Intrinsic electrical transport and magnetic properties of $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ MOCVD thin films and bulk material

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An investigation designed to display the intrinsic properties of perovskite manganites was accomplished by comparing the behavior of bulk samples with that of thin films. Epitaxial 1500 Å films of perovskite $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ were grown by solid source chemical vapor deposition on $LaAlO_3$ and post annealed in oxygen at 950 °C. Crystals were prepared by laser heated pedestal growth. The magnetic and electrical transport properties of the polycrystalline pellets, crystals, and annealed films are essentially the same. Below $T_C/2$ the intrinsic magnetization decreases as T^2 (as can be expected for itinerant electron ferromagnets) while the intrinsic resistivity increases proportional to T^2. The constant and T^2 coefficients of the resistivity are largely independent of magnetic field and alkaline earth element (Ca, Sr, or Ba). Hall effect measurements indicate that holes are mobile carriers in the metallic state. We identify three distinct types of negative magnetoresistance. The largest effect, observed near the Curie temperature, is 25% for the Sr and 250% $[\Delta R/R(H)]$ for the Ca compound. There is also magnetoresistance associated with the net magnetization of polycrystalline samples which is not seen in films. Finally a small magnetoresistance linear in H is observed even at low temperatures. The high temperature (above T_C) resistivity of $La_{0.67}Ca_{0.33}MnO_3$ is consistent with small polaron hopping conductivity with a slight transition at 750 K, while $La_{0.67}Sr_{0.33}MnO_3$ does not exhibit activated conductivity until about 500 K, well above T_C. The limiting low and high temperature resistivities place a limit on the maximum possible magnetoresistance of these materials and may explain why the ''colossal'' magnetoresistance reported in the literature correlates with the suppression of T_C. [S0163-1829(96)04421-9]

I. INTRODUCTION

The $R_{0.67}A_{0.33}MnO_3$ perovskite manganites, where R and A are some rare earth and alkaline earth elements, respectively, display the unusual property of being paramagnetic insulators at high temperatures and ferromagnetic metals at low temperatures.[1–4] Both end members of $La_{1-x}A_xMnO_3$ are antiferromagnetic insulators,[5] but become ferromagnetic metals upon doping. The theory of double exchange[6–8] has been developed in order to explain this phenomenon and correctly predicts $x=1/3$ to be optimal doping.[9] Recent calculations show that a second mechanism such as a Jahn-Teller distortion may be required to explain the magnetoresistance within the double exchange model.[10,11]

Until recently, much of the experimental work on the manganites has been motivated by their utility as a cathode materials in solid oxide fuel cells. Thus many compounds of the type $R_{1-x}A_xMnO_{3+\delta}$ have been studied in polycrystalline form.[12–15] Much has been learned about their defect chemistry and high temperature electronic and ionic conductivity. Most of these compounds are not metallic above room temperature but have electronic conductivity, presumably due to (small) polaron hopping, sufficient to make good electrodes.

Interest in the perovskite manganites has expanded since their fabrication as epitaxial thin films.[16,17] Some films have shown the insulator to ferromagnetic metal transition at lower temperatures with a large magnetoresistance near this transition.[18,19] $\Delta R/R(H)$ of greater than 10^6% has been reported for fields of several T.[20–23] Since giant magnetoresistance (GMR) films have a $\Delta R/R(H)$ of typically 20% (which saturates in a few thousand Oe), the manganite films have been proposed as possible replacements for GMR read heads in the magnetic recording industry. However, since magnetic recording devices work at room temperature with low magnetic fields, the temperature range and field sensitivity of the manganites in their present state do not make them competitive with GMR materials. Nevertheless, the rather imprecise term ''colossal magnetoresistance'' (CMR) has been coined for this phenomenon. [It should be noted, however, that such a large magnetoresistance is not unique to the manganates. Doped EuO and EuS show magnetoresistances of 10^4%, using the above definition, and therefore can be considered a CMR material. Furthermore, it has been shown that in some Chevrel phase compounds,[24] a magnetic field makes the material superconducting—which would make them ''supermagnetoresistance'' (SMR) materials.] However, since it has been widely adopted we will employ it here where CMR is defined when $\Delta R/R(H)>10$.

Although the films are quite stable and the measurements reproducible even after several months, it is clear that growth

TABLE I. Physical properties of polycrystalline pellets.

	$La_{0.67}Sr_{0.33}MnO_8$	$La_{0.67}Ca_{0.33}MnO_3$
T_C	376 K	270 K
M_S	3.59 μ_b/Mn	3.39 μ_b/Mn
a	3.88 Å	3.86 Å
H_C	20 Oe	10 Oe
Curie Weiss μ_{eff}	5.61 μ_b	5.96 μ_b
Hall carrier density (of films)	2.1 holes/Mn	0.9 holes/Mn

and annealing conditions greatly influence the properties of the manganite films.[25] Furthermore, the electrical and magnetic properties of the CMR films are often very different than those of the materials produced by bulk ceramic techniques or single crystals with the same nominal composition. Thus, in order to understand these materials, we should distinguish between the properties intrinsic to perfect crystalline $La_{0.67}A_{0.33}MnO_3$ and those caused by microstructure, strain, disorder, and/or compositional variations. From the work described below, we conclude that the low temperature, CMR phenomenon is not intrinsic to the thermodynamically stable phases with composition $La_{0.67}Sr_{0.33}MnO_3$ or $La_{0.67}Ca_{0.33}MnO_3$.

In this study, we attempt to establish the inherent properties of $La_{0.67}A_{0.33}MnO_3$ by comparing measurements among polycrystalline pellets, single crystals, and thin films, supplemented with literature data when available. Whereas most reported $La_{0.67}A_{0.33}MnO_3$ films have been grown by laser ablation, we show that organometallic chemical vapor deposition (MOCVD) produces high quality films upon annealing. We will demonstrate singular behavior which can be obtained in bulk and thin films.

II. EXPERIMENT

A. Sample preparation

Three types of samples were prepared: polycrystalline pellets, float zone crystals, and thin films. Polycrystalline samples of $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ were made using standard ceramic synthesis techniques. La_2O_3, $SrCO_3$, or $CaCO_3$, and MnO were repeatedly reacted in air at 1250 °C for several days. Pellets were cold pressed and sintered under the same conditions. Powder x-ray diffraction showed single-phase nearly cubic perovskite patterns with cell lengths given in Table I. Under these conditions, the material should be fully or slightly over oxygenated.[26]

From this material, float zone crystals were grown using a CO_2 laser heated pedestal growth system.[27,28] The approximately 1 mm diameter crystals were grown at about 1 cm/h. Back reflection Laue and transmission rotation x-ray photographs showed broad but discrete reflections, with only weak powder rings.

The solid source MOCVD reactor used to grow the films in this study has been described previously.[29] The 2,2,6,6-tetramethyl-3,5-heptanedionato (TMHD) organometallics used for La, Sr, Ca, and Mn were, respectively tris(TMHD) lanthanum, bis(TMHD) strontium hydrate, bis(TMHD) calcium, and tris(TMHD) manganese. $LaAlO_3$ substrate temperatures of 600–800 °C (as measured by a thermocouple in the susceptor—actual surface temperatures were ~100–150 °C lower) were used in an oxygen partial pressure of 3–4 torr 1500 Å thick films were grown at approximately 45 Å/min. The films were then annealed in flowing oxygen at 950 °C for several h and cooled slowly (ca 20° h) to room temperature. X-ray diffraction of annealed films showed only single phase [100] oriented cubic perovskite. Unannealed films particularly at the lower growth temperatures showed only weak or no crystallization. The composition of the source material was adjusted so that Rutherford back scattering of the films were within 1% of the desired composition.

B. Magnetization measurements

A Quantum Design $MPMS_2$ SQUID magnetometer was used for magnetization and transport measurements from 2 to 400 K; thus low field magnetization and resistivity can also be measured simultaneously. The absolute temperature reliability is 1 K, whereas the relative error is much better.

Thin film samples were held in a plastic straw. Measured data contained contributions from the film and the $LaAlO_3$ substrate which is diamagnetic with a small paramagnetic impurity. [Approximating $\chi=\chi_0+C/(T+\Theta)$ gives $\chi_0=-2.219(2)\times10^{-7}$ emu/g/G, $C=6.8(2)\times10^{-7}$ emu K/g G, and $\Theta=11.3(6)$ K.] A small paramagneticlike contribution to the low temperature (<15 K) M vs T data was found in the film samples only. Since we are not certain this effect is due to the film, as opposed to the substrate or an interfacial phase, we omit the affected data.

C. Electronic transport measurements

Four leads were attached with indium for measurements less than 400 K or polyimide based silver epoxy for above 400 K (in air) either in the van der Pauw[30] or conventional configuration. dc currents were chosen well within the ohmic regime. Offset voltages were subtracted by reversing the current. Voltages were measured at several slightly (up to 20%) different currents to calculate the precision. Differences between the transverse and longitudinal magnetoresistances are small and the subject of a future publication.

The Hall effect was measured using the van der Pauw geometry on thin films. The magnetoresistance must be subtracted in order to obtain the Hall resistance. Because the magnetoresistance is so large in these materials, we only show the Hall effect measurement at 5 K.

III. RESULTS

A. Magnetism

The polycrystalline samples have relatively square hysteresis loops (Fig. 1), with forced magnetization at 70 kOe of only a few percent. The saturation magnetizations are close to that expected for high spin manganese in octahedral coordination: for spin only (orbital contribution quenched) moment $\mu=gs\mu_b$, $g=2$ and then $\mu=2\mu_b[0.67\times2$ (from Mn^{3+})$+0.33\times3/2$ (from Mn^{4+})$]=3.67\mu_b$. The measured ferromagnetic and Curie temperatures are the same within experimental error of a few degrees. The physical properties of the polycrystalline materials summarized in Table I are consistent with previous results.[1–3,31–33] Since the precise

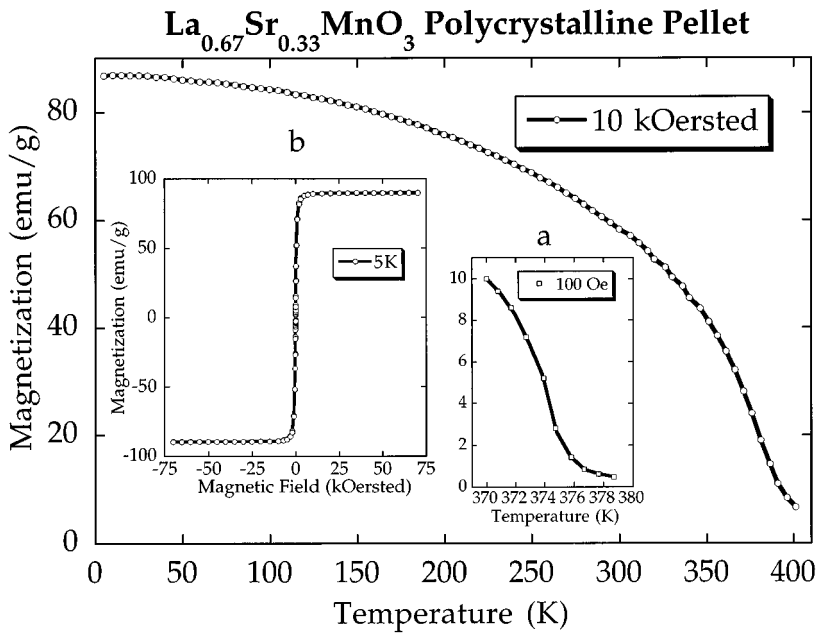

FIG. 1. Magnetization of $La_{0.67}Sr_{0.33}MnO_3$ polycrystalline pellet at 10 kOe. Inset (a), magnetization at 100 Oe used to determine T_C=375 K. Inset (b), full hysteresis loop at 5 K.

oxygen concentration has a noticeable effect on T_C and M_S,[34] slight differences are expected. Float zone grown crystals have similar magnetic properties.

The transition temperatures of the annealed films are close to those of the polycrystalline material, and are summarized in Table II. The saturation magnetization, measured at 5 kOe, also decreases as T^2 for both samples. The annealed films exhibit a (5 K) coercivity of about 100 Oe and a sheared hysteresis loop expected from demagnetization or uniaxial anisotropy effects (Figs. 2 and 3).

The saturation magnetization decreases approximately proportional to T^2 at low temperatures (Fig. 4). This temperature dependence of M which has not been previously reported is expected for metallic ferromagnets, in which single particle excitations are dominant.

B. Electronic transport

Both $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ have an abrupt drop in resistivity below the magnetic Curie temperature in both films and bulk samples (Figs. 5 and 6). The magnetoresistance [defined as $R(0)$-$R(H)$] peaks near the Curie temperature as shown in Figs. 5 and 6 and previous experiments (Refs. 31 and 34).

Low temperature resistivity data were analyzed using a polynomial expansion in temperature T. Since the resistivity is essentially constant for temperatures less than 10 K for all samples, it is clear that the resistivity data both with and without an applied field require a temperature independent (R_0) term. As shown previously for related compounds,[31,34,35] R_0 is a function of magnetization in polycrystalline $La_{0.67}A_{0.33}MnO_3$ (Fig. 7). In contrast, the magnetoresistance of films and crystals at 5 K is over 100 times less: it is not even measurable in the $La_{0.67}Ca_{0.33}MnO_3$ crystal where the precision is 0.5%. Due to the higher resistance of the films, the magnetoresistance at 5 K is measurable and is approximately linear with field (Fig. 7). This effect is small enough for the analysis to be carried out with R_0 independent of magnetic field.

Since polycrystalline material contains significant contribution to the resistivity from grain or domain boundaries, as shown by microwave measurements[36] and higher R_0 values, analysis of the resistivity data is made only for the well annealed films and crystals. Data up to 70 and 100 K for

TABLE II. Magnetoresistance of annealed films.

Sample	T_C (K)	T_{MR} (K)	T_{MI} (K)	R_0 (10^{-3} Ω cm)	R_2/R_0 (10^{-6} K^{-2})	$R_{4.5}$(0 T)/R_0 (10^{-12} K$^{-4.5}$)	$R_{4.5}$(7 T)/R_0 (10^{-12} K$^{-4.5}$)	E_a/k_b (K)
LSM1[a]	360	365	455	0.15	55	28	15	
LCM*X*	267	272	275	0.10	102	67	54	849
LCM13	240	250	250	0.10	61	122	87	967
LCM10	260	275	280	0.12	66	85	72	740
LCM15	260	265	265	0.15	73	87	73	725
LCM17	260	262	264	0.16	60	133	82	865
LCM21	240	245	245	0.28	61	114	60	1116
LBM (Ref. 60)	310	310	330	0.34	52			

[a]LSM=$La_{0.67}Sr_{0.33}MnO_3$; LCM and LBM are the Ca and Ba analogues. *X* refers to float zone growth crystals.

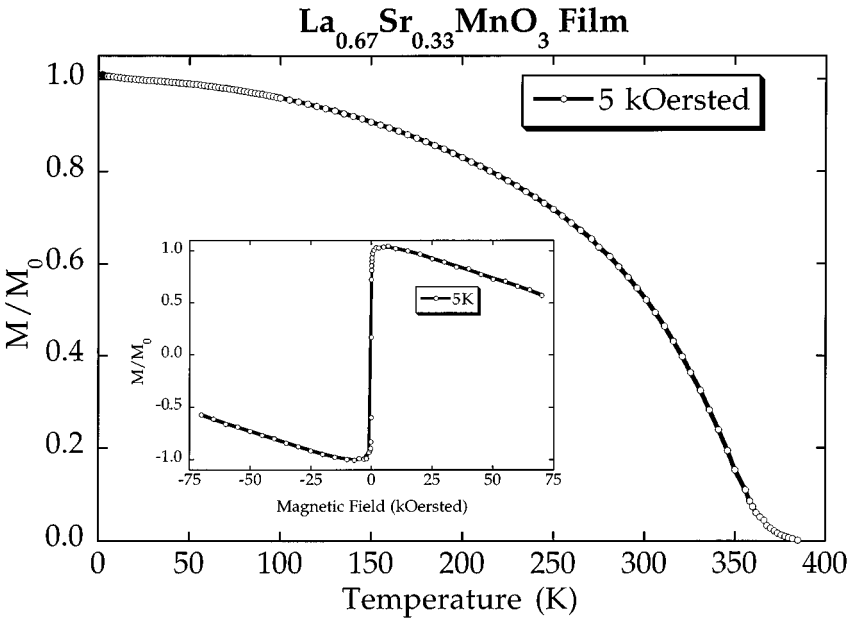

FIG. 2. Magnetization of $La_{0.67}Sr_{0.33}MnO_3$ film (LSM1) on $LaAlO_3$ at 5 kOe. Inset, full hysteresis loop at 5 K of film and (diamagnetic) substrate.

$La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$, respectively, are well described with an additional (R_2) term proportional to T^2 (Fig. 8). A linear term in T did not significantly improve the fit and was not used in later calculations in order to keep the number of free parameters to a minimum. The field dependence of R_2 is so small (less than 10% variation) we have not been able to measure it.

The range of validity can be extended to about 200 K for $La_{0.67}Ca_{0.33}MnO_3$ and 350 K for $La_{0.67}Sr_{0.33}MnO_3$ with the addition of a T^n term where $4<n<5$. We have chosen to analyze the data with a fit to $R_0+R_2T^2+R_{4.5}(H)T^{4.5}$ since a $T^{4.5}$ temperature dependence has been predicted for electron-magnon scattering in the double exchange theory.[37] We cannot claim from our data that we see evidence for a $T^{4.5}$ term (as opposed to T^4 or T^5) only that it allows the determination of the R_0 and R_2 terms to higher accuracy in a much larger temperature range. The maximum temperature for which we analyzed the data was determined by finding the maximum temperature where the free parameters remained stable and the fit was visibly accurate.

The results of this analysis are given in Table II. As expected, $R_{4.5}(H)$ decreases as the magnetic field increases. In a field of 70 kOe $R_{4.5}(H)$ decreases by 25–50 % (Table II).

Above T_C, the zero field resistivity (Fig. 9) of $La_{0.67}Ca_{0.33}MnO_3$ fit best to $R_hT\exp(E_a/k_bT)$ predicted by small polaron hopping conductivity.[38] Other forms predicted by variable range hopping[39] or band semiconductor type conductivity were also fit with two parameters to the data with less accurate and less consistent results. In contrast to the Ca and Ba analogs[31,34] the $La_{0.67}Sr_{0.33}MnO_3$ resistivity (Fig. 10) does not reach a maximum until about 100 K above T_C.[14]

The Hall effect data at 5 K (Fig. 11) were analyzed according to the equation $R=R_0+HR_H+|H|R_{\mathrm{MR}}$, where R_H is the Hall resistance and R_{MR} is the magnetoresistance. The

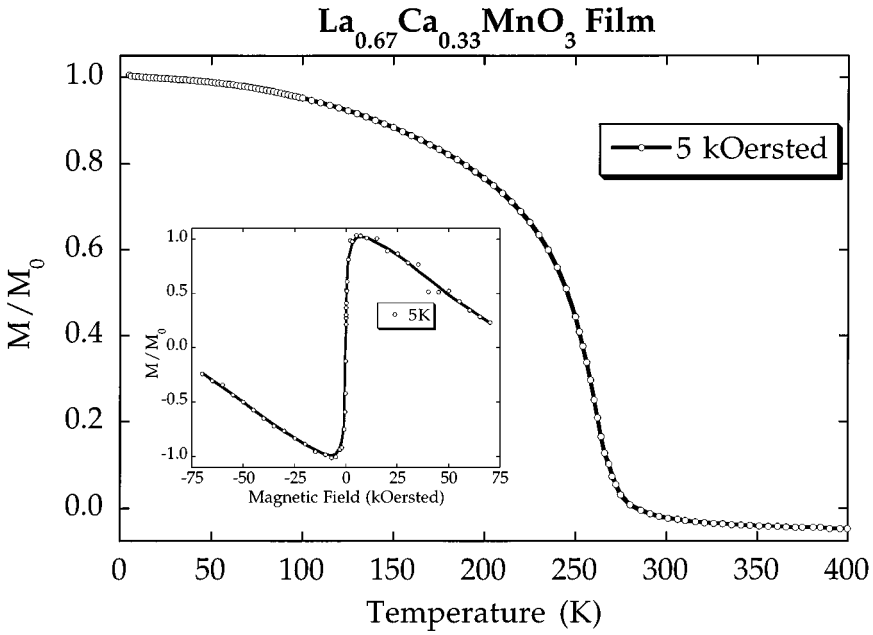

FIG. 3. Magnetization of $La_{0.67}Ca_{0.33}MnO_3$ film (LCM15) on $LaAlO_3$ at 5 kOe. Inset, full hysteresis loop at 5 K of film and (diamagnetic) substrate.

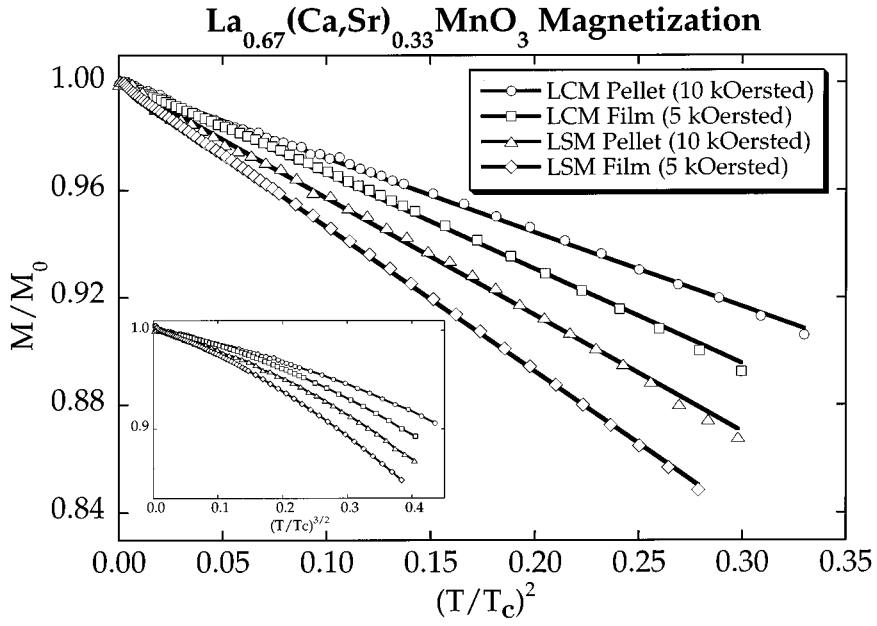

FIG. 4. Magnetization of $La_{0.67}(Ca/Sr)_{0.33}MnO_3$ films and polycrystalline samples showing the T^2 dependence of the magnetization. Inset, same data as a function of $T^{3/2}$ for comparison.

contribution due to the anomalous Hall effect was not detected at this temperature. From the simple single band interpretation of the Hall effect,[40] our measurements at 5 K show hole conductivity with concentrations of the expected order of magnitude (Table I).

IV. DISCUSSION

In order to produce the thermodynamically stable phase, we anneal the material at high temperatures for long times and cool slowly. This produces films, polycrystalline pellets, and single crystals with very similar properties, as shown above. Properties which are common to all these samples are called ''intrinsic'' to the thermodynamically stable phase. The remaining differences can then be attributed to inhomogeneities, noncrystallinity, microstructure, and strain. Major changes in the magnetization and electrical transport have been observed in $R_{0.67}A_{0.33}MnO_{3+\delta}$ compounds (A =Ca,Sr,Ba) when the oxygen stoichiometry was varied; these have been discussed mainly in terms of nonstoichiometry doping and carrier localization.[12–15,34,41]

In order to compare experimental properties certain terms need to be defined. Here we define T_C, the magnetic Curie temperature, to be the temperature where the bulk of the zero field magnetization disappears. T_{MI} (metal to insulator temperature) is the temperature where the resistivity is a maximum. T_{MR} is the temperature where the magnetoresistance $[R(0)\text{-}R(H)]$ is the largest. The term ''CMR'' is used here when the magnetoresistance ratio $\Delta R/R(H)$ is greater than 10 (or 1000%).

In general, manganite films reported in the literature which exhibit CMR (Refs. 20, 22, 25, 42, and 43) (1) do not have square hysteresis loops at low temperatures, leading some to believe superparamagnetic behavior exists in those

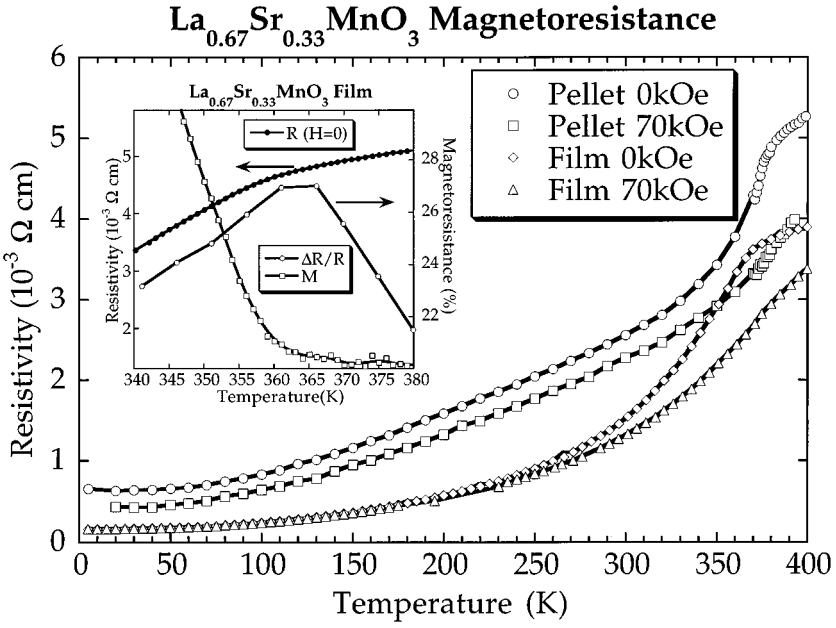

FIG. 5. Magnetoresistance of $La_{0.67}Sr_{0.33}MnO_3$ polycrystalline pellet and film (LSM1). Inset, simultaneous magnetization and resistivity of the film at 20 Oe, along with the magnetoresistance $[R(H=0$ kOe$)-R(H=70$ kOe$)]$.

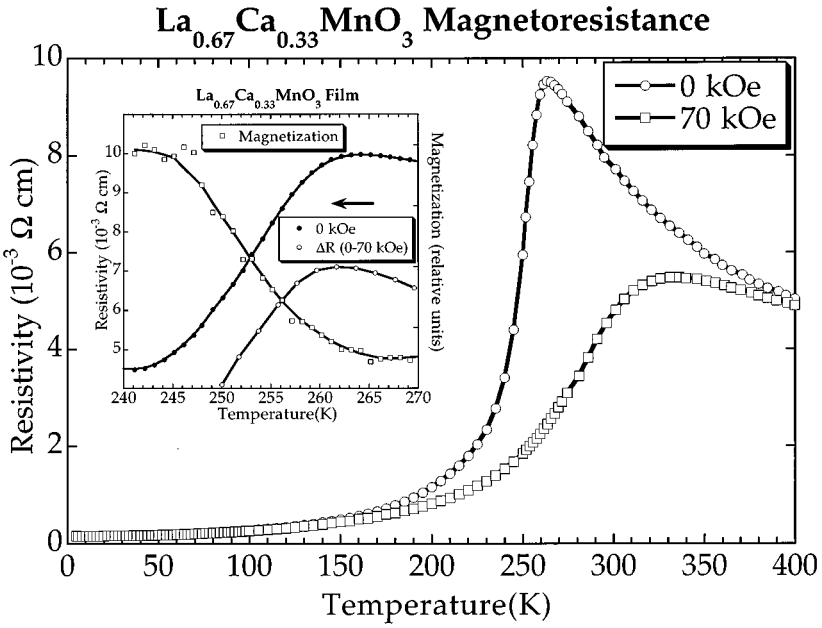

FIG. 6. Magnetoresistance of $La_{0.67}Ca_{0.33}MnO_3$ film (LCM17). Inset, simultaneous magnetization and resistivity at 20 Oe, along with the magnetoresistance $[R(H=0\ \text{kOe}) - R(H=70\ \text{kOe})]$.

materials; (2) have ill-defined T_C's which are much less than those reported for the bulk materials with the same nominal composition; (3) have T_{MI} well below T_C, with T_{MR} slightly less than T_{MI}; and (4) have high resistivities in the metallic state, at low temperatures.

The annealed films in this study (which do not exhibit CMR) are much like bulk polycrystalline or single crystal material: They are clearly itinerant electron ferromagnets with reasonably square hysteresis loops, T^2 dependence of the saturation magnetization, and sharp T_C's. They have T_C and T_{MR} all approximately equal and along with T_{MI} are comparable to those of the bulk polycrystalline material. Finally, the films have low resistivities like those observed in single crystals.[36,44–48] We therefore conclude that these films are displaying properties inherent to $La_{0.67}(Sr/Ca)_{0.33}MnO_3$ and less influenced by microstructure, strain, and/or compositional variations than films with suppressed T_C and CMR.

The resistance of $La_{0.67}Ca_{0.33}MrO_3$ reaches a maximum near the Curie temperature whereas that of $La_{0.67}Sr_{0.33}MrO_3$ maximizes about 100 K above T_C. This is best seen from simultaneous magnetization and resistance measurements (Figs. 5 and 6), where there is no error in relative temperature. Both $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ have $T_{MR} \approx T_C$ within a few K. For $La_{0.67}Ca_{0.33}MnO_3$ T_{MI} is approximately equal to $T_C \approx T_{MR}$. $La_{0.67}Sr_{0.33}MnO_3$ however shows a much more gradual transition to a hopping conductivitylike transport with T_{MI} (approximately 455 K) well above $T_C = 360$ K.

At T_C a maximum in $d\rho(H=0)/dT$ is expected for a metallic ferromagnet.[49] This is observed for both compounds studied within experimental uncertainty. The added resistance at a ferromagnetic Curie temperature is due to electron

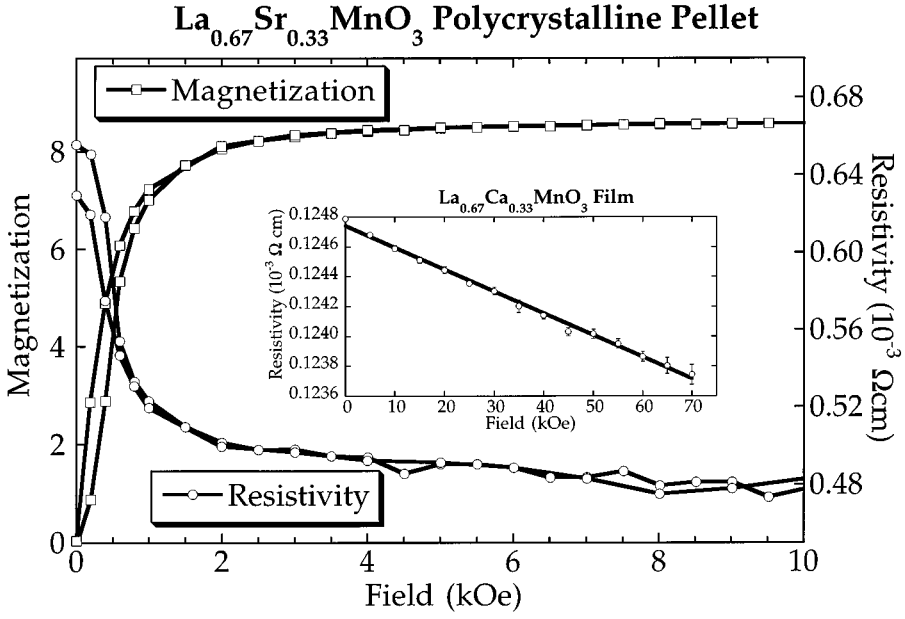

FIG. 7. Simultaneous magnetization and resistivity in a magnetic field of $La_{0.67}Sr_{0.33}MnO_3$ polycrystalline pellet at 5 K. Data for both increasing and decreasing field are shown. Inset, magnetoresistance of $La_{0.67}Ca_{0.33}MnO_3$ film (LCM10) at 5 K.

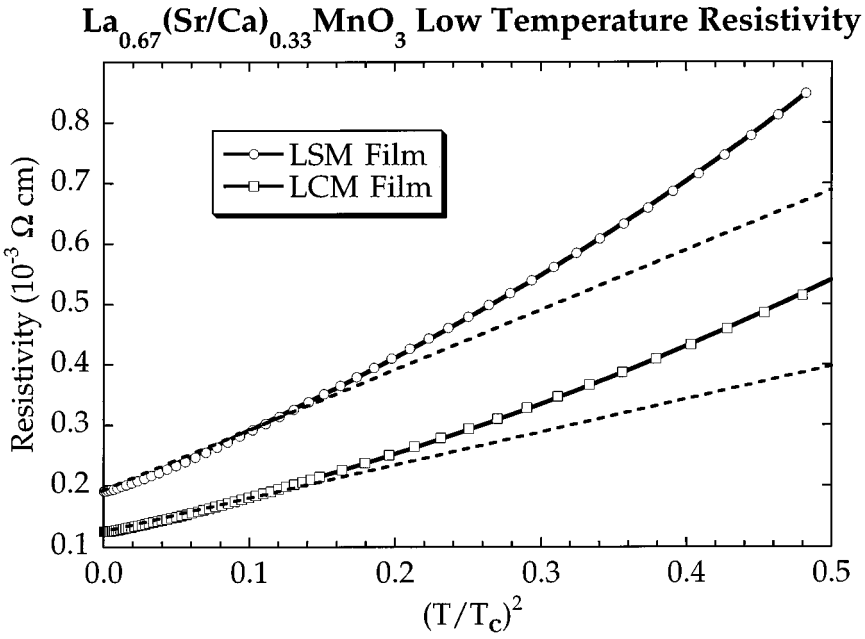

FIG. 8. Low temperature resistivity (in zero field) of $La_{0.67}(Sr/Ca)_{0.33}MnO_3$ films (LSM1 and LCM10). Solid lines are the fit to $R_0+R_2T^2+R_{4.5}T^{4.5}$ up to 250 and 200 K for LSM and LCM, respectively. The dashed lines show the constant and T^2 terms of the best fit.

scattering off disordered spins and, particularly in the case of the manganites, polaron formation. Since a magnetic field can easily suppress spin fluctuations in the critical region, the resistance associated with magnetic disorder will be reduced in a magnetic field. In a good metal such as Fe or $SrRuO_3$ (Ref. 50) this normally is a small effect of about a few percent. It has been shown theoretically that this effect is much larger for a semimetal (or semiconductor) at T_C, particularly within the double exchange model;[8,49,51,52] however, this conclusion has been recently questioned.[10,11] Nevertheless, this explanation has been used to explain the magnetotransport properties of semiconducting magnetic chalcogenides such as EuO,[53] Gd_2S_3,[54] and various spinels[55] where the resistance may drop by several orders of magnitude at T_C.

The negative magnetoresistance associated with the domain orientation is only observed in polycrystalline samples.[31,34] If this is due to domain wall scattering, then films and crystals with fewer domain boundaries would be expected to show a much smaller effect.

The low temperature negative magnetoresistance linear in H is very small in the films but somewhat larger in the polycrystalline samples (Fig. 7, and Refs. 31 and 34). This negative magnetoresistance may be due to the M^2 dependence of the resistivity[45,46] combined with a small forced magnetization. Classic magnetoresistance of metals is generally positive but is often negative in ferromagnets.

A T^2 dependence of the magnetization is predicted by the Moriya theory of spin fluctuation in itinerant electron ferromagnets, as shown by a calculation for the weak metallic ferromagnet Ni_3Al.[56] A T^2 dependence has been observed in bulk $SrRuO_3$,[57] which is a metallic ferromagnet with a sub-

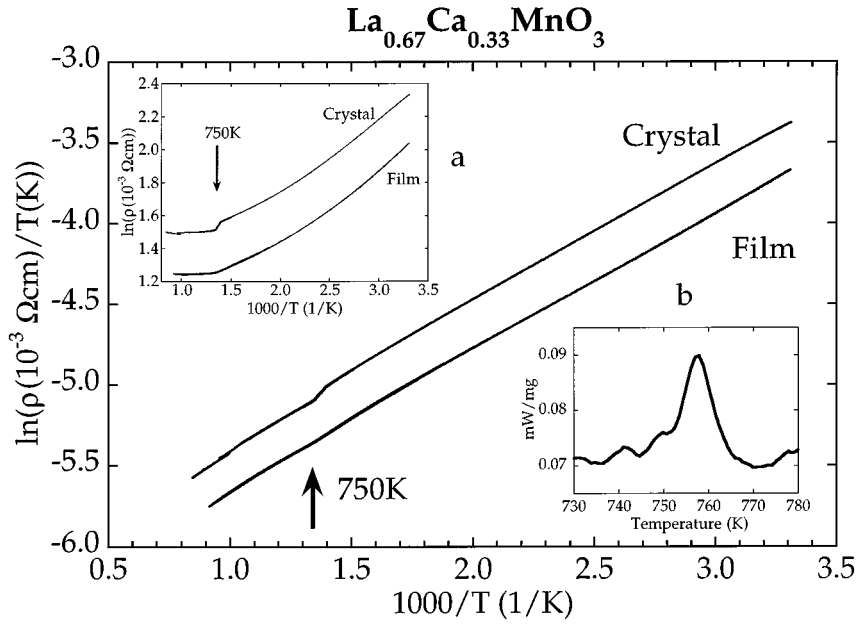

FIG. 9. High temperature resistivity (warming and cooling) of $La_{0.67}Ca_{0.33}MnO_3$ film (LCM17) and crystal in zero field. Inset (a), same data with different abscissa to compare small polaron and semiconductor models. Inset (b), differential scanning calorimetry trace of polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ showing the heat of the high temperature structural transition.

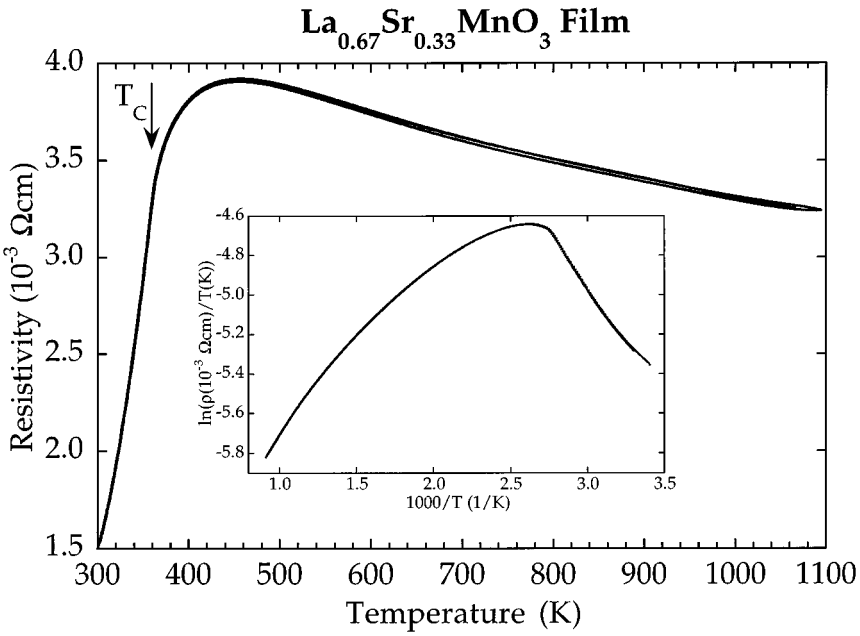

FIG. 10. High temperature resistivity (warming and cooling) of $La_{0.67}Sr_{0.33}MnO_3$ film (LSM1) in zero field. Inset, same data displayed as in Fig. 7.

stantial saturation moment (i.e., $p_{sat}/p_{cw}>0.5$) like the manganites. In the simplest model, a T^2 dependence is due to single (k-space) particle spin-flip excitations, while a $T^{3/2}$ law is expected for collective excitations (spin waves). A predominantly $T^{3/2}$ law has also been seen in thin film $SrRuO_3$.[58]

The temperature independent term in the resistivity can be ascribed to scattering processes such as impurity, defect, grain boundary, and domain wall scattering. From this value, one can make a rough estimate of the (0 K) mean free path of 26 Å.[40] The temperature independent term in the polycrystalline samples is somewhat larger than that observed in films or crystals (Fig. 5, Ref. 31). This indicates a significant grain boundary resistance and/or a significantly restricted conduction path in the polycrystalline samples. The temperature independent terms for the various $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ films and crystals (Table I) concur with recent measurements on other well annealed $La_{0.67}A_{0.33}MnO_3$ (Refs. 59 and 60) films and single crystals.[44] This limiting resistivity which is largely independent of A-site atoms may be due to the inherent disorder on the A site.

The T^2 term in the resistivity is also universal with respect to different samples and type of alkaline earth element (Table II). Furthermore, this term is independent (within 10%) of magnetic field. The significant magnetoresistance observed in the temperature range used to fit the conductivity data is absorbed primarily in the $T^{4.5}$ term. This universality with respect to growth, composition, and magnetic field leads us to conclude that the T^2 term in the resistivity represents intrinsic behavior of $La_{0.67}A_{0.33}MnO_3$ compounds.

Significant T^2 dependencies in resistivity[61] are often observed in metallic ferromagnets such as Fe, Co, and Ni where

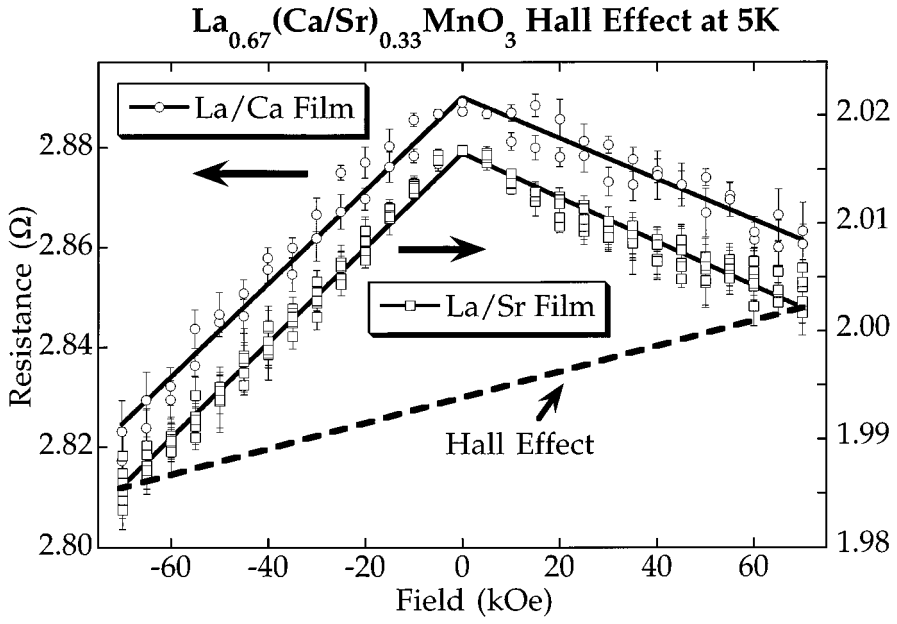

FIG. 11. Resistance as a function of field $La_{0.67}(Ca/Sr)_{0.33}MnO_3$ films (LSM1 and LCM19) in the Hall effect configuration at 5 K. The Hall effect is calculated from the slope of the line indicated (see text).

the coefficient[62] is 10^{-11} Ω cm/K^2. The magnitude of R_2 is expected[63,64] to scale with $1/M_0$, which explains the larger 5×10^{-8} Ω cm/K^2 value for R_2 found in the weak itinerant electron ferromagnets Sc_3In and $ZrZn_2$. The term in $La_{0.67}A_{0.33}MnO_3$ (Table II) is about 1000 times larger than that in Fe, Co, and Ni, which have comparable M_0's. Furthermore, the value of R_2 is expected to decrease in a magnetic field (proportional to $H^{-1/3}$) due to the suppression of spin fluctuations; however, the field dependence of R_2 in the manganites is too small for us to detect. Thus the theory of spin fluctuations does not completely explain the observed T^2 dependence of the resistivity.

General electron-electron scattering mechanisms within the Fermi liquid model give a T^2 dependence of the resistivity which is not necessarily field dependent. A value of R_2 as large as that seen in this work has been found in the nonmagnetic semimetal TiS_2.[65]

Recently other authors have analyzed the resistivity data for $R_{0.67}A_{0.33}MnO_3$ compounds using models different than the one presented above. The resistivity of polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ has been fit to $R_0+R_CT^C$,[31] while a polynomial fit such as the one used in this work will also fit their data. We find the $R_0+R_2T^2+R_{4.5}T^{4.5}$ fit, which has the same number of free parameters, preferable since there seems to be some universality in R_2. The low temperature zero field resistivity of $La_{0.67}Ba_{0.33}MnO_3$ films[60] has been fit to $R_0+R_1T+R_2T^2$, where $R_1<0$. As previously stated, we find R_1 insignificant even though a small correction is necessary to explain the almost constant resistivity at the lowest temperatures. A dominant T^2 term has been also recently found in the resistivity of single crystals.[66]

A quite interesting correlation[48,59,67] has been found between the magnetization and the resistivity, namely $\rho=R_e\exp[-M(t,h)/M_r]$, where R_e and M_r are fitting parameters. This is clearly preferable to a polynomial fit in the critical region near T_C. If, at low temperatures, $M=M_0(1-M_2T^2)$ where M_2 is largely independent of field, then this expression predicts the resistivity will vary as $R_2T^2+R_4T^4$. Thus a three parameter fit to $\rho=R_e\exp[-M(t,h)/M_r]$ is essentially equivalent to $R_0+R_2T^2+R_4T^4$ and therefore fits our data very well. However, this equivalency breaks down when one considers the field dependency: since both R_e and M_r are independent of field, the field dependence of ρ comes from the field dependence of M_2 which would affect R_2 and R_4 equally. In summary, the exponential fit combined with a T^2 dependence of the magnetization uses four free parameters: R_0, R_e, M_r, and M_2(7 T) which does not fit the low temperature data as well as the four free parameters R_0, R_2, $R_{4.5}$(0 T), $R_{4.5}$(7 T) used in this work.

In the regime above T_C the resistivity of $La_{0.67}Ca_{0.33}MnO_3$ closely follows the law predicted by small polaron hopping, $\ln(\rho/T)=\ln(R_h)+E_a/k_bT$, as opposed to that predicted for a semiconductor, $\ln(\rho)\propto1/T$ (Fig. 9). Therefore we conclude that the temperature dependence of the resistivity is due to the temperature dependence of the mobility while the carrier concentration remains constant. In the above equations E_a is the hopping energy, $R_h\approx k_b/[e^2a^2p(1-x)\nu]$, where k_b is Boltzman's constant, e is the charge of the hole, a is the distance between hopping sites, p is the carrier density, x is the doping fraction (1/3 in this case), and ν is the optical phonon or attempt frequency. A least squares fit of the high temperature data gives a hopping activation energy of 865 K and attempt frequency $\nu=6\times10^{13}$ s.

At 750 K, we observe in the resistivity a nearly discontinuous jump as well as a significant change in slope. The jump is much more noticeable in the crystals indicating a structural transition which is suppressed to some extent by the epitaxy in the thin films. This transition has been confirmed by differential scanning calorimetry (Fig. 9). An orthorhombic to rhombohedral transition is seen in at low temperatures in $La_{0.83}Sr_{0.17}MnO_3$.[68]

A change in slope is only noticeable in the $\ln(\rho)$ vs $1/T$ plot but not in the $\ln(\rho/T)$ vs $1/T$ plot. This indicates that the change in $d\rho/dT$ can be interpreted within the small polaron hopping conductivity model.[69] Below 750 K thermally activated hopping of the charge carriers dominates the conductivity, while above 750 K scattering of these carriers begins to dominate.

The presence of small polarons implies the existence of local lattice distortions which localize the charge carriers. A Jahn-Teller distortion about the Mn^{3+} ion is expected from its d^4 configuration in an octahedral environment. It has been postulated that such a distortion is necessary to explain the magnetoresistivity of these compounds.[10,11]

Above T_C the resistivity of $La_{0.67}Sr_{0.33}MnO_3$ may be explained by a crossover between two types of polaron conduction.[38] Just above T_C the polarons are heavy free carriers scattered by phonons, which gives a positive $d\rho/dT$. Quantitatively, this is expected to add a term to the conductivity proportional to $\exp(-T/\Theta_D)/T$.[69] At T_{MI}, which should be about half the Debye temperature (Θ_D), the phonon scattering becomes so strong that the mean free path is about one lattice spacing, and therefore localizes the carriers. Above T_{MI} the polarons conduct via thermally activated hopping, which has a negative $d\rho/dT$. Although this qualitatively explains the data, the quantitative predication of the temperature dependence does not fit the data very well.

If one assumes that the resistivity behaves as $T\exp(E_a/k_bT)$ above T_{MI} and at least R_2T^2 in an infinite field below T_C, then the maximum magnetoresistance $[\Delta R/R(H)$ at $T=T_{MR}=T_{MI}]$ follows $\exp(E_a/k_bT_{MI})/(T_{MI})$. This predicts ''colossal'' magnetoresistance only at low temperatures, as a consequence of the depressed T_{MI}. Such a strong dependence of the magnetoresistance on a film's particular T_{MI} has been documented[70] from the various values reported in the literature.

Hole conduction observed in our Hall measurements at 5 K complements the concurring Seebeck measurements above room temperature.[71] Since $LaMnO_3$ is a high spin d^4 insulator, the e_g orbitals must be split, possibly by the Jahn-Teller effect. Thus doping with an alkaline earth element on the La site, should put mobile holes in the lower e_g state. The magnitude of the carrier concentration calculated from the Hall effect is somewhat too large compared with the above model and therefore such a simple interpretation is clearly inadequate.

V. CONCLUSION

Well annealed MOCVD thin films show properties of bulk $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$. The limiting

low temperature resistivity of 0.2 mΩ cm, which gives a mean free path of roughly 20 Å, is independent of alkaline earth element and only slightly dependent on field for single crystal material (bulk or film). The manganites show a significant T^2 dependence of the resistivity which is also independent of alkaline earth element and magnetic field. The maximum in the magnetoresistance occurs at the Curie temperature, which is not necessarily where $d\rho/dT$ changes sign. A large magnetoresistance can occur well above room temperature, but the effect decreases significantly with temperature.

We identify three regions of magnetoresistance in these materials. The largest effect is likely due to the suppression of magnetic critical scattering near the Curie temperature. There is also a negative magnetoresistance associated with the net magnetization of polycrystalline samples but not seen in single crystal materials. Finally there is a small magnetoresistance linear in field even at low temperatures.

The compounds $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ are strong metallic ferromagnets. The saturation magnetization is found to decrease proportional to T^2 which indicates that spin-flip excitations dominate below $T_C/2$.

The high temperature resistivity of $La_{0.67}Ca_{0.33}MnO_3$ clearly follows the law predicted by small polaron hopping conductivity both in the thermally activated regime and at higher temperatures where scattering becomes important. There appears to be a structural transition at about 750 K.

The resistivity of $La_{0.67}Sr_{0.33}MnO_3$ above the Curie temperature shows a crossover from a metallic to a hopping regime at higher temperatures.

We conclude that the CMR effects in materials of the same compositions as those studied here but with much lower transition temperatures, are not intrinsic to the thermodynamically stable phase. Local inhomogeneities or noncrystallinity in not fully annealed films may suppress the magnetic and metal-insulator transitions. This presumably causes the observed superparamagnetic type magnetism and conduction via percolation.

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[1] H. van Santen and G. H. Jonker, Physica **16**, 599 (1950).
[2] H. van Santen and G. H. Jonker, Physica **16**, 337 (1950).
[3] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[4] H. Y. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).
[5] J. B. Goodenough and J. M. Longo, in *Crystallographic and Magnetic Properties of Perovskite and Perovskite-Related Compounds*, edited by K.-H. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 4a (Springer, Berlin, 1970).
[6] C. Zener, Phys. Rev. **82**, 403 (1951).
[7] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
[8] P.-G. deGennes, Phys. Rev. **118**, 141 (1960).
[9] S. Zhang (unpublished).
[10] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
[11] A. J. Millis, B. I. Shraiman, and R. Mueller (unpublished).
[12] T. Kobayashi, H. Takizawa, T. Endo, T. Sato, and M. Shimada, J. Solid State Chem. **92**, 116 (1991).
[13] H. Taguchi, M. Nagao, and M. Shimada, J. Solid State Chem. **97**, 476 (1992).
[14] J. A. M. van Roosmalen, J. P. P. Huijsmans, and L. Plomp, Solid State Ion. **66**, 279 (1993).
[15] A. Hammouche, E. J. L. Schouler, and M. Henault, Solid State Ion. **28–30**, 1205 (1988).
[16] H. L. Ju, C. Kwon, Q. Li, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2108 (1994).
[17] J. Cho, M. Gomi, and M. Abe, Jpn. J. Appl. Phys. **29**, 1686 (1990).
[18] K. C. Chanara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).
[19] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[20] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[21] G. C. Xiong, Q. Li, H. L. Ju, S. N. Mao, L. Senapati, X. X. Xi, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **66**, 1427 (1995).
[22] J. Z. Sun, L. Krusin-Elbaum, S. S. P. Parkin, and G. Xiao, Appl. Phys. Lett. **67**, 2726 (1995).
[23] S. Jin, M. McCormack, T. H. Tiefel, and R. Ramesh, J. Appl. Phys. **76**, 6929 (1994).
[24] S. Kawamata, N. Kobayashi, M. Ikebe, and Y. Muto, Physica B **148**, 130 (1987).
[25] G. C. Xiong, Q. Li, H. L. Ju, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **66**, 1689 (1995).
[26] J. H. Kuo, H. U. Anderson, and D. M. Sparlin, J. Solid State Chem. **83**, 52 (1989).
[27] R. S. Feigelson, D. Gazit, D. K. Fork, and T. H. Geballe, Science **240**, 1642 (1988).
[28] C. A. Burrus and L. A. Coldren, Appl. Phys. Lett. **31**, 383 (1977).
[29] R. Hiskes, S. A. DiCarolis, J. Fouquet, Z. Lu, R. S. Feigelson, R. K. Route, F. Leplingard, and C. M. Foster, in *Metal-Organic Chemical Vapor Deposition of Electronic Ceramics*, edited by S. B. Desu, D. B. Beach, B. W. Wessels, and S. Gokoglu, MRS Symposia Proceedings No. 335 (Materials Research Society, Pittsburgh, 1994), p. 299.
[30] L. J. van der Pauw, Philips Tech. Rev. **20**, 220 (1958).
[31] P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[32] I. O. Troyanchuk, JETP **75**, 132 (1992).
[33] T. M. Perekalina, T. A. Sivokon', S. A. Cherezyan, and I. É. Lipin'ski, Sov. Phys. Solid State **31**, 1524 (1989).
[34] H. L. Ju, J. Gopalakrishnan, J. L. Peng, G. C. X. Qi. Li, T. Venkatesan, and R. L. Greene, Phys. Rev. B **51**, 6143 (1995).
[35] R. Mahendiran, A. K. Raychaudhuri, A. Chainani, D. D. Sarma, and S. B. Roy, Appl. Phys. Lett. **66**, 233 (1995).

[36] M. Domínguez, S. M. Bhagat, S. E. Lofland, J. S. Ramachandran, G. C. Xiong, H. L. Ju, R. L. Greene, and T. Venkatesan, Europhys. Lett. **32**, 349 (1995).
[37] K. Kubo and N. Ohata, J. Phys. Soc. Jpn. **33**, 21 (1972).
[38] N. Mott, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1971).
[39] J. M. D. Coey, M. Viret, and L. Ranno, Phys. Rev. Lett. **75**, 3910 (1995).
[40] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).
[41] R. von Helmolt, J. Wecker, K. Samwer, and K. Bärner, J. Magn. Magn. Mater. **151**, 411 (1995).
[42] S. Jin, H. M. O'Bryan, T. H. Tiefel, M. McCormack, and W. W. Rhodes, Appl. Phys. Lett. **66**, 382 (1995).
[43] M. McCormack, S. Jin, T. H. Tiefel, R. M. Fleming, J. M. Philips, and R. Ramesh, J. Appl. Phys. **64**, 3045 (1994).
[44] J. Z. Liu, I. C. Chang, S. Irons, P. Klavins, R. N. Shelton, K. Song, and S. R. Wasserman, Appl. Phys. Lett. **66**, 3218 (1995).
[45] C. W. Searle and S. T. Wang, Can. J. Phys. **47**, 2703 (1969).
[46] C. W. Searle and S. T. Wang, Can. J. Phys. **48**, 2023 (1970).
[47] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, Physica B **155**, 362 (1989).
[48] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and N. Furukawa, J. Phys. Soc. Jpn. **63**, 3931 (1994).
[49] M. E. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).
[50] S. C. Gausepohl, M. Lee, K. Char, and C. B. Eom, Phys. Rev. B **52**, 3459 (1995).
[51] P. G. deGennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).
[52] C. Haas, Phys. Rev. **168**, 531 (1968).
[53] S. von Molnár and S. Methfessel, J. Appl. Phys. **38**, 959 (1967).
[54] S. von Molnár, I. Terry, T. Penney, and P. Becla, Physica B **197**, 151 (1994).
[55] M. R. Oliver, J. O. Dimmock, A. L. McWhorter, and T. B. Reed, Phys. Rev. B **5**, 1078 (1972).
[56] G. G. Lonzarich and L. Taillefer, J. Phys. C **18**, 4339 (1985).
[57] G. J. Snyder, K. A. Moler, A. Kapitulnik, M. R. Beasley, and T. H. Geballe (unpublished).
[58] L. Klein, J. S. Dodge, T. H. Geballe, A. Kapitulnik, A. F. Marshall, L. Antognazza, and K. Char, Appl. Phys. Lett. **66**, 2427 (1995).
[59] M. F. Hundley, M. Hawley, R. H. Heffner, Q. X. Jia, J. J. Neumeier, J. Tesmer, J. D. Thompson, and X. D. Wu, Appl. Phys. Lett. **67**, 860 (1995).
[60] S. E. Lofland, S. M. Bhagat, H. L. Ju, G. C. Xiong, T. Venkatesan, and R. L. Greene, Phys. Rev. B **52**, 15 058 (1995).
[61] I. Mannari, Prog. Theor. Phys. **22**, 335 (1959).
[62] I. A. Campell and A. Fert, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, New York, 1982), Vol. 3, Chap. 9.
[63] K. Udea and T. Moriya, J. Phys. Soc. Jpn. **39**, 605 (1975).
[64] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
[65] A. H. Thompson, Phys. Rev. Lett. **35**, 1786 (1975).
[66] A. Urushibara, Y. Moritomo, T. Arima, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14 103 (1995).
[67] Y. Tokura, A. Urushibara, Y. Moritomo, A. Asamitsu, Y. Tomioka, T. Arima, and G. Kido, J. Mater. Sci. Eng. B **31**, 187 (1995).
[68] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature **373**, 407 (1995).
[69] J. B. Goodenough, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1971), Vol. 5, Chap. 4, pp. 145–400.
[70] M. F. Hundley, J. J. Neumeier, R. H. Heffner, Q. X. Jia, X. D. Wu, and J. D. Thompson, J. Appl. Phys. (to be published).
[71] R. Hildrum, S. Aasland, and Ø. Johannesen, Solid State Ion. **66**, 207 (1993).