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Crossover from charge-localized state to charge-ordered state in $Pr_{2/3}Ca_{1/3}MnO_3$

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In $Pr_{2/3}Ca_{1/3}MnO_3$, we have found a crossover from a charge-localized state to a charge-ordered (CO) state. Linear-thermal-expansion and magnetostriction measurements up to 14 T show that for temperatures below $T_p \sim 400$ K a charge localization is present as in the case of $La_{2/3}Ca_{1/3}MnO_3$. Below $T_{CO} \approx 210$ K, a charge ordering, as found in some $R_{0.5}A_{0.5}MnO_3$ (R-A=La-Ca, Pr-Ca, Pr-Sr, Nd-Sr) compounds, is observed. A magnetic field suppresses the CO state below T_{CO} giving rise to a first-order structural transition. A continuous change in volume is measured between $T_{CO} < T < T_p$. The electrical behavior is similar to the structural behavior, and is the result of the strong spin-charge-lattice coupling present in the colossal-magnetoresistance perovskites. [S0163-1829(96)50242-0]

One of the keys to understanding the colossal magnetoresistive (CMR) behavior of manganese perovskites is to understand the role that the coupling between the carriers and the lattice plays in these compounds. Since the simple double-exchange picture is unable to explain the experimental results,[1] several models have been proposed, including one based on lattice-carrier coupling.[2] In this article we present experimental results on the relationship between the electrical and structural behavior in $Pr_{2/3}Ca_{1/3}MnO_3$. This compound has been found to be an example where a crossover from a charge-localized (CL) state to a charge-ordered (CO) state takes place. It was found in pure and doped $La_{2/3}Ca_{1/3}MnO_3$ (Refs. 3–5) compounds that an anomalous linear thermal expansion (LTE) over the phonon Grüneissen-like contribution to the LTE is present. That was associated to the onset of charge localization. Below a certain temperature (T_p), there is a gradual charge localization which brings about a local distortion. When the long-range ferromagnetic order appears in $La_{2/3}Ca_{1/3}MnO_3$, the charge localization and the associated distortion are released with a $\sim$0.1% reduction of the cell volume at T_c. That CL state occurs without a real-space ordering of the Mn^{3+} and Mn^{4+} ions as has been shown by electron diffraction in $La_{2/3}Ca_{1/3}MnO_3$.[6] The existence of CO states has been found in $R_{0.5}A_{0.5}MnO_3$ [R-A=La-Ca (Ref. 6), Pr-Ca (Ref. 7), Pr-Sr (Ref. 8), Nd-Sr (Ref. 9)] compounds. The CO states had been predicted from transport and magnetic susceptibility measurements. However, the detection of superlattice spots below T_{CO} by electron diffraction in $La_{0.5}Ca_{0.5}MnO_3$ has provided a direct evidence of their existence.[6]

Although CL and CO states have in common that they both reduce the mobility of the carriers there are important differences between them. It is commonly accepted that some type of polarons are present in the CL state. However, the nature of these polarons is still a matter of speculation. Mn^{3+} is a Jahn-Teller ion whose three low-energy t_{2g} states are occupied while one of the twofold degenerated high-energy e_g states can lower its energy if the octahedron formed by the O^{2-} ions around the Mn atom is distorted. This low-energy e_g state can house an electron (or hole) that becomes localized, which would be the origin for a small Jahn-Teller-type polaron.[10] Zhao *et al.*[11] have measured a shift of >20 K on T_c replacing ^{16}O with ^{18}O in $La_{1-x}Ca_xMnO_3$, which supports their existence. Park *et al.*[12] claim that other kinds of small polaron effects would be more important. Such small polarons would arise when the e_g electrons (or holes) are localized and then a charge fluctuation energy appears in the process of hopping of the electrons between Mn^{3+} and Mn^{4+} sites. In $La_{2/3}Ca_{1/3}MnO_3$ it has been found that this CL state happens simultaneously with the interplay of a short-range ferromagnetic order.[5] That gives rise to magnetic clusters. Their presence and the associated anomalous LTE well above T_c were related to the conductivity, whose behavior can be explained above T_c as due to hopping of magnetic polarons.[13] On the other hand, the mechanism which gives rise to the appearance of CO states with real-space ordering of the Mn^{3+}/Mn^{4+} ions is still an open question. Tomioka *et al.* [14] suggested that the repulsive Coulomb interaction between electrons or the electron-lattice interaction may explain the CO state but, as mentioned above, no mechanism for the CO state has been really developed so far. The CO state has been found in ferro-antiferromagnetic transitions like in $La_{0.5}Ca_{0.5}MnO_3$ (Ref. 15) or $Pr_{0.5}Sr_{0.5}MnO_3$ (Ref. 14) and in the paramagnetic state like in $La_{1-x}Ca_xMnO_3$ ($0.63 \leqslant x \leqslant 0.67$) (Ref. 16) or in $Pr_{0.5}Ca_{0.5}MnO_3$.[7] Up to now only the CO state was proposed to occur in $Pr_{2/3}Ca_{1/3}MnO_3$. In this article we will show that both states, CL and CO, are present in $Pr_{2/3}Ca_{1/3}MnO_3$, with the CL state across the temperature range $T_{CO} < T < T_p$ and the CO state below T_{CO} ($T_p \sim 400$ K, $T_{CO} \approx 210$ K).

The series $Pr_{1-x}Ca_xMnO_3$ has been exhaustively studied. Pollert *et al.*[17] performed a pioneer study of the structural properties. Jirák *et al.*[7] proposed a phase diagram of the series with the help of magnetic and neutron diffraction measurements. Tomioka *et al.*[18] and Lees *et al.*[19] studied the magnetic and magnetoresistive behavior of the series and Yoshizawa *et al.*[20] studied $Pr_{0.7}Ca_{0.3}MnO_3$ with neutron diffraction. From these studies the following information is obtained. The structure is orthorhombic and can be indexed in the space group *Pbnm* (there is lack of data of the evolution of the lattice parameters with temperature). At $T \approx 210$ K there is charge order reminiscent of the 1:1 ordering of Mn^{3+}/Mn^{4+} in $Pr_{0.5}Ca_{0.5}MnO_3$. The compound is an insulator down to low temperature, but a first-order insulator-metal transition can be obtained below T_{CO} by applying a magnetic field. At $T \sim 150$ K the compound orders antiferromagnetically and at $T \sim 100$ K a canted magnetic structure is developed. Much effort has been devoted to show the close relationship between the magnetic and electrical behavior. We aim to include the lattice effects in this intriguing spin-charge-lattice coupling in CMR perovskites. In that direction, the thermal expansion and magnetostriction measurements are very valuable.

Polycrystalline $Pr_{2/3}Ca_{1/3}MnO_3$ samples were prepared by standard solid-state reaction techniques. Stoichiometric quantities of Pr_6O_{11}, $CaCO_3$, and Mn_2O_3 were ground and reheated several times at 1400 °C for 24 h. Then the powder was pelletized and heated in air for another 24 h at the same temperature. The structure and phase purity were checked by x-ray diffraction. Linear thermal expansion, magnetoresistance, and magnetostriction up to 12 T measurements were performed in a superconducting coil that produces steady fields up to 12 T. Magnetostriction up to 14 T was measured by using a pulsed magnetic field setup. The resistance was measured with the four-points technique using a dc current parallel to the applied magnetic field. The contacts were made with silver paste. The LTE below room temperature and magnetostriction measurements were done with the strain-gauge technique.[3] In the magnetostriction measurements the strain was measured parallel ($\lambda_{\parallel}$) and perpendicular ($\lambda_{\perp}$) to the applied magnetic field. The volume magnetostriction ω is calculated as $\omega = \lambda_{\parallel} + 2\lambda_{\perp}$. Above room temperature the LTE was measured with a push rod and differential transformer method.

In Fig. 1(a) the LTE of $Pr_{2/3}Ca_{1/3}MnO_3$ at 0, 6, and 12 T is presented. Without an applied magnetic field, the LTE does not show any abrupt change. However, two features are clearly detected. We have calculated the anharmonic lattice contribution by fitting the high-temperature LTE. That gives a Debye temperature $\Theta_D \approx 500$ K. It allows detecting the presence of extra-lattice effects when the measured LTE curve differs from the anharmonic lattice contribution. Below $T \sim 400$ K there is an extra contribution in the LTE that is a hallmark of charge localization, similar to that found in $La_{2/3}Ca_{1/3}MnO_3$.[3–5] The process of localization takes place gradually below T_p as the temperature is lowered. In $La_{2/3}Ca_{1/3}MnO_3$ this process was accompanied by the appearance of short-range ferromagnetic correlations.[5] From the susceptibility measurements in $Pr_{2/3}Ca_{1/3}MnO_3$ (Ref. 19) a positive Weiss temperature is deduced above T_{CO}, which can be an indication of such ferromagnetic correlations. The localized charge orders spatially at T_{CO} as is seen by neutron diffraction.[20] It is remarkable that the crossover from the CL state to the CO state occurs without a discontinuous change in volume. In the LTE curve for $H = 0$ T, the onset of the CO state is detected only with the appearance of a small kink. An abrupt change in the lattice parameters may occur at T_{CO}, but without a significant change in the cell volume. At 6 T and above 80 K the LTE is basically identical to the one at zero field. But at $T \approx 80$ K a structural transition with a $\approx 0.14\%$ change in volume takes place. With $H = 12$ T the onset of this transition is shifted to $T \approx 220$ K. From our experimental results we cannot infer whether the CO state sets in at 12 T. This behavior can be understood as follows: within the double-exchange framework, the magnetic field favors the charge delocalization, as the field is able to align the magnetic moments. The distortion linked to the localized charge is also suppressed and consequently a change in volume is observed. At low temperatures the 6 and 12 T LTE curves essentially coincide with the lattice contribution as no localized charge is present. In the inset of Fig. 1(a) the extra contribution to the LTE over the phonon one at different magnetic fields is shown. The LTE results are in close agreement with the resistance

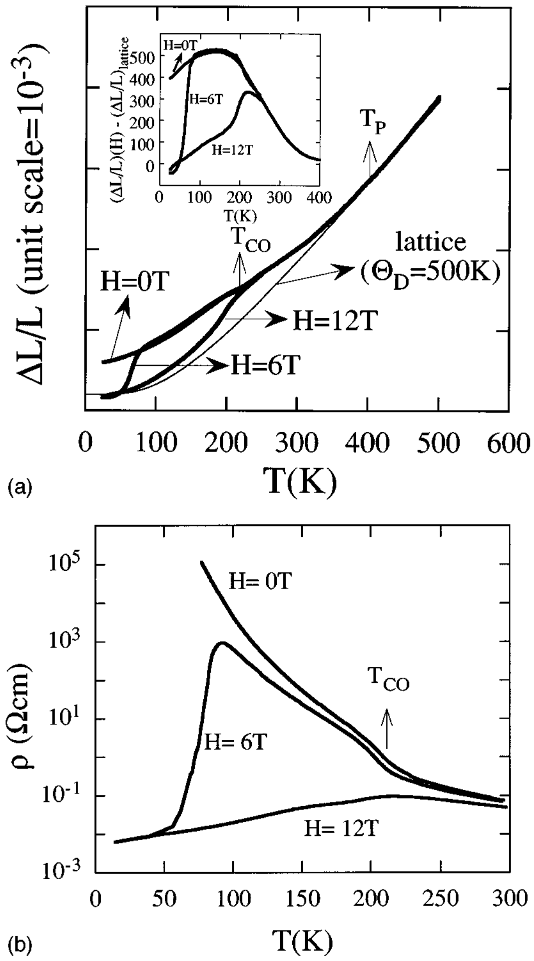

FIG. 1. (a) Linear thermal expansion ($\Delta L/L$) vs temperature at magnetic fields of 0, 6, and 12 T. The phonon lattice contribution (see text) is also shown. The inset shows the difference curves $(\Delta L/L)(H) - (\Delta L/L)_{\mathrm{lattice}}$ for the same magnetic field values. (b) Resistivity vs temperature at magnetic fields of 0, 6, and 12 T.

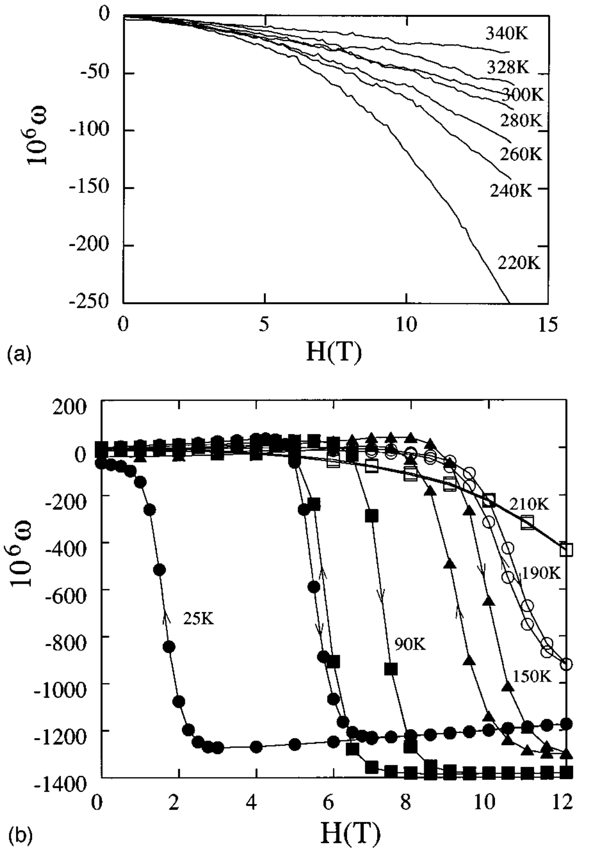

FIG. 2. (a) Volume magnetostriction ω at temperatures above T_{CO}. (b) Volume magnetostriction ω at temperatures below T_{CO}.

data. In Fig. 1(b) the resistivity as a function of temperature is shown. In zero magnetic field the compound behaves as a semiconductor below 300 K. At T_{CO} a kink is seen in the resistance curve. At 6 T an insulator-metal transition appears at $T \approx 80$ K in agreement with the LTE data. Under 12 T the transition occurs at $T \approx 200$ K and it is rather smooth according to the LTE behavior.

The analysis of the magnetostriction and magnetoresistance isotherms allows us to obtain complementary information. In Fig. 2(a) the volume magnetostriction above T_{CO} is shown. The volume magnetostriction in the paramagnetic regime shows a continuous volume change with applied magnetic field. It has the same origin as in $La_{2/3}Ca_{1/3}MnO_3$,[3–5] where a progressive charge delocalization is produced by the magnetic field. A magnetic field greater than our maximum available field (14 T) would be necessary to delocalize the charge completely. In Fig. 2(b) the volume magnetostriction below T_{CO} is shown. The change in volume with applied magnetic field is a first-order transition as suggested by the hysteretical behavior that accompanies the transition. The CO state is destroyed when a high-enough magnetic field is applied and the charge is delocalized, which brings about the volume change.

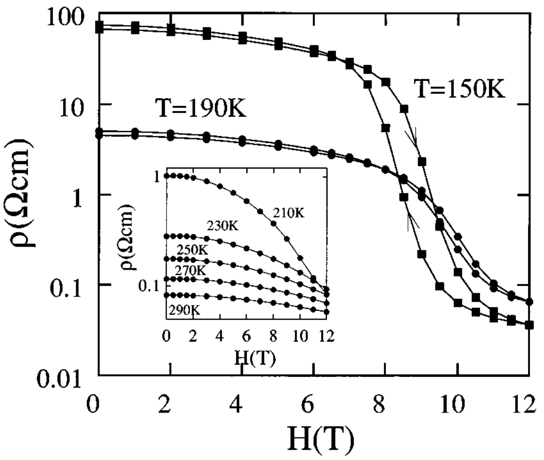

FIG. 3. Resistivity as a function of the applied magnetic field below T_{CO}. The inset shows the isotherms above T_{CO}.

The close relationship between the lattice and the charge is confirmed by the magnetoresistance isotherms (see Fig. 3). Above T_{CO} (inset) the resistance decreases continuously with the magnetic field as in $La_{2/3}Ca_{1/3}MnO_3$.[4,5] Below T_{CO} a first-order insulator-metal transition occurs. The extraordinary resemblance between the MS and MR isotherms supports the idea of a strong charge-lattice coupling in this compound and consequently the possible Jahn-Teller origin for the underlying polaronic behavior. The set of results of $Pr_{2/3}Ca_{1/3}MnO_3$ reveals that there are many competing interactions in this system. Above T_{CO} the positive Weiss temperature supports the presence of a ferromagnetic double-exchange interaction. Between $T_{CO} < T < T_p$ a charge localization, arising from small polarons formation effect, is observed. Below T_{CO} a charge ordering takes place possibly owing to repulsive Coulomb interaction between electrons. Below T_N the compound orders antiferromagnetically due to the superexchange interaction. It is not surprising that the magnetic fields affect the magnetic, electrical, and structural properties so greatly.

To sum up, remarkable lattice effects have been found in $Pr_{2/3}Ca_{1/3}MnO_3$ which stem from the strong spin-charge-lattice coupling in this CMR perovskite. For the first time, to the best of our knowledge, a crossover from a charge-localized state to a charge-ordered state is reported, the result of the different competing interactions in this system. That crossover takes place without a change in volume whereas a first-order structural transition occurs below T_{CO} if a high enough magnetic field is applied.

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