ESRF	**Experiment title:** Evolution of the orbital occupation in single-crystalline MnFe(P,Si) resolved by temperature dependent X-ray linear dichroism at P K-edge	**Experiment number**: HC-5008
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Names and affiliations of applicants (* indicates experimentalists):

Francois Guillou, College of Physics and Electronic Information, Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, 81 Zhaowuda Road, Hohhot 010022, Inner Mongolia, PR China

Report:

MnFe(P,Si) is one of the rare materials presenting a volume preserving isostructural first-order ferromagnetic magnetic transition at ambient conditions. This system attracts a continuous attention, both for its potential applications in thermal managment or waste heat recovery and for the scientific interest to unravel the underlying transition mechanism. Debates on the nature of the changes in electronic structure continue up to today. (Non-magnetic) X-ray absorption and linear dichroism which can provide element selective, orbital and orientation specific information were uniquely suited to address this issue. We initially intended to measure Fe, Mn and foremost P K-edge XLD spectra across the ferromagnetic transition of MnFe(P,Si) single crystals.

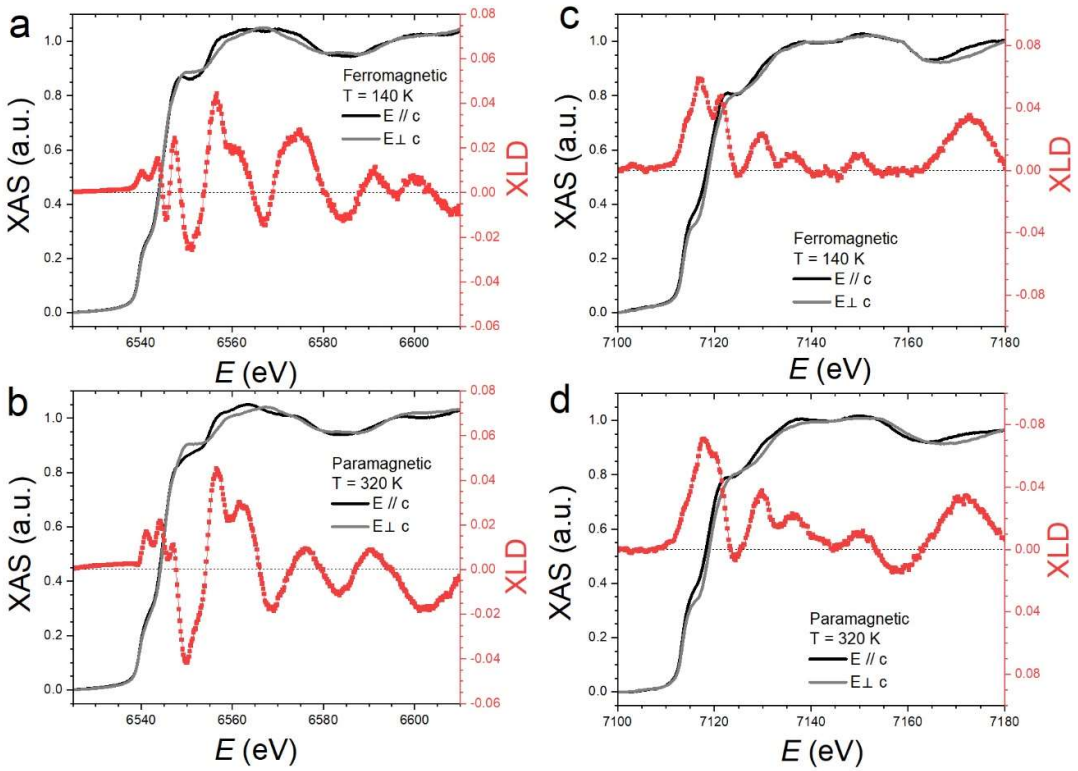

Figure 1: Mn K-edge x-ray absorption spectra and their difference below (a) and above (b) the Curie temperature of a $Mn_{0.70}Fe_{1.30}P_{0.68}Si_{0.30}$ single-crystal. Fe K-edge in similar conditions (c and d). Raw spectra are presented, without background subtraction nor re-absorption correction.

In accordance, x-ray absorption experiments and their dichroism were carried out at the Fe and Mn (Figure 1) and P K-edges (Figure 2) of a $Mn_{0.70}Fe_{1.30}P_{0.68}Si_{0.30}$ single crystal below (T = 140 and 190 K) and above (T = 300 and 320 K) its Curie temperature (T_C = 280 K). The measurements were carried out using a photodiode in backscattering geometry while changing the polarization of the undulator.

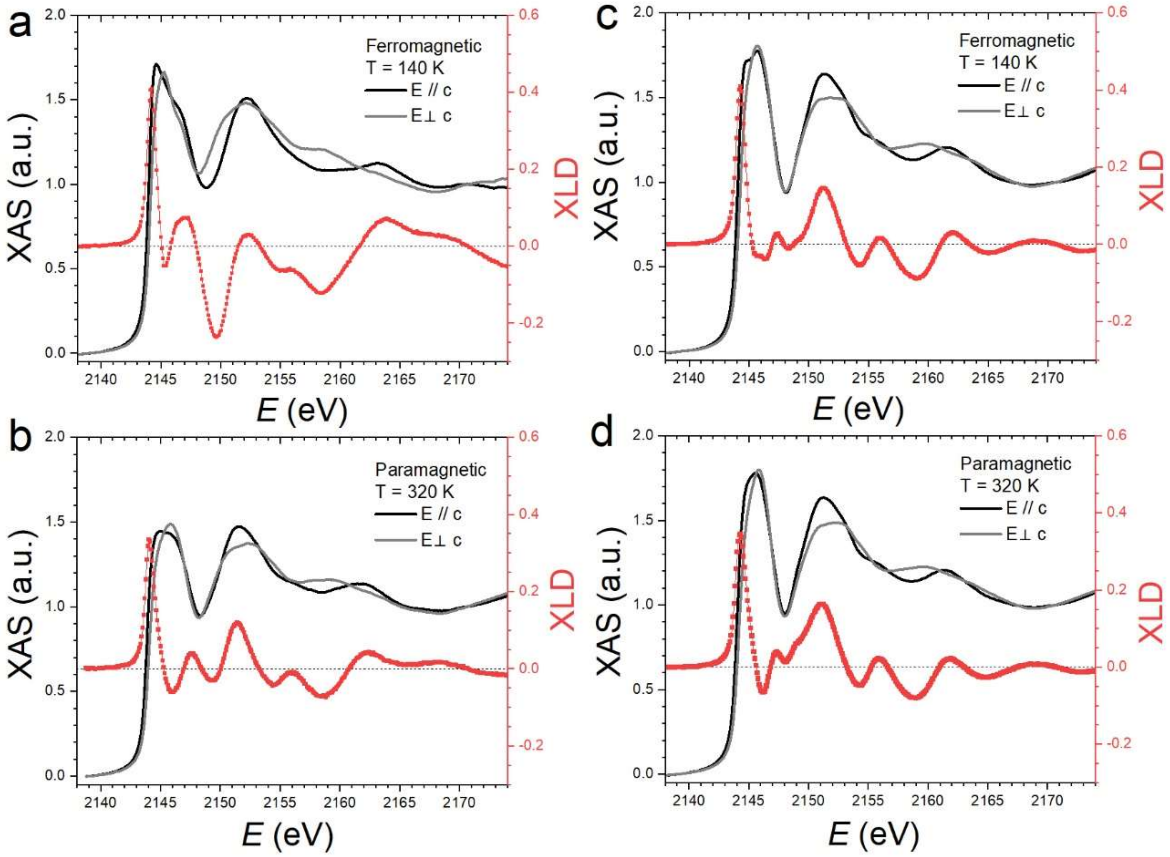

Figure 2: P K-edge x-ray absorption spectra and their difference below (a) and above (b) the Curie temperature of a $Mn_{0.70}Fe_{1.30}P_{0.68}Si_{0.30}$ single crystal. Similar spectra below (a) and above (b) the Curie temperature of a Fe_2P single crystal. Raw spectra are presented, without background subtraction nor re-absorption correction.

As expected, due to their nature and non-equivalent site occupancies, Mn and Fe spectra are different, yet both show only minor evolutions across the transition. In stark contrast, the XLD spectra at the P K-edge experience a major change with the development in the ferromagnetic state of a large feature (nearly 25% of the edge jump) at about 6-7 eV above the edge. While both $Mn_{0.70}Fe_{1.31}P_{0.68}Si_{0.31}$ and its Fe_2P (T_C = 212 K) parent material are known to present a distortion on the *c/a* ratio of the cell parameters at their ferromagnetic transition, only the former shows a truly significant reconstruction of its unoccupied phosphorous *p* states. To deepen the interpretation and address the hybridization scheme between transition metal and metalloid elements, several actions are in progress: first, experimental data will be corrected for background and re-absorption to facilitate the comparison with theory; second, further band structure calculations and spectral simulations are required to unravel the origin of the evolution at the P K-edge in $Mn_{0.70}Fe_{1.31}P_{0.68}Si_{0.31}$ single-crystal.
We note that complementary XLD measurements were carried out at room temperature on several $Mn_{2-x}Fe_xP_{1-y}Si_y$ crystals with different Mn/Fe site occupancy to serve as references.

To sum up this experimental session, temperature dependent XAS and XLD experiments were successfully caried out at ID12 according to the original proposal. Intriguing insights are anticipated on the evolution of the lattice and electronic structures of MnFe(P,Si) materials across their ferromagnetic transition. Data analysis, interpretation and report are in progress.