

Direct Observation of High-Temperature Polaronic Behavior in Colossal Magnetoresistive Manganites

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The temperature dependence of the electronic and atomic structure of the colossal magnetoresistive oxides $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$) has been studied using core and valence level photoemission, x-ray absorption and emission, and extended x-ray absorption fine structure spectroscopy. A dramatic and reversible change of the electronic structure is observed on crossing the Curie temperature, including charge localization on and spin-moment increase of Mn, together with Jahn-Teller distortions, both signatures of polaron formation. Our data are also consistent with a phase-separation scenario.

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Agreement is still lacking on the correct theoretical description of the colossal magnetoresistive (CMR) manganites, which are among the most studied materials in condensed matter physics [1]. Although the long-standing double-exchange (DE) model [1,2] provides a qualitatively correct description of these materials, more complex, but not necessarily mutually exclusive, mechanisms such as charge localization via Jahn-Teller distortion (JTD) with polaron formation [3–6] and phase separation [7] have also been proposed.

In particular, manganites with composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) are still a matter of controversy: They have commonly been referred to as “canonical” (i.e., capable of description via the DE model alone) by some authors [1,2], but have been suggested by others to exhibit more complex behavior due to JTDs and polaron formation [3,6].

In an attempt to resolve some of these issues, we have studied the ferromagnetic-to-paramagnetic transition in the CMR compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.3, 0.4$) by temperature-dependent core and valence level photoemission spectroscopy (PS), x-ray absorption and x-ray emission spectroscopy (XAS and XES, respectively), and extended x-ray absorption fine structure (EXAFS). Our measurements reveal significant charge localization onto the Mn atom at high temperature, coupled with local JTD, thus providing a direct observation of polaron formation. These results suggest that the presence of polarons above the Curie temperature (T_C) is a general defining characteristic of all the CMR materials.

The LSMO compounds studied are metallic and in a rhombohedral crystal structure for the full temperature range accessed by our measurements ($110 \leq T \leq 600$ K) [8]. A magnetic phase transition from ferromagnetic to paramagnetic metal occurs at $T_C \approx 370$ K. The PS, XAS,

and XES spectra have been measured on undulator beam line 4.0.2 at the Berkeley Advanced Light Source on high-quality single crystals fractured *in situ* at room temperature in ultrahigh vacuum (ca. $1-2 \times 10^{-10}$ torr). Quantitative PS analysis of core-level spectra confirmed the expected stoichiometries to within experimental accuracy and further showed minimal degrees of surface stoichiometry alteration (within $\pm 5\%$ for all species) or surface contamination (e.g., less than 0.07 monolayers of C contaminant) during the entire length of a given set of experiments (ca. 24 h). Additional bulk-sensitive EXAFS measurements were carried out at the Stanford Synchrotron Radiation Laboratory on BL 4-1.

We have first detected temperature-dependent electronic structure changes by core and valence PS (Figs. 1 and 2). In Fig. 1(a), we show a set of Mn 3s photoelectron spectra obtained in a single temperature scan on a sample of composition $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. These spectra exhibit a doublet due to multiplet splitting of the binding energy (BE), a well-known effect in transition metals which provides a unique probe of the local spin moment of magnetic atoms [9,10], and which has recently been analyzed for several CMR materials [11]. The multiplet energy separation ΔE_{3s} depends on the net valence spin S_v of the emitter (Mn in this case) via $\Delta E_{3s} = (2S_v + 1)J_{3s-3d}^{\text{eff}}$, where J_{3s-3d}^{eff} denotes the effective exchange integral between the 3s and the 3d shells after allowing for final-state intrashell correlation effects [9,10,12]. The Mn 3s splitting changes markedly from 4.50 to 5.55 eV as the temperature is raised from T_C to a higher “saturation” temperature $T_{\text{SAT}} \approx 470$ K beyond which no change is observed. The splitting also tends to return to its original value upon cooling the sample [Figs. 1(a) and 2(a)], but with hysteresis. These data thus indicate a significant increase in the Mn spin moment S_v at high temperature.

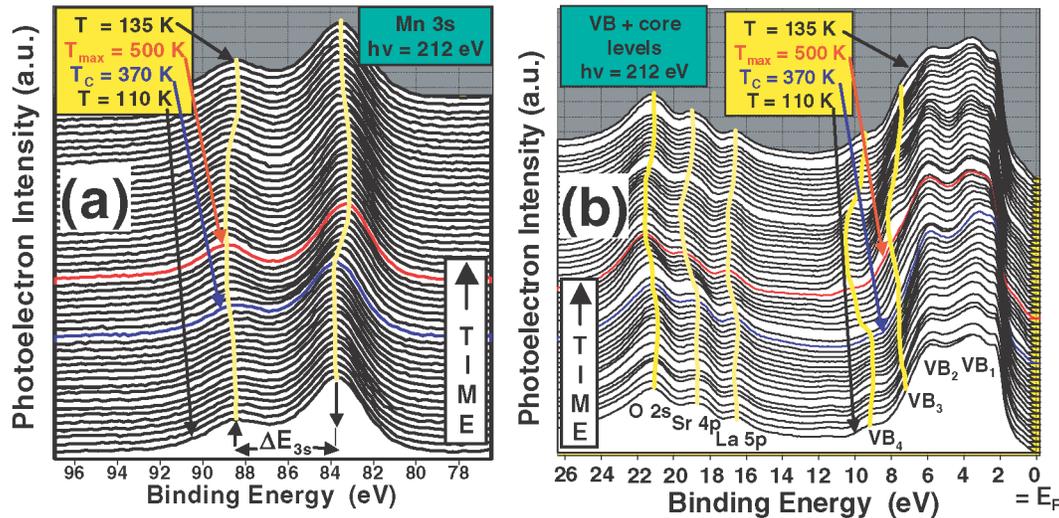


FIG. 1 (color online). Temperature dependent core and valence PS spectra from a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ single crystal. The photon energy was set to 212.5 eV for the Mn 3s spectra (a) and the high-lying core-level (O 2s, Sr 4p, La 5p) and valence band spectra (b), and 652 eV for O 1s spectra (not shown), so that the O 1s photoelectrons had very nearly the same kinetic energy (and thus escape depth, $\Lambda_e \approx 5 \text{ \AA}$) as the Mn 3s electrons. The temperature range was 110 K–500 K, with a step of approximately 20 K. Note core-level shifts at high T , reversible changes in valence features VB_1 – VB_4 , and the lack of any Fermi level shift to within $\approx 50 \text{ meV}$.

Prior experimental results for a range of inorganic Mn compounds yield $J_{3s,3d}^{\text{eff}} \approx 1.1 \text{ eV}$ [9–11,13,14]; our observed change in the Mn 3s splitting thus implies an increase in the average spin moment of Mn from ≈ 3 to $\approx 4\mu_B$, corresponding to about one electron transferred to the Mn atom. Note also that the average position of the Mn 3s doublet changes very little with temperature [Fig. 2(a)]. Simultaneous with the Mn 3s spectra, other core-level (O 1s, O 2s, La 4d, La 5p, Sr 4p) and valence-band spectra were also recorded, with all but O 1s and La 4d being shown in Fig. 1(b). The BEs of all of the O, La, and Sr core peaks increase by between 0.4 and 0.6 eV as the temperature changes from T_C to T_{SAT} , concomitant with the change of the Mn 3s splitting. The high- T increases of the core BEs for the O, La, and Sr core levels thus suggest charge transfer from the O, La, and Sr atoms to the Mn atom, fully consistent with the increase of the

Mn 3s splitting. If charge from the O, La, and Sr atoms is transferred to and localized on the Mn atom, La, Sr, and O core electrons will experience a more positive environment and therefore be detected at higher BE. The absence of any shift in the Fermi level E_F (to within approximately 50 meV) ensures that the observed increase of the core levels BEs is not an artifact due to sample charging.

On cooling the sample, both the Mn 3s splitting and the core BEs return to their original values, but with $\approx 200\text{-K}$ -wide hysteresis loops centered around T_C , and with a time constant of several hours (Fig. 2). The BE loops for O, Sr, and La close on the time scale of our measurement, whereas the Mn splitting closes on a slightly longer time scale. We attribute this difference to additional collective magnetic character in the Mn 3s spectrum, perhaps due to ferromagnetic cluster formation, resulting in a slower time scale.

To explore the depth distribution of these effects below the surface, we studied the same temperature-dependent effects when the core spectra were excited with higher photon energies so as to change the photoelectron escape depth Λ_e from $\approx 5 \text{ \AA}$ (cf. Figs. 1 and 2) to $\approx 15 \text{ \AA}$ (corresponding to an average emission depth of roughly three unit cells); these data indicate that the observed electronic structure changes affect more than the outermost surface layers. Moreover, although not shown here, more bulk-sensitive XAS spectra measured over the O K and Mn L edges and detected with secondary electrons of $\approx 100 \text{ eV}$ kinetic energy, as well as fluorescence photons, show remarkable changes when the temperature is varied through T_C and up to T_{SAT} . Finally, the most bulk-sensitive XES data reveal a strong temperature dependence of the O $2p \rightarrow \text{O } 1s$ and Mn $3d \rightarrow \text{Mn } 2p$

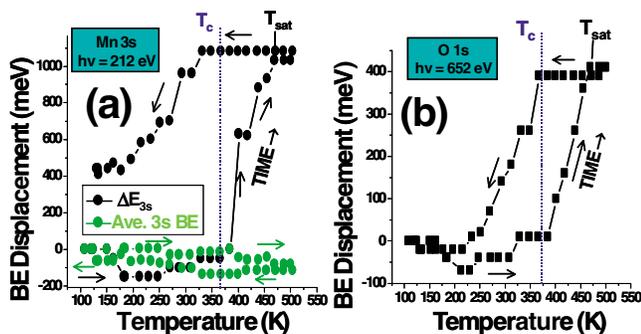


FIG. 2 (color online). Reversibility and hysteresis in the temperature dependence of (a) Mn 3s and (b) O 1s core level BEs of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, including the Mn 3s multiplet splitting.

transitions on crossing T_C and approaching T_{SAT} . Thus, we estimate that these effects take place over at least the first 30–50 Å inward from the surface, or roughly 6–10 unit cells, and are likely to be bulk phenomena. We have also seen identical effects in experiments on $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, with the only difference being that T_{SAT} does not occur until about 150 K above T_C , as compared to 100 K above T_C for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

We now ask whether these dramatic electronic structure changes are accompanied by local JTDs of atomic positions in the oxygen octahedra surrounding each Mn atom, often considered a structural signature of polaron formation. Several prior structural studies provided evidence for the existence of polarons in other “noncanonical” manganites, suggesting that the existence of polarons is directly related to JTDs [4,5], but we now consider the presence of JTDs in these canonical compounds. As a first point, the long-time-scale hysteresis of the temperature-driven change of the electronic structure (Fig. 2) qualitatively suggests the presence of slower-relaxing atomic displacements that are in turn responsible for the perturbations of the core and valence levels we observe. However, no obvious modification of the long-range crystal structure is shown by x-ray crystallography, since our samples are rhombohedral at all temperatures studied [8]. We have thus explored the possibility of short-range modifications in structure on passing T_C via bulk-sensitive Mn K -edge EXAFS measurements performed on a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample in the fluorescence-yield mode.

The EXAFS data permit extracting the variance of the Mn-O bond length distribution, σ^2 (Fig. 3) [5]. At low temperatures, the σ^2 of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ approaches that of the JTD-free CaMnO_3 material [5]. As the temperature increases toward T_C , σ^2 increases more rapidly than expected from a purely vibrational analysis via the correlated-Debye model [15]. Above T_C , σ^2 increases more gradually, again consistent with a Debye-model broadening. These data for LSMO suggest a JTD that develops with increasing temperature and saturates once the system becomes paramagnetic, as observed in a previous EXAFS study of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (cf. Fig. 3) [5]. The size of the apparent JTD in our Sr-doped compound is only about half that in the Ca-doped compound, a difference which may be the microscopic cause of the metallic state that survives in the paramagnetic state of the Sr-doped (but not Ca-doped) materials.

Our data thus provide direct experimental evidence for the presence of polarons in the LSMO compounds, since they show both charge localization onto the Mn atom and JTDs. There is theoretical support for this, since Millis *et al.* predicted that, for $x > 0.2$ in LSMO, strong electron-phonon coupling should localize the electrons via polarons, with the JT energy remaining important even in the metallic state [3]. It may at first sight seem that polaronic electron localization and metallic

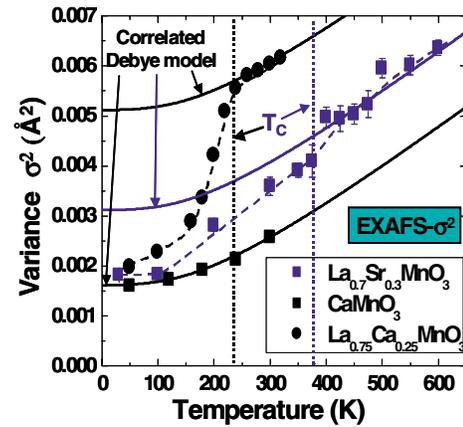


FIG. 3 (color online). EXAFS results for the variance of the Mn-O bond length distribution σ^2 as a function of temperature for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, compared with similar data from [5] for CaMnO_3 and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$. The solid line through the CaMnO_3 data is a correlated-Debye fit with $\Theta_{CD} = 860$ K. The same curve is drawn through the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ data with 0.0015 Å² and 0.0035 Å² offsets, respectively. Dashed curves represent the experimental data. Curie temperatures of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are indicated.

conduction (our samples are metallic for all temperatures) are mutually exclusive, but there is experimental evidence suggesting that in fact they are not. For example, neutron scattering measurements with pair distribution function analysis (PDF) have shown that for LSMO up to $x = 0.4$ local JTDs are observed even in the metallic phase [6], with somewhat larger magnitudes than reported here. Our results are in better agreement with another recent EXAFS study in which a distortion in the metallic phase is observed but to a lesser degree than in the PDF analysis [16].

It is also possible, and consistent with our data, that the polarons have a magnetic character, i.e., that above T_C the carriers become localized as the lattice is distorted and magnetically polarize the neighboring Mn atoms, forming ferromagnetic clusters. Experimental evidence for the existence of such “magnetic polarons” has in fact been reported for a related class of compounds [4]. Recent theoretical studies also predict the presence of ferromagnetic clusters in the temperature range $T_C \leq T \leq T^*$, with T^* adding a new temperature scale, and these clusters growing in size when the temperature is reduced from T^* to below T_C [17]. All of our results are consistent with this scenario as well, and it is possible that the temperature T^* could be identified with our temperature T_{SAT} .

Finally, we comment on the possibility of phase separation in the LSMO system, which has been discussed previously from both experimental and theoretical viewpoints [6,7,18]. In order to determine whether the change in electronic structure that we observe is consistent with such a scenario, we have fitted the Mn 3s

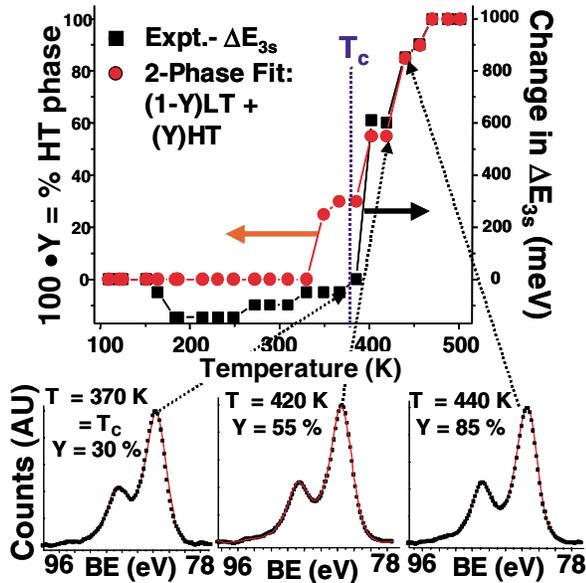


FIG. 4 (color online). Two-phase fits of the Mn 3s temperature-dependent core spectra of Fig. 1(a) with a linear superposition of the spectra at low ($T < 200$ K) and high temperatures ($T \geq T_{\text{SAT}}$). The variation of the multiplet splitting ΔE_{3s} (black points and curve in top panel) is shown for comparison. Fits to spectra at three specific temperatures are shown in the lower panels.

temperature-dependent core spectra with a linear superposition of the spectra at low (< 200 K) and high temperature ($\geq T_{\text{SAT}}$). The only free parameter is the fraction Y of the high-temperature spectrum, and Fig. 4 demonstrates the excellent agreement between experiment and these two-phase fits. Similar agreement was found for fits of the O, La, and Sr core-level spectra taken over $T_C < T < T_{\text{SAT}}$ (not shown), thus further implying the presence of unique low and high-temperature electronic states and spectroscopic behavior that is at least consistent with the presence of phase separation in these materials. Since our core-level measurements probe only the short-range electronic structure, they do not provide any information on the sizes of the domains of these two phases.

This study thus provides unexpected results which act to clarify and unify our understanding of the CMR materials. In particular, polaron formation, which in LSMO is directly observed via both electronic and atomic structure changes, is shown to be an important defining characteristic of the high-temperature paramagnetic state of the CMR materials, even when the electronic phase is metallic. Future temperature-dependent studies of this type, involving both core and valence level spectroscopies, could shed important light on these and other strongly correlated materials.

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