direct observation of electron doping in La$_{0.7}$Ce$_{0.3}$MnO$_3$ using x-ray absorption spectroscopy

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We report on a X-ray absorption spectroscopic (XAS) study on a thin film of La$_{0.7}$Ce$_{0.3}$MnO$_3$, a manganite which was previously only speculated to be an electron doped system. The measurements clearly show that the cerium is in the Ce(IV) valence state and that the manganese is present in a mixture of Mn$^{2+}$ and Mn$^{3+}$ valence states. These data unambiguously demonstrate that La$_{0.7}$Ce$_{0.3}$MnO$_3$ is an electron doped colossal magnetoresistive manganite, a finding that may open up new opportunities both for device applications as well as for further basic research towards a better modelling of the colossal magnetoresistance phenomenon in these materials.

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Hole doped rare-earth manganites of the form R$_{1-x}$A$_x$MnO$_3$ (R = rare-earth, A = divalent cation) have been at the focus of attention in recent times in the field of ferromagnetic oxides. 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. 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.

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. The divalent cation in these compounds brings the manganese from a Mn$^{3+}$ valence state in the parent compound into a mixture of Mn$^{3+}$ and Mn$^{4+}$. Double exchange between the Mn$^{3+}$ and the Mn$^{4+}$ cations drives the insulating antiferromagnetic ground state present in the parent compound (LaMnO$_3$) into a ferromagnetic metallic ground state for $x > 0.2$ in the doped compound. Above $T_c$, for compounds such as La$_{0.7}$Ca$_{0.3}$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 Mn$^{3+}$ gives rise to a polaronic insulating state. 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 LaMnO$_3$? Electron doping is expected to drive the manganese into a mixture of Mn$^{2+}$ and Mn$^{3+}$.

The crucial issue that we have to address now is whether it is really possible to electron dope LaMnO$_3$. One compound, which displays properties remarkably similar to La$_{0.7}$Ca$_{0.3}$MnO$_3$, is the cerium doped manganite La$_{0.7}$Ce$_{0.3}$MnO$_3$. La$_{0.7}$Ce$_{0.3}$MnO$_3$ has a ferromagnetic metallic ground state with $T_c \sim 250$ K. 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. It has been shown very recently that a tunnel junction made of the hole doped La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ce$_{0.3}$MnO$_3$ exhibits rectifying characteristics 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 Mn$^{2+}$ and Mn$^{3+}$ valencies, there has been so far no direct evidence for electron doping in this compound. One of the main difficulty in this compound is that the system forms in single phase only in the epitaxial thin film form deposited through the energetic pulsed laser ablation process (other methods...
failed in this respect. 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 Mn$^{4+}$ towards the electro positive Mn$^{3+}$, in view of the observation that formally tetravalent CeO$_2$ has an extremely large amount of oxygen holes.

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

Bulk polycrystalline targets of La$_{0.7}$Ce$_{0.3}$MnO$_3$ and LaMnO$_3$ were prepared by a solid state reaction route as reported earlier. Using these targets, epitaxial films were deposited by pulsed laser deposition (PLD) on SrTiO$_3$ (STO) substrate, using a KrF excimer laser. The substrate temperature was kept between 790°C and 800°C at all times. The laser energy density was approximately 3 J/cm$^2$ with a repetition rate of 9 Hz and the laser wavelength was 248 nm. The La$_{0.7}$Ce$_{0.3}$MnO$_3$ film was grown at an oxygen pressure of 400 mTorr whereas the LaMnO$_3$ film was deposited at 100 mTorr. The lower oxygen pressure during growth of the 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. 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 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. Also, a weak ferromagnetic moment in the A-type antiferromagnet LaMnO$_3$ is believed to arise from the Dzyaloshinskii-Moryia interaction. The temperature dependence of the magnetization for the film of interest, La$_{0.7}$Ce$_{0.3}$MnO$_3$, is shown in Fig. 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. A a maximum of the resistance in dependence on temperature near $T_C$. There is a similarity in the magnetic properties of La$_{0.7}$Ce$_{0.3}$MnO$_3$ and its hole doped analogue La$_{0.7}$Ca$_{0.3}$MnO$_3$ in the sense that both have similar Curie temperatures. It is known that perovskite rare-earth manganites such as LaMnO$_3$ can accept a large excess of oxygen via the formation of cation vacancies inducing hole doping in the parent compound. Therefore, to confirm that the system La$_{0.7}$Ce$_{0.3}$MnO$_3$ is indeed electron doped and the magnetic ordering does not occur due to the existence of Mn$^{4+}$ and 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 Ce-M$_{4.5}$ and 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 Mn-L$_{2,3}$ and 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 3d 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. Fig. shows the Ce-M$_{4.5}$ XAS spectrum of La$_{0.7}$Ce$_{0.3}$MnO$_3$. For comparison, the spectra of the reference materials CeO$_2$ and CeF$_3$ are also included. The Ce-M$_{4.5}$ XAS spectrum of the formally tetravalent Ce-compound 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 La$_{0.7}$Ce$_{0.3}$MnO$_3$ can be easily recognized since the spectral features are very similar to those of CeO$_2$. In tetravalent compounds like CeO$_2$, the Ce–4f and O–2p covalence can be described in a configuration interaction scheme, in which the ground state is given by $|g\rangle = \alpha|4f^0\rangle + \beta|4f^1L\rangle$ ($L\rangle$ refers to the ligand hole) while the final states can be labelled as the bonding and anti-bonding states of $3d^04f^1$ and $3d^04f^2L$. These two final states give rise to the main peak and the higher energy satellite. By an interference effect the intensity of the anti-bonding 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 anti-bonding 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[^9].

In contrast to the single-peaked structure in Ce(IV)-compounds, the main spectral features of the trivalent Ce-compound CeF₃ exhibits a more complicated multiplet structure which could be very well reproduced by atomic multiplet calculations. It is well known that the Mn-L₂,₃ spectrum of trivalent rare-earth elements is very sensitive to trivalent impurities. One can see that even CeO₂ has some very small Ce³⁺ content as suggested by the small asymmetry in the two peaks near the low energy side. The main peaks of the Ce M₄,5-edge in La₀.₇Ce₀.₃MnO₃, 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 CeO₂ remains unreacted though the epitaxial thin film of La₀.₇Ce₀.₃MnO₃ forms in single phase[^8]. Thus, to conclusively establish that it is indeed an electron doped system one has to search for a corresponding replacement of Mn³⁺ by Mn²⁺ as well. We have measured the Mn-L₂,₃ XAS spectra to investigate the valence state of Mn in the ground state. Fig. 3 shows the Mn-L₂,₃ spectra of La₀.₇Ce₀.₃MnO₃ (a) and for comparison of MnO₂, LaMnO₃ (b) and MnO for Mn⁴⁺, Mn³⁺ and Mn²⁺ references, respectively. The LaMnO₃ spectrum is similar to that obtained previously[^20]. It is a well known fact[^21] that an increase of the metal ion valence by one results in shift of the L₂,₃ 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 Mn²⁺ (MnO) to Mn³⁺ (LaMnO₃) and further to Mn⁴⁺ (MnO₂). In comparison to undoped LaMnO₃, in La₀.₇Ce₀.₃MnO₃ we can see new and sharp low energy structures at nearly the same energy position as in the 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 Mn²⁺ component in addition to Mn³⁺ in the single phase La₀.₇Ce₀.₃MnO₃ compound. In order to estimate the Mn²⁺ content, the normalized spectrum of LaMnO₃

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[^8]: Reference text about Mn-L₂,₃ XAS spectra in Ce(IV) compounds.
[^9]: Reference text about Mn-L₂,₃ XAS spectra in Ce(IV) compounds.
[^10]: Reference text about Mn-L₂,₃ XAS spectra in Ce(IV) compounds.
[^11]: Reference text about Mn-L₂,₃ XAS spectra in Ce(IV) compounds.

FIG. 2: Ce-M₄,₅ XAS spectra of La₀.₇Ce₀.₃MnO₃ and of CeO₂ for a tetravalent and CeF₃ for a trivalent reference.

FIG. 3: Mn-L₂,₃ XAS spectra of La₀.₇Ce₀.₃MnO₃ (a) and for comparison of MnO₂, LaMnO₃ (b) and MnO for Mn⁴⁺, Mn³⁺ and Mn²⁺ references, respectively. The curve labeled “difference” ((a)-(b)) is the difference between the La₀.₇Ce₀.₃MnO₃ and the LaMnO₃ spectra. In comparison to the MnO spectrum, this difference curve clearly indicates the existence of Mn²⁺ in La₀.₇Ce₀.₃MnO₃.
has been subtracted from that of La$_{0.7}$Ce$_{0.3}$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 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 MnO spectrum (as indicated by the vertical line in Fig. 3) and the overall appearance of the difference and the MnO spectra is very similar. However, the difference spectrum in its details is not exactly the same as that of MnO. As an example, there is a sharp shoulder (at around 641 eV) below the main peak found in 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.

In order to estimate the contents of Mn$^{2+}$ and Mn$^{3+}$ from the corresponding spectral weights (18% and 82%, respectively) one needs to bear in mind that, formally, Mn$^{2+}$ has 5 holes in the 3d-orbital whereas Mn$^{3+}$ has 6 holes. Assuming completely ionic Mn$^{2+}$ and Mn$^{3+}$, the content of Mn$^{2+}$ is about 20%. However, the strong covalence of 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 Mn$^{2+}$ and hence, we estimate the Mn$^{2+}$-content in La$_{0.7}$Ce$_{0.3}$MnO$_3$ to 20(±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 Mn$^{3+}$-content.

In summary, we have shown from XAS measurements that La$_{0.7}$Ce$_{0.3}$MnO$_3$ is an electron doped manganite where the formally tetravalent cerium drives the manganese into a mixture of Mn$^{2+}$ and Mn$^{3+}$ valence states. Thus, it is tempting to think that the ferromagnetism in this compound is brought about by the double exchange between Mn$^{2+}$/Mn$^{3+}$ ions. The remarkable similarity between this compound and its hole doped counterpart, La$_{0.7}$Ca$_{0.3}$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 La$_{0.7}$Ce$_{0.3}$MnO$_3$. Recent observation of a large positive magnetoresistance in ferromagnetic tunnel junctions involving La$_{0.7}$Ce$_{0.3}$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. This would significantly modify our understanding of the origin of CMR in this compound in terms of on-site Hund’s rule coupling. We hope that this work will motivate further studies on the electron doped phase of rare-earth manganites.

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