ESRF	**Experiment title:** XCMD experiments in doped $La_{2/3}Ca_{1/3}MnO_3$ perovskites.	**Experiment number:** HC545
Beamline: ID12-BL6	**Date of experiment:** from: April 11,1996 to: April 16,1996	**Date of report:** 20/02/1997
Shifts: 18	**Local contact(s):** Andrei Rogalev	*Received at ESRF:* 28 FEV. 1997

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Report:

The mixed valence compounds $La_{1-x}Ca_xMnO_3$ have been recently subject of renewed attention due to the close interplay between magnetism and transport properties (1,2). This system displays several magnetic transitions as a function either of temperature or doping, some of them associated with sharp changes of the electrical conductivity. Several studies have shown that for compositions x=1/3, the magnetoresistive effect associated to the ferromagnetic-paramagnetic transition is strongly enhanced. Recent investigations show that lanthanum substitution in the compound $La_{2/3}Ca_{1/3}MnO_3$ by other trivalent atoms, as Y, Pr or Tb, induces a lowering of the transition temperature and an enhancement of the magnetoresistence (giant magnetoresistence). These materials are formally a mixed valence Mn^{4+}/Mn^{3+} compounds and the metallic conductivity in the ferromagnetic phase has been traditionally ascribed to the double exchange mechanism between Mn^{3+} and Mn^{4+} ions.

XCMD, the effect of the magnetic field on the XANES spectra and XANES as a function of temperature across the phase transition of $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ and $La_{0.85}Ca_{0.15}MnO_3$ were carried out at the beamline 6.

The high reproducibility in energy of the monochromator has allowed us to determine chemical shifts of about 0.01 eV. XCMD spectra of the aboved mentioned samples were measured in the ferromagnetic phase. Right-circularly polarized X-rays were employed. Sucessive scans of field up and field down were subtracted in order to get the dichroic signal. The effect of the magnetic field on the XANES spectra at a fixed temperature was obtained by averaging the scans taken with field up and field down and subtracting to the resulting average, the spectrum recorded at zero magnetic field. Also, scans recorded at different temperatures, below and above the transition temperature at zero magnetic field, were subtracted.

The conclusions can be summarized as follows: Our results do not support the description of these materials as an ionic picture with only d^3 and d^4 configurations for Mn atoms. The behaviour of the XANES spectra of $La_{2/3}Ca_{1/3}MnO_3$ and $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ as a function of temperature or magnetic field across the MI transition shows very small changes. These results indicate that no dramatic changes occur in the local electronic and geometrical structure at the manganese site during the phase transition, suggesting that the mechanism responsible of the magnetoresistance and the MI transitionis is not based on a localization of the carriers at the Mn atom.

The XCMD experiments in the ferromagnetic phase show, for the first time, the effect of the magnetic polarization of the empty p states, showing a change in the sign of the polarizability. Moreover, magnetic multiple scattering contributions and the detection of a two-electron excitation process were observed. As it occurs for the XANES spectra, an unique dichroic signal has been observed, showing clearly that only one type of manganese is present in this system. This result is also in contrast with the simple description of a strong mixed valence mechanism.

These results together with the XANES data taken at beamline 18, have been submitted to Phys. Rev. B for publication.

(1) S. Jin, H.M. O'Brian, T.H. Tiefel, M. McCormack, W.W. Rhades, Appl. Phys. Lett. 66 (1995) 382

(2) R. Mahendiran, A.K. Raychandhuri, A. Chainani, D.D. Sarma, S.B. Roy, Appl. Phys. Lett. 66, (1995) 233.