


Experiment title:

The crucial role of Mn^{2+} ions in lanthanum-deficient La_xMnO_3 thin films studied by Mn L_3 edge RIXS

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Report:

The aim of the proposed experiment was the determination of the electronic structure of strained and unstrained lanthanum deficient (or Mn-rich) La_xMnO_3 (LMO) thin films, as a function of several controlled structural parameters. More specifically, we exploited the almost unique capability of L-edge Resonant Inelastic X-ray Scattering spectroscopy (RIXS) to measure the set of the local dd excitations to unambiguously assign the crystallographic site of divalent Mn^{2+} ions, which have been proved to be the key-players in the newly discovered Multiple Double-Exchange transport mechanisms in strongly correlated electron manganite materials [ref1].

In order to investigate the electronic properties and the local structure of manganite thin, we performed polarization dependent X-ray Absorption Spectroscopy (XAS) at the Mn $L_{2,3}$ absorption edge (by using the initial 3 shift, as planned in the proposed time-scale). In particular, X-ray Magnetic Circular Dichroism (XMCD) and Linear Dichroism (LD) XAS allowed us to experimentally determine the orbital reconstruction and the magnetic order in manganite films. Heavy-ion La/Mn stoichiometric ratio was varied from La-deficient, to 1:1-stoichiometric LaMnO_3 , and finally to La-rich. Moreover, $(\text{La,Sr})_x\text{MnO}_3$ (LSMO) off-stoichiometric samples ($x \neq 1$) grown on SrTiO_3 (STO) substrates, with different (La,Sr)/Mn ratio were also investigated. Similarly to the LMO samples, also for LSMO samples, the x content varies from 0.66 to 1.07. Finally, different bi-axial strain was induced by growing LMO films on different substrates: namely STO and LaAlO_3 (LAO), where the films are expected to experience negligible strain and a compressive strain of 3.0%, respectively. In detail, the following 4 sets of manganite samples were investigated by XAS:

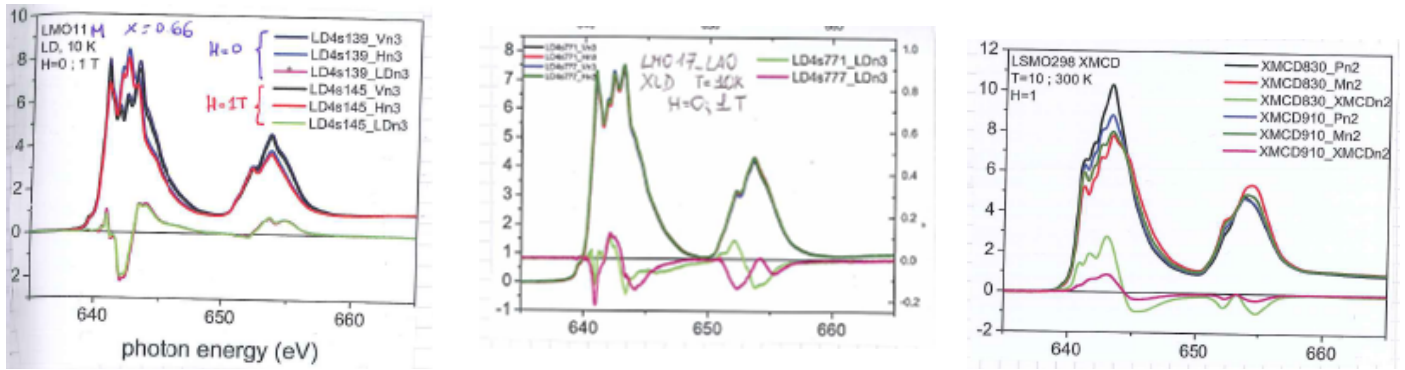
- I. LMO films N-series: set of 4 LMO samples grown on STO, with different La/Mn stoichiometric ration (namely, $x = 0.66, 0.88, 0.98$ and 1.05) and annealed for 54-hours (i.e. optimally doping procedures for oxygen content).
- II. LMO films M-series: set of 4 LMO samples grown on STO and annealed for 24-hours (i.e. slightly underdoped-samples) with same La/Mn stoichiometry of M-series.
- III. LMO films on LAO: set of 2 LMO samples grown on LAO annealed for 54-hours (i.e. same oxygen content of N-series); the La/Mn ratio were 0.66 and 1, so being compositionally identical to two LMO samples of N-series but experiencing different substrate induced strain (i.e. compressive).

IV. LSMO films :

set of 5 (La,Sr)_xMnO₃ (LSMO) samples grown on STO, with different (La,Sr)/Mn stoichiometric ratio. Similarly to the LMO samples, also for LSMO samples, the x content varies from x < 1 to x > 1.

La/Mn or (La,Sr)/Mn stoichiometric ratio				
Set of samples	0.67	0.88	0.98	1.05
I. LMO films N-series on STO	Lmo11N	Lmo13N	Lmo14N	Lmo16N
II. LMO films M-series on STO	Lmo11M	Lmo13M	Lmo14M	Lmo16M
III. LMO films on LAO	Lmo19LAO		Lmo17LAO	
IV. LSMO films on STO	Lsmo298 Lsmo296* *(x = 0.70)	Lsmo291 Lsmo303# #(x = 0.80)		Lsmo287 [§] [§] (x = 1.07)

Linear and circular dichroism (LD and XMCD) at Mn L-edge were performed on all the listed samples, in zero-field-cooled (ZFC) at two selected temperatures (i.e. 300K and 10K), both with and without 1T applied magnetic field and in Grazing and in Normal Incidence (GI and NI) to check the magnetic anisotropy. In case of Mn-excess with respect to the ideal La/Mn = 1 stoichiometric ratio, a strong signal associated to Mn²⁺ presence appears (XMCD for LMO film on STO, LMO film on LAO and LSMO film on STO, respectively, are reported below).

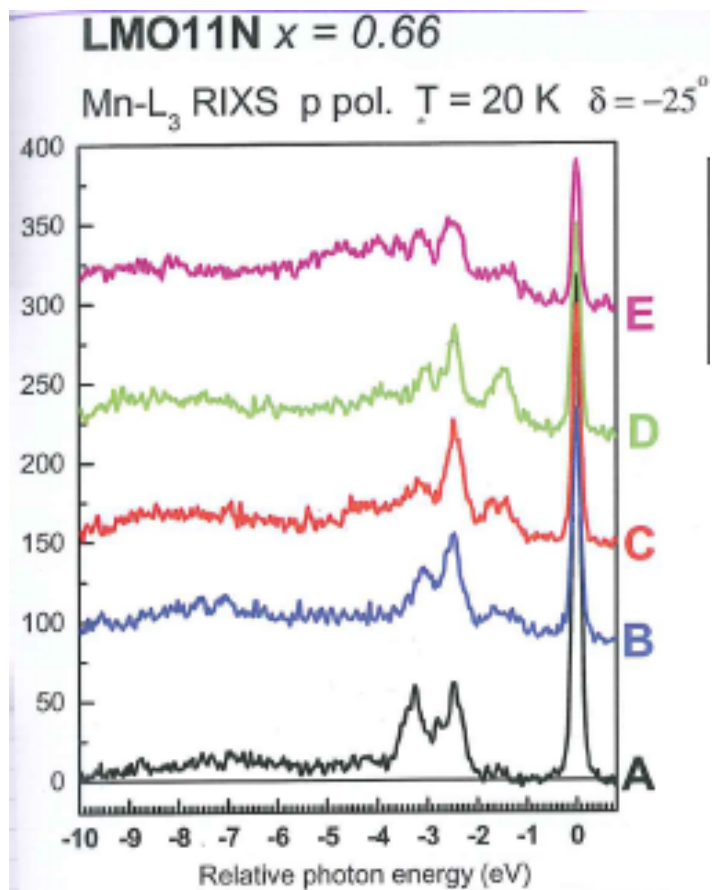


Such a peak, usually associated to spurious bulk Mn₃O₄ and/or surface MnO phases, is only present in Mn-rich thin films. More significantly, also in LSMO thin films with Mn-excess, such a Mn²⁺-peak has been observed. In all Mn²⁺-rich samples, either LMO or LSMO films, transport properties were found sizably increased, therefore supporting a newly proposed theoretical scenario based on Mn²⁺-ions behaviour as dopant and as element electronically involved in hopping mechanisms [ref.1]. Preliminary analysis of the experimental data, beyond the confirmation of some already reported (i.e. HE-3123) [ref. 1-2], opens new scenarios about orbital ordering in manganites induced by structural effects (i.e. strain mechanism) in insulating samples and hopping mechanism in metallic samples. All this results are presently under deep investigation also by theoretical point of view. Knowing this, we pointed to the core aim of the experiment which is to definitively determine the localization of Mn²⁺-ions in both Mn-rich LMO and LSMO films.

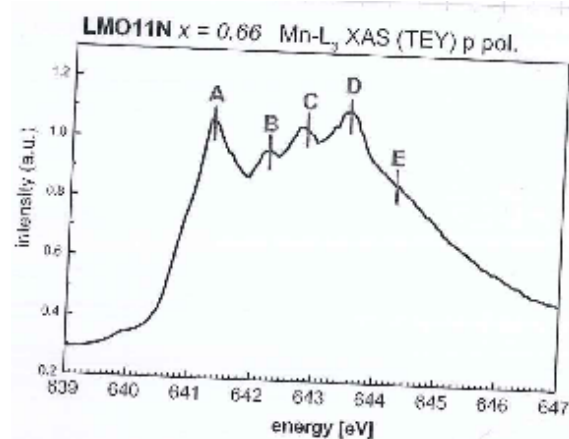
Based on the XAS spectra, we selected the six following LMO/LSMO samples to be investigated by RIXS:

Sample	Physical properties	Structural properties	XAS feature
Lmo11N_STO	metallic and ferromagnetic	strainless	presence of Mn ²⁺ features
Lmo14N_STO	metallic and ferromagnetic		presence of Mn ²⁺ features
Lmo16N_STO	insulating		absence of Mn ²⁺ features
Lmo17_LAO	worse metallic phase	compressive	presence of Mn ²⁺ features
Lmo19_LAO	(compared to samples on STO)	strain	absence of Mn ²⁺ features
LSMO296_STO	metallic and ferromagnetic	strainless	presence of Mn ²⁺ features

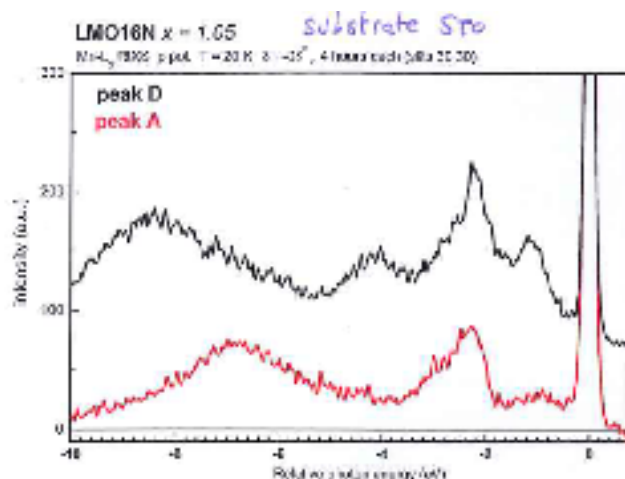
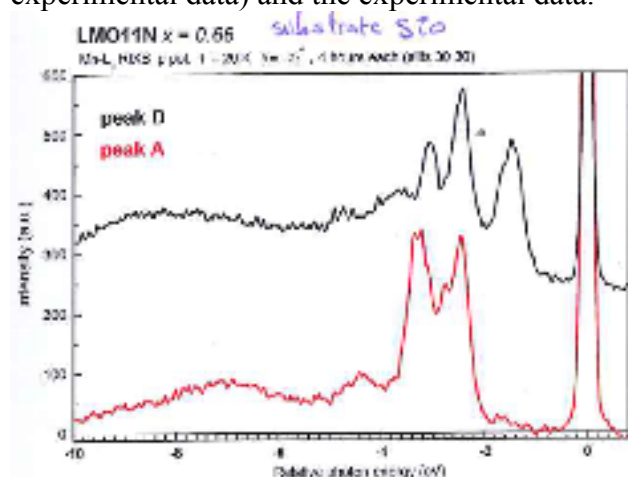
As previously said, RIXS spectra provide an extremely accurate information about the degree of hybridization of Mn_{3d} and O_{2p}, which substantially depends on the Mn-O structural arrangement. Such an occurrence is indeed strongly influenced by the ionic coordination (i.e. first neighbors) of the Mn-ions. In particular, at the corner of the cubic cell, the atom is tetrahedrally coordinated with 6 oxygen atoms, while in the center of the cell, the atom has 12 first-neighbors in an almost-spherical coordination. As a consequence, sizeable differences in RIXS spectra are expected to occur (for instance) in these two limit-cases.



As a preliminary step, XAS experiments were also performed in RIXS chambers on all the samples (see for instance XAS spectrum of Lmo11N sample below). After that, five significant energies (namely, labelled as A-E in the graph) at which run RIXS experiments were selected. In particular, A-peak, C-peak and E-peak correspond to Mn^{2+} , Mn^{3+} and Mn^{4+} transition energies, respectively, while B-peak and D-peaks show Mn^{2+}/Mn^{3+} and Mn^{3+}/Mn^{4+} intermediate characteristic, respectively. Such a procedure was followed for all investigated samples.



The Mn-rich and Mn-deficient (i.e. $x < 1$ and $x > 1$ samples, respectively) samples give very different results. The spectra at point A in Mn-rich samples are very different, with respect to the spectra at point D (corresponding to the Mn^{3+} transition energies), indicating a very different crystal field in the two situations. Based on the acquired spectra, we further selected two significant energies (namely the A and the D points, corresponding to Mn^{2+} and Mn^{3+}/Mn^{4+} mixed transition energies, respectively) at which run long RIXS scans. Such a procedure allowed us to sizeably increase the signal-to-noise ratio of the single measurement, thus revealing underneath fine structures in the RIXS spectra, which were otherwise covered by the noise. Such an improved quality of the RIXS spectra will put us in the most favorable condition to compare theoretical calculations of the RIXS spectra for Mn^{2+} for different crystal field (mandatory to understand experimental data) and the experimental data.



We are presently elaborating all the data (magneto-transport, magnetic, structural, XAS and RIXS) within a complete and self-consistent theoretical framework. As a matter of fact, although the dd excitations can be relatively easily interpreted within the single ion crystal field model made by ourselves, the support of theoretical calculations within the effective single band model will be crucial for obtaining the full picture of the role played by Mn^{2+} ions in manganite thin films.

By considering the original proposal, all the aimed goals were successfully achieved.