



<b>Experiment title:</b> Electronic structure and local moments in single-crystalline MnFe(P,Si) probed by linear dichroic XES and HERFD-XAS	<b>Experiment number:</b> HC-4931	
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 14 <sup>th</sup> June 2022 to: 20 <sup>th</sup> June 2022	<b>Date of report:</b> 8 <sup>th</sup> September 2022
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#### Report:

MnFe(P,Si) compounds show an isostructural, yet volume preserving, first-order magnetic transition (FOMT) at ambient conditions. Since the discovery of their giant magnetocaloric effect, this system attracts continuing attention, both for its potential applications and for the scientific interest to unravel the underlying physical mechanisms of the FOMT. While the magneto-elastic aspect with opposite lattice discontinuities at the FOMT is well established, several debates persist on the changes in electronic structure and in magnetic moments across the ferromagnetic transition.

This experiment sought to gain new insights on the evolution of the magnetic moments, irrespectively of the disappearance of a magnetic order, by analyzing the temperature evolution of the XES emission spectra at Fe and Mn  $K\beta$  edges. In addition, to clarify the changes in the electronic structure across the FOMT and pinpoint them to specific elements and orbitals, we intended to exploit the improved resolution offered by high energy resolution fluorescence detected HERFD-XAS, as well as the directionality of XES linear dichroism.

Despite the loss of about 5 shifts due to various experimental challenges (radiation damage, beamline control issues and cryostat difficulties), the work was carried out as initially proposed. XES Fe and Mn  $K\beta$  spectra, as well as the HERFD-XAS Mn and Fe K-edge spectra, and their temperature evolution were measured for a  $\text{Mn}_{0.80}\text{Fe}_{1.26}\text{P}_{0.64}\text{Si}_{0.30}$  single crystal mounted with the  $c$ -axis nearly parallel and nearly normal to the emission direction (*i.e.*, with respect to the analyzer). In addition, the XES  $K\beta$  spectra of various polycrystalline materials ( $\text{Fe}_2\text{P}$ ,  $\text{MnFe}_{0.95}\text{P}_{0.66}\text{Si}_{0.34}$ ,  $\text{Mn}_{1.28}\text{Fe}_{0.67}\text{P}_{0.5}\text{Si}_{0.5}$ , Fe metal, Mn metal,  $\text{Sc}_{0.28}\text{Ti}_{0.72}\text{Fe}_2$ ) were measured to serve as references.

Figure 1 illustrates the temperature evolution of the K-edge HERFD-XAS and  $K\beta$  XES spectra for the  $\text{Mn}_{0.80}\text{Fe}_{1.26}\text{P}_{0.64}\text{Si}_{0.30}$  single crystal at Mn and Fe edges. On the HERFD-XAS spectra, tiny, yet clear, burst-like spectral changes are observed between 270 and 280 K: at about 10 eV above the edge for both Fe and Mn and on the pre-peak for Fe only. First, these changes that occur at the Curie temperature detected from bulk magnetic measurements confirm that the FOMT was crossed during the present experiment. These HERFD-XAS spectral changes suggest that Fe and Mn 4p states are affected by the FOMT. This observation is at odds with former XAS results measured in transmission or in total fluorescence and highlights the gain in resolution and the interest of the present HERFD-XAS experiments. Complementary calculations are in progress to further interpret these spectra.

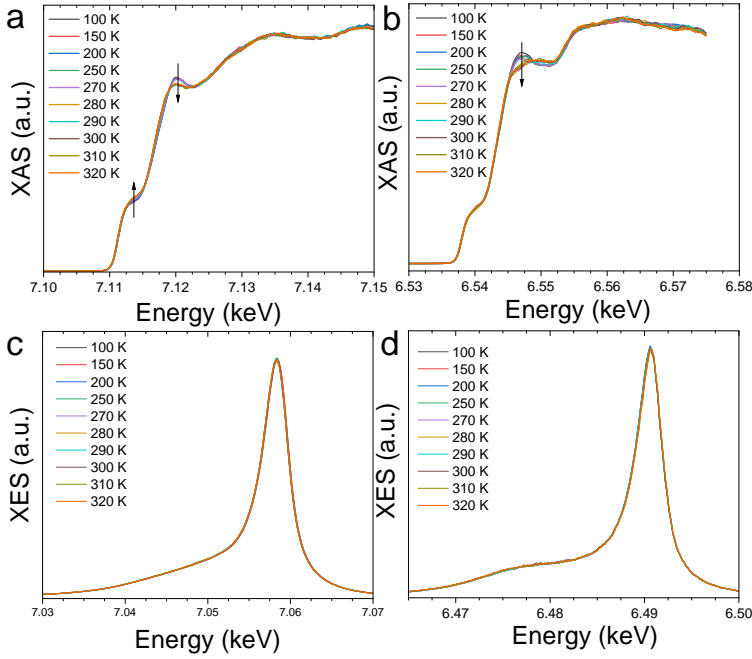


Figure 1: Temperature dependence of the HERFD-XAS (a,b) and XES (c,d) spectra at Fe and Mn edges for  $\text{Mn}_{0.80}\text{Fe}_{1.26}\text{P}_{0.64}\text{Si}_{0.30}$  single crystal (crystallographic  $c$  axis grazing to the emission direction). In panels a and b, the arrows mark out the spectral evolution with the increase in temperature.

In contrast to HERFD-XAS data, no noteworthy changes could be detected on XES  $K\beta$  spectra across the FOMT, neither for Fe nor Mn. This is a first qualitative indication that inner-shells, local charges and spin-densities are hardly affected by the FOMT.

We turned toward the  $K\beta$ -IAD method for a more quantitative estimate of the spin state. The analysis is presented in Figure 2 and was carried out by normalizing XES area to unity and using (Sc,Ti) $\text{Fe}_2$  alloy at 250 K and Mn metal as references for Fe and Mn, respectively. No significant evolution of the IAD across the FOMT could be distinguished, neither for Mn nor Fe. The IAD at the Mn edge of the crystal is comparable to that of  $\text{MnFe}_{0.95}\text{P}_{0.66}\text{Si}_{0.34}$ , in agreement with the moments of  $\sim 2.9 \mu_B/\text{Mn}$  expected in both compounds, and as expected significantly larger than that of  $\text{Mn}_{1.28}\text{Fe}_{0.67}\text{P}_{0.5}\text{Si}_{0.5}$  or Mn metal references. The average IAD value for Fe is in-between that of  $\text{MnFe}_{0.95}\text{P}_{0.66}\text{Si}_{0.34}$  and  $\text{Fe}_2\text{P}$  which is in line with the common expectations for the site occupancy of Fe and the Fe moments in these compounds. At the end, while the IAD method provides a reasonable estimate of the Mn or Fe moments in  $\text{Fe}_2\text{P}$  compounds, it does not reveal any significant evolution when crossing the FOMT as a function of the temperature, at least not within a  $\sim 0.3 \mu_B$  uncertainty. The absence of a significant moment evolution calls for revisiting the mechanism of the FOMT.

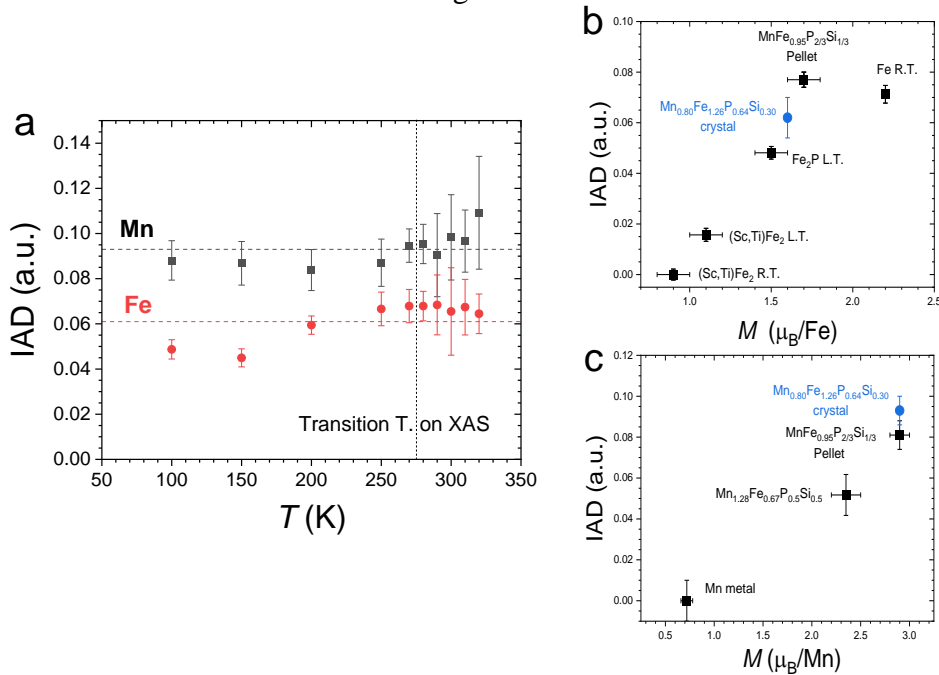


Figure 2: (a) Thermal evolution of the Integrated Absolute Difference (IAD) from XES measurements at Mn and Fe  $K\beta$  edges on  $\text{Mn}_{0.80}\text{Fe}_{1.26}\text{P}_{0.64}\text{Si}_{0.30}$  single crystal. (b) IAD scaling as a function of the expected Fe magnetic moment. (c) IAD scaling as a function of the expected Mn magnetic moment.

Measuring XES dichroic signals was attempted by changing the orientation of the sample after a full set of measurements was carried out in the same position. Unfortunately, the observed amplitude for the XES dichroic signal is on par with the noise level quantified as the dispersion between two measurements in identical conditions. A different approach should be looked for in order to measure such small signals on relatively small single crystals.