ESRF	**Experiment title:** XMCD study on the change in electronic configuration of Fe and Mn at the magnetocaloric transition of FeMn(P,Si)	**Experiment number**: HC-686
Beamline: ID08	**Date of experiment**: from: 04/04/2013 to: 07/04/2013	**Date of report**: 17/10/2014
Shifts: 9	**Local contact(s)**: Erika Jiménez Romero	*Received at ESRF:*

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Report:

In the high-performance and low-cost $(Mn,Fe)_2(P,Si)$ magnetocaloric compounds the ferromagnetic phase transition is accompanied by a large latent heat. The transition temperature can be conveniently tuned around room temperature by changing the chemical composition (Mn/Fe and P/Si ratios). As a result, this system is a promising candidate for magnetic cooling and power conversion applications. Recent first principle electronic-structure calculations indicate that at the first-order phase transition a strong electronic reconstruction takes place where in the paramagnetic state the Fe atoms lose their moment, while the Mn moments are conserved[1].

The aim of this experiment was to experimentally test these predictions and probe the evolution of the magnetic moments in an element specific manner across the ferromagnetic phase transition, *i.e., both* in the ferromagnetic and paramagnetic states. The X-ray Magnetic Circular Dichroism (XMCD) experiments were performed at the ID08 beamline. The measurements were taken by tuning the energy at both the Mn and Fe $L_{2,3}$ edges ($2p \rightarrow 3d$ transition). The X-ray absorption spectra were recorded using the Total-Electron Yield (TEY) mode, and normalized to the intensity of incident beam. The sample temperature was regulated in the temperature range from 230 to 330 K.

The X-ray absorption (XAS) spectra correspond to the sum of positive (μ^+) and negative (μ^-) absorption signals, while the XMCD spectrum is calculated from the difference between μ^+ and μ^-. Three polycrystalline materials $MnFe_{0.95}P_{0.582}B_{0.078}Si_{0.34}$, $Mn_{1.25}Fe_{0.7}P_{0.52}Si_{0.48}$ and $Mn_{1.25}Fe_{0.7}P_{0.5}B_{0.01}Si_{0.49}$ were measured. The bulk samples (plates of 10 mm diameter and 2

mm thickness) were placed in a ultra-high vacuum (UHV) system equipped with a 5 T split coil superconducting magnet. The incident X-ray beam and magnetic field are parallel to each other and oriented perpendicular to the sample surface. In order to assure the cleanliness of sample surface and remove surface oxidation, the pellets were scrapped *in situ* with a diamond file in the preparation chamber before the measurements. The extraction of the Fe and Mn moment from the experimental XMCD data has been performed using the sum rules and multiplet calculations.

As illustrated in Fig. 1, from XAS, it is found that no significant valence change and generally speaking no spectral shape modification is observed at the FOMT. From XMCD, the magnetic field and temperature dependences of the magnetic moments were obtained for the Fe and Mn moments for two Fe/Mn ratios. It is observed that the manganese exhibits a much lower magnetization on the *3f* site than on the *3g*. In contrast to theoretical predictions, it is observed that neither the Mn nor the Fe moments are fully quenched in the paramagnetic state (see Fig. 2). These results suggest that the magnitude of the reduction of the Fe *3f* moments at T_C is overestimated by ab-initio calculations. On one hand, part of this discrepancy might arise from the measurements that are done in the vicinity of the FOMT. The reduction in moment might be gradual due to the developing short-range order above the transition. On the theoretical side, the change in the balance between bond formation and magnetism for Fe and its neighbouring atoms might be overestimated. The paper on this work has been submitted.

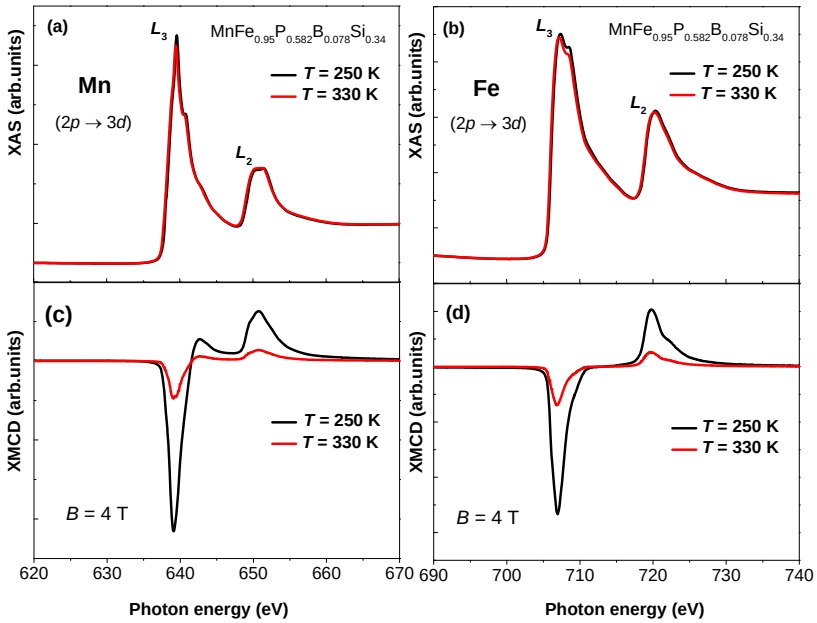

Fig.1 XAS and XMCD spectra for $MnFe_{0.95}P_{0.582}B_{0.078}Si_{0.34}$ measured at the Mn-$L_{2,3}$ edge (left panel) (a) and (c), and Fe-$L_{2,3}$ edge (right panel) (b) and (d). Black and red spectra are measured at 250 K (ferromagnetic state) and 330 K (paramagnetic state), under an applied magnetic field of 4 T, respectively.

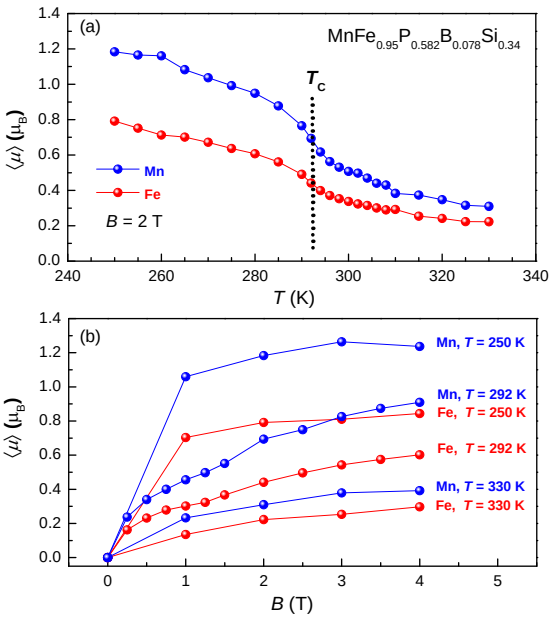

Fig.2 The XMCD magnetic moment as a function of temperature (a) and magnetic field (b) for $MnFe_{0.95}P_{0.582}B_{0.078}Si_{0.34}$. Top curves were measured in a field of 2T, below curves were measured at 250 K (Ferromagnetic state), 292 K (near transition) and 330 K (Paramagnetic state). The XMCD magnetic moments were derived as described in the text.

Reference

[1] N.H. Dung, Z.Q. Ou, L. Caron, L. Zhang, D.T. Cam Thanh, G.A. de Wijs, R.A. de Groot, K.H.J. Buschow, E. Brück, *Adv. Energy Mater. 1 (2011) 1215*.