



	Experiment title: Metal-insulator transition and charge disproportionation in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ as seen by x-ray absorption spectroscopy	Experiment number: HS-3079
Beamline: BM29	Date of experiment: from: 18-Jun-06 to: 23-Jun-06	Date of report: 25-09-07
Shifts: 12	Local contact(s): Olivier Mathon	<i>Received at ESRF:</i>
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Report:

The substitution of La^{3+} with Sr^{2+} in the perovskite series $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($0 \leq x \leq 1$) produces a formal change in the valence state of Fe ion from +3 ($x=0$) to +4 ($x=1$). This leads to the decrease of T_N and the increase of electronic conductivity. One of the most striking properties in this series occurs at a critical concentration of $x \sim 2/3$. $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ samples undergoes a metal-insulator (MI) transition at ~ 200 K evidenced by a jump in the resistivity of more than one order of magnitude with decreasing temperature. This MI transition has been then interpreted as a charge disproportionation from an average-valence state ($\text{Fe}^{+3.67}$) in the paramagnetic phase above 200 K into a mixture of 2Fe^{3+} and 1Fe^{5+} in the antiferromagnetic charge ordering (CO) state below 200 K. The Fe^{5+} comes from the disproportionation of Fe^{4+} into Fe^{3+} and Fe^{5+} .

The present work [1] was undertaken to investigate the changes of the electronic and local structure of Fe atoms upon varying the La/Sr ratio by x-ray absorption spectroscopy (XANES and EXAFS). It also focuses on the changes observed at the so-called CO transition at the critical concentrations of $x=2/3$ and $x=3/4$. XANES and EXAFS spectra were recorded at the BM29 beam line in transmission mode on powder samples and at selected temperatures between 40 and 295 K. The beam was monochromatized by a fixed-exit Si(111) double-crystal and harmonic rejection better than 10^{-5} was achieved by using the Si mirror coating of the double flat mirror installed after the monochromator. The energy resolution, $\delta E/E$, was estimated to be about 8×10^{-5} at the Fe K-edge and a Fe foil was simultaneously measured for energy calibration.

Figure 1 (left panel) shows the Fe K-edge XANES spectra of the whole series at room temperature. We observe a systematic chemical shift of the edge position as the Sr content increases indicating that the Fe valence also increases. The chemical shift between LaFeO_3 (formal Fe^{3+}) and $\text{SrFeO}_{2.96}$ (formal Fe^{4+}) was

found to be 1.26 eV and the absorption edge for the doped samples lies between the end members, indicating intermediate valence states for iron. However, we cannot determine what kind of mixed valence exists along the whole series $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$, i.e. if it is pure intermediate valence $\text{Fe}^{3,x+}$ or a mixture of Fe^{3+} and Fe^{4+} . We can nicely reproduce the XANES spectra of the series members by the weighted addition of XANES spectra from $(1-x)\text{LaFe}^{3+}\text{O}_3$ and $(x)\text{SrFe}^{4+}\text{O}_3$. This is true even at low temperatures where is thought that the Fe^{4+} disproportionates into Fe^{3+} and Fe^{5+} for $x \sim 2/3$, as shown in Fig. 1 (right panel).

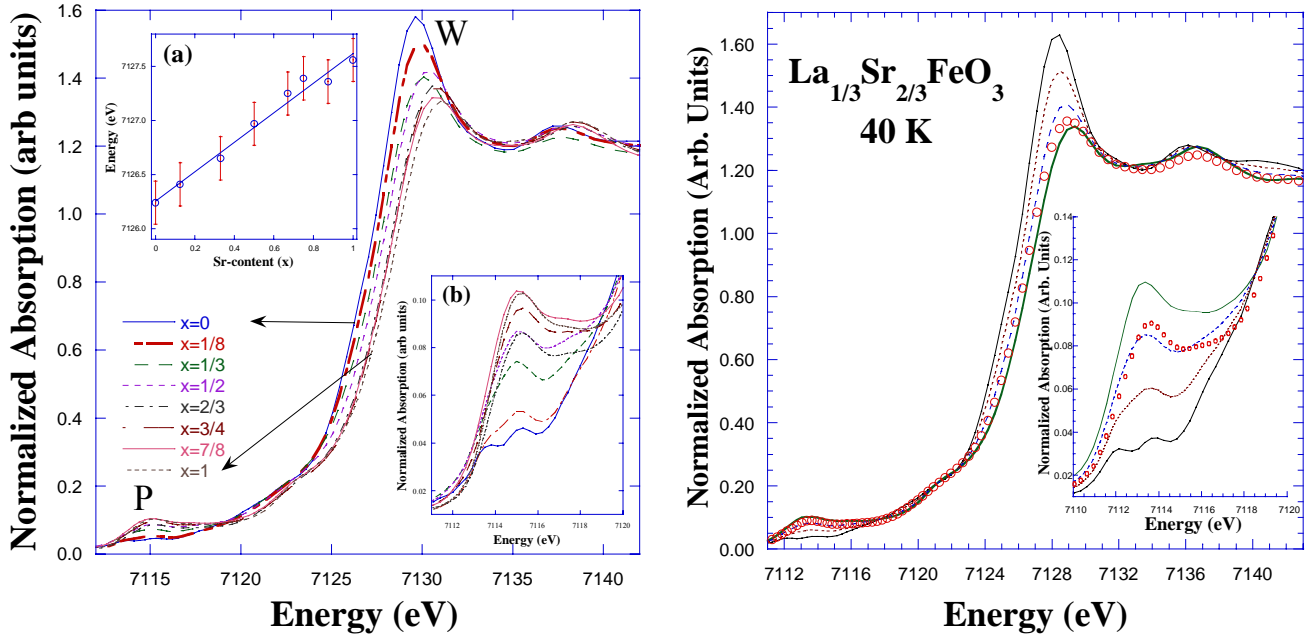


Fig. 1. Left panel: Fe K-edge XANES for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples at room temperature. P and W denote pre-peak and white line features, respectively. Inset (a): Plot of the edge position vs. chemical composition. Inset (b): Detail of the pre-edge region. **Right panel:** Comparison between normalized XANES spectra of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ (circles) and the following additions of reference XANES: $1/3\text{LaFeO}_3 + 2/3\text{SrFeO}_3$ (dashed line) and $2/3\text{LaFeO}_3 + 1/3\text{SrFeO}_3$ (dotted line). Normalized XANES of parent LaFeO_3 (thin straight line) and SrFeO_3 (thick straight line) are also plotted for comparison.

EXAFS results concur with XANES data, the Fe-O bond-length decreases with increasing x and accordingly, the oxidation state of Fe atoms increases. However, large DW factors are observed for all samples except LaFeO_3 , which indicates that the hole-doping produces local disorder around the Fe ions. The DW factors for this first Fe-O shell show unusually large values below the metal-insulator (MI) transition for $x=2/3$ or $3/4$. This indicates an additional disorder at low temperature, which mainly affects to the Fe-O sublattice. We show that a significant charge disproportionation of the type $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ cannot account for the local structure observed below the MI transition temperature of these samples. In conclusion, we propose a structural transition from uncorrelated FeO_6 octahedra at room temperature to a low-temperature phase with an ordering of the local distortion as the most suitable explanation for the metal-insulator phase transition observed in the $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ and $\text{La}_{1/4}\text{Sr}_{3/4}\text{FeO}_3$.