Magnetic Inhomogeneity and Magnetotransport in Electron-Doped Ca$_{1-x}$La$_x$MnO$_3$  
($0 \leq x \leq 0.10$)

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The dc magnetization ($M$) and electrical resistivity ($\rho$) as functions of magnetic field and temperature are reported for a series of lightly electron doped Ca$_{1-x}$La$_x$MnO$_3$ ($0 \leq x \leq 0.10$) specimens for which magnetization [Phys. Rev. B 61, 14319 (2000)] and scattering studies [Phys. Rev. B 68, 134440 (2003)] indicate an inhomogeneous magnetic ground state composed of ferromagnetic (FM) droplets embedded in a G-type antiferromagnetic matrix. A change in the magnetic behavior near $x = 0.02$ has been suggested to be the signature of a crossover to a long-ranged spin-canted phase. The data reported here provide further detail about this crossover in the magnetization, and additional insight into the origin of this phenomenon through its manifestation in the magnetotransport.

In the paramagnetic phase ($T \geq 125$ K) we find a magnetoresistance $\Delta \rho/\rho = -C(M/M_S)^2$ ($M_S$ is the low-$T$ saturation magnetization), as observed in many manganites in the ferromagnetic (FM), colossal magnetoresistance (CMR) region of the phase diagram, but with a value of $C$ that is two orders of magnitude smaller than observed for CMR materials. The doping behavior $C(x)$ follows that of $M_S(x)$, indicating that electronic inhomogeneity associated with FM fluctuations occurs well above the magnetic ordering transition.

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I. INTRODUCTION

Inhomogeneous magnetic ground states, consisting of ferromagnetic (FM) or spin-canted clusters embedded within an antiferromagnetic (AF) background, characterize both the lightly hole-doped$^{12}$(Mn$^{4+}$-rich) and lightly electron-doped$^{2,4,5,6,7,8,9,10,11,12,13,14,15}$ (Mn$^{4+}$-rich) perovskite manganites. There is growing consensus that such inhomogeneity is intrinsic$^{16}$ an example of phase separation induced by a competition between double-exchange (DE) and superexchange (SE) interactions between magnetic ions.

The anomalous magnetic behavior of the electron-doped compounds is reflected in the appearance of a small FM magnetization that turns on below the antiferromagnetic Néel temperature ($T_N$), saturates in an applied magnetic field of $H \geq 1 - 2$ T, and has a low-$T$ value ($M_S$) that exhibits a change in slope as $x$ increases$^{6}$ occurring near $x = 0.02$ for Ca$_{1-x}$La$_x$MnO$_3$ (Fig. 1). The origin of this slope change and its manifestation in magnetotransport is the focus of the present investigation.

A competition between DE and SE underlies the magnetic phase behavior in electron doped manganites. Recent neutron scattering studies$^{15}$ of lightly doped Ca$_{1-x}$La$_x$MnO$_3$ compounds evidence a novel ground state wherein electron doping introduces FM polarons of nanometric size that increase in density (but not size) with increasing $x$. For $x \geq 0.06$ these studies indicate the development of a long-range spin-canted state. It was postulated that the crossover near $x = 0.02$ reflects the large-scale aggregation of intermediate-sized spin-canted regions that coexist with isolated FM droplets of smaller size. Whereas magnetization measurements effectively sum over all the magnetic species present, we anticipate that the magnetotransport will be more sensitive to the hypothesized larger-scale spin-canted regions.

Here we examine measurements of magnetization and magnetoresistance (MR) of Ca$_{1-x}$La$_x$MnO$_3$ ($0 \leq x \leq 0.10$) in the range $1.5K \leq T \leq 250$ K and fields $H \leq 9$ T. The low-$T$ magnetization ($M$) curves, measured to higher fields than previously reported$^6$ reveal a doping dependent susceptibility that can be deconvolved into field-independent AF and field-dependent FM components, the latter presumably reflecting the growth of FM and/or spin-canted domains. The magnetotransport exhibits a

![Fig. 1: T = 5K saturation magnetization vs x from Ref. 6.](image-url)
crossover in behavior near \( x = 0.02 \) in both the magnetically ordered and PM phases. We observe that \( \Delta \rho/\rho = C(M/M_S)^2 \) describes the PM phase MR well, but with \( C \) two orders of magnitude smaller than found for CMR compounds due to the small volume fraction of DE bonds in the present materials. Particularly interesting is the doping behavior of \( C \) which follows that of the low-\( T \) \( M_S \), indicating that paramagnetic phase FM fluctuations have the same inhomogeneous character as the magnetic ground state.

II. EXPERIMENT

\( \text{Ca}_{1-x}\text{La}_x\text{MnO}_3 \) polycrystals were prepared by standard solid-state reaction; the preparation methods along with magnetization and resistivity measurements are reported elsewhere.\(^6\) Iodometric titration indicated the oxygen content of all specimens fell within the range \( 3.00 \pm 0.01 \). 6-probe Hall-bar specimens of approximate dimensions \( 3 \times 1 \times 0.15 \text{ mm}^3 \) were prepared with silver paint contacts for dc Hall and magnetoresistivity (MR) measurements in a 9T magnet. The magnetic field was applied perpendicular to the plane of the plate-like specimens in which the current flowed. Both current and field reversal were employed in the Hall measurements; the MR was measured for both forward and reverse field orientations. The temperature was controlled with a Cernox sensor. Magnetization and zero-field resistivity for these compounds have been reported previously,\(^6\) as well as thermopower and Hall mobility in the paramagnetic phase.\(^6\) The latter measurements indicate an electron density near room temperature in good agreement with values of \( x \). The very high resistivity of the \( x = 0 \) compound restricted measurements of its magnetotransport to \( T \geq 75 \text{ K} \) and thus it is excluded from the subsequent presentation.

III. RESULTS AND ANALYSIS

A. Magnetically Ordered Phase \((T < T_N)\)

1. Magnetization

Figure 2(a) shows the \( T = 5 \text{ K} \) magnetization, \( M(H) \), for a series of specimens measured to higher field than that reported previously in Ref.\(^2\) and with a data density in magnetic field that allows for a careful examination of the differential susceptibility, \( dM/dH \), shown as a function applied field in Fig. 2(b). These curves show an interesting trend: above \( H \approx 2 \text{ T} \) (a saturation field for reorienting FM domains), \( dM/dH \) is nearly independent of field, increases approximately linearly with doping up to \( x = 0.02 \), and becomes strongly field dependent for \( x \geq 0.03 \). The intermediate compositions, \( x = 0.02, 0.03 \) exhibit \( dM/dH \) curves that appear transitional between these behaviors: field-independent for \( 2 \leq \mu_0 H \leq 4 \text{ T} \) and more strongly field dependent for \( H \geq 4 \text{ T} \). That a crossover in behavior occurs near \( x = 0.02 \) is more clearly seen in Fig. 3 where \( dM/dH(x) \) is plotted for several fixed values of magnetic field.

If contributions to the FM magnetization come from isolated regions (e.g. FM droplets or spin-canted clusters) embedded in an AF background, the doping-
dependent susceptibility should be a simple sum of terms weighted by their volume fractions,

\[ \chi = (1 - x)\chi_{AF} + x\chi_{FM} \]  

(1)

where \( \chi_{AF} \) represents the constant susceptibility of the AF background and \( \chi_{FM} \), in general field dependent, describes the growth in the isolated FM regions with applied field. This simple model describes the Hall number vs \( T \) for \( x = 0.005, 0.01 \) specimens. Curves are guides to the eye.

A negative MR, \( \Delta \rho/\rho \equiv [\rho(H) - \rho(0)]/\rho(0) \), is observed for all specimens, the magnitude of which increases with decreasing \( T \) (Fig. 4), particularly at \( T < T_N = 110 - 125 \) K. The field dependence of the MR at the lowest \( T \) also exhibits a crossover in behavior near \( x = 0.02 \). We choose to present the low-\( T \) magnetotransport as magnetoresistance (MC), \( \Delta \sigma/\sigma \equiv [\sigma(H) - \sigma(0)]/\sigma(0) \), since we find that it affords a more direct comparison to the behavior of the susceptibility and the occurrence of a saturating FM component. The \( T = 1.5 \) K MC is shown in Fig. 4 For \( x = 0.005, 0.01 \) [Fig. 4 (a)] the MC is well represented by a power law, \( \Delta \sigma/\sigma \propto H^m \) with \( m \approx 2 \) at low fields and \( m \approx 3 \) at the highest fields [inset, Fig. 4 (a)]. There is no evidence for a contribution that saturates like the FM component of magnetization (Fig. 2) for \( \mu_0 H \gtrsim 2 \) T, and thus the power-law behavior of the MC appears to be a characteristic of the lightly doped system. For \( x = 0.07, 0.10 \) the MC is larger at low field and smaller at high field [Fig. 4 (b)] in comparison with the lightly doped compounds, and a contribution that saturates for \( H \gtrsim 2 \) T is evident [inset, Fig. 4 (b)]. The MC’s for compositions \( x = 0.02, 0.03 \) appear to be transitional in form between those of low and high doping. The doping dependence of the MC at fixed fields (Fig. 5) reveals a maximum magnitude for \( x = 0.02 \) at the highest fields.
B. Paramagnetic Phase \((T > T_N)\)

The MR in the PM phase is quadratic in field as shown for \(T = 200\, \text{K}\) in Fig. 9. Note that the magnitude of the MR for \(x = 0.10\) is smaller than that for \(x = 0.07\), suggesting that the MR is a simple function of the saturation magnetization, \(M_S\) (Fig. 1). This motivates an analysis along the lines typical for CMR compositions.
where $\Delta \rho/\rho = -C[M(H,T)/M_s]^2$ is found to describe combined magnetization and MR data near the Curie temperature. Figure 10 (a) shows that this scaling provides a good description of the MR data at five temperatures in the PM phase. Particularly interesting is the observation that the doping variation of the slopes of these curves, $C(x)$, follows that of $M_s(x)$ remarkably well [Figure 10 (b)], and thus also exhibits a slope change near $x = 0.02 - 0.03$. We find that $C(x) \propto x/2$ for $x \leq 0.02$, and $C(x) \propto 3x$ for $0.02 \leq x \leq 0.07$ (dashed lines).

IV. DISCUSSION

The small angle neutron scattering (SANS) study by Granado et al. evidences the presence of FM droplets of diameter 10 Å that are decoupled from the G-type AF background. Yet these droplets could account for less than half of the measured dc saturation magnetization at $x = 0.02$. Indeed, the density of droplets is about 60 times smaller than the electron density (their minimum spacing at $x = 0.02$ is $\sim 40$ Å), implying that most electrons reside outside of the FM droplets. The development of a long-ranged spin-canted state, evidenced in neutron scattering by Ling et al. for $x \geq 0.06$, motivated these authors to postulate that the long-range spin-canted state emerges through a gradual coalescence, with increasing $x$, of intermediate-scale spin-canted clusters not identified in the SANS studies. Thus it is proposed that most doped electrons reside in these spin-canted clusters.

The changes in the doping and magnetic field dependencies of the susceptibility that occur near $x = 0.02$ (Fig. 3) are consistent with a either a growth of the spin-canted cluster size or the canting angle. The mean distance between dopants, $d = (4\pi n/3)^{-1/3}$ (where $n \approx x/V_{f.u.}$ is the carrier density) is $\sim 8.4$ Å at $x = 0.02$, about twice the Mn ion separation. This is just the expected point of overlap for symmetric, 7-site FM polarons (a central Mn$^{3+}$ ion spin aligned with those of its nearest neighbor Mn$^{4+}$), predicted to be the stable magnetic-polaron state for this system. But this appears to be a coincidence since, as noted previously, the low-doping regime ($x \approx 0.02$) has $dM_s/dx \approx 1\mu_B$/Mn ion doped electron (Fig. 4), much smaller than would be expected if each electron created an isolated 7-site FM polaron. The slope for $0.02 \leq x \leq 0.07$ is close to that expected for isolated 7-site FM polarons, but in this regime long-ranged spin canting emerges. Thus the correct picture is evidently more complicated.

The transport data give further insight into the issue of magnetic inhomogeneity. At the lowest $T$ the zero-field electrical conductivity for $x = 0.005$ is higher than that for $x = 0$ by five orders of magnitude. This fact, along with the large, positive MC argue against the coexistence, for $x \leq 0.02$, of the FM droplets with an unaltered G-type AF spin background; isolated droplets separated by $\sim 40$ Å or more cannot dramatically improve electron transfer relative to that of the background lattice. Intervening non-percolating, spin-canted regions between droplets appear to be the simplest modification capable of reconciling the magnetization, neutron, and trans-
port data. The particular spin structure remains to be determined, but a plausible symmetric candidate has a FM droplet surrounded by a spin-canted region. This arrangement might naturally account for liquid-like correlations in the distribution of the droplets observed in neutron scattering.

For impurity band conduction, $\rho_0$ and $\varepsilon$ represent the overlap of impurity-level wave functions and their average energy difference, respectively. The results of Fig. 5 indicate that in the low-$T$ ordered state both of these are substantially reduced in an applied field. Since $\Delta\sigma/\sigma = [\rho_0(0)/\rho_0(H)] \exp(\Delta\varepsilon/k_BT) - 1$, the factor $\rho_0(0)/\rho_0(H)$ clearly predominates. Thus increased overlap of localized states underlies most of the MC and this effect is maximal near $x = 0.02$.

Regarding the PM phase MR, the empirical expression $\Delta\rho/\rho = -C[M(H,T)/M_S]^2$ has been widely employed for the PM CRM manganites for $M/M_S < 0.3$. Originally, the more general expression, $\rho = \rho_0 \exp[1 - (M/M_S)^2]$, was proposed to describe Eu chalcogenides $^{23}$ with an activation energy reduced in proportion to $M^2$. Models based on $\text{D}_{\text{P}}$ $^{25,26}$ and those invoking magnetization-dependent variable range hopping barriers $^{27,28,29}$ have been proposed. For metallic ferromagnets and magnetic semiconductors this empirical correlation between MR and magnetization emerges in generic models of magnetic scattering due to FM fluctuations $^{30}$. As noted above and in Ref. 17 the PM phases of the present compounds are best described as heavily-doped semiconductors with nearly constant carrier densities and temperature-dependent mobilities. Thus a magnetization-dependent mobility would appear to be a more suitable description of the present system, with FM fluctuations in the PM phase tending to reduce $\rho$ by providing DE pathways. Regardless of whether a hopping barrier or scattering picture is more appropriate, it is interesting to examine the magnitude and doping dependence of the coefficient $C$ for the electron-doped compounds in comparison to the CMR manganites for which much data is available.

The magnitude of $C$ is quite small (CMR compounds have $C \sim 1 - 7$) $^{46,47}$, This is to be expected given that for doping $x$, the fraction of Mn$^{4+}$O$^2-\text{Mn}^{4+}$ bonds for which FM DE can operate is only $2x$, and thus Mn$^{4+}$O$^2-\text{Mn}^{4+}$ SE interactions dominate the magnetic fluctuations. Assuming that only the fluctuation contribution to the conduction is field dependent, we have $\Delta\rho/\rho \approx 2x(\Delta\rho MF/\rho MF)$, where $\Delta\rho MF/\rho MF$ is the hypothetical MR that would occur in a uniform system where all bonds are DE active. Thus the value $C \approx 0.13$ found at $x = 0.07$ is roughly equivalent to $C \sim 0.13/2x \approx 1$ for a uniform system, comparable to values for pure DE systems.

The finding $C(x) \propto M^3_S(x)$ (Fig. 11) $^{30}$ provides compelling evidence that the PM-phase MR is associated with FM fluctuations. Furthermore, since the crossover behavior near $x = 0.02 - 0.03$ is also evident in $C(x)$, we conclude that these fluctuations have the same inhomogeneous structure present in the ground state: fluctuating FM droplets and/or spin-canted clusters begin developing well above the ordering temperature. It is reasonable to view this as a natural consequence of the need to maintain local charge neutrality; doped electrons tend to spend more time near La dopants with decreasing temperature, and eventually become trapped in the vicinity of these donor sites at low $T$.

In summary, magnetization and magnetotransport in electron-doped Ca$_{1-x}$La$_x$MnO$_3$ ($0 \leq x \leq 0.10$) evidence a crossover in behavior near $x = 0.02$ in both magnetically-ordered and PM phases. These phenomena are attributed to an inhomogeneous magnetic structure of both the ground state magnetism and the FM fluctuations at $T > T_N$. The present data lend support to the scenario motivated by recent neutron scattering studies $^{48}$ that non-percolating, spin-canted clusters coexist with smaller-scale FM droplets in this system.

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