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Doping-induced transition from double exchange to charge order in $La_{1-x}Ca_xMnO_3$ near $x=0.50$

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We study a series of the perovskite manganite compounds $La_{1-x}Ca_xMnO_3$ closely spaced in doping near $x=0.50$ where the ground state undergoes a doping-dependent metal-insulator transition (MIT) from a metallic to a charge-ordered state. A significant difference is found between the value of x and the Mn^{+4} fraction which defines the metal-insulator phase boundary. In the immediate doping regime of the MIT, the resistivity data can be quantitatively described by a model based on the coexistence of two carrier types: nearly localized carriers in the charge-ordered state exhibiting variable-range hopping and a parasitic population of free carriers which is tunable by either magnetic field or stoichiometry. [S0163-1829(98)05234-5]

There has been much recent interest in the properties of perovskite manganites with the composition $R_{1-x}A_xMnO_3$, where R^{+3} is a rare earth ion such as La, Pr, or Nd, and A^{+2} is a divalent ion such as Ca, Ba, Sr, or Pb. These materials were first studied in the early 1950s,[1,2] but recent work has revealed an unexpectedly rich variety of behavior originating in the strong coupling between the electronic, magnetic, and structural degrees of freedom.[3–6] Associated with this close coupling, recent studies have shown that a metal-insulator transition (MIT) can be induced in these materials by changing temperature[3] or magnetic field,[7] or even by more exotic mechanisms such as incident x rays or visible light.[8]

Most of the recent research on these materials has focused on compounds with $x\sim0.3$ which display intrinsic magnetoresistance of such great magnitude that they have been dubbed ''colossal magnetoresistance'' or CMR materials.[9] The large magnetoresistance for $x\sim0.3$ coincides with a phase transition into a ferromagnetic conducting ground state. The physics of this transition has long been explained by double exchange,[10] a ferromagnetic exchange process in which the e_g electron is exchanged between Mn^{+3} and Mn^{+4} ions, and it has been recently demonstrated that the strong Jahn-Teller distortion associated with the Mn^{+3} ions also plays an important role.[11]

At larger values of x, the conducting ferromagnetic ground state becomes unstable to a charge ordered ground state which is associated with the same Jahn-Teller distortion.[4–6] In the charge-ordered state, the e_g electrons (and therefore the distortions) are localized in a periodic array on the crystalline lattice creating a spatial ordering of Mn^{+3} and Mn^{+4} ions,[6,12] and this localization suppresses double exchange so that the spins order antiferromagnetically due to superexchange between the Mn ions.[2,13]

In an intermediate doping regime, where the energy scales of double exchange and charge ordering are comparable, one obtains a MIT between the conducting and charge-ordered ground states. Compounds in this intermediate doping regime (typically near $x=0.50$) often display *both* ferromagnetic conducting and charge ordered states with first order transitions between them such that the electronic state can be tuned by thermal and magnetic history.[14] Recent measurements have shown the electronic and structural properties of compounds in the intermediate doping regime are correspondingly rather different from those in either the purely charge-ordered or ferromagnetic regimes.[5,14–17]

We have performed a detailed study of the doping dependent MIT in the CMR manganites in a series of $La_{1-x}Ca_xMnO_3$ samples closely spaced in doping with $x\sim0.50$ and with well-characterized percentages of Mn^{+4} (p_4). In the proximity of the MIT, we find the material properties are extraordinarily sensitive to changes in doping and that the differences between x and p_4 become critical in determining the state of the system. The low temperature electronic state appears to be well described by the presence of a small density of free carriers (which can be induced either stoichiometrically or by application of a magnetic field) superimposed on the charge order. Our data suggest that it is the increasing density of these carriers that leads to the ''melting'' of the charge lattice by an applied magnetic field.[14,15]

Samples of $La_{1-x}Ca_xMnO_3$ were prepared with compositions and Mn^{+4} concentrations of x $(p_4)=0.33$ (37.2), 0.4.2 (34.8), 0.48 (49), 0.48 (53.2), 0.49 (52.8), 0.50 (53.8), 0.51 (53.6), 0.52 (49.2), 0.52 (55.2), and 0.55 (58.2). Stoichiometric quantities of La_2O_3, $CaCO_3$, and MnO_2 were combined and calcined at 1000 °C. The powder was subse-

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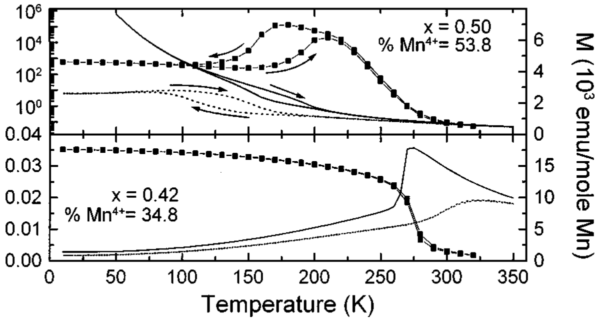

FIG. 1. The temperature dependent resistivity at $H=0$ T (solid line) and $H=6$ T (dashed line) and magnetization at $H=1$ T (solid square) for $x=0.42$ and $x=0.50$.

quently fired at 1250 °C and 1350 °C with intermediate grindings and then pressed into a pellet and fired at 1400 °C in flowing oxygen, followed by slow cooling to room temperature. The resulting dense black pellets were all single phase as adjudged by powder X-ray diffraction. We determined p_4 to $\pm 1\%$ Mn^{+4} for each sample by redox titration,[18] with the precision determined by running several (typically 5–10) separate runs on each sample. As measure of the accuracy of the method, a sample of $La_{0.79}Ca_{0.21}MnO_{3.155}$ ($\delta=0.155$ determined by thermogravimetric analysis[19]) was analyzed. The redox titration gave a value of $p_4=52.8\%$, equivalent to $\delta=0.159$. The differences between p_4 and x probably arise from small ($\lesssim 1\%$) oxygen off-stoichiometries.

In Fig. 1 we show representative resistivity (ρ) and magnetization (M) data taken on warming and cooling.[20] At $x=0.42$, we see behavior typical of a sample in the lower doping regime, a ferromagnetic transition with an accompanying drop in $\rho(T)$ and no hysteresis. At $x=0.50$ we observe behavior typical of the intermediate regime with an apparent transition upon cooling to a ferromagnetic state and then a lower temperature first-order transition to the charge-ordered and antiferromagnetic state [signified by a drop in $M(T)$ and a maximum in $-d\rho/dT$].[21] In the presence of a magnetic field, ρ is suppressed by orders of magnitude and *decreases* with temperature at low temperatures, behavior which will be discussed in detail below. For $x=0.55$, in the fully charge-ordered regime, $\rho(T)$ is activated down to the lowest temperatures even at $H=6$ T, and $M(T)$ is less than 10% of saturation magnetization at all temperatures. Even in the charge-ordered doping regime $M(T)$ shows a peak, but this is associated with the charge ordering transition and reflects the reduction in ferromagnetic double exchange accompanying the charge ordering.[5,6,13]

The importance of the difference between x and p_4 is illustrated by the data in Fig. 2 from two pairs of samples with $x=0.48$ and 0.52. The sample with $x=0.48$ and $p_4=53.2\%$ has $\rho(T,H)$ similar to that of samples with larger value of x. On the other hand, $\rho(T,H)$ for the $x=0.48$ sample with $p_4=49\%$ has a single maximum on cooling which is typical of a sample with a FM ground state. Perhaps more interesting, in this latter sample $\rho(T)$ displays strong hysteresis on warming with second maximum—indicating the presence of a first order charge ordering as in the samples with larger x.[22] The decreasing low temperature $\rho(T)$ and the low $\rho(T\rightarrow 0)$ suggest that conduction in this latter sample in the charge-ordered ground state is through the presence of free carriers in the charge lattice—a concept on which we will elaborate below. While the material properties vary with p_4 for a given x, they are not determined solely by p_4 but rather depend on the combination of x and p_4 in a given sample. This can be seen from $\rho(T,H)$ for the sample with $x=0.52$ and $p_4=49.2\%$, which is almost identical to $\rho(T,H)$ for the sample with $x=0.52$ and $p_4=55.2\%$ [although $M(T)$ of the former sample is considerably larger].

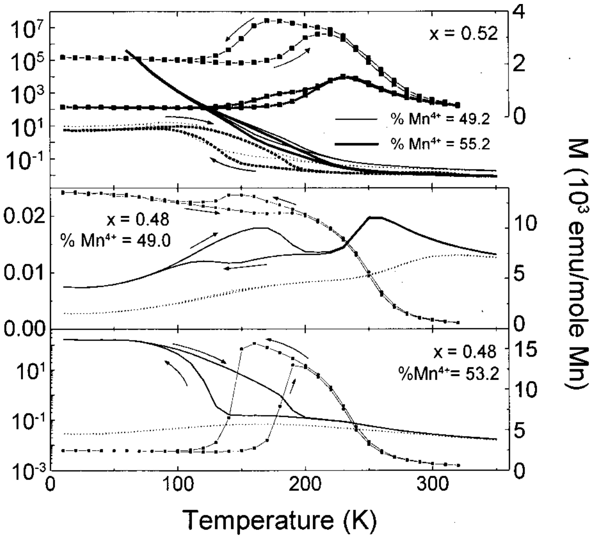

FIG. 2. The temperature dependent resistivity at $H=0$ T (solid line) and $H=6$ T (dotted line) and magnetization at $H=1$ T (solid square) of samples at $x=0.52$ and 0.48 with different Mn^{+4} contents.

The importance of the difference between x and p_4 is demonstrated again in Fig. 3 where we plot the low temperature magnetization and resistivity vs both x and p_4. As seen in the figure, the doping dependent MIT occurs at $x=0.49$ but at $p_4=53\%$—a significant difference since the transition

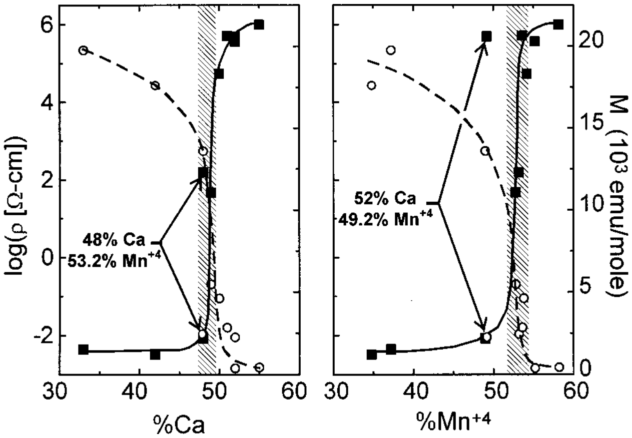

FIG. 3. The metal insulator transition as a function of %Ca (x) and %Mn^{+4} (p_4) as observed through $\rho(T=60\text{ K}, H=0)$ [solid squares] and $M(T=10\text{ K}, H=1\text{ T})$ [open circles]. The lines are guides to the eye, and the arrows indicate the samples which are inconsistent with the general trends as discussed in the text. The shaded regions give an estimated maximum range for the MIT based on the precision of our knowledge of p_4 and x and the slope of the data.

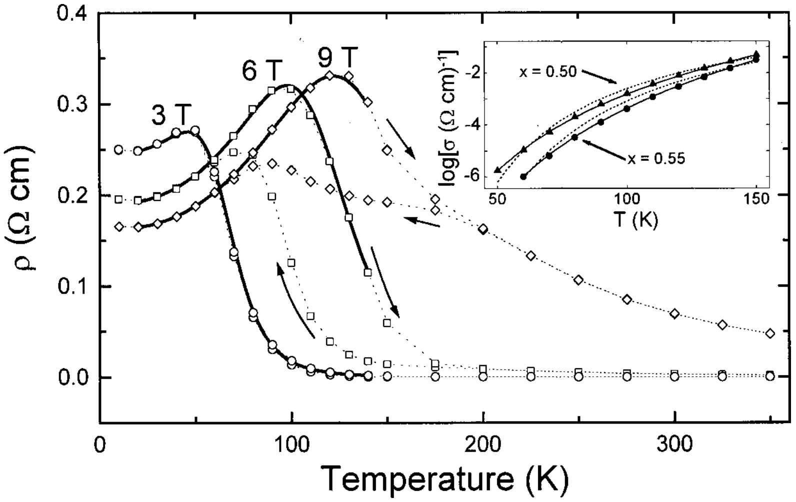

FIG. 4. Linear scale plot of $\rho(T)$ for $La_{0.50}Ca_{0.50}MnO_3$ (data at 3 T are divided by a factor of 10 000 and data at 6 T by a factor of 25). The bold lines are fits to the data as described in the text. Inset: Best fits to low temperature $\rho(T)$ at $H=0$ with a simple activated form ($\rho=C\ \exp[D/T]$, dashed line) and a variable range hopping form ($\rho=C\ \exp[-(D/T)^{1/4}]$, solid line) for $x=0.50$ and $x=0.55$.

width is $\sim 1\%$. This difference, as well as the presence of a sample in each case which does not follow the trend of the others, demonstrates that *both x and the difference between x and* p_4 are critical in determining the material properties in this doping regime, and that neither parameter alone is sufficient in characterizing the MIT. The extreme sensitivity to doping is perhaps implied by the strong first order nature of the MIT in this doping regime. The present results, however, demonstrate that p_4 can be critically important within the intermediate doping regime, even though it is typically not measured in studies of materials in this regime.[5,6,12,14,16,17]

At low temperatures we find $\rho(T)$ decreases drastically with increasing applied magnetic field as has been observed previously in compounds with $x \sim 0.50$.[14,15,17] This large magnetoresistance has been explained as the melting of the charge lattice into a double-exchange-based ferromagnetic conducting state. In addition to large magnetoresistance, we find that at temperatures well below the charge ordering transition $\rho(T)$ reaches a maximum and subsequently decreases with decreasing temperature as $T \rightarrow 0$ as is illustrated in Fig. 4 for the $x=0.50$ sample. As can been seen in the figure, the extent of the decrease in $\rho(T)$ and temperature range of this behavior both increase with applied field. The decreasing low temperature $\rho(T)$ is seen at all fields for samples with $x<0.50$ and in all of the samples when a sufficiently large magnetic field of gT is applied (except $x=0.55$). The decreasing low temperature $\rho(T)$ can also be observed in previously published data on both polycrystalline and high quality single crystal samples.[14,15,17]

We attempt to explain the large magnetoresistance and decreasing low temperature $\rho(T)$ through the presence of free carriers in the charge-ordered state whose population is enhanced either by the application of a magnetic field or by doping to $x<0.50$ (as in the case of the $x=0.48$ sample with $p_4=49\%$ shown in Fig. 2). Assuming that the total conductivity is due to parallel conduction through variable range hopping of bound polarons in the charge lattice[23] and a small population of free carriers (with scattering from defects as well as a combination of phonons, electrons, and spin fluctuations), we expect

$$1/\rho = 1/(A+BT^{2.5}) + C\ \exp[-(D/T)^{1/4}]$$

where the exponent of 2.5 is an empirical fit.[5] This form fits the data rather well through the entire range of compounds we studied, and typical fits are shown by the thick solid lines in Fig. 4. We chose the variable range hopping form for conduction within the charge-ordered state since, for $H=0$ where a wide temperature range is available for fitting, a simple activated form ($\rho=C\ \exp[D/T]$) cannot fit the data nearly as well as $\rho=C\ \exp[(D/T)^{1/4}]$ (see inset to Fig. 4). As expected, the fitting parameters C and D which characterize the variable range hopping both increase with increasing x through the MIT.[20]

In a simple Drude model, both A (associated with temperature-independent scattering from defects) and B (associated with temperature dependent scattering from other excitations) would be inversely proportional to the density of the free carriers (for either type of scattering $\rho \propto 1/n\tau$ where n is the carrier density and τ is the scattering time). As can be seen from Fig. 5, the quotient A/B is independent of field even though both A and B change by orders of magnitude. Since $A(H)$ should depend on magnetic field only through n,

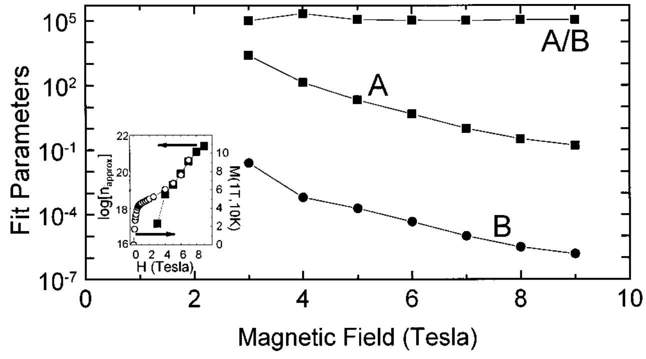

FIG. 5. The fit parameters A (in Ω cm) and B (in Ω cm/K^2) and their ratio A/B as a function of field. The inset shows the field dependence of both the field-cooled magnetization (in 10^3 emu/mole) for $x=0.50$ after field cooling to $T=10$ K and the approximate number density per molar volume of free carriers as discussed in the text.

the experimental finding that $B(H) \propto A(H)$ implies that B also depends on magnetic field only through the number of free carriers. Within this simple framework, our data thus indicate that the magnetoresistance is controlled by a field-induced increase of carrier density rather than a reduction in scattering.

We can use a fit to the $x=0.42$ sample (in which we expect ~ 0.4 free carriers per formula unit) to obtain an estimate of the field dependence of the approximate scattering time associated with B, and from that scattering time obtain an approximate number density $[n_{\mathrm{approx}}(H)]$ in the $x=0.50$ samples from $B(H)$. This is plotted in the inset to Fig. 5 along with $M(T=10\ \mathrm{K})$. While the magnetization reaches $\sim 35\%$ of full saturation, the number density of free carriers reaches only about 1% of its maximum value ($\sim 3\times 10^{23}$) implying that even at such high magnetization the charge lattice is largely intact.

The quality of our fits and the qualitative nature of the data (particularly those of the $x=0.48$ and $p_4=49\%$ sample) strongly suggest that charge order and free carriers can coexist in the doped perovskite manganites. Our results further suggest that underlying charge order may influence the material properties even in the ferromagnetic regime where double-exchange results in a metallic ferromagnetic state.[24] Indeed, the influence of charge order could perhaps explain the rather high $T\rightarrow 0$ resistivity which has been observed in even the best manganite samples.

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[20] Resistivity measurements were conducted by a four in-line ac bridge technique. Magnetization measurements were conducted on a Quantum Design SQUID magnetometer. Complete data sets with fits will be included in a future publication.

[21] The low temperature limiting magnetization in samples of $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ for $x \gtrsim 0.50$ is anomalously large for a nominally antiferromagnetic state [see Refs. 5, 15, 17, and G. Papavassiliou *et al.*, Phys. Rev. B **55**, 15 000 (1997)] suggesting that the spins are easily canted by a field in this doping regime, or perhaps coexistence of islands of ferromagnetic state in the charge-ordered state.

[22] The same hysteretic double peak behavior was observed in an $x=0.48$ sample studied in Ref. 5 [P. Schiffer (unpublished)].

[23] We expect that variable range hopping conduction in the charge lattice is by Jahn-Teller polarons as in the high temperature paramagnetic state. M. Jaime *et al.*, Phys. Rev. B **54**, 11 914 (1996); T. T. M. Palstra *et al.*, *ibid.* **56**, 5104 (1997).

[24] The potential importance of an underlying charge order has also been recently proposed based on features in the phase diagram of $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ [S.-W. Cheong *et al.* (unpublished)].