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# Irreversible electronic and magnetic transformations in colossal magnetoresistance compositions close to charge ordering

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We report the measurements of resistivity and ac susceptibility in two colossal magnetoresistanace compositions ($La_{1-x}Ca_xMnO_3, x=0.50$, 0.52) close to charge ordering, which have been prepared in air. With time and thermal cycling ($T<300$ K) there is an *irreversible* transformation of the low-temperature phase from a partially ferromagnetic and metallic to one that is less ferromagnetic and highly resistive. The time changes in the magnetization are logarithmic in general and activation energies are consistent with those expected for electron transfer between Mn ions. The data suggest that oxygen nonstochiometry results in mechanical strains in this two-phase system, leading to the development of metastable states which relax towards the more stable charge-ordered and antiferromagnetic microdomains.

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## I. INTRODUCTION

The unusual properties of the colossal magnetoresistance (CMR) manganites involve, in general, a combination of charge, lattice, spin, and orbital degrees of freedom.[1–6] A typical formula for the perovskite-type CMR compounds is $A_{1-x}B_xMnO_3$ where $A$ represents a rare-earth atom (e.g., La) and $B$ an alkaline earth (e.g., Ca). For $0.2\lesssim x\leqslant 0.5$ the materials undergo an insulator-to-metallic and paramagnetic-to-ferromagnetic (FM) transition. For $x>0.5$ the materials are, however, insulating and antiferromagnetic (AFM), and display a variety of charge and orbital ordering configurations. In the intermediate-doping regime (typically near $x=0.50$) the compounds can display both ferromagnetic and antiferromagnetic and charge-ordered states, depending on the thermal and magnetic history and preparation conditions, e.g., oxygen or air ambient and preparation temperatures.[7–12] It has been observed that those prepared in oxygen show stronger antiferromagnetic and insulating characteristics at low temperatures while the same compositions prepared in air show relatively more ferromagnetic and metallic effects. The exact oxygen concentration affects both the $Mn^{4+}/Mn^{3+}$ ratio as well as the prevalence of Jahn-Teller (JT) distortions. These latter have the effect of stabilizing the antiferromagnetic and charge-ordered configurations.

Phase separation in the manganites between hole-undoped AFM and hole-rich FM regions was theoretically predicted[13] and a variety of measurements[14,15] have lent support to this scenario. For the $x=0.50$ composition both electron and x-ray diffraction measurements[3,6,16] have shown the coexistence of ferromagnetism and charge ordering in the form of microdomains. The FM-to-AFM transition is characterized by an evolution of the charge-ordered domains. Recent measurements[15] have also shown the presence of metastable states in the two-phase region of these compositions and the conversion of one phase into another when perturbed *externally*.

There is considerable literature[17] on the transformation from a ferromagnetic to an antiferromagnetic (canted) and/or an insulator to a metallic state for compositions on the borderline of charge ordering. These transformations have been seen to be field and temperature induced and are clearly *reversible*. After thermal cycling to above the charge ordering regime, subsequent cooling reproduces the initial states.

Our recent experiments reported here on charge-ordered compositions ($x=0.50$ and $x=0.52$) of $La_{1-x}Ca_xMnO_3$ manganites prepared in air and at slightly low temperatures ($T<1400\,^{\circ}C$) provide clear evidence for *irreversible* transformations within the low-temperature phase. Our susceptibility and resistivity measurements show the as-prepared samples initially exhibiting a ferromagnetic component at low temperatures, in addition to the antiferromagnetic and insulating component expected to be dominant in this composition range. However, with time and/or thermal cycling the samples relax *irreversibly* into a highly resistive state with a pronounced decrease of the ferromagnetic-metallic component. Our primary results show the presence of a two-phase system which has a metastable ferromagnetic and metallic part.

These results are unique in that no such *irreversible* changes from one magnetic phase to another (or from metallic to insulating) have been reported in the manganites until now and they allow insight into the dynamics of the conversion of one phase into the other.

## II. EXPERIMENT

The samples were prepared by the standard solid-state reaction method. Powders of $La_2O_3$, $MnO_2$, and $CaCO_3$ were finely ground and initially reacted at 1000 °C. The powders were reground and heated up to 1100 °C for 17 h in air. A final heat treatment was given to the pellets at 1275 °C for 17 h, again in air. The same procedure was adopted for the preparation of various compositions of the type $La_{1-x}Ca_xMnO_3$, for $x=0.35$, 0.48, 0.50, 0.52, and 0.55. The x-ray patterns were studied for all the compositions. At room temperature all the compositions could be indexed to a tetragonal unit cell, as reported previously.[18] The in-plane lattice constants decrease from 5.460 to 5.409 Å as $x$ is varied

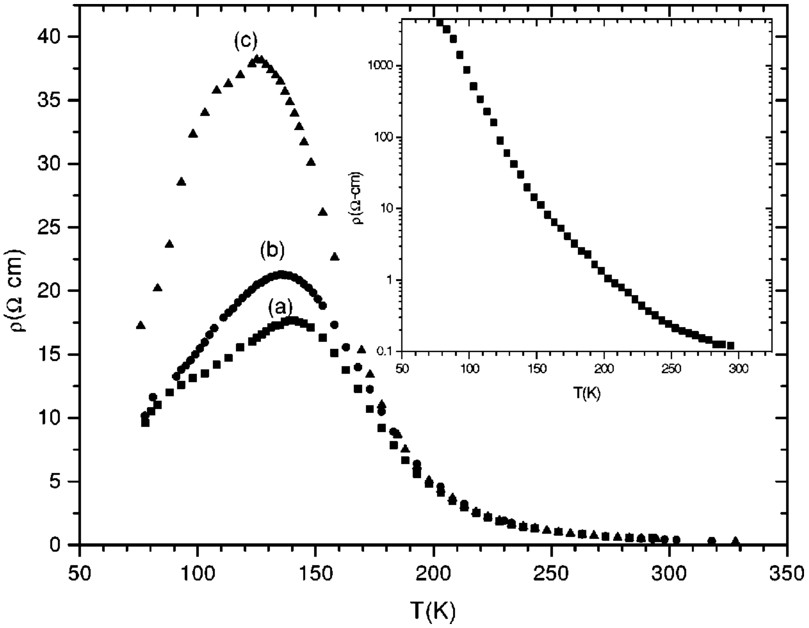

FIG. 1. Main figure: temperature dependence of the resistivity for $La_{0.50}Ca_{0.50}MnO_3$. Data labeled as (a) were taken during cooling of a fresh sample and (b) obtained on heating after completion of (a), while (c) were obtained subsequent to the (a) and (b) measurements during heating, after waiting at 80 K for 16 h. The pronounced increase at low temperatures is evident and was irreversible. Inset: resistivity of the $x=0.52$ sample as a function of temperature.

from 0.35 to 0.52, while $c$ decreases from 7.730 to 7.662 Å over the same range. No unidentified peaks could be seen in any of the compositions, testifying to the structurally single-phase nature of the materials, at least at room temperature. For $x<0.50$ the samples exhibit the usual, i.e., paramagnetic-to-ferromagnetic and insulator-to-metal, transition, while for $x=0.55$ the material is insulating and there is a clear paramagnetic-to-antiferromagnetic transition. Thus, while all the compositions are prepared under identical conditions and there is a smooth change of lattice constants with composition, it is only the compositions on the borderline of charge ordering, viz., $x=0.50$ and 0.52, that display the anomalous transient or irreversible behavior described below. Iodometric titration experiments were also performed to determine the oxygen content of the compositions. We find that both compositions have an excess of oxygen. For both compositions $La_{1-x}Ca_xMnO_{3+\delta}$ ($x=0.50$ and $x=0.52$) we obtain $\delta=+0.015$.

dc resistivity was performed by the usual four-probe method, in the temperature range $77<T<300$ K. For all measurements, resistive as well as magnetic, it is important to distinguish between the response of the fresh samples and the samples that have been thermally cycled. They will be referred to as as-prepared and thermally cycled, respectively. Figure 1 shows the resistivity of the $x=0.50$ sample in various conditions. (a) is for the as-prepared sample and is taken while cooling down. Here the peak at $T\sim141$ K is evident, below which temperature the decline is consistent with weakly metallic behavior. On waiting at the lowest temperature 81 K, the resistance was observed to be increasing with time. The data labeled (b) in Fig. 1 show the subsequent resistive behavior on heating. The increased value of resistivity in (b) (at, e.g., the maximum) of 23 Ω cm compared to the corresponding value for the initial state (a) of 18 Ω cm is evident. The same sample was again cooled down from room temperature to 81 K and allowed to stay at the temperature for about 16 h. A very pronounced increase in the resistivity between 81 and 160 K is evident from curve (c) in the figure. The final value of the resistivity was ~38 Ω cm. It is apparent that the low-temperature state becomes increasingly insulating and the peak in the resistance shifts to lower temperatures, with time and thermal cycling. It may be noted that these changes in the conducting behavior are *irreversible* in the sense that subsequent cooldowns from room temperature to low temperatures do not recover the initial low resistance state of Fig. 1(a). Hence it is clear that the effect of thermal cycling has been to convert at least part of the metallic microdomains into insulating or highly resistive ones, leading to an overall increase of the resistivity.

The $x=0.52$ sample (see inset of Fig. 1) displayed insulating behavior in the entire temperature range ($T>77$ K) even in the as-prepared state, and the resistivity was $\rho\sim4000$ Ω cm at 80 K. The changes in the resistivity with time and thermal cycling in this composition, though present, were much less pronounced ($\sim+10\%$) as compared to the $x=0.50$ composition.

The dc magnetization $[M(H)]$ of these compositions was also studied. At 77 K and $H=10$ kOe we obtained for the $x=0.50$ sample a moment of 2.44 $\mu_B$/Mn while the 0.52 sample had a moment of 0.97 $\mu_B$/Mn. The same samples after repeated thermal cycling showed a pronounced decrease (25% and 18%, respectively) in the magnetic moments. dc magnetization measurements as a function of temperature $[M(T)]$ for the $x=0.50$ composition are shown in the inset of Fig. 2. The field-cooled (100 Oe) measurements [Figs. 2(g) and 2(h)] showed a ferromagnetic transition at around 220 K and a slight decrease in the moment starting at about 125 K. Zero-field-cooled measurements [Figs. 2(k) and 2(l)], on the other hand, showed a very clear transition into the antiferromagnetic state at low temperature, with $T_N\sim170$ K. On thermally cycling the sample a significant (~10%) decrease in the value of the low-temperature moment, compared to the initial (as-prepared) value, was noticeable. A decrease of the moment was noticeable when waiting

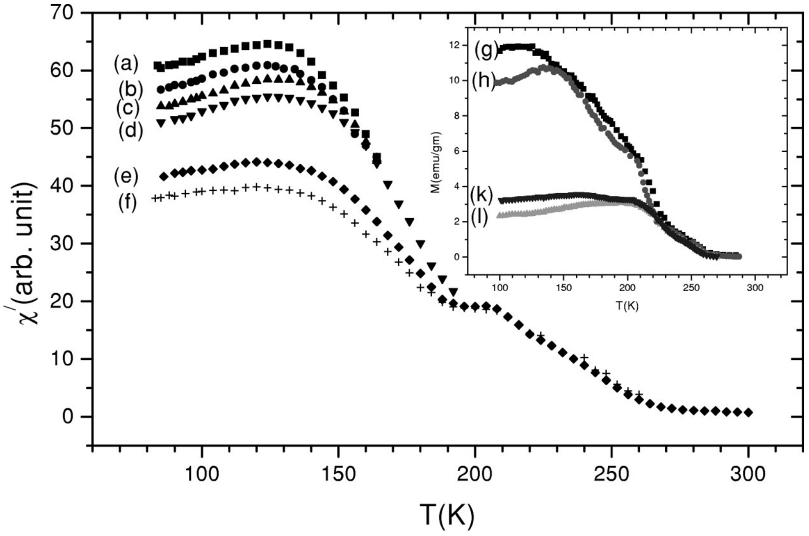

FIG. 2. Temperature dependence of the in-phase part of the ac susceptibility $\chi'$ of $La_{0.50}Ca_{0.50}MnO_3$ for a 5-Oe ac field and frequency $f = 131$ Hz. Data labeled as (a), (b), (c), (d), (e), and (f) taken successively as described in the text. Inset: dc magnetization of the same sample [(g) and (h) are field cooled while (k) and (l) are zero-field cooled]. An irreversible decrease in the moment from (a) to (f) and from (g) to (h) is evident.

for long periods of time. However, in the presence of an applied dc field changes in the moment with time were too slow to be accurately determined by us. We thus decided to investigate the irreversible changes taking place using weak ac fields.

ac susceptibility measurements were repeated on three specimens for each of the compositions, starting from fresh as-prepared samples for each one. The behavior reported here was observed consistently in each of the specimens. The ac technique has been described by us elsewhere.[19] In Fig. 2 (main figure) we show the data for the in-phase part of the susceptibility for the $x = 0.50$ sample measured successively over a period of 1 day. The initial data [Fig. 2(a)] show a small plateau at $T \sim 200$ K followed by a sharp rise down to 125 K below which there is again a small decrease in the moment. The low-temperature decrease of the ac susceptibility is very similar to the dc magnetization behavior already discussed. Also shown in Figs. 2(b), 2(c), and 2(d) are the changes in the susceptibility as the $x = 0.50$ sample was heated up to a particular temperature below 200 K and then cooled down again. It is apparent that with time and thermal cycling the *low-temperature* moment decreases to about 55% of its initial value while there is virtually no change above 190 K. The ferromagnetic component of the total moment is apparently substantially weakened and the antiferromagnetic regions expand, with concomitant decrease of conductivity, as discussed earlier. The measurements in Fig. 2 were taken over a period of 10 h and it was noticeable that after the temperature had been cycled several times to above 200 K, there was no further change in the low-temperature behavior. Thus it is noted that similar to the case for the resistivity discussed above, the effect of thermal cycling has been to decrease the ferromagnetic component of this two-phase system in an irreversible way. Subsequent cooldowns from high temperature (300 K) do not recover the initial state. As mentioned above there are no changes in the magnetization above 190 K. Gong *et al.*[17] discuss the fact that the charge-ordered lattice begins to melt at around 160 K in this composition and the process is completed at around 200 K. It therefore appears that the changes we observe in the magnetization are confined to the region below the charge ordering temperature $T_{co}$. This would suggest that the magnetic and resistive changes we observe are triggered by the onset of charge ordering in the system.

The changes shown in Fig. 2 were an outcome of the combined effects of time and temperature. To separate out the time dependence we measured the magnetic relaxation of an as-prepared $x = 0.50$ sample, which was cooled down rapidly by inserting it into the cryostat, precooled to 90 K. The data were recorded for a period of 2 h, omitting the data for the first 50 s, during which the sample may not be in equilibrium. The ac susceptibility was observed to decrease systematically with time and the fit of the data to a logarithmic function

$$\chi'(t) = \chi_{(0)}\left[1 - S\ln\left(1 + \frac{t}{t'}\right)\right] \tag{1}$$

is shown in Fig. 3 (main figure). Here $\chi_{(0)}$ and $t'$ are parameters obtained from the fit. It can be seen that the fit is in general quite good. From the fit to Eq. (1) we obtain the rate of relaxation $S = 0.052$. Logarithmic relaxation has been observed in spin glass systems and a mixture of small ferromagnetic particles.[20] It has been attributed to the distribution of energy barriers separating local minima, which correspond to different equilibrium states.[21] For typical thermal activation with relaxation time $\tau = \tau_0 \exp(U/k_BT)$ and for the special case of activation barriers $U$ distributed uniformly in a range $U_1 < U < U_2$, one obtains[22] logarithmic relaxation in the intermediate time region $\tau_1 < t < \tau_2$. Here $\tau_1$ and $\tau_2$ are the relaxation times corresponding to the activation energies $U_1$ and $U_2$, respectively. In this limit, the rate of relaxation

$$S = \frac{1}{m_0}\left(\frac{dm}{d\ln t}\right),$$

where $m_0$ is the initial moment, approximates[22] to

$$S \sim \frac{1}{\ln(\tau_2/\tau_1)} = \frac{k_BT}{(U_2 - U_1)}. \tag{2}$$

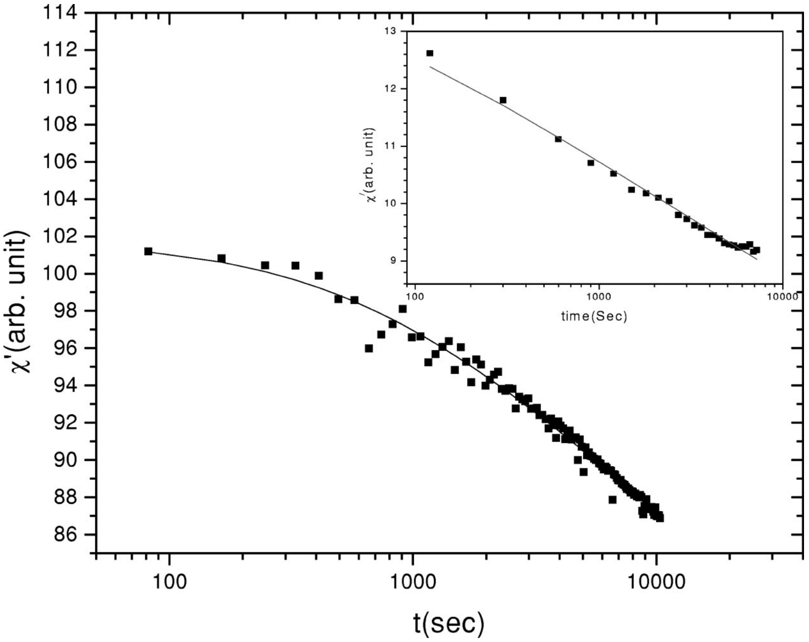

FIG. 3. Main figure: typical time dependence of the ac susceptibility for the $La_{0.50}Ca_{0.50}MnO_3$ sample at $T=90$ K. The data are for an as-prepared sample. The change indicates a lesser moment. The fit is to the $\ln(1+t/t')$ form as discussed in the text. Inset: time dependence of the susceptibility of the $x=0.52$ sample showing the fit to the logarithmic form.

The relaxation rate can thus be used[23] to obtain an approximate width of the distribution of activation barriers, $W=U_2-U_1$. From the value of $S$ measured at 90 K we obtain $W=149$ meV. Thus the effective range of activation energies corresponding to the observed relaxation of the ferromagnetic-conducting part is seen to be comparable to the values quoted[24] in general for activation energies required for electronic rearrangements in oxides.

Figure 4 (inset) shows the in-phase part of the susceptibility $\chi'$ for one of the as-prepared $x=0.52$ samples. The data are taken during warming up from 80 K. The susceptibility peaks at about 216 K, followed by a decline until about 160 K, which is followed by another increase in the moment. At 81 K the moment has increased by about 50% over the minimum value attained at 160 K. This is consistent with an antiferroalignment starting at $\sim 126$ K and continuing until 160 K, which is followed by redomination of the ferromagnetic alignment at lower temperature. The occurrence of the antiferromagnetic behavior is consistent with the sharp increase in resistivity we observe below 200 K, as well as with the reported charge ordering in this composition with $T_{co}$ $\sim 190$ K (on warming). The nonmonotonic temperature dependence of the susceptibility in our as-prepared samples is very similar to that reported, e.g., by Gong *et al.*[17] for the low-field dc magnetization of their 0.50 sample. They do not refer to any transient behavior, however.

Figures 4(a)–4(f) are the changes in the susceptibility as the $x=0.52$ sample (as prepared) was heated up to a particular temperature below $T_{co}$ and then cooled down again. It is apparent that the low-temperature moment, in the ferromagnetic region, decreases successively until the upturn in $\chi'$ is completely eliminated and an almost temperature-independent behavior is seen. It was again noticeable that after the temperature had been cycled to above 200 K there

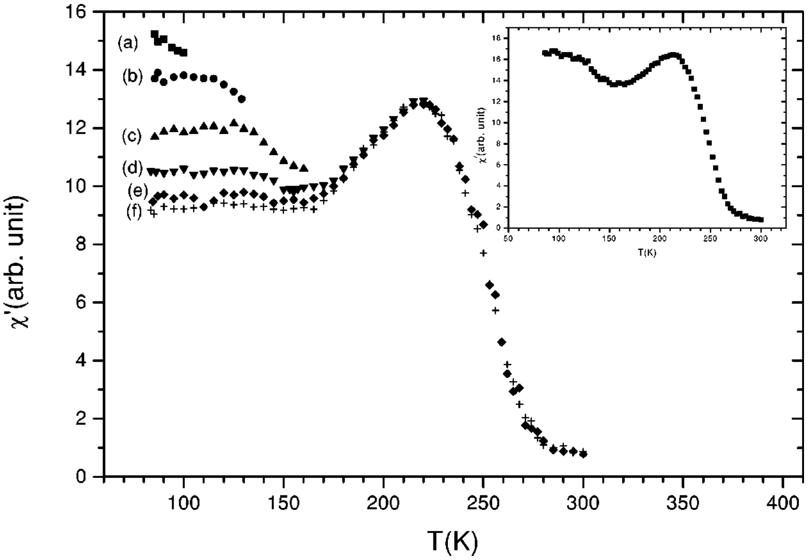

FIG. 4. Main figure: temperature variation of the ac susceptibility of the $La_{0.48}Ca_{0.52}MnO_3$ composition for a 5-Oe ac field and frequency $f=131$ Hz. The data of curves labeled (a)–(f) have been obtained successively heating up to the temperature indicated by the final data point in each set of data. The decrease of the ferromagnetic component at low temperatures ($T<200$) is evident. Inset: temperature dependence of the susceptibility for the same sample in the as-prepared state.

was no further change in the low-temperature behavior. Further no thermal cycling or relaxation effects were observed for $T > 170$ K. Magnetic relaxation of an as-prepared $x = 0.52$ sample at 83 K (inset of Fig. 3) yielded the activation energy distribution width $W = 106$ meV. It is noticeable looking at the activation energy range $W$ measured in these compositions that they are comparable to the energy gap $2D$ measured optically[25] (82 meV) as well as to the typical activation energies measured resistively[2] for the $x = 0.50$ composition. It would thus appear that the electronic rearrangements between Mn ions, at least at low temperatures, occur over energy barriers with a distribution width comparable to the gap in the electronic density of states.[25]

We recall that the structural studies[3] at low temperatures clearly show the development of static JT distortion of the oxygen octahedra for $T < 220$ K and the lattice parameters change significantly down to $T \sim 150$ K. Our magnetic relaxation experiments establish an interesting connection between the magnetic relaxation and the creation of a metastable state on passing through the temperature region of pronounced Jahn-Teller activity ($T < 220$ K). After an $x = 0.50$ sample had apparently relaxed to equilibrium at 125 K (relaxation was no longer measurable) it was reheated to 250 K. On cooling down to 125 K again, renewed relaxation was noticeable. What is very significant here is that cycling of temperature through the region of high Jahn-Teller activity apparently initiates further instability. Thus the conclusion we draw is that each time the sample is cycled through this region it produces additional microstructural changes and the consequent instability further triggers a relaxation towards the eventual stable state, which is more antiferromagnetic and insulating.

## III. DISCUSSION AND CONCLUSIONS

It is clear that the changes in the magnetic and resistive state of our samples show a metastable condition in the temperature region where charge ordering and antiferromagnetic behavior would be dominant. This is in line with the phase separation scenario[13] where the ferromagnetic (metallic) and antiferromagnetic (insulating) phases coexist. Our experiments show the conversion of one of the phases into the other. With increasing time the increase in the resistivity and the decrease in the ferromagnetic part, as well as the measured activation energies of the changes, are consistent with the transfer of electrons from some of the $\mathrm{Mn}^{3+}$ ions to some of the $\mathrm{Mn}^{4+}$ ions such as to make more of the system charge ordered and insulating. In other words, more of the ferromagnetic microdomains convert into antiferromagnetic and charge-ordered regions. It is noticeable that the changes in the susceptibility only occur for the region below $T \sim 200$ K, where the Jahn-Teller effects create the lattice distortions which are understood to stabilize the charge-ordered state. The magnetic relaxation experiments give further confirmation of the relation between the passage through the temperature region close to $T_{co}$, on the one hand, and the initiation of the transformations, on the other.

We note that there have been a number of studies on 50-50 compositions which have not shown the behavior we report. We believe that the unusual behavior of our samples may stem from the relatively low-temperature annealing (1275 °C). This is understood to result in excess oxygen retention. The presence of excess oxygen is borne out by iodometric titerations on our samples. The effect of excess oxygen is to create cation vacancies.[11,12] The effect of these vacancies is both to create an excess of $\mathrm{Mn}^{4+}$ (holes) in the samples and also to develop mechanical strains in the lattice. These combine to inhibit the prevalence of the antiferromagnetic and charge ordering usually seen in these compositions and the system develops phase seperation with the coexistence of the ferromagnetic (metallic) and charge-ordered domains, initially. The question then is what causes the metastability of the ferromagnetic phase in this two-phase situation. We believe that the presence of mechanical strains is crucial to understanding the behavior. Podzorov *et al.*[15] have argued that a metastable phase arises in the two coexistant phase compositions due to the strain induced by the lattice mismatch between the two phases. These strains are further enhanced by the Jahn-Teller distortion which occurs within the charge-ordered regions but is absent within the ferromagnetic ones. Millis *et al.*[26] showed that biaxial strain due to the Jahn-Teller distortion could lead to the localization of charges and a decrease of the Curie temperature. Thus a plausible explanation is that upon thermal cycling, the Jahn-Teller distortion of the $\mathrm{Mn}^{3+}\mathrm{O}_6$ octahedras increases the interfacial elastic energy between microdomains of the two phases, and the system relaxes to lower energy by growth of the charge-ordered and antiferromagnetic regions. This is consistent with our results where the sensitivity of the ferromagnetic to antiferromagnetic and insulating behavior is closely linked to cycling through the Jahn-Teller region, as discussed above. In conclusion we have seen that in the two-phase systems there can be a spontaneous and *irreversible* tendency for the conversion of one of the phases into another due, most probably, to the presence of strains associated with the mismatch of the two phases. Further experiments are in progress to observe if the initial metastable state can be reattained after high-temperature thermal annealing in an oxygen or air ambient.

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