



Experiment title:
Study of the charge ordering state in manganese perovskites by means of anomalous X-ray powder diffraction.

Experiment number:
 HE-103

Beamline: ID 20
Date of experiment: from: February 5, 1998 to: February 9, 1998

Date of report:
 25/02/1998

Shifts: 15
Local contact(s): Jean-Louis Hodeau

Received at ESRF:
02 MAR. 1998

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Report:

Mixed valence manganese perovskites $RE_{1-x}A_xMnO_3$ (RE= rare earth, A= Ca, Sr) have become during the last few years, one of the hot topics in solid-state physics due to the complex phenomenology and rich variety of properties they show. In this series, a charge ordering (CO) state is developed for $x \geq 0.5$ when decreasing the temperature. This CO phase transition has been observed in $RE_{0.5}A_{0.5}MnO_3$ compounds with R= La, Pr, Nd, Tb and A= Ca, Sr by several techniques. Different Mn^{3+}/Mn^{4+} arrangements in the primitive cubic cell, in alternate (111), (100) and (110) planes, have been proposed to describe this new structure.

In order to obtain a direct evidence of this charge ordering state and discriminate among the different models, we have performed x-ray anomalous diffraction experiments in powder samples of $Tb_{0.5}Ca_{0.5}MnO_3$. This compound shows a structural transition at around room temperature that can be described in a monoclinic unit cell, derived from the high-temperature orthorhombic one by doubling the a-axis, with stripes of Mn^{3+} and Mn^{4+} in the ac-plane [J. Blasco et al., J. Phys.: Condens. Matter 9, 10321 (1997)]. Powder diffraction spectra were measured at 300 K and at 150 K (below T_{CO}) at photon energies of 6.52 KeV and 6.552 KeV, below and close to the absorption K-edge of

manganese in this compound, i.e. between the Mn^{3+} and Mn^{4+} K-edges. Besides, in the low temperature CO phase, we have also measured particular diffraction peaks at several energies in order to differentiate between the contribution of the charge disproportionation and the structural changes associated to the modification of the electronic state of the Mn atom.

The diffraction patterns recorded at 150 K and at 6.52 and 6.552 KeV, up to $2\theta = 60^\circ$, are shown in figure I. The characterization of the structure and the analysis of the anomalous effect is in progress. The preliminary results can be summarized as follows. We have performed computer simulations of the diffraction data, using theoretical f' and f'' values, which indicate us that (200) and (220) reflections of the monoclinic cell are originated by a perfect charge ordering of Mn^{3+} and Mn^{4+} . However, our measurements of the (200) reflection at different energies are not in agreement with this result, indicating that a charge disproportionation does not occur. We are also analyzing the anomalous effect on the (201) and (020) reflections in order to confirm the previous result.

Since this subject is of great importance to understand the charge ordering mechanism, and it is still quite controversial, we think that further experiments, on other systems which present charge ordering behaviour, are needed to obtain a definitive conclusion.

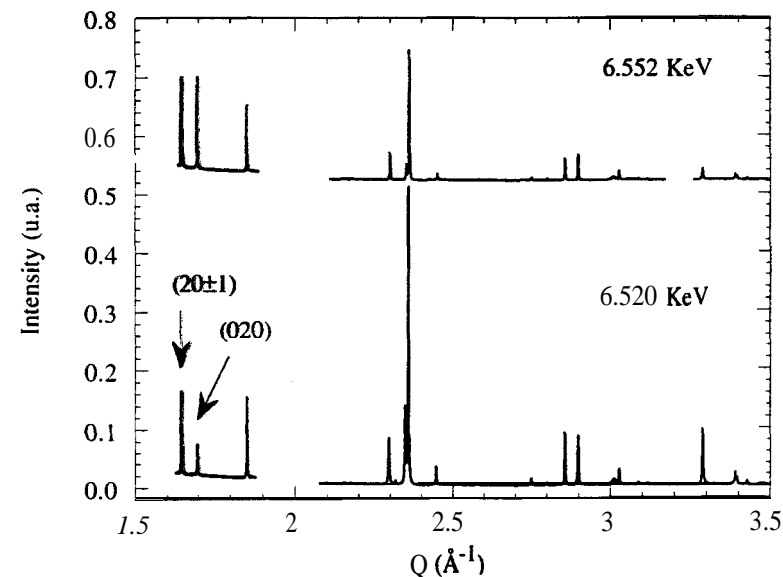


Figure 1. Powder diffraction patterns recorded at 150 K for $Tb_{0.5}Ca_{0.5}MnO_3$ at two different energies below and close to the absorption K-edge of manganese.