M. Phillips, and R Ramesh, Appl. Phys. Lett. 64: 3045 (1994). S. Jin, M. McCormack, T.H. Tiefel, and R. Ramesh, J. Appl. Phys. 76: 6929 (1994).

[2] G.H. Jonker and J.H. Van Santen, Physica 16: 337 (1950). J. H. Van Santen and G.H. Jonker, ibid. 16: 599 (1950).

[3] J. Volger, Physica 20: 49 (1954).

[4] C. Zener, Phys. Rev. 2: 403 (1951).

[5] P.W. Anderson and H. Hasegawa, Phys. Rev. 100: 675 (1955).

[6] I. Mannari, Prog. Theor. Phys. 22: 325 (1959).

[7] T. Kasuya, Prog. Theor. Phys. 22: 227 (1959).

[8] P.G. de Gennes, Phys. Rev. 118: 141 (1960).

[9] K. Kubo and N. Ohata, Jou. Phys. Soc. Japan 33: 21 (1972).

[10] J. Mazaferro, C. A. Balseiro, and B. Alascio, J. Phys. Chem. Solids 46: 1339 (1985).

[11] N. Furukawa, Jou. Phys. Soc. Japan 63: 3214 (1994).

[12] C.M. Varma, Phys. Rev. B54: 7328 (1996).

[13] R. Allub and B. Alascio, Phys. Rev. B 55: 14113 (1997).

[14] E.O Wollan, K.C. Kochler, Phys. Rev. 100: 545 (1955).

[15] R.M. Kusters, J. Singleton, D.A. Keen, R. McGreevy, and W. Hayes, Physica B 155: 362 (1989).

[16] K. N. Clausen, W. Hayes, D.A. Keen, R.M. Kusters, R.L. McGreevy, and J. Singleton, J. Phys.: Condens. Matter 1: 2721 (1989).

[17] R. von Helmolt, L. Haupt, K. Bärner, and U. Sonderman, Sol. St. Comm. 82: 693 (1992).

[18] A. Maigan, F. Damay, A. Barnabe, C. Martin, M. Hervieu, and B. Raveau, Phil. Trans. A 356: 1635 (1998 ).

[19] A. Arulraj, R. Mahesh, G.N. Subbanna, R. Mahendiran, A.K. Raychaudhuri, and C.N.R. Rao, Jou. Sol. St. Chem. 127: 87 (1996 ).

[20] R. Mahendiran, S.K. Tiwary, A.K. Raychaudhuri, T.V. Ramakrishnan, R. Mahesh, N. Rangavittal, and C.N.R. Rao, Phys. Rev. B 53: 3348 (1996). Also R. Mahendiran, S.K. Tiwary, and A.K. Raychaudhuri, Sol. St. Comm. 98: 701 (1996).

[21] S. Satpathy, Z.S. Popovic, and F.R.Vukajlovic, Phys. Rev. Lett. 76: 960 (1996).

[22] K. Khazeni, Y.X. Jia, L. Lu, C.H. Crespi, M. Cohen, and A. Zettl, Phys. Rev. Lett. 76: 295 (1996).

[23] J.J. Neumeier, M.F. Hundley, J.D. Thompson, and R.H. Heffner, Phys. Rev. B 52: R7006 (1995).

[24] H.Y. Hwang, T.T.M. Palstra, S-W. Cheong, and B. Batlogg, Phys. Rev. B 52: 15046 (1995).

[25] M.R. Ibarra, P.A. Algarabel, C. Marquina, J. Blasco, and J. García, Phys. Rev. Lett. 75: 3541 (1995).

[26] P.G. Radaelli, D.E. Cox, M. Marezio, S-W. Cheong, P.E. Schiffer, and A.P. Ramirez, Phys. Rev. Lett. 75: 4488 (1995).
[27] P. Dai, J. Zhang, H.A. Mook, S.-H. Liou, P.A. Dowben, and E.W. Plummer, Phys. Rev. B 54: R3694 (1996).
[28] J.M. De Teresa, M.R. Ibarra, C. Marquina, P.A. Algarabel, and S. Oseroff, Phys. Rev. B 54: R12689 (1996).
[29] J. Tanaka, M. Umehara, S. Tamura, M. Tsukioka, and S. Ehara, Jou. Phys. Soc. Japan 51: 1236 (1982).
[30] M. Jaime, M.B. Salamon, K. Pettit, M. Rubinstein, R.E. Trece, J.S. Horwitz, and D.B. Chrisey, Appl. Phys. Lett. 68: 1576 (1996).
[31] V.H. Crespi, L. Lu, Y.X. Jia, K. Khazeni, A. Zettl, and M. Cohen, Phys. Rev. B 53: 14303 (1996).
[32] M. Jaime, M.B. Salamon, M. Rubinstein, R.E. Trece, J.S. Horwitz, and D.B. Chrisey, Phys. Rev. B 54: 11914 (1996).
[33] J.-S. Zhou, W. Archibald, and J.B. Goodenough, Nature 381: 770 (1996).
[34] T.T. Palstra, A.P. Ramirez, S-W. Cheong, B.R. Zegarski, P. Schiffer, and J. Zaanen, Phys. Rev. B 56: 5104 (1997).
[35] M.F. Hundley and J.J. Neumeier, Phys. Rev. B 55: 11511 (1997).
[36] M. Jaime, H.T. Hardner, M.B. Salamon, M. Rubinstein, P. Dorsey, and D. Elin, Phys. Rev. Lett. 78: 951 (1997). Also M. Jaime, H. Hardner, M.B. Salamon, M. Rubinstein, P. Dorsey, and D. Elin, J. Appl. Phys. 81: 4958 (1997).
[37] S.G. Kaplan, M. Quijada, H.D. Drew, D.B. Tanner, C.G. Xiong, R. Ramesh, C. Kwon, and T. Venkatesan, Phys. Rev. Lett. 76: 2081 (1996).
[38] Y. Yamada, O. Hino, S. Nohro, R. Kanao, T. Inami, and S. Katano, Phys. Rev. Lett. 77: 904 (1996).
[39] S.J.L. Billinge, R.G. DiFrancesco, G.H. Kwei, J.J. Neumeier, and J.D. Thompson, Phys. Rev. Lett. 77: 715 (1996).
[40] P.G. Radaelli, M. Marezio, H.Y. Hwang, S-W. Cheong, and B. Batlogg, Phys. Rev. B54: 8992 (1996).
[41] D. Louca, T. Egami, E.L. Brosha, H. Röder, and A.R. Bishop, Phys. Rev. B 56: R8475 (1997).
[42] G. Zhao, K. Conder, H. Keller, and K.A. Müller, Nature 381: 676 (1996).
[43] G. Zhao, M.B. Hunt, and H. Keller, Phys. Rev. Lett. 78: 955 (1997).
[44] I. Isaac and J. P. Franck, Phys. Rev. B 57: R5602 (1998).
[45] C.H. Booth, F. Bridges, G.J. Snyder, and G.T. Geballe, Phys. Rev. B 54: R15606 (1996).
[46] C.H. Booth, F. Bridges, G.H. Kwei, J.M. Lawrence, A.L. Cornelius, and J.J. Neumeier, Phys. Rev. B 57: 10440 (1998).
[47] A. Shengelaya, G. Zhao, K. Heller, and K.A. Müller, Phys. Rev. Lett. 77: 5296 (1996).
[48] J.L. Cohn, J.J. Neumeier, C.P. Popoviciu, K.J. McClellan, and Th. Leventouri, Phys. Rev. B 56: R8495 (1997).
[49] R.H. Heffner, L.P. Le, M.F. Hundley, J.J. Neumeier, G.M. Luke, K. Kojima, B. Nachumi, Y.J. Uemura, D.E. MacLaughlin, and S-W. Cheong, Phys. Rev. Lett. 77: 1869 (1996).
[50] H.Y. Hwang, S-W. Cheong, P.G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. 75: 914 (1995).
[51] J.B. Goodenough, J.-S. Zhou, Mat. Res. Soc. Symp. Proc. 494: 335 (1998).
[52] H. Yoshizawa, R. Kajimoto, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B 55: 2729 (1997).
[53] L.M. Rodriguez-Martinez, J.P. Attfield, Phys. Rev. B 54: R15622 (1996).
[54] A. Sundaresan, A. Maigan, and B. Raveau, Phys. Rev. B 56: 5092 (1997).
[55] G.H. Rao, J.R. Sun, J.K Liang, W.Y. Zhou, Phys. Rev. B 55: 3742 (1997). Also F. Damay, C. Martin, A Maignan, and B. Raveau, J. Appl. Phys. 82: 6181 (1997).
[56] J.L. García-Muñoz, J. Fontcuberta, B. Martínez, A. Seffar, S. Piñol, and X. Obradors, Phys. Rev. B 55: R666 (1997).
[57] J.N. Eckstein, I. Bozovic, J. ODonnell, M ONellion, M.S. Rzchowski, Appl. Phys. Lett. 69: 1312 (1996).
[58] T. Holstein, Ann. Phys. 8: 343 (1959).
[59] L. Friedman and T. Holstein, Ann. Phys. (N.Y.) 21: 494 (1963).
[60] N.F. Mott and E.A. Davis, in Electronic Processes in Non-Crystalline Materials (Clarendon Press, Oxford, 1971).
[61] D. Emin, in Electronic Structure Properties of Amorphous Semiconductors, edited by P.G. Le Comber and N.F. Mott (Academic Press, New York, 1973). Also M.S. Hillery, D. Emin and N.H. Liu, Phys. Rev B 38: 9771 (1988).
[62] R. Raffaelle, H.U. Anderson, D.M. Sparin, and P.E. Parris, Phys. Rev. B 43: 7991 (1991).
[63] P.M. Chaikin, and G. Beni, Phys. Rev. B 13: 647 (1976).
[64] F. Prado and A. Caneiro (unpublished).
[65] A. Caneiro, P. Bavdaz, J. Fouletier, and J. P. Abriata, Rev. of Sci. Instr. 53: 1072 (1982).
[66] R.R. Heikes, in Thermoelectricity, edited by P.H. Egli (Wiley, New York, 1965). Also R.R. Heikes, in Transition Metal Compounds, edited by E.R. Schatz (Gordon and Breach, New York, 1963).
[67] A. Rojo, private communication.
[68] J.W. Lynn, R.W. Erwin, J.A. Borchers, A. Santoro, Q. Huang, J.L. Peng, and R.L. Greene, Jou. Appl. Phys. 81: 5488 (1997).
[69] P. Nagels in The Hall Effect and its Applications, edited by C.L. Chien and C.R. Westgate (Plenum, New York, 1980), p. 253.
[70] D. Emin and T. Holstein, Ann. Phys. (N.Y.) 53: 439 (1969).
[71] D.C. Worledge, L. Miéville, and T.H. Geballe, Phys. Rev. B 57: 15267 (1998).
[72] J.E. Nunez-Regueiro, D. Gupta, and A.M. Kadin, J. Appl. Phys. 79: 5179 (1996). G.J. Snyder, M.R. Beasley, T.H. Geballe, R. Hiskes, and S. diCarolis, Appl. Phys. Lett. 69, 4254 (1996).
[73] P. Matl, N.P.Ong, Y.F. Yan, Y.Q. Li, D. Studebaker, T. Baum, and G. Doubinira, Phys. Rev. B 57: 10248 (1998). G. Jakob, F. Martin, W. Westerburg, and H. Adria, ibid. B 57: 10252. P. Mandal, K. Barner, L. Haupt, A. Poddar, R. vonHelmolt, A.G.M. Jansen, and P. Wyner, ibid. B 57: 10256. K. Li, R. Cheng, Z. Chen, J. Fang, X. Cao, and Y. Zhang, Jou. Appl. Phys 84: 1467 (1998).
[74] M. Jaime, P. Lin, M.B. Salamon, and P.D. Han, Phys. Rev. B 58: R5901 (1998).
[75] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B 51: 14103 (1995).
[76] P. Schiffer, A.P. Ramirez, W. Bao, and S-W. Cheong, Phys. Rev. Lett. 75: 3336 (1995).
[77] G.J. Snyder, R. Hiskes, S. Dicarolis, M.R. Beasley, T.H. Geballe, Phys. Rev. B 53: 14434 (1996).
[78] J-H. Park, et al. Nature 392: 794 (1998).
[79] W.E. Pickett and D.J. Singh, Phys. Rev. B 53: 1146 (1996). Also D.J. Singh and W.E. Pickett Phys. Rev. B 57: 88 (1998).
[80] J.W. Lynn et al., Phys. Rev. Lett. 76: 4046 (1996).
[81] J.A. Fernandez-Baca, P. Dai, H.Y. Hwang, C. Kloc, and S.W. Cheong, Phys. Rev. Lett. 80: 4012 (1998).
[82] K. Kadowaki, and S.B. Woods, Sol. St. Comm. 58: 507 (1986).
[83] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Sauders College Publishing, 1976) p.33
[84] J.J. Hamilton, E.L. Keatley, H.L. Ju, A.K. Raychaundhuri, V.N. Smolyaninova, and R.L. Greene, Phys. Rev. B 54: 14926 (1996).
[85] A.J. Millis, P.B. Littlewood, and B.I. Shraiman, Phys. Rev. Lett. 74: 5144 (1995).
[86] A.J. Millis, B.I. Shraiman, and R. Mueller, Phys. Rev. Lett. 77: 175 (1996).
[87] A.J. Millis, Phys. Rev. B 53: 8434 (1996). A.J. Millis, Phys. Rev. B 55: 6405 (1997).
[88] A. J. Millis, R. Mueller, and B. I. Shraiman, Phys. Rev. B 54: 5389 (1996), ibid. B 54: 5405 (1996).
[89] D.C. Worledge, G.J. Snyder, M.R. Beasley, and T. Geballe, J. Appl. Phys. 80: 5158 (1996).
[90] D. Emin, Philos. Mag. 35: 1189 (1977).
[91] C. Wood and D. Emin, Phys. Rev. B 29: 4582 (1984).
[92] S. Yoon, H.L. Liu, G. Schollere, S.L. Cooper, P.D. Han, D.A. Payne, S.W. Cheong, and Z. Fisk, Phys. Rev. B 58: 2795 (1998).
[93] C. H. Booth, F. Bridges, G.H. Kwei, J.M. Lawrence, A.L. Cornelius, and J.J. Neumeier, Phys. Rev. Lett. 80: 853 (1998). Similar resuls are discussed by A. Lanzara et al., Phys. Rev. Lett. (to be published).
[94] R.D. Bernard, Thermoelectricity in Metals and Alloys (Taylor and Francis, London, 1972) p.140.
[95] D. C. Mattis, The Theory of Magnetism II, (Springer-Verlag, Berlin, 1985) p. 22.
[96] D.H. Goodwing, J.J. Neumeier, A.H. Lacerda, and M.S. Torikachvili, Mat. Res. Soc. Symp. Proc. 494: 95 (1998).
[97] J. Gardner, J. Thompson, and J. Sarrao, private communication.
[98] P. Lin, M.B. Salamon, and M. Jaime, Bull. Am. Phys. Soc. 43: 293 (1998).
FIGURES

FIG. 1. a) Lattice structure of LaMnO$_3$ b) MnO planes showing the characteristic periodic distortion c) Mn$^{3+}$ electronic levels $t_{2g}$ and $e_g$ split as a result of the Mn-O bond length distortion qualitatively displayed in b)

FIG. 2. Phase diagram for A$_x$B$_{1-x}$MnO$_3$ manganites. Modified from Schiffer et al. [76], mesh is coexistence region discussed below.

FIG. 3. Strain field induced in the structure by a non-JT, $s = 3/2$ spin, Mn$^{4+}$ atom.

FIG. 4. Different relevant temperature ranges for transport properties in CMR manganites for doping levels $x \approx 1/3$. At low temperatures DE effects are dominant, while at high temperature dynamic structural effects control the transport properties.

FIG. 5. Transition temperature vs. tolerance factor for the A$_{0.37}B_{0.3}MnO_3$ family of compounds, modified from ref. 53. PI: paramagnetic insulator, PM: paramagnetic metal, CFI: canted ferromagnetic insulator, FGC: ferromagnetic glass conductor, FM: ferromagnetic metal, O and O: orthorhombic, R: romboedric phases. The shadowed area indicates coexistence of extended and localized electronic states. Some samples discussed bellow were included: (⊗) (La$_{0.33}$Gd$_{0.33}$)Ca$_{0.33}$MnO$_3$, (□) (La$_{0.5}$Gd$_{0.17}$)Ca$_{0.33}$MnO$_3$, (●) La$_{0.67}$Ca$_{0.33}$ MnO$_3$, and (■) La$_{0.67}$(Ca$_{0.11}$Pb$_{0.22}$)MnO$_3$.

FIG. 6. Resistance vs temperature for a polycrystalline sample in zero field (□) and H=5T (●) and exponential fit. The data follows very well the model for adiabatic small polarons. b) The thermoelectric power vs temperature and fit to a function of the form A/T + B.

FIG. 7. The resistance for a polycrystalline sample of composition La$_{0.67}$Ca$_{0.33}$ MnO$_3$ plotted in two different scales, the one expected for adiabatic small polaron hopping and for Variable Range Hopping.

FIG. 8. The 1000 °C isotherm for La$_{0.67}$Ca$_{0.33}$MnO$_3$.

FIG. 9. a) Thermopower vs. 1000/T for polycrystalline samples of composition La$_{0.67}$ Ca$_{0.33}$MnO$_3$, La$_{0.67}$Ca$_{0.33}$MnO$_{2.49}$ and La$_{0.75}$Ca$_{0.25}$MnO$_3$. b) $S_\infty$ vs Mn$^{4+}$ content for our samples and theoretical predictions discussed in the text.

FIG. 10. The Hall coefficient vs T for film samples of composition (La$_{1-y}$Gd$_y$)$_{0.67}$Ca$_{0.33}$MnO$_3$, $y = 0$ (□) and $y = 0.25$ (▲). The dashed line correspond to a fit of the form $R_H = R_H^0 \exp[E_H/k_B T]$. Inset a): 1/$R_H$ vs T, for $y = 0.25$ showing an extrapolation to 245 K $>> T_C = 142$ K. Inset b) ln $|R_H|$ vs 1000/T, for $y = 0.25$, showing an activation energy $E_H = 91 \pm 5$ meV.
FIG. 11. Left: the resistivity vs $T^2$ for magnetic fields up to 70 kOe in a single crystal sample of composition La$_{0.67}$(Ca,Pb)$_{0.33}$MnO$_3$. Right: the magnetization deviation from saturation vs temperature on a log-log plot, with $T^{3/2}$ and $T^{5/2}$ contributions.

FIG. 12. Left: the experimental resistivity $\rho(T)$ after subtraction of the residual value $\rho_0^{exp}$, divided by $\alpha_H T^2$ vs temperature. The dashed line is the result of the one-magnon calculation described in the text. Right: $\rho(T)$ after subtraction of the fitted value $\rho_0^{fit}$ vs temperature in a log-log plot. In both plots significant deviations from the $T^2$ behavior displayed in Fig. 12 are observed.

FIG. 13. The Seebeck coefficient $S$ vs temperature. It is positive and metal-like at low temperature, has an anomalous kink near 30 K, and develops a positive field dependence above 40 K. The dashed line is a linear fit in the low temperature regime.

FIG. 14. a) Resistivity vs temperature in zero field. The broken lines indicate extrapolations of the fits to the low and high temperature regions of the curve. The solid line is the parallel combination of the two conductivities using the magnetization (inset) as a mixing factor. b) Similar results for the Seebeck coefficient.

FIG. 15. a) Magnetization data for this sample. b) Resistivity data as functions of field and temperature. The dashed curve is a parallel admixture using the reduced magnetization measured at 10 kOe.

FIG. 16. a) The mixing factor $c(H,T)$ extracted from the resistivity as described in the text. b) Seebeck coefficient data and results of a computation using $c(H,T)$ from a) in Eq. 8.

FIG. 17. a) the mixing factor $c(H,T)$ calculated in the mean-field model with $\alpha =0.02$ and $\gamma =0.3$. b) The magnetization calculated with the same parameters. The dotted line shows the non-interactive case for comparison.

FIG. 18. a) Inverse magnetic susceptibility $H/m$ vs temperature near the M-I transition. The appearance of free carriers induce the rise of the effective $T_C$, in qualitative agreement with data by Goodwing et al. b) Calculated resistivity using $c(H,T)$ from Fig. 17a) in Eq. 7.
This figure "Figure1_4.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Figure5_8.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Fig9_10.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Fig11_12.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Fig13_14.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Fig15_16.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1
This figure "Fig17_18.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/9902284v1