	Experiment title: Characterization of pressure-induced structural and magnetic changes in iron(II) hexacyanochromate(III) by soft XAS and XMCD studies	Experiment number: HE 2223
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Shifts: 18	Local contact(s): Dr. Flora YAKHOU	
Names and affiliations of applicants (* indicates experimentalists): Dr. Julio Criginsky CEZAR*, X-ray Absorption and Magnetic Scattering Group, ESRF. Dr. Tomasz KORZENIAK*, Instituto de Ciencia Molecular, Universidad de Valencia. Dr. Francisco M. ROMERO*, Instituto de Ciencia Molecular, Universidad de Valencia.		

Report:

The aim of the experiment was to employ the X-ray absorption (XAS) and magnetic circular dichroism (XMCD) techniques at the $L_{2,3}$ absorption edges of Fe and Cr to characterize the structural and magnetic changes of the Prussian blue analogue $K_{0.4}Fe_4[Cr(CN)_6]_{2.8} \cdot 16H_2O$ (*KFC* for short) that occur at moderate pressures.

We had already reported that *KFC*, a soft ferromagnet with critical temperature $T_C = 19$ K and coercive field (at 2 K) $H_c = 0.06$ T, undergoes a pressure-induced partial structural transformation that is accompanied by a decrease of magnetic moment and ordering temperature.¹ The phenomenon is completely reversible. However, at pressures higher than 1200 MPa, the behaviour is irreversible and the sample can be trapped in a *metastable state* after pressure release. Since soft X-ray experiments are usually not available at high pressures, we chose to perform XAS and XMCD experiments on this metastable material and compare them with data recorded for the original sample.

Figure 1a shows the comparison of data recorded at the Fe $L_{2,3}$ edges for both the original and metastable samples. The absorption spectrum of *KFC* closely resembles that obtained previously for iron (II) hexacyanochromate(III). The L_3 edge presents a double structure: the main peak observed at low energies (707 eV) corresponds to Fe^{II} bonded to nitrogen. With this metal environment, a shoulder has to be expected around 709 eV. Instead, a more intense feature appears in this energy range as a sharper peak. In the metastable sample, the relative intensity of this high-energy peak is higher and, interestingly, a new third feature appears around 712 eV. The same observations can be made for the L_2 edge. The absorption spectrum of *KFC* exhibits, as expected, a single peak at 720 eV together with a large shoulder at higher energy. Instead, the metastable sample shows clearly a double peak spectrum in this range together with a third feature around 725 eV. Spectra were also recorded at the Cr L edge. No remarkable differences between fresh and pressure-treated samples were observed.

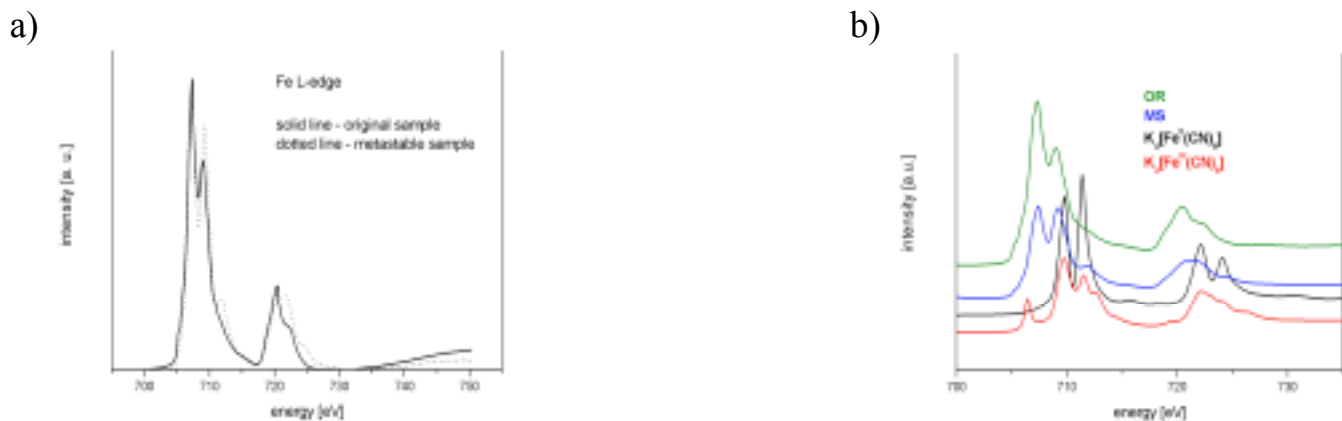


Figure 1. a: Iron $L_{2,3}$ -edges spectra of KFC (original sample) and the metastable sample obtained after pressure treatment. b: Iron $L_{2,3}$ -edges spectra of the original (OR) and metastable (MS) sample compared to model compounds $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

In order to get a proper explanation of the changes observed in the spectra, ligand field multiplet (LFM) calculations are currently being performed in collaboration with Prof. De Groot (Utrecht University, Netherlands). At present, we can only extract some qualitative information from the spectra by comparing them with model compounds. In Figure 1b, we compare the absorption spectrum of the original and metastable sample with model compounds potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III). Note that the distinctive pre-edge feature observed in the spectrum of the Fe^{III} model compound is not present in the spectrum of the metastable material. This clearly discards the Fe^{III} -CN configuration. On the other hand, the two doublets observed in the spectrum of the Fe^{II} model compound appear at energy values that match perfectly the peaks that appeared after the pressure treatment. It seems that the metastable sample contains an important fraction of iron sites with the Fe^{II} -CN configuration, in agreement with data obtained from Raman and Mössbauer spectroscopy. In any case, this has to be confirmed by simulation of the spectra using LFM calculations, which will provide also a quantitative description of the process.

The fact that the pressure-induced transformation involves a linkage isomerization of the cyanide ligand without changes in the oxydation state ($Cr^{III}-C\equiv N-Fe^{II} \rightarrow Cr^{III}-N\equiv C-Fe^{II}$) explains perfectly the decrease in magnetic moment and critical temperature observed upon pressure application: when the cyanide anion isomerises, the electronic configuration of the iron metal ions changes from high-spin ($S = 2$) to low-spin ($S = 0$). Both the number of spin carriers and the connectivity of the magnetic lattice decrease dramatically. This behaviour should be clearly seen in XMCD studies. Indeed (Figure 2), the XMCD spectrum of the metastable sample is less intense than that of the original material, as expected for a lower fraction of paramagnetic centers.

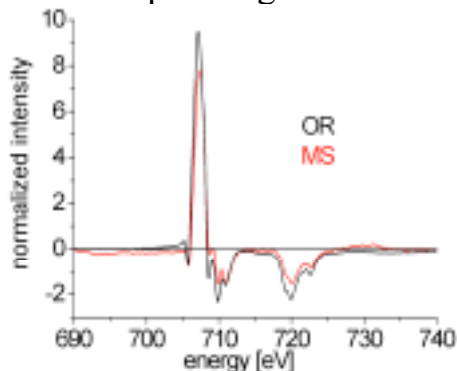


Figure 2: Iron XMCD spectra for OR and MS.