

**Direct observation of electron doping in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  using x-ray absorption spectroscopy**C. Mitra,<sup>1,\*</sup> Z. Hu,<sup>2,†</sup> P. Raychaudhuri,<sup>3,‡</sup> S. Wirth,<sup>1</sup> S. I. Csiszar,<sup>4</sup> H. H. Hsieh,<sup>5</sup> H.-J. Lin,<sup>5</sup> C. T. Chen,<sup>5</sup> and L. H. Tjeng<sup>2</sup><sup>1</sup>Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany<sup>2</sup>II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany<sup>3</sup>School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom<sup>4</sup>Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands<sup>5</sup>Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan

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We report an x-ray absorption spectroscopic (XAS) study on thin films of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ . The measurements clearly show that the cerium is in the Ce(IV) valence state, and that the manganese is present in a mixture of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  valence states. These data demonstrate that  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  is an electron-doped colossal magnetoresistive manganite, a finding that may open up opportunities for device applications as well as for further research on the colossal magnetoresistance phenomenon in these materials.

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Hole doped rare-earth manganites of the form  $R_{1-x}A_x\text{MnO}_3$  ( $R$ =rare earth,  $A$ =divalent cation) have been at the focus of attention in recent times in the field of ferromagnetic oxides.<sup>1,2</sup> The interest in these compounds stems from a variety of reasons. These compounds exhibit a large magnetoresistance, coined as ‘‘colossal magnetoresistance’’ (CMR), close to their ferromagnetic transition temperature ( $T_c$ ) which makes them potential candidates for device applications. These materials exhibit a strong interplay between spin, charge, and orbital degrees of freedom, due to the competition of the various relevant energy scales that are of comparable magnitude. All these give rise to a wide variety of phenomena such as electronic phase separation, charge ordering, spin glass order, and half metallicity.<sup>2</sup> It is therefore of prime fundamental interest to study the rich phase diagram of these compounds as a function of doping  $x$  and size of the  $R/A$  cation.<sup>3</sup>

The basic physics of the hole doped rare-earth manganites can be understood from an interplay of a strong Hund’s rule coupling in the manganese and the Jahn-Teller distortion.<sup>4</sup> The divalent cation in these compounds brings the manganese from a  $\text{Mn}^{3+}$  valence state in the parent compound into a mixture of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . Double exchange between the  $\text{Mn}^{3+}$  and the  $\text{Mn}^{4+}$  cations drives the insulating antiferromagnetic ground state present in the parent compound ( $\text{LaMnO}_3$ ) into a ferromagnetic metallic ground state for  $x \geq 0.2$  in the doped compound. Above  $T_c$ , for compounds such as  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , the decrease in mobility of the electrons due to spin disorder localizes the carriers via the formation of Jahn-Teller polarons. This local deformation around the Jahn-Teller cation  $\text{Mn}^{3+}$  gives rise to a polaronic insulating state.<sup>5</sup> At temperatures close to  $T_c$ , i.e., at the transition between the two phases, an external magnetic field can give rise to CMR. A salient question to ask in this context is: Can one induce a ferromagnetic metallic ground state by doping electrons instead of holes in the parent compound  $\text{LaMnO}_3$ ? Electron doping is expected to drive the manganese into a mixture of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ . This question is particularly relevant in manganites since manganese can exist in many valence states. In addition, the system has an intrinsic symmetry since  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  are both non Jahn-

Teller ions whereas  $\text{Mn}^{3+}$  is a Jahn-Teller ion. Thus, the basic physics in terms of Hund’s rule coupling and Jahn-Teller effect could operate in the electron doped phase as well. The existence of an electron doped manganite is not merely of academic interest since it also opens up possibilities for fabricating bipolar devices<sup>6</sup> using the electron and hole doped manganites where both spin and charge are utilized.

The crucial issue that we have to address now is whether it is really possible to electron dope  $\text{LaMnO}_3$ . One compound, which displays properties remarkably similar to  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ , is the cerium doped manganite  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ .  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  has a ferromagnetic metallic ground state with  $T_c \sim 250$  K.<sup>7-9</sup> The ferromagnetic transition is accompanied by a metal-insulator transition and the system has a magnetoresistance  $[\rho(0) - \rho(H)]/\rho(0)$  in excess of 70% at a field of 1.5 T.<sup>8</sup> It has been shown very recently that a tunnel junction made of the hole doped  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  exhibits rectifying characteristics<sup>6</sup> in the polaronic insulating state at temperatures  $T > T_c$ . While this result may suggest that cerium doping drives the manganese in a mixture of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  valencies, there has been so far no direct evidence for electron doping in this compound. One of the main difficulties in this compound is that the system forms in *single phase* only in the epitaxial thin film form,<sup>9</sup> deposited through the energetic pulsed laser ablation process (other methods failed in this respect<sup>10</sup>). This precludes the possibility of using conventional techniques such as chemical analysis. In addition, it is *a priori* not obvious that cerium has enough reducing power to drive  $\text{Mn}^{3+}$  towards the electro-positive  $\text{Mn}^{2+}$ , in view of the observation that formally tetravalent  $\text{CeO}_2$  has an extremely large amount of oxygen holes.<sup>11</sup>

In this paper we provide a direct evidence of the Ce and Mn valence states in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  through x-ray absorption measurements on epitaxial thin films of these compounds.

Bulk polycrystalline targets of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and  $\text{LaMnO}_3$  were prepared by a solid state reaction route as reported earlier.<sup>9</sup> Using these targets, epitaxial films were

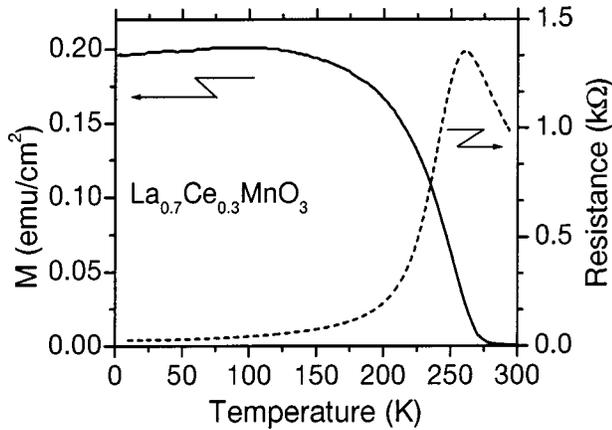


FIG. 1. Temperature dependence of the magnetization (full line, left scale) and resistance (dashed line, right scale) of the investigated  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  thin film sample. The magnetization measurement was conducted in an applied field of 1 kOe.

deposited by pulsed laser deposition (PLD) on  $\text{SrTiO}_3$  (STO) substrate, using a KrF excimer laser. The substrate temperature was kept between 790 and 800 °C at all times. The laser energy density was approximately 3 J/cm<sup>2</sup> with a repetition rate of 9 Hz and the laser wavelength was 248 nm. The  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  film was grown at an oxygen pressure of 400 mTorr whereas the  $\text{LaMnO}_3$  film was deposited at 100 mTorr. The lower oxygen pressure during growth of the  $\text{LaMnO}_3$  film was necessary to avoid over-oxygenation which can induce considerable hole doping in this compound. After deposition, the laser ablation chamber was vented with high purity oxygen and the substrate cooled down to room temperature. Details of the x-ray characterization can be found in Ref. 9. Several reflections were taken in the x-ray analysis to ascertain the single phase nature of the films.

Magnetization was measured using a Quantum Design superconducting quantum interference device (SQUID). The  $\text{LaMnO}_3$  had a weak ferromagnetic transition around 115 K. This weak ferromagnetism could be due to a slight oxygen non-stoichiometry in the film as has been observed before in bulk samples.<sup>12</sup> Also, a weak ferromagnetic moment in the *A*-type antiferromagnet  $\text{LaMnO}_3$  is believed to arise from the Dzyaloshinsky-Moryia interaction.<sup>2</sup> The temperature dependence of the magnetization for the film of interest  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  is shown in Fig. 1. A  $T_c \approx 260$  K can be inferred. From the magnetization data there is no sign of any magnetic impurity phase in our sample. In addition, the hallmark of the CMR material is depicted in Fig. 1: a maximum of the resistance in dependence on temperature near  $T_c$ . There is a similarity in the magnetic properties of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and its hole doped analog  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  in the sense that both have similar Curie temperatures. It is known that perovskite rare-earth manganites such as  $\text{LaMnO}_3$  can accept a large excess of oxygen via the formation of cation vacancies inducing hole doping in the parent compound.<sup>12</sup> Therefore, to confirm that the system  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  is indeed electron doped and the magnetic ordering does not occur due to the existence of  $\text{Mn}^{4+}$  and

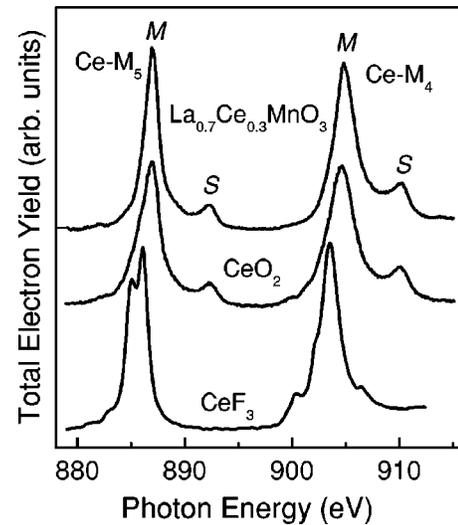


FIG. 2.  $\text{Ce-}M_{4,5}$  XAS spectra of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and of  $\text{CeO}_2$  for a tetravalent and  $\text{CeF}_3$  for a trivalent reference.

$\text{Mn}^{3+}$  valence states resulting from over-oxygenation of the film one must study both the Ce as well as the Mn valence states.

The  $\text{Ce-}M_{4,5}$  and  $\text{Mn-}L_{2,3}$  XAS measurements were performed using the Dragon beamline at the Synchrotron Radiation Research Center (SRRC) in Taiwan. The experimental photon energy resolution was approx. 0.2 and 0.3 eV at the  $\text{Mn-}L_{2,3}$  and  $\text{Ce-}M_{4,5}$  thresholds, respectively. The spectra were recorded at room temperature, employing the total electron-yield method by measuring the sample drain current to ground. In addition, the incident beam flux was monitored simultaneously with a gold mesh in the beam line which allowed the obtained spectra to be normalized very accurately.

It is well known that the x-ray absorption spectra at the rare-earth  $M_{4,5}$  and the 3*d* transition metal  $L_{2,3}$  thresholds are highly sensitive to the valence state and the distribution of valence electrons between the metal ion and the ligand orbitals since the experimental spectral structures can be well reproduced by atomic multiplet calculations.<sup>13-17</sup> Figure 2 shows the  $\text{Ce-}M_{4,5}$  XAS spectrum of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ . For comparison, the spectra of the reference materials  $\text{CeO}_2$  and  $\text{CeF}_3$  are also included. The  $\text{Ce-}M_{4,5}$  XAS spectrum of the formally tetravalent Ce-compound  $\text{CeO}_2$  consists of a single main structure (*M*) at 887 eV and a satellite (*S*) at  $\approx 6$  eV above the main peak. The tetravalence of the Ce in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  can be easily recognized since the spectral features are very similar to those of  $\text{CeO}_2$ . In tetravalent compounds such as  $\text{CeO}_2$ , the Ce-4*f* and O-2*p* covalence can be described<sup>14</sup> in a configuration interaction scheme, in which the ground state is given by  $|g\rangle = \alpha |4f^0\rangle + \beta |4f^1\bar{L}\rangle$  ( $\bar{L}$  refers to the ligand hole) while the final states can be labeled as the bonding and antibonding states of  $3d^9 4f^1$  and  $3d^9 4f^2\bar{L}$ . These two final states give rise to the main peak and the higher energy satellite. By an interference effect<sup>14</sup> the intensity of the antibonding state is strongly reduced, especially if the charge transfer energy between the two configurations in the ground state and the final state is

nearly the same. Therefore, the higher energy antibonding state appears usually as a weak satellite. Nevertheless, the presence of such a weak satellite indicates that the  $4f$  occupancy is about 0.5, as a careful theoretical analysis has shown.<sup>14</sup>

In contrast to the single-peaked structure in Ce(IV)-compounds, the main spectral features of the trivalent Ce compound  $\text{CeF}_3$  exhibits a more complicated multiplet structure which could be very well reproduced by atomic multiplet calculations.<sup>13</sup> It is well known<sup>18</sup> that the  $M_{4,5}$  spectrum of trivalent rare-earth elements is shifted to lower energy by more than 1 eV with a decrease in their valence. Here, we observe a shift of  $\cong 1.5$  eV towards lower energy in the  $\text{CeF}_3$  spectrum with respect to the spectra of  $\text{CeO}_2$  and  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ . Therefore, the Ce- $M_{4,5}$  spectrum of Ce(IV) compounds is very sensitive to trivalent impurities. One can see that even  $\text{CeO}_2$  has some very small  $\text{Ce}^{3+}$  content as suggested by the small asymmetry in the two peaks near the low energy side. The main peaks of the Ce  $M_{4,5}$ -edge in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ , however, are perfectly symmetric, indicating a pure Ce(IV) valence state of Ce in this compound.

The existence of Ce(IV), however, still does not confirm that the sample is electron doped. In the past it has been shown that in a bulk polycrystalline sample some amount of  $\text{CeO}_2$  remains unreacted though the epitaxial thin film of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  forms in single phase.<sup>9</sup> Thus, to conclusively establish that it is indeed an electron doped system one has to search for a corresponding replacement of  $\text{Mn}^{3+}$  by  $\text{Mn}^{2+}$  as well. We have measured the Mn- $L_{2,3}$  XAS spectra to investigate the valence state of Mn in the ground state. Figure 3 shows the Mn- $L_{2,3}$  spectra of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and—for comparison—of  $\text{MnO}_2$ ,  $\text{LaMnO}_3$  and  $\text{MnO}$  for  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{2+}$  references, respectively. The  $\text{LaMnO}_3$  spectrum is similar to that obtained previously.<sup>19,20</sup> It is a well known fact<sup>21-23</sup> that an increase of the metal ion valence by one results in shift of the  $L_{2,3}$  XAS spectra to higher energy by about 1 eV or more. In Fig. 3 we can see a shift towards higher energy from bottom to top in a sequence of increasing Mn valence from  $\text{Mn}^{2+}$  ( $\text{MnO}$ ) to  $\text{Mn}^{3+}$  ( $\text{LaMnO}_3$ ) and further to  $\text{Mn}^{4+}$  ( $\text{MnO}_2$ ). In comparison to undoped  $\text{LaMnO}_3$ , in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  we can see new and sharp low energy structures at nearly the same energy position as in the  $\text{MnO}$  spectrum. These sharp structures at around 642 eV are a reliable benchmark of the appearance of a divalent Mn state since they are hardly smeared by background or other structures. The observed spectral features indicate the existence of a  $\text{Mn}^{2+}$  component in addition to  $\text{Mn}^{3+}$  in the single phase  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  compound. In order to estimate the  $\text{Mn}^{2+}$  content, the *normalized* spectrum of  $\text{LaMnO}_3$  has been subtracted from that of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  (the resultant difference spectrum is labeled “difference” in Fig. 3). The most reasonable difference spectrum was obtained if the spectral weight of the subtracted  $\text{LaMnO}_3$  spectrum was taken as 82%. The main structures of the difference spectrum are found at the same energy position as the prominent features of the  $\text{MnO}$  spectrum (as indicated by the vertical line in Fig. 3) and the overall appearance of the difference and the  $\text{MnO}$  spectra is very similar. However, the difference spectrum in its details is not exactly

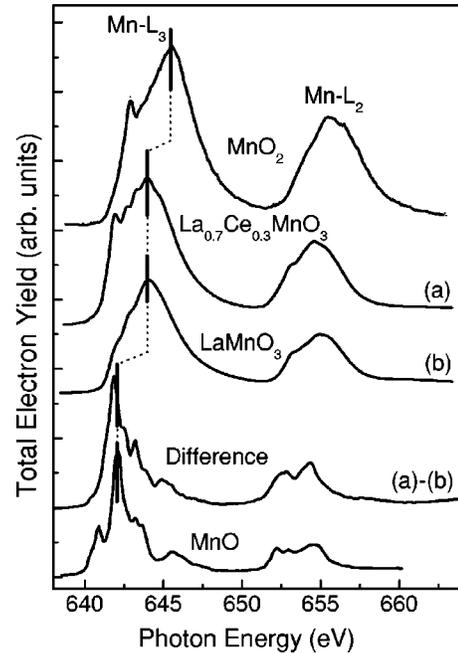


FIG. 3. Mn- $L_{2,3}$  XAS spectra of  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  (a) and for comparison of  $\text{MnO}_2$ ,  $\text{LaMnO}_3$  (b) and  $\text{MnO}$  for  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  references, respectively. The curve labeled “difference” [(a),(b)] is the difference between the  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and the  $\text{LaMnO}_3$  spectra. In comparison to the  $\text{MnO}$  spectrum, this difference curve clearly indicates the existence of  $\text{Mn}^{2+}$  in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ .

the same as that of  $\text{MnO}$ . As an example, there is a sharp shoulder (at around 641 eV) below the main peak found in  $\text{MnO}$  which is nearly absent in the difference spectrum. Such subtle distinctions are to be expected because of the difference in the local symmetry of Mn in these two compounds. In fact, there is an additional feature just above the main peak in the  $L_3$  edge of the difference spectrum and the main peak is further shifted to lower energy by 0.2 eV. Also, a change at the Mn  $L_2$  edge is clearly seen. Moreover, the appearance of minority spin carriers (with spin antiparallel to the magnetization) at the Fermi energy  $E_F$  was proposed recently<sup>24,25</sup> which may possibly lead to an intermediate spin state. The latter, however, requires further experimental evidence since Mn is much more commonly observed in a high spin state (as in  $\text{MnO}$ ) due to the usually large on-site Hund’s rule coupling.

In order to estimate the contents of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  from the corresponding spectral weights (18 and 82 %, respectively) one needs to bear in mind that, formally,  $\text{Mn}^{2+}$  has five holes in the  $3d$  orbital whereas  $\text{Mn}^{3+}$  has six holes. Assuming completely ionic  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ , the content of  $\text{Mn}^{2+}$  is about 20%. However, the strong covalence of  $\text{Mn}^{3+}$  may reduce this number slightly. Even though the latter effect is difficult to account for the main error originates from the uncertainty in determining the spectral weight of  $\text{Mn}^{2+}$  and hence, we estimate the  $\text{Mn}^{2+}$ -content in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  to  $20(\pm 4)\%$ . The deviation from the nominal 30% Ce doping may be due to the fact that the system might have been over-oxygenated which gives rise to an excess of  $\text{Mn}^{3+}$  content.

In summary, we have shown from XAS measurements that  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  is an electron doped manganite where the formally tetravalent cerium drives the manganese into a mixture of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  valence states. Thus, it is tempting to think that the ferromagnetism in this compound is brought about by the double exchange between  $\text{Mn}^{2+}/\text{Mn}^{3+}$  ions. The remarkable similarity between this compound and its hole doped counterpart  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  provides further motivation to explore the electron doped phase in detail. One issue of particular interest is the spin state of manganese in  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ . The recent observation of a large positive magnetoresistance in ferromagnetic tunnel junctions involving  $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$  and a hole doped manganite as the ferromagnetic electrodes suggests that the manganese in this

compound may be in an intermediate spin state.<sup>25</sup> This might modify our understanding of the origin of CMR in this compound in terms of on-site Hund's rule coupling. We hope that these results will motivate further studies on the electron doped phase of rare-earth manganites.

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