



	<b>Experiment title:</b> The role of pnictogen in magnetism of rare-earth cobalt pnictides	<b>Experiment number:</b> HC-2689
<b>Beamline:</b> ID12	<b>Date of experiment:</b> from: 30/08/2016 to: 05/09/2016	<b>Date of report:</b> 02/02/2017
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## Report:

This project was aiming to investigate rare-earth cobalt pnictides  $\text{RCo}_2\text{P}_2$  ( $\text{R}=\text{Pr}, \text{Eu}, \text{La}$ ) showing a unique interplay between local and itinerant magnetism, resulting in multiple magnetic transitions. The character of the coupling between the local  $4f$  and the itinerant  $3d$  magnetic moments and the magnetic properties of Co-pnictides are often assumed to be mediated by the position of the pnictogen atom in the lattice, and the pnictogen-Co phonon modes. We were originally planning to carry out x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) experiments upon pressure on the antiferromagnetic (AFM) parent phases  $\text{PrCo}_2\text{P}_2$  and  $\text{EuCo}_2\text{P}_2$ , as well as the mixed chemically compressed ferromagnetic (FM) compound  $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ . High pressure XMCD measurements were intended for the latter, as it is expected to become AFM, similar to the high pressure phase of  $\text{EuCo}_2\text{P}_2$ .

It appeared however necessary to carry out some preliminary measurements before starting such highly challenging XMCD experiments under pressure: first, to measure the XMCD at ambient pressure, and second, to explore the changes in Eu valence and more generally the changes in electronic structure at high pressure by XAS measurement. Thus the beamtime granted for HC-2689 has been equally spent on two quite independent issues: i) XMCD measurements in  $\text{RCo}_2\text{P}_2$  ( $\text{R}=\text{Pr}, \text{Eu}, \text{La}$ ) materials; ii) high pressure XAS measurements on  $\text{EuCo}_2\text{P}_2$ .

### i) XMCD measurements on $\text{RCo}_2\text{P}_2$ ( $\text{R}=\text{La}, \text{Pr}, \text{Eu}$ ) materials

XMCD measurements were carried out at ambient pressure on two selected FM compositions in the  $\text{RCo}_2\text{P}_2$  system.  $\text{LaCo}_2\text{P}_2$  ( $T_C \sim 130$  K) represents a material whose magnetism solely originates from the cobalt sublattice. On the contrary,  $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$  forms a nice example of rich mutual behavior of rare-earth and Co magnetic sublattices. Polycrystalline powders of each composition were mixed with black C and pressed into pellets. The XMCD experiments were carried out in the 17 T end station, using Si photodiode as fluorescence detector.

For  $\text{LaCo}_2\text{P}_2$ , XMCD spectra were recorded at 15 K and 5 T at the La  $L_3$  and  $L_2$ , Co K and P K edges. Sizable XMCD signals were observed at the La  $L$  edges and P K edge, demonstrating the development of induced magnetic moments on the La  $d$  and P  $p$  states due to hybridization with Co states. For each spectrum an energy point was selected and its field dependence recorded up to 8 T. The XMCD vs B profile shown in Fig. 1(a) is typical of that observed in bulk magnetic measurements and confirms the predominant role played by Co in  $\text{LaCo}_2\text{P}_2$ .

For  $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ , XMCD spectra were measured at Pr  $L_2$  and  $L_3$ , Eu  $L_2$  and  $L_3$ , Co K and P K edges at 15 K and 5 T. Sizable XMCD signals were detected at all edges. Eu XAS and XMCD spectra indicate a Eu mixed valence state. The field dependence of the XMCD was recorded for all absorption edges, Fig. 1 (b). While the field dependence of the Eu magnetization shows a usual FM trend, the Co sublattice shows a more complex behavior, without any saturation. The differences between Eu and Co sublattices indicate that

$\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$  is not a simple FM at low temperatures. More work is needed on this material, which has been the object of a dedicated proposal for the round of September 2016 (HC-2989).

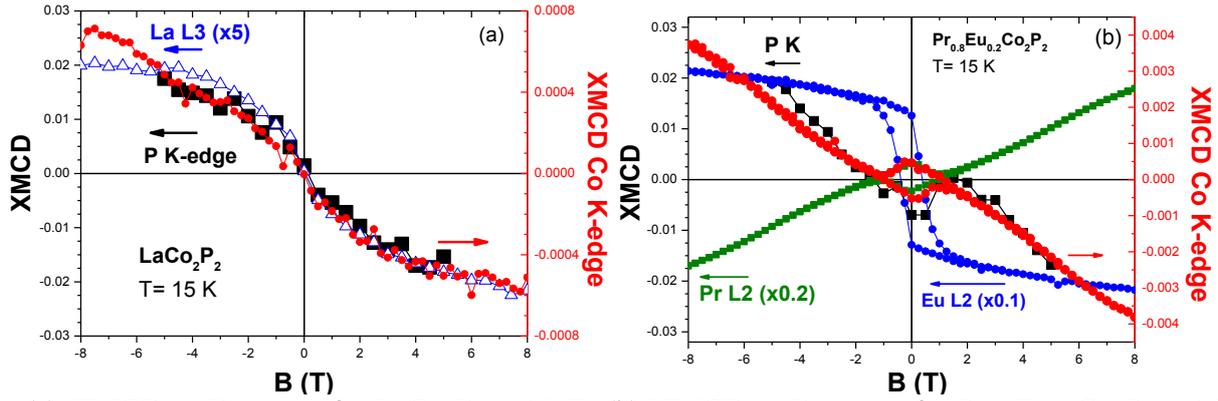


Fig1. (a) XMCD vs B curves for  $\text{LaCo}_2\text{P}_2$  at 15 K. (b) XMCD vs B curves for  $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$  at 15 K.

## ii) High pressure XAS measurements on $\text{EuCo}_2\text{P}_2$

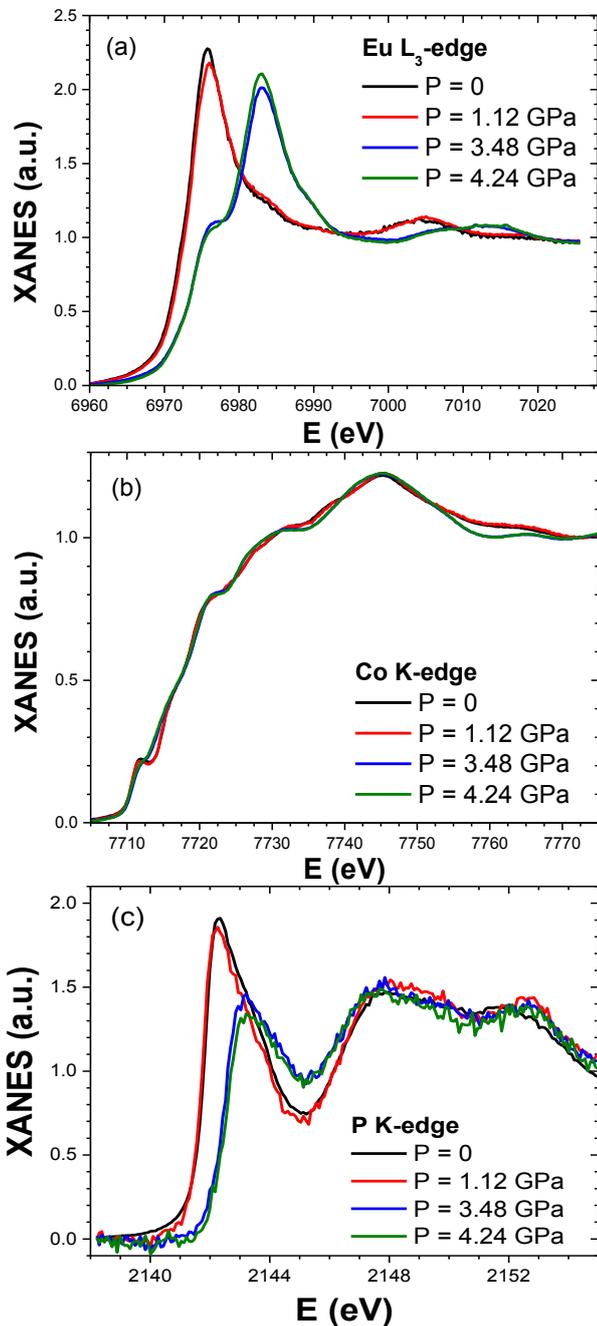


Fig. 2. XAS of  $\text{EuCo}_2\text{P}_2$  upon pressure at room temperature

$\text{EuCo}_2\text{P}_2$  is one of the “122” rare-earth pnictides having attracted a large interest. It represents rather complex magnetic structure with in-plane FM ordering of Eu moments and AFM ordering among the planes, which results in an incommensurate spiral AFM structure along the tetragonal  $c$  axis below  $T_N \sim 66.5$  K. Besides,  $\text{EuCo}_2\text{P}_2$  undergoes a discontinuous structural phase transition under pressure of about 3.1 GPa with a drastic reduction of the lattice parameter  $c$  ( $\Delta c/c \sim -13\%$ ), accompanied by a small increase in the lattice constant  $a$  ( $\Delta a/a \sim +3\%$ ). This pressure induced transition is accompanied by a change in Eu valence, which was confirmed by XAS and Mössbauer experiments. However a simultaneous investigation of the changes in electronic structure for all elements was still lacking. The XAS spectra measured at room temperature for Eu  $L_3$ , Co  $K$  and P  $K$  edges at 4 pressures (2 below and 2 above the transition) are shown in Fig. 2. High pressure conditions were achieved using the method developed at ID12 based on fully perforated DAC with diamond plate windows. One observes an incomplete valence change for Eu in line with former reports. The Co  $K$  edge shows the disappearance of the prominent shoulder in the rising part of the edge. This fingerprint of a metallization across the transition is a direct confirmation of former theoretical works in this system. A longstanding question has been, whether the excess electrons for a  $d$ -band filling originates only from the pressure-induced Eu valence transition [ $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ ], or does the formation of the P-P bond [ $2\text{P}^{3-} \rightarrow \text{P}^{4-}_2$ ] take part in this process as well. The pronounced electronic reconstruction observed on the phosphorus  $3p$  states in Fig. 2(c) brings new direct experimental insight on this issue. Comparison between these experimental results and theoretical simulations are currently in progress.