



Experiment title: Local structure and electronic properties of rombohedral colossal magnetoresistive manganites by Mn-K edge EXAFS and XANES

**Experiment number:
HS-1952**

Beamline: BM29	Date of experiment: from: 13 September 2002 to: 16 September 2002	Date of report: 21 August 2003 <i>Received at ESRF:</i>
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Report:

Mn-K edge EXAFS and XANES spectra of Na doped and Ca doped lanthanum manganites with different crystal structures (orthorhombic and rombohedral), different oxygen stoichiometries and different oxygen contents have been acquired at various temperatures ranging from RT to 30 K. The main result of this investigation are:

- 1) The Mn(IV) content of the samples as determined by the chemical shift of the Mn-K edge is in fairly nice agreement with that calculated on the basis of the quasi-chemical equilibria leading to doping on the La site and to oxygen non-stoichiometry. In particular, doping with Ca injects one hole per doping atom, while doping with Na injects two holes per doping atom. The holes are destroyed by oxygen under-stoichiometry via the formation of cation vacancies;**
- 2) The pre-edge peak shows a transfer of spectral weight with temperature which is greater in the samples orthorhombic with respect to the rombohedral ones (see Fig. 1): this can be attributed to the presence of a greater static disorder in the orthorhombic manganites;**
- 3) The EXAFS Fourier transforms of the various samples at room temperature suggest an increase of the local order around Mn with increasing Mn(IV) content: this effect has been attributed to the non Jahn-Teller nature of the MN(IV) ions;**

4) In the rhombohedral samples a single Mn-O distance (nearest neighbours) is found. In addition, the trend of the EXAFS Debye-Waller factors for the Mn-O distance can be fitted with a simple Einstein model, with no static disorder at low temperature (see Fig. 2). This suggest a dynamic nature of the Jahn-Teller effect in the rhombohedral samples, which is in contrast with the static and cooperative Jahn-Teller effect found for the orthorhombic samples.

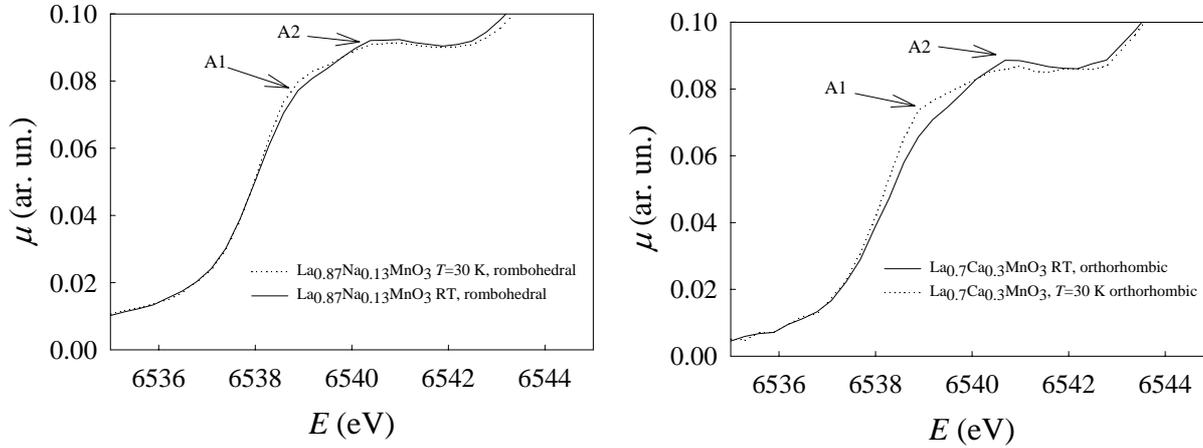


Figure 1: Mn-K edge pre-edge peak at different temperatures and for different doped lanthanum manganites

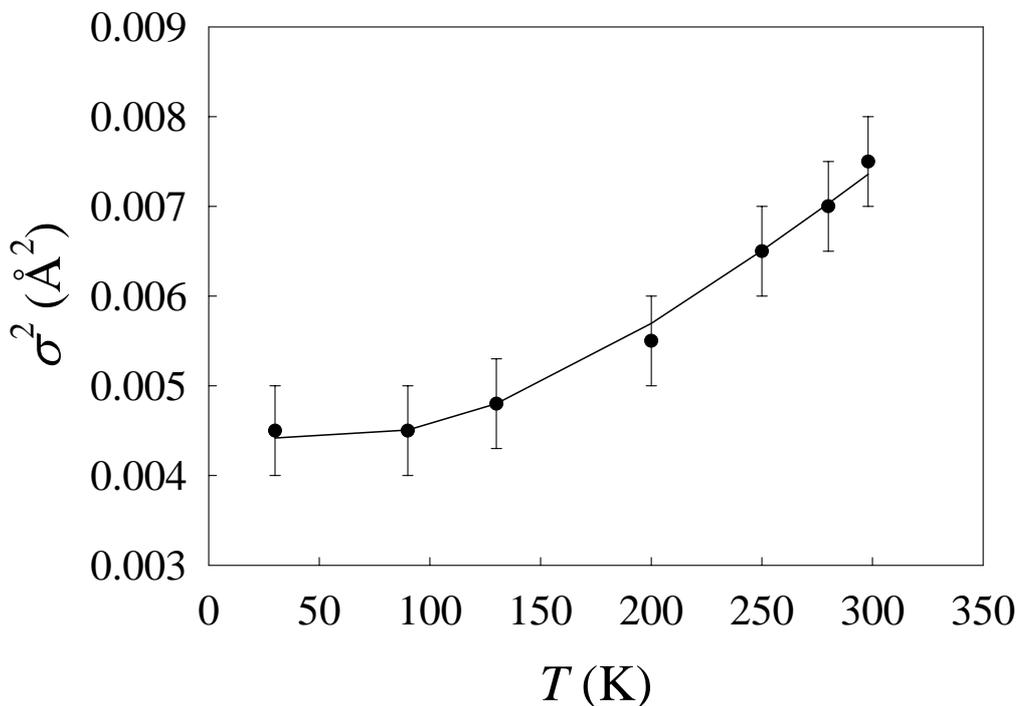


Figure 2: Mn-O Debye-Waller factors for the rhombohedral manganite $\text{La}_{0.87}\text{Na}_{0.13}\text{MnO}_3$, as a function of temperature. The full line is a fit according to the Einstein model.