Unusual Electric Field Effects in $Nd_{0.7}Sr_{0.3}MnO_3$

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Enhanced electric field (E) induced modulation of the resistance of epitaxial thin films of $Nd_{0.7}Sr_{0.3}MnO_3$ has been observed. The results show several remarkable features: first, field-direction-independent decrease of the resistance above the temperature at which the peak in resistivity occurs (T_p); second, proportionality of the modulation to E^2; third, a reduction in the magnitude and field-direction-independent reversal of the sign of $\Delta R/R$ just below T_p; and fourth, a prompt time response at high temperatures and a slower response near T_p. These results are consistent with a model of a polarization-induced lattice distortion coupling with both spin and charge transport. [S0031-9007(96)00809-5]

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The observation of a colossal magnetoresistance (CMR) effect in the $R_{1-x}M_x MnO_3$ ($R =$ La, Nd, etc., $M =$ Sr, Ca, Ba, etc.) family of oxides has renewed research on these materials because of their anticipated significant implications for science and technology [1–4]. There have been several studies in the past on the structure-property relationships in these perovskites and the results have emphasized a possible connection between local structural (Jahn-Teller type) distortions, magnetism, and transport therein [5–7], hinging upon the electronic states and charge dynamics of the basic Mn^{3+}-O-Mn^{4+} configuration [8,9]. In particular, Millis *et al.* and other groups [10–13] emphasize the importance of Jahn-Teller distortions on the transport properties, as opposed to only double exchange mechanisms, underscoring the strong coupling of lattice dynamics and electronic transport in these systems. In a recent work Asamitsu *et al.* [14] report magnetic field induced modification of the structural phase diagram in CMR materials though with a somewhat different composition. Thus, there is adequate precedence to suggest that in these manganites structural distortions are influenced strongly by external fields, which then affect the transport properties.

One interesting way to obtain new insight into the nature of the transport is to perturb the system with an electric field, fields of several MV/cm being possible in simple field effect transport configurations. Electric field effects have been studied in high-T_c superconducting perovskites [15–18], and most of these appear to be well explained by field induced modulation of mobile carrier density.

The thin film multilayer under study was prepared by pulsed laser deposition yielding a 35 nm film of the CMR material $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO) grown on a $LaAlO_3$(100) substrate followed by a 400 nm film of $SrTiO_3$ (STO) dielectric and a thick layer of *in situ* deposited gold. The conditions used for the deposition of NSMO are given in Ref. [19], while those for the deposition of dielectric STO along with the patterning procedure are given in Refs. [17,20]. A potential difference of 1 V across the 400 nm thick dielectric will result in a field of 2.5×10^4 V/cm. Assuming a dielectric constant of about 20 for NSMO [21], this leads to a displacement field at the NSMO interface $\simeq$0.5 MV/cm. The dynamics of the effect was measured by a frequency mixing study involving use of two different frequencies for the channel current and the gate voltage bias, and monitoring the difference frequency components of the output (representing electronic coupling in the channel) as a function of the applied gate bias frequency [22].

We have studied four out of eight devices fabricated. These four devices met the criterion of the gate current less than 1 nA under a 2 V bias. The modest working device yield is explained by the difficulty of depositing a good quality gate insulating layer on top of an ultrathin CMR film. In Fig. 1 are shown the results for R vs T for the NSMO system with zero, positive (+2 V) and negative (−1.5 V) bias applied to the gate. An electrometer was used to measure the resistance of the channel due to the high resistivity of this material. It may first be noted that the observed effect is significant (a few percent) considering the 35 nm film thickness used. Further, above the temperature at which the resistivity peak (T_p) occurs, the resistance is suppressed irrespective of the field direction, in clear contrast to the nature of the electric field effect observed in high-T_c superconductors. Remarkably, there is a shift in T_p to lower temperatures. The magnitude of the effect is reduced significantly for the temperatures below T_p which clearly signifies a change in the nature of the transport mechanism and its modulation.

In Fig. 2(a) are shown the data for the electric field modulation, $-\Delta R/R$, as a function of temperature as well as R vs T. It may be noted that, over a temperature range between 300 and 200 K, $-\Delta R/R$ is nearly constant; however, below 200 K it shows a considerable increase, down to a temperature of about 165 K. Below this temperature (which is about 10–12 K above T_p) $-\Delta R/R$ exhibits a sharp drop, with a change in its sign a few degrees below T_p. It is interesting that the temperature dependence of $-\Delta R/R$ is similar to the temperature dependence of dR/dT, though the significance of this

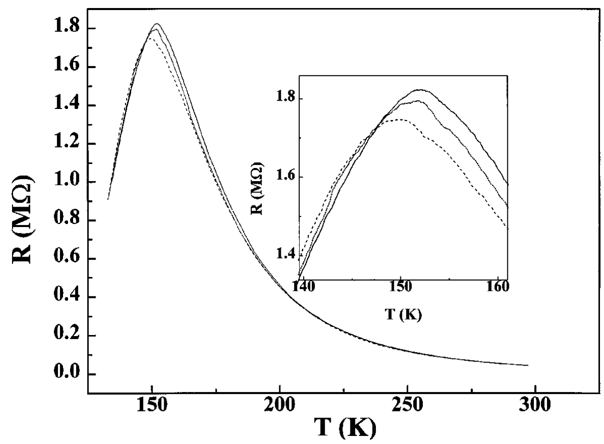

FIG. 1. R vs T for the gate voltages zero (solid line), $+2.0$ V (broken line), and -1.5 V (dotted line); the inset shows the behavior near T_p on an expanded scale.

correspondence is not yet clear. The very low gate leakage currents (under 1 nA) help to rule out thermal effects.

In Fig. 2(b) is shown the dependence of the modulation $-\Delta R/R$ on the value and direction of the applied field at a typical temperature of 210 K. Similar features are seen at other temperatures as well. This dependence has a parabolic (E^2) nature with an apparent small asymmetry. This asymmetry can be attributed to the properties of the

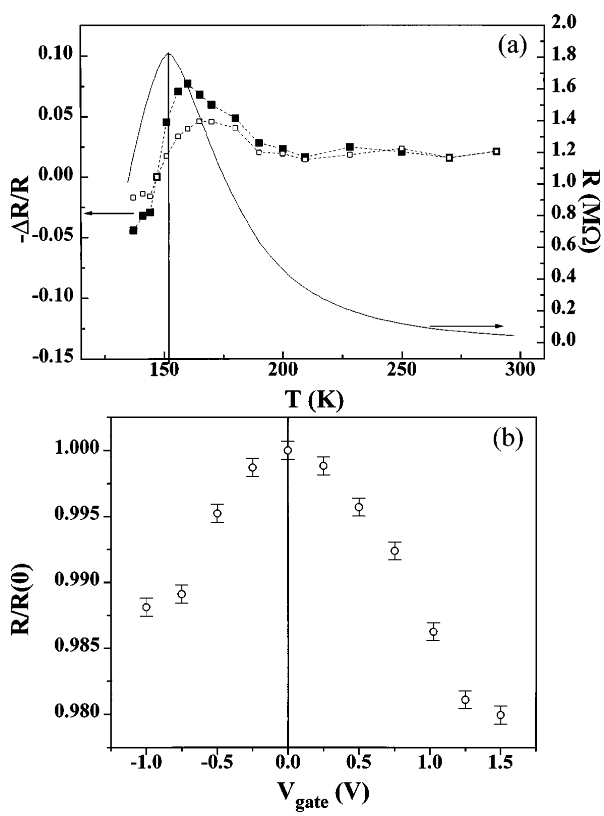

FIG. 2. (a) R vs T (the solid line) and $-\Delta R/R$ vs T for the gate voltages $+2.0$ V (solid squares) and -1.5 V (open squares); (b) the dependence of $R/R(0)$ on the gate voltage at 210 K.

gate dielectric STO, as reported earlier [17,20]. Once again, proportionality to E^2 possibly reflects the role of field induced strain or field-dipole interaction rather than charge density modulation.

In the case of a similar metal oxide conductor such as the cuprate superconductors, the field modulation of the resistivity could be completely explained on the basis of charge transfer effects. However, in the case of manganites the data do not support a charge transfer mechanism. First, the modulation is gate polarity independent, and second, the field dependence is quadratic rather than linear as has been seen for the cuprates. The peak resistivity of the film is 3.5 Ω cm, and at room temperature the value of about 0.2 Ω cm corresponds to a fairly resistive material having a long screening length. In addition, the mobility of carriers in this type of materials is known to be quite low, which also results in poor screening of an external electric field [23]. Hence the electric field most likely penetrates the entire 35 nm thickness of the film whereby most of the film is subjected to a considerable electric field.

One may attempt to explain the data as a possible shift of the ferromagnetic transition temperature resulting from a strain effect. The strain could arise from an electric field induced electroelastic effect in the STO layer which is then transmitted to the film below. There are experimental results which argue against this possibility. First, it has been shown that there are negligible electric field effects in STO films prepared at lower temperatures where the degree of crystallinity is not high enough. This is characteristically true for films with dielectric constants below 300 [20]. Second, using uniaxial compressive pressure experiments the peak resistivity temperature is upshifted at the rate of 4 K/GPa [24]. To explain a downshift of 3–4 K would require a tensile stress of the order of 1 GPa, too high to be realistic for piezoelectric effects. Thus we have to conclude that the effect observed arises from direct electric field interaction with the manganite film. In fact, we present below a scenario which does not involve any shift of the ferromagnetic transition temperature.

Our current understanding of the transport in this material suggests a two-component system consisting of a paramagnetic semiconducting matrix shunted by a ferromagnetic network [25]. Above T_p the transport is dominated by the matrix, but below T_p the conductivity is dominated by the metallic ferromagnetic regions, where the spins line up. A good correlation has been seen with T_p and the ferromagnetic transition temperature T_c. The electric field would be expected to affect the matrix and the ferromagnetic regions in different ways. At temperatures well above T_p, the semiconducting nature arises from the bond distortion of the Mn^{3+}-O-Mn^{4+} which reduces the overlap of the highly directional electronic orbitals of the oxygen and the Mn atoms [26]. This bond distortion arises primarily from the small radius of the rare earth ion and the Curie temperature in these materials can in fact be tuned by varying the radius of the rare earth ion [26]. Charge conduction occurs in this phase by hopping transport between the Mn^{3+} and Mn^{4+} atoms via the O atom, with a characteristic barrier energy (typically $\sim$100 meV). Below T_p, a ferromagnetic order sets in and a metallic behavior is observed due to a reduction in the spin-spin scattering.

The understanding of even the zero field transport in these materials is at an evolutionary stage, with proposed models of both an activated energy process as well as a simple variable range hopping model. The resistivity behavior of the material in the semiconducting region can be (and has been) [11,26] fitted by an activated form of the type

$$R(T) = R_0 \exp(\Phi/k_B T). \tag{1}$$

The actual value of Φ extracted from the fit to these data in Fig. 3 is $\simeq$108 meV. This activation energy is close to the published value for NSMO materials with different oxygen contents and with resistivity spanning over 5 orders of magnitude [27]. Also shown are similar fits for the two different applied fields, shifted by a constant for clarity.

In Eq. (1), Φ denotes the semiconducting barrier, and R_0 depends on the attempt frequency as well as the number of charge hopping sites. At any temperature

$$\Delta R/R = \Delta R_0/R_0 + \Delta\Phi/k_B T. \tag{2}$$

At 200 K, for a gate bias of -1.5 and 2 V, the barrier term is reduced by 24.3% and 26.6%, and the prefactor in enhanced by 21.6% and 24.0%, respectively. Using Eq. (2), the barrier reduction hence dominates over the hopping site reduction giving rise to a net decrease of resistance of the order of about 3%, as seen in Fig. 2(a). The physics behind this most likely is related to the effect of polarization of the oxygen octahedra, which in turn may affect the Mn^{3+}-O-Mn^{4+} bond configuration. A recent report of a large magnetovolume effect in LCMO suggests strong interplay between magnetoelastic effects and transport in these manganites [28]. Analogously, one could expect electroelastic effects in the CMR materials as well, and any resultant bond reconfiguration is likely to affect the transport properties. The applied field at the STO/CMR interface ($\sim$0.5 MV/cm) is a reasonable fraction of the crystal fields in typical solids ($\sim$10–100 MV/cm). Since the Jahn-Teller distortion in the manganites arises from such crystal fields, one would expect a perturbation on this distortion by an applied electric field producing electroelastic effects in the CMR layer.

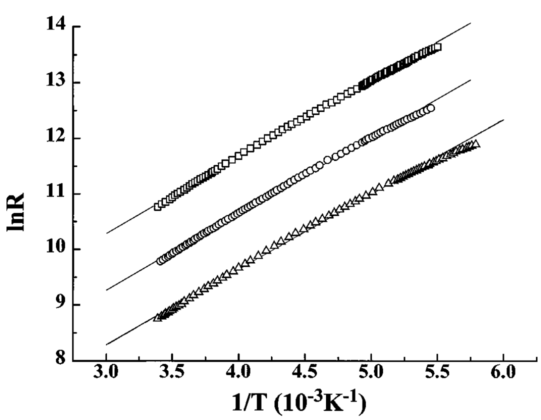

FIG. 3. A linear fit of ln R vs $1/T$ at the gate voltages zero (squares), $+2.0$ V (triangles), and -1.5 V (circles). The plots are separated for clarity.

It is worth noting here that in all experiments involving a perturbation of the oxygen octahedra such as applying high pressure [22], oxygen doping [27], cationic doping [26], or a magnetic field, a T_p increase was accompanied by a resistivity decrease and vice versa. The electric field effect is a departure in this respect, since both the resistivity and T_p are reduced simultaneously. While the magnetic field interacts with the spins in the system, the electric field interacts with the induced polarization, and thus the two types of interaction are fundamentally different in nature. However, pressure and elemental doping do affect the distortion of the oxygen octahedra directly, and thus this difference is indeed puzzling. At temperatures below T_p, where the ferromagnetic ordering sets in and the bond configuration is least distorted [29], the external electric field causes a small resistivity increase presumably implying an increase in the bond distortion.

The above idea of the strong coupling between lattice disorder and transport in the system also implies a strong correlation with the spins in the system. An implication would be that lattice dynamics ought to be significantly different above and below T_p. This is partly borne out in the dynamical study of the system as described below. In Fig. 4 are shown the results of a frequency mixing study to examine the time response of the electric field effects. The results show the dependence of the modulation $-\Delta R/R$ on the driving gate frequency at two temperatures. The respective values of $1/RC$ of the device configuration are also shown. It can be noted that the response at 300 K is fast enough to be limited by the RC time constant only, which itself is rather high because of the high value of the channel resistance. At the temperature of 173 K, which is above but near T_p, the response begins to drop at a frequency much lower than the value of $1/RC$ at that temperature. Much above T_p, where there is negligible ferromagnetic interaction, the lattice dynamics is fast. As one approaches T_p, there is a strong magnetic spin interaction which could slow down the lattice dynamics, as has been observed for magnetoelasticity in Jahn-Teller materials [30].

In conclusion, we have observed remarkable features in the transport properties of pulsed laser deposited epitaxial thin films of $Nd_{0.7}Sr_{0.3}MnO_3$ subjected to an external electric field. Specifically, the resistance is seen to decrease independently of the field direction above the temperature at which the peak in resistivity occurs (T_p).

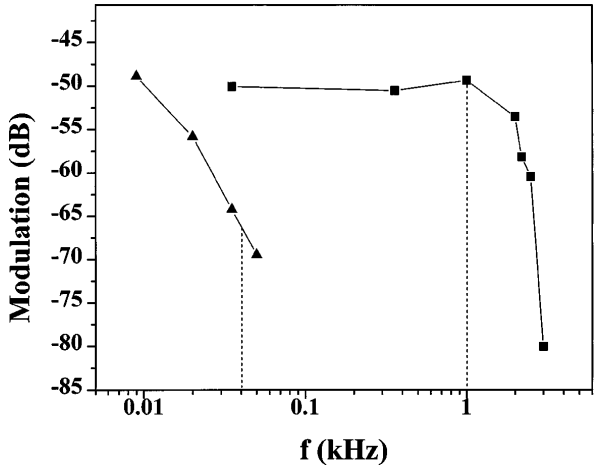

FIG. 4. The dependence of the electric field induced modulation $-\Delta R/R$ on the driving gate frequency at 173 K (triangles) and 300 K (squares).

The modulation is found to be proportional to E^2 (excluding charge density modulation effects and pointing towards field induced lattice distortions). The effect is seen to undergo a dramatic reduction in the magnitude and field direction independent reversal of the sign of $\Delta R/R$ below T_p, which can be attributed to the ferromagnetic ordering effects on transport. The time response is observed to be limited by the *RC* time constant of the device at high temperatures, but by some intrinsic mechanism near T_p. The results are consistent with a model whereby the electric field affects the lattice distortions in the CMR layer causing the observed changes. The electric field effect is the first demonstration of the modulation of the hopping barrier energy in the semiconducting region in this class of materials. There is a fundamental difference in the shift of the T_p and the resistivity peak value in this case in comparison with other forms of perturbation.

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