Lattice effects and phase competition in charge ordered manganites

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A complete characterization of the magnetotransport and magnetoelastic properties of two classical examples of half doped manganites, $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) and $La_{0.5}Ca_{0.5}MnO_3$ (LCMO), was carried out by electrical resistivity, magnetoresistance, thermoelectric power, electron spin resonance (ESR), and thermal expansion measurements. We have identified a mixed paramagnetic (charge localized) plus ferromagnetic (FM) (conductive) state between the low temperature antiferromagnetic (AF) and high temperature paramagnetic (itinerant) phases, which in the case of LCMO exists over a temperature range of about 100 K. The magnetic field completely separates the FM and AF phases, suppressing the intermediate paramagnetic-localized phase. This mixed state is only observed in a narrow temperature interval for NSMO, and shows how the relative strength of the competing phases can be tuned by the lattice distortion. We also observed a large gap at the charge ordering temperature in the activation energy of the resistivity, which is almost independent of the sample. ESR results will be presented to show that this technique could be a very useful tool with which to investigate the multiphase microscopic state characteristic of manganites. [DOI: 10.1063/1.1447285]

In the last two years, manganites have suffered a second renaissance since it was suggested that some kind of electronic phase segregation could be the origin of many of the intriguing properties of these compounds.[1] As a result, previous work is now being reexamined in light of this new evidence and much experimental and theoretical effort is being devoted to determining the exact nature of this inhomogeneous state. However, the origin of this tendency towards phase segregation is not completely clear at the moment and more research needs to be done in this direction.

Here we propose a comparison between two well-known charge ordered (CO) manganites: $Nd_{0.5}Sr_{0.5}MnO_3$ (NSMO) and $La_{0.5}Ca_{0.5}MnO_3$ (LCMO). These particular compounds were chosen for two reasons: (i) at 1:1 (Mn^{3+}:Mn^{4+}) composition CO is particularly feasible, leading to a rich variety of charge/orbital ordered (CO/OO) structures,[2] and (ii) in spite of having the same hole density, their so very different values of the mean ionic radius at the rare earth position, $\langle r_A \rangle$ (1.236 Å for NSMO and 1.198 Å for LCMO) make them ideal candidates with which to explore different zones of the phase diagram of half doped manganites.

The ceramic samples used for this study were synthesized by solid-state reaction. Room temperature x-ray diffraction patterns indicate that the samples are single phase (orthorhombic, *Pnma*). Electron spin resonance (ESR) measurements were performed at 9.4 GHz (*X* Band) with a EMX Bruker spectrometer between 100 and 400 K.

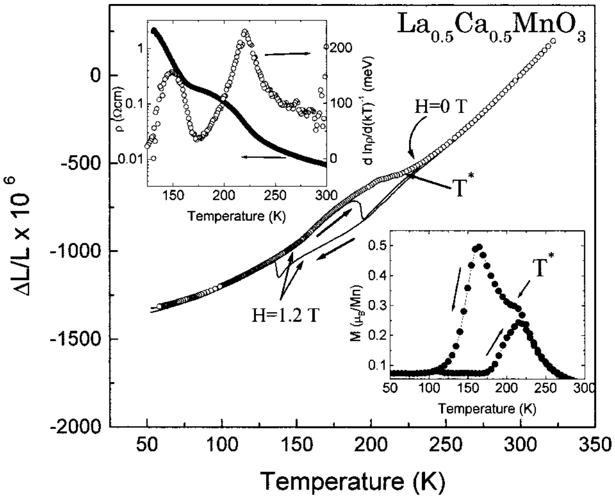

FIG. 1. Results for LCMO. Main panel: Thermal expansion without field (open circles) and with field (1.2 T, lines) and decreasing and increasing temperature. Note how the magnetic field suppresses the anomaly at T^* and defines the PM-FM-AF regions. Inset, bottom right: Thermal evolution of the magnetization measured at 3.3 kOe in field cooling-zero field cooling conditions. Inset, top left: Resistivity and activation energy of the resistivity. The peaks in the activation energy coincide with anomalies in the magnetization and resistivity curves.

In Fig. 1 we show many of the main results for LCMO. By cooling down the compound from the high temperature paramagnetic (PM) state, it undergoes a second-order transition towards a ferromagnetic (FM) state at 225 K, and then becomes antiferromagnetic (AF) at $T_N \sim 160$ K. The strong thermal hysteresis of the magnetization resembles the first-order character of the AF transition. Associated with those magnetic transitions we observed two anomalies in the resistivity which are reflected also in the activation energy. But,

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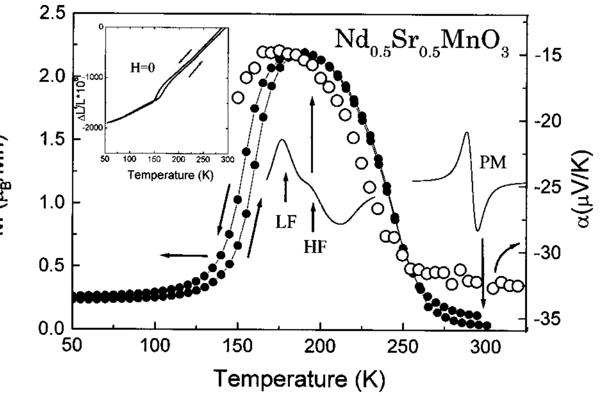

FIG. 2. Results for NSMO. Main panel: Thermal evolution of the magnetization in field cooling-zero field cooling conditions (closed circles) and of the thermopower (open symbols). Some ESR lines are shown at the corresponding temperature (300 and 200 K). Inset, top left: Thermal expansion without field and increasing and decreasing temperature. Only the transition at T_N is observed.

perhaps, the most interesting results that will be shown in this work are those concerning thermal expansion, shown in the main panel of Fig. 1. By reducing the temperature through $T\sim225$ K, sample volume increases, as compared with the high-T extrapolation, which indicates that some kind of carrier localization takes place at this temperature. But when a magnetic field as small as 1.2 T is applied, the sample shows the typical (small) volume reduction associated with the PM to FM transition, and the FM and AF states are completely separated.

In Fig. 2 shown is the thermal evolution of the magnetization, thermal expansion, and some of the EPR lines obtained at different temperatures for NSMO. This compound undergoes an insulator-to-metal transition associated to the FM-to-PM transition (not shown), and then becomes AF-CE (CO/OO) at low temperature.[3] Differences in the thermal expansion with respect to LCMO are also evident.

But, let us first discuss our results for LCMO. As we mentioned, a second-order transition takes place at $T\sim225$ K $(=T^*)$. This cannot be considered a truly Curie temperature since no long-range FM is achieved below it but FM clusters, probably near the percolation threshold, have formed. On the other hand, the activation energy of the resistivity continuously increases upon approaching T^* from above, indicating a transition from Zener (two-Mn) to small (one-site) polarons, with a typical value of the activation energy of $\sim$200 meV. Thermopower $\alpha(T)$, measurements confirmed this hypothesis: the almost temperature independent value of α well above T^* is also characteristic of polaronic conduction, and the progressive increment of $\alpha(T)$ as T decreases towards T^* indicates trapping out of mobile Zener polarons, confirming the behavior of the activation energy (see, for example, the results for NSMO in Fig. 2). Below T^*, the activation energy decreases again showing the more conductive character of the FM clusters with respect to the matrix. From these experiments it follows that at T^* there is segregation between a hole-poor conductive FM phase ($x\sim0.4$, estimated from the value of T^*, and hence ferromagnetism is produced via double-exchange interaction)[4] and a hole-rich matrix in which conductivity takes place through small-polaron activation. Moreover, from ESR experiments we deduced that the charge-localized matrix is PM and not AF, as we will discuss later. This transition from the high temperature PM delocalized state to the intermediate mixed state (PM+FM) produces a positive thermal expansion (main panel of Fig. 1) due to larger Mn–O bonds in the charge-localized-PM matrix below T^* with respect to smaller Mn–O bonds in the high temperature PM state at $T>T^*$.[4] Upon further cooling, a transition towards a low temperature AF-CE charge and orbitally ordered phase takes place[5] (also observable as a jump in the activation energy). Due to localization effects in the CO phase, the Mn–O bond lengths must be similar to those in the PM-localized phase below T^*, and must be the reason why it is not observed in the magnetovolume. When a magnetic field is applied (1.2 T in this case), it can be seen that there is a small thermal expansion anomaly around 200 K (the volume of the mixed state is smaller than in the zero field situation), due to the suppression of the PM localized state below T^* by the applied field. The short Mn–O average bond FM phase is kept down to $\sim$130 K when the first-order transition to the AF-CE phase takes place.

So, it is clear that at T^* a transition takes place between a high temperature PM-delocalized phase (from the low values of resistivity at high temperature, Fig. 1, it could be considered to be a bad metal) and a low temperature mixed PM-localized plus FM-conductive clusters. Note that there is no any crystallographic transition at T^* (see Ref. 5). The magnetic field grows FM clusters beyond percolation, suppressing the PM-localized state and producing a large magnetoresistive effect.[6]

On the other hand, the behavior of NSMO is quite different, in spite of the similar structure and doping level to LCMO. Looking at the magnetization versus temperature curve, a second-order transition at $\sim$250 K (T^*) towards FM phase takes place although, again, the FM order is not actually long range (although it is closer to 3.5 μ_B than LCMO). To study the magnetic nature of the phase segregated state below T^* in more detail, we have performed careful ESR experiments at different temperatures in both LCMO and NSMO throughout these transitions. Some results are shown in Fig. 2 for NSMO. At high temperature, in the PM-delocalized state, we observed a single ESR line (Lorentzian in shape) centered at $H_r\sim3.3$ kOe, characteristic of PM behavior. Below T^*, two lines appear in the ESR spectra: a low field (LF) line and a high field (HF) line. We have fitted the spectra and obtained the characteristic resonance fields for both lines. This allowed us to attribute the LF line to a FM state, and the HF line to a PM in both LCMO and NSMO. Previous studies by ^{139}La nuclear magnetic resonance (NMR) and ESR in $La_{0.5}Ca_{0.5}MnO_3$ suggested the coexistence of FM/AF phases between T_N and T_C.[7] But, our results point towards a PM nature of the incommensurate-CO phase in $La_{0.5}Ca_{0.5}MnO_3$ between T_N and T^*. Our hypothesis of the PM character of this phase is supported by neutron diffraction studies by Huang *et al.*,[8] who showed the existence of a new crystallographic phase below ~230 K in LCMO, which becomes AF-CE below 150 K.

If we look now to the thermal expansion of NSMO, it can be seen that the there is no anomaly at T^*, showing that the FM order that developed below this temperature, although not completely, is more pronounced than that in LCMO (the compound becomes metallic below this temperature, indicating percolation of FM domains). However at T_N, there is a reduction in the volume with respect to the FM phase, which cannot be explained in terms of charge localization in the AF structure. Mahendiran *et al.*[9] actually showed that the low temperature AF-CO state has a monoclinic structure with a unit cell volume smaller than the volume of the high temperature FM (orthorhombic), hence explaining the volume contraction observed in this compound.

In order to compare the relative stability of the low temperature AF-CE (CO/OO) phase in both compounds (note the coincidence of T_N), we calculated the ratio between the gap at the charge ordering temperature (from the resistivity) and the thermal energy at this temperature, $E_\alpha(\mathrm{CO})/k_BT$. This ratio is $E_\alpha(\mathrm{CO})/k_BT \sim 13$, independent of the compound studied. This result is perfectly compatible with recent calculations, which point toward a low-temperature-CO/OO state independent of electron–phonon coupling (λ) for a large enough value of J_{AF}.[10] However, it should be noted that the value of the gap calculated from the resistivity can be influenced by variations in the carrier concentration or mobility at the transition and the data should be checked with the Hall effect or spectroscopy data.

But there is an important question that should be addressed: How does the intermediate two-phase state give place to the low-temperature AF-CE phase? In our opinion, suppression of double exchange in the PM-localized state introduces a AF state via superexchange interaction. Due to the doping level ($x = 0.5$) this AF state is CE type. However, we have recently obtained ESR evidence of the existence of small FM clusters immersed in this AF-CE matrix, even at low temperature.[6]

In summary, we have demonstrated the coexistence FM-conductive (hole poor) and PM-localized states between T_N and T^* in LCMO and NSMO. The relative strength of the competing interactions can be fine-tuned by electron–lattice coupling. Also, we have shown the importance of techniques like thermal expansion and ESR for exploring the nature of the mixed phase state in manganites. On the basis of our results, LCMO should be considered an intermediate-λ compound, while NSMO represents an example of a low-λ compound.

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