

Electroresistance and Electronic Phase Separation in Mixed-Valent Manganites

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The sensitivity of transport in colossal magnetoresistance (CMR) manganites to external electric and magnetic fields is examined using field effect configurations with $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO), $\text{Na}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$, and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (0.5-doped LCMO) channels, and ferroelectric $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) or dielectric (SrTiO_3) gates. A large electroresistance (ER) of $\sim 76\%$ at 4×10^5 V/cm is found in LCMO with PZT-ferroelectric gate, but the magnitude of the effect is much smaller (a few percent) in the other three channels. The ER and CMR effects are remarkably complimentary. The size and systematics of the effect strongly favor a percolative phase separation picture.

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Colossal magnetoresistance (CMR)—a huge decrease in resistivity in mixed-valent manganites by magnetic field—has triggered intense scientific activity in recent years; yet, the mechanism of the effect is still not fully understood [1–3]. One aspect of the phenomenon is a bulk metal-to-insulator transition tuned by changing spin correlations, but possibly involving other degrees of freedom also [4]. Recent studies, however, suggest that the largest magnetoresistance in these systems is associated with spatial inhomogeneity related to multiphase coexistence [5–15] which generically causes a sensitivity of physical properties to external perturbations. We examine the sensitivity to external electric and magnetic fields in the case of CMR manganites using ferroelectric- or dielectric-based field effect configurations with $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO, $x = 0.3$ and 0.5), $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (NSMO), and $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ (LBMO) channels. A large change in resistance ($\sim 76\%$) is observed at modest E -field ($\sim 4 \times 10^5$ V/cm) for LCMO with a $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) gate, but the effect is much smaller for other channels. The electroresistance (ER) and CMR effects are found to be complimentary in nature.

An early study using a dielectric gate revealed interesting ER phenomena [16], and this was followed by the demonstration of a large field effect using a ferroelectric gate [17,18]. However, the systematics were not studied nor was a mechanism determined. In these previous papers, the channel layer was the first layer grown on a substrate followed by the gate layer; this leads to lower quality films, perhaps because of substrate induced stress and “dead layers” in the interface region [19]. Current induced switching of resistive states in manganites has also been reported [20–23]. However, such schemes raise the possibility of local heating due to highly filamentary conduction.

In this paper we present results of a systematic study of ER effects using a new, inverted device configuration

(inset of Fig. 1), resulting in a new understanding of the phenomenon. A (100)-oriented single crystal of n -type SrTiO_3 (STO) doped with 1 at. % Nb is used as the substrate, and as the conducting gate. On this we grew a 150 nm gate layer of PZT or STO, and then a 50 nm manganite channel layer. The gate and channel layers were grown by pulsed laser deposition under O_2 pressure of 100 mTorr and 400 mTorr, respectively, as a substrate temperature of 650°C . The surface preparation procedure of Kawasaki *et al.* [24] was found to be crucial for obtaining high quality devices. Our new geometry is a significant improvement on previous designs [16–18]. Strain in the channel layer is minimized. Further, for the device

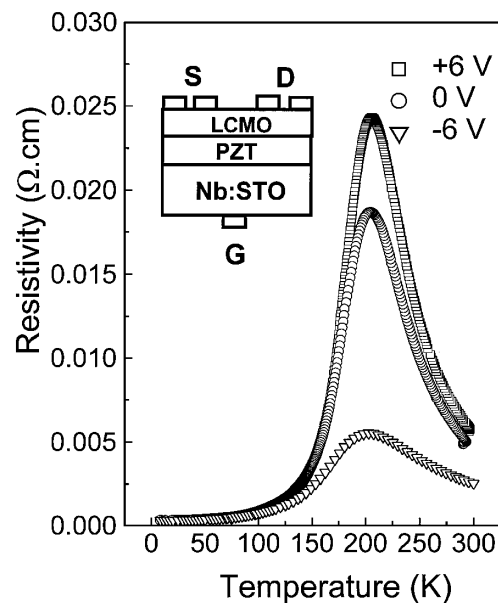


FIG. 1. Dependence of resistivity of the LCMO channel on temperature, for field biasing with a PZT gate over an applied gate voltage range from +6 to -6 V. Inset shows the device configuration.

with a PZT gate, there is no gate current at all, while, for the device with a STO gate, the gate current is negligible (<1 nA). Clearly, there is no concern for local heating.

Figure 1 shows the dependence of resistivity (ρ) of the LCMO channel with the PZT gate on temperature (T), for field biasing (V_{gate} from $+6$ to -6 V). The new features seen are as follows: First, the effect is much stronger ($ER_{\text{max}} = [R(E) - R(0)]/R(0) = 76\%$ for $E = 4 \times 10^5$ V/cm near T_p) than reported previously [16–18]. Second, the ER changes sign with the field direction. Third, the magnitude of ER is not symmetric *vis-a-vis* the field direction, implying channel asymmetry for hole vs electron-type carrier modulation. Finally, the gate field leaves the temperature T_p , at which resistivity peaks, almost unchanged. In the PZT device the polarization dependence on field is nonlinear, but Fig. 2 shows that the behavior is very similar in devices based on the dielectric material STO. The inset shows that the channel resistance increased and saturated for positive bias, but for negative bias a nonlinear decrease with no evidence for saturation was seen.

The results for NSMO, LBMO, and 0.5-doped LCMO channels obtained by using the new device geometry are shown in Figs. 3(a), 3(b), and 3(c), respectively. In NSMO, the sign of $-\Delta R/R$ is seen to be polarity independent. The magnitude of the effect is rather small; it peaks above T_p for both polarities, and drops with the decrease of T below T_p , as seen previously [16]. A new feature, not evident in previous work [16], is the polarity dependence of the magnitude (not sign) of the effect at higher T , where NSMO resistivity is much lower than its value near T_p . To summarize, the general similarity of the present and previous NSMO results indicates that we are measuring intrinsic properties, while the improved resolution, which allows the observation of new features

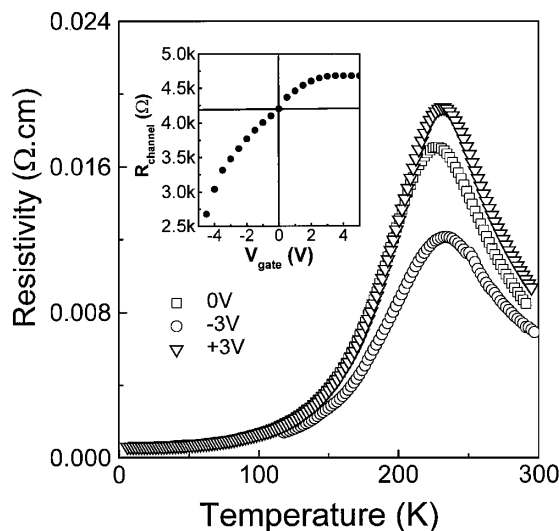


FIG. 2. Dependence of resistivity of the LCMO channel on temperature, for field biasing with an STO gate over an applied gate voltage range from $+3$ to -3 V. Inset shows the channel resistance dependence on gate voltage.

in the detailed behavior, testifies to our improved device geometry and sample preparation. We also examined the device in magnetic (H) field. Just above T_p , where a polarity independent effect was seen without the H -field,

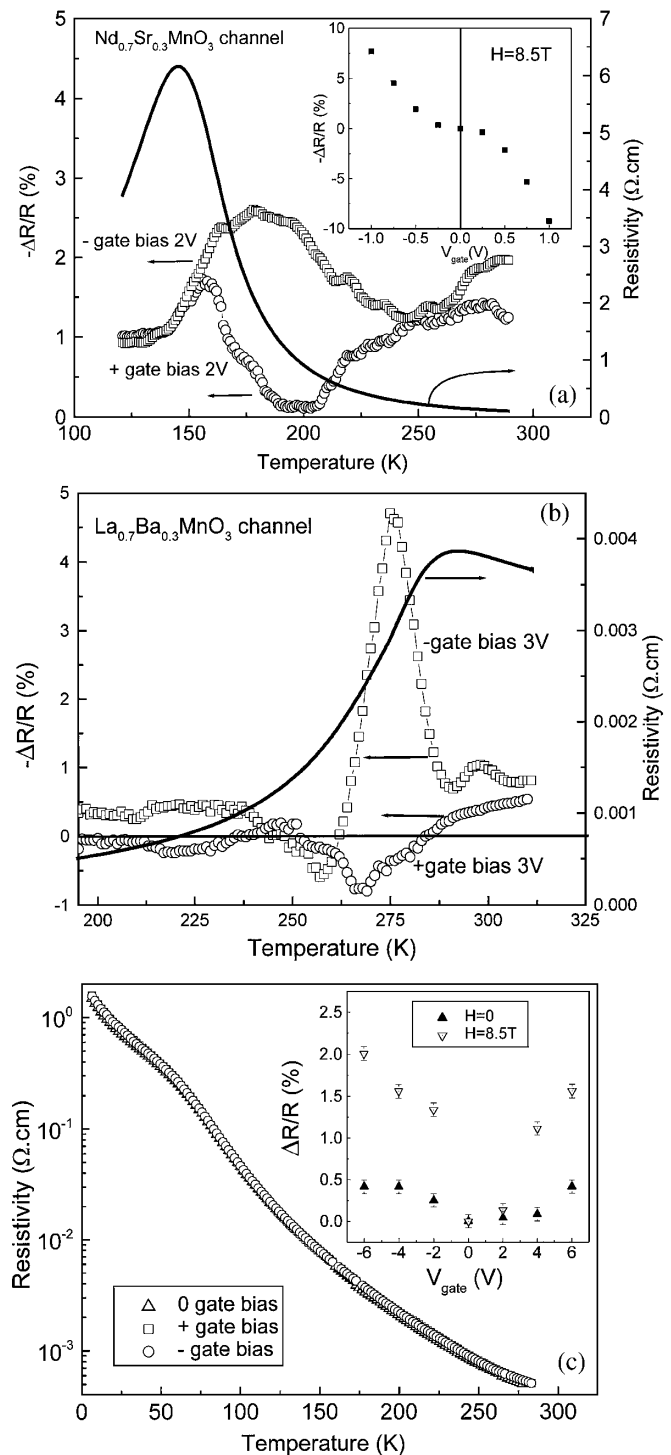


FIG. 3. Dependence of resistivity of (a) the NSMO channel, (b) the LBMO channel, and (c) the 0.5-doped LCMO channel, on temperature, for field biasing with an STO gate. The electroresistance represented by $-\Delta R/R$ (%) is also shown. The inset in (a) is the ER with $H = 8.5$ T. The inset in (c) compares ER for $H = 0$ and $H = 8.5$ T.

a growing polarity dependent fraction was seen with increasing H , reflecting the contribution of growing metallic regions in the channel. Above a field of a few tesla, the polarity dependent fraction was seen to dominate [inset of 3(a)], as expected. Figure 3(b) shows that for LBMO the behavior is similar to that for LCMO, but the magnitude of the effect is much lower. Figure 3(c) shows that the effect is negligibly small in the charge ordered insulator $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The inset in the figure (filled triangles) shows that, even for a high E -field (2×10^5 V/cm), the effect is $\leq 0.5\%$ and is polarity independent. Interestingly, when a field of 8.5 T is applied, the effect increases to $\sim 2\%$ without changing its polarity independence. It is important to state here that the ρ - T of this sample (not shown) exhibited insulating character even under the H -field, though ρ dropped by a factor of ~ 15 at 100 K at which the ER data shown in the inset of Fig. 3(c) were recorded.

Figure 4 compares the E - and H -field effects on transport in LCMO, showing ρ vs T for the unbiased and field-biased (4×10^5 V/cm) channel, with and without 6 T H -field. We observe that an E -field of 4×10^5 V/cm produces a change in ρ which is almost as large as that produced by an H -field of 6 T. Curves B and C in Fig. 4 show that, for equal conductivity values, the electroresistance [magnetoresistance (MR)] is lower (higher) for $T < T_p$ than that for $T > T_p$. Thus, the E - and H -fields have a complementary effect on transport. Comparison of curves B and D, or of C and D, shows that the application of an H -field of 6 T to the E -field-biased channel, or an E -field to the channel subjected to a 6 T H -field, produces an additional large drop in ρ . The H -field shifts the temperature at which ρ with ER peak. The insets show MR vs T in 6 T, for the unbiased and E -field-biased CMR channel, and ER vs T , for the channel with and without an H -field of 6 T. The difference seen in the ER case arises from the peak shift characteristic of CMR.

We now consider the interpretation of our results. If the carrier density in the channel was uniformly equal to the chemical density (0.7 electrons/Mn $\cong 10^{22}$ cm $^{-3}$), any applied electric field would be screened within one or two lattice constants of the interface, and could not affect bulk transport, even to the extent observed in NSMO or LBMO, much less as in LCMO. In our films, therefore, some process has opened a gap in the electronic spectrum, thereby reducing the effective carrier density by orders of magnitude and allowing the E -field to penetrate deeply into the film. Of course this gap is also evident in the rapid temperature dependence of ρ . The gap could be due to polaron formation, i.e., electron trapping by spatially incoherent lattice distortions, as proposed in [25] and [26], but in these models it is difficult to obtain the very rapid upturn of ρ between 300 and 200 K, and the predicted screening lengths are a few lattice constants [27]. We believe our data are more naturally interpreted as a consequence of *inhomogeneous* charge ordering (CO) in our films.

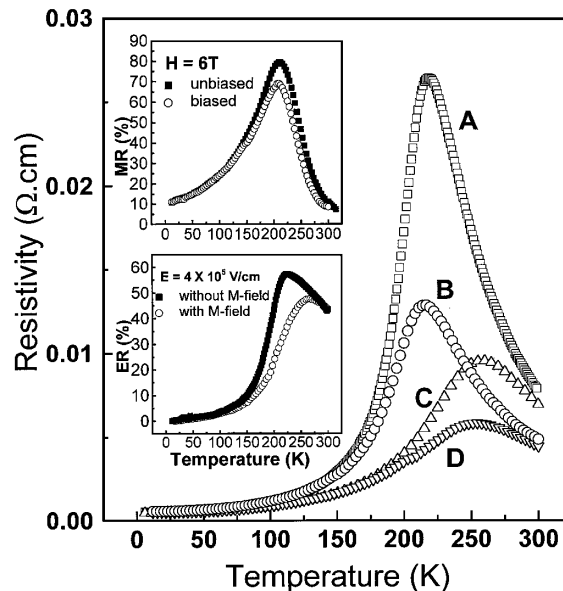


FIG. 4. Dependence of LCMO channel resistivity on temperature for the unbiased (A) and electric-field-biased [(B), 4×10^5 V/cm] channel, in the absence of magnetic field. The dependence (A) changes to (C), and (B) changes to (D) under a magnetic field of 6 T. The insets show MR vs T in 6 T for the unbiased and E -field-biased CMR channel, and ER vs T for the channel with and without a magnetic field of 6 T.

In an electronically inhomogeneous channel, partly metallic (M) and partly insulating (I), the E -field would change the relative volume fractions of the M and I regions by accumulation of charge between M and I phases, thereby causing the interface to move. The nature of accumulating charge, holes vs electrons, will depend on field polarity and thereby control the direction of interface movement. In our system, as T is lowered, “droplets” of ferromagnetic (FM) metal appear. Applying a negative gate voltage causes electrons to accumulate at I - M interfaces, which pushes the interfaces away from the electrodes, causing increased metallicity with a nonlinear V dependence. A positive voltage does the opposite, leading to a ρ which saturates at the intrinsic insulating value for the given T , which is not high. This picture also naturally explains the experimentally observed complementary character of the E - and H -field influence on the CMR channel. The H -field makes the intrinsic behavior of the I regions more metallic, while the E -field changes the connectivity of the M regions by modifying the volume fractions of the FM and CO components.

A large and growing body of evidence supports the idea that multiphase coexistence is important in manganites generally and in LCMO in particular [15]. Jamie *et al.* [12] showed that thermopower data on $x = 0.3$ LCMO implies a two-phase mixture near T_c , and Heffner *et al.* [13] found neutron scattering evidence for two relaxation times in similar samples and temperature regimes. Very recently Lynn and co-workers [14] presented direct neutron scattering evidence that in $x = 0.3$ LCMO the coexistence near T_c is between a conventional FM metal

and a phase with a very substantial degree of short range orbital order of the $(1/4, 1/4, 0)$ type observed as long range order in $x = 0.5$ samples. Note that the observability of this short range orbital order implies the existence in the sample of very strong short range charge ordering.

Multiphase coexistence apparently requires that charge/orbital order (long range or at least large amplitude) exists in the material, which depends on chemical composition and microstructure. If Ca is replaced by Sr the high temperature phase becomes much more metallic and no evidence of multiphase coexistence is reported, while, as La is replaced by Pr, the evidence of multiphase behavior over a wide range becomes much stronger [8]. Further, strain in films, due to the substrate [28,29], microstructure, or damage [30], has been shown to induce insulating behavior.

That the ER in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is much larger than in NSMO, LBMO, or the 0.5-doped LCMO has a natural interpretation in the phase coexistence model. Essentially all of the 0.5-doped LCMO is in a strongly insulating state; essentially all of the NSMO is in a weakly insulating state; hence there is no ER. The lower resistivity and the higher T_c of LBMO show that it is mostly metallic. Only in the LCMO film are the two phases sufficiently closely balanced to give a truly large ER. Applying a magnetic field to the NSMO and LCMO (0.5) samples increases the ER somewhat.

In conclusion, we have observed a large ER in a LCMO channel subjected to E -field through a PZT gate, exhibiting peculiar characteristics in the presence and absence of H -field. The magnitudes of the effects observed in NSMO, LBMO, and 0.5-doped LCMO channels are much smaller. These observations find a consistent explanation in the two-phase picture of mixed-valent manganites. Search for ER effects across the phase diagram and inclusion of electric field into the recent computational studies of disordered manganites, which focus on coexisting metallic and insulating domains [31], would be very interesting.

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