ESRF

Experiment title:	Experiment number:
XANES and EXAFS studies of a mixed valency oxide thin film $La_{0.8}MnO_{3-\delta}$ deposited by a novel MOCVD process.	CH-673

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Report:

In ths experiment we originaly studied by XAS thin films of vacancy doped manganites: $La_{1-x}MnO_{3-\delta}$. Two epitaxial films of $La_{0.8}MnO_{3-\delta}$ (sample A and B) have been deposited on $SrTiO_3$ using a novel injection MOCVD process[1]. One of the two samples (sample B) has been annealed at 750 °C during 3 hours to reduce the oxygen deficiency δ. Films have been fully characterized by XRD, resistivity and magnetoresistivity measurements. In particular, the annealing produces an increase in the Curie temperature from 240 K, in the as-prepared sample, to 310 K in the annealed film. From our previous XAS experiments performed at LURE, this evolution has been interpreted in terms of manganese oxidation giving rise to different Mn^{4+}/Mn^{3+} ratio.

The aim of this experiment was to evaluate the Mn^{4+}/Mn^{3+} ratio trough a detailed analysis of the XANES region and to follows the evolution of the Mn local structure across the metal to insulator transition.

12 XAS spectra of A and B samples were recorded in fluorescence geometry in the temperature range 180 - 350 K. XANES region was sampled with an energy step of 0.02 eV.

The figure 1 shows the XANES region of the XAS spectra for two samples measured at 0 °C on both samples. In the lower part also the derivative is reported. It is evident from this data that the XANES region of both samples are identical in evident contrast with previous data measured at LURE. This is probably due to the higher resolution and improved stability of the setup used at ESRF.

The absence of sizable effects on the XANES region is an interesting and unexpected result in fact seem to indicate that the annealing, does not affect electronic state of Mn even though it widely modify the Curie temperature of the material (figure 1, lower panel).

This result suggest that the ratio Mn^{4+}/Mn^{3+} is not the principal responsible of the differences observed in the susceptibility curves of these two samples.
To investigate structural effects in the Mn surrounding we are performing an accurate analysis of the EXAFS region of the spectra including the multiple scattering effects.
A preliminary analysis has already been done by using the GNXAS package (figure 2) and demonstrated not only a high sensitivity of EXAFS data to the Mn-O bond length distribution but also the possibility to determine the next neighbor distribution including informations about Mn-O-Mn bond angle.

Preliminary results show:
i) a bimodal Mn-O bond length distribution with 4 short bonds at about 1.9 Å and 2 longer bonds at about 1.95Å indicative of a Q_3 type Jahn-Teller distortion effect. This value is about three times smaller than the values found on hole doped parent compounds like $La_{1-x}Ca_xMnO_3$.
ii) The Mn-O-Mn bond angle is about 160 deg. in the as prepared sample (sample A) and raises to about 165 on the annealed film (sample B).

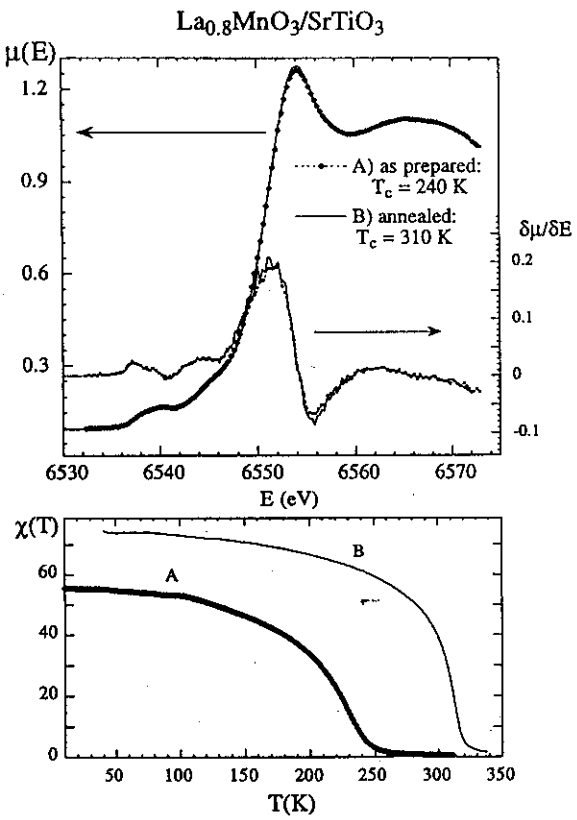

Fig. 1: XANES measured at 0 °C for sample A and B (upper panel). Lower panel shows the susceptibility plots.

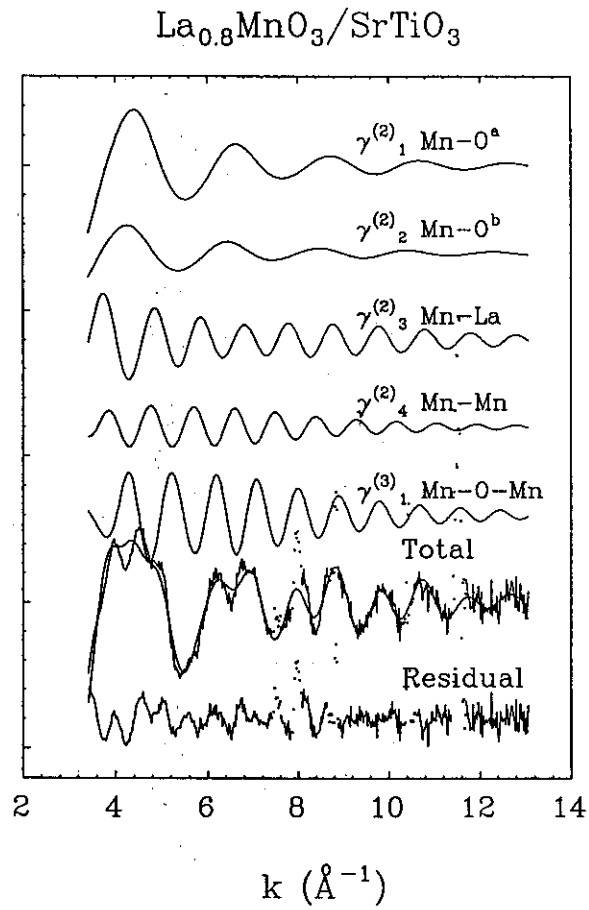

Fig. 2: Example of fitting of EXAFS data using multiple scattering approch (GNXAS). Notice the large three body contribution coming from Mn-O-Mn almost collinear configurations of the perovskite structure.