



ESRF

Experiment title:

X-ray absorption study of mixed valence
 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ perovskites.

Experiment

number:

HC518

Beamline:

BL18

Date of experiment:

from: March 18,1996 to: March 21,1996

Date of report:

20/02/1991

Shifts:

9

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Report:

We have performed a systematic study of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0, 0.15, 0.33, 0.5, 1$) and $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ compounds by means of XANES, with the aim of studying the electronic state of Mn.

XANES spectra at the Mn K-edge of metallic manganese, MnO, Mn_2O_3 , MnO_2 , LaMnO_3 , TbMnO_3 and CaMnO_3 were recorded in transmission mode at room temperature. A chemical shift of 4.2 eV is observed for Mn_2O_3 with respect to MnO_2 and for LaMnO_3 with respect to CaMnO_3 , as expected for Mn^{3+} and Mn^{4+} states.

XANES spectra of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ series and the doped sample $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ at room temperature are reported in figure 1. The spectra are very similar to each other, showing a preedge structure, the intensity of which rises by increasing the Ca content. These prepeaks arise from transitions to bounded Mn 3d states which are allowed by symmetry due to the mixing with the oxygen 2p band as it occurs in related perovskites. We can distinguish a main peak at the edge (labelled A in fig.1) and a second resonance (labelled B), the intensity and shape of which depend strongly on the scattering of the outgoing electron by coordination shells beyond the first one. The main difference, in comparison with other perovskites oxides, is related

to the peak C that is associated to a double-electron transition due to the simultaneous excitation of a Mn 3d electron.

The spectra show minor changes that follow a continuous evolution from LaMnO_3 up to CaMnO_3 . The main difference is related to the chemical shift. The energy positions of the doped samples lie between the end members of the series, indicating an intermediate valence state for manganese. However, the chemical shift cannot show if the two manganese atoms with 3+ and 4+ valence state are present or if there is only one kind of Mn fluctuating from one state to the other. In order to distinguish between the two possibilities, we have simulated the spectra of the doped compounds by means of a linear combination of the end members. The simulation reproduces nicely the energy position of the absorption edge but it does not reproduce the intensity of the resonances that is lower than in the experimental spectrum. As a conclusion, we can say that XANES does not support the ionic picture with only d^3 and d^4 configurations for Mn atoms, being this system better described as a nearly half-metallic compound.

The results of this investigation, together with the CMXD and temperature and field dependent XANES data taken at beamline 6, has been submitted to Phys. Rev. B for publication.

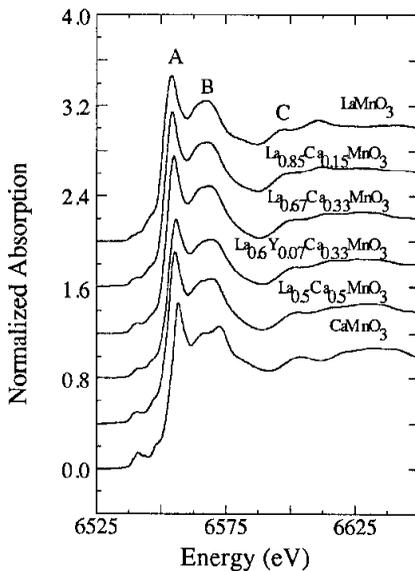


Figure 1. The normalized XANES spectra at the Mn K-edge at room temperature for the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ series and the doped sample $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$.