



	Experiment title: The effect of nanoconfinement on photomagnetic properties of CoFe Prussian Blue Analogs unraveled by Fe and Co K-edge HERFD-XAS and RXES	Experiment number: CH-5021
Beamline: BM20	Date of experiment: from: June 26 th 2017 to: July 4 th 2017	Date of report: Feb 14 th 2018
Shifts: 18	Local contact(s): Kristina Kvashnina	<i>Received at ESRF:</i>
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Our group successfully synthesized two CoFe Prussian Blue Analogs (PBAs; $\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7}$ and $\text{Rb}_2\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3}$) at the nanoscale by confining their growth into the porosity of mesoporous silica monolith. But some differences arose in their crystallographic and electronic structure and magnetic properties with respect to the macroscopic PBA, even if the photomagnetic properties of the macroscopic PBA are retained at the nanoscale. Therefore the goal of the experiment was to determine the electronic structure and local symmetry of the Co and Fe ions in the ground and excited states of photomagnetic PBAs nanoparticles by high-energy resolution fluorescence detected XAS through a detailed analysis of the Fe and Co K pre-edge.

The proposal initially aimed at measuring the HERFD-XANES spectra of the macro- and nano-PBAs at room temperature and at 10K under light excitation using the new 1 crystal spectrometer of BM20, in order to probe both the ground and excited states. Nevertheless, not enough space was free around the spectrometer to install the minicryostat of the Sample Environment Support Service (and the required liquid He container). We thus decided to change the plan and we concentrated on room-temperature measurements but with an additional series of samples : molecular derivatives of CoFe-PBA; this choice enable to get three different sizes of the same PBA (a polymer with particles around 150-200 nm, nanoparticles of 5 nm and molecules of 5Å). We also investigated additional macroscopic PBA containing Cs and Na cations instead of Rb, in order to study the effect of the nature of the alkali cation; it is known to significantly impact the photomagnetic properties, but the reason is still unknown. The effect of the nature of the alkali cation was also investigated for the molecule. We could record HERFD-XAS spectra (monitoring the $\text{K}\alpha_1$ line) at both the Co and Fe K edges (using respectively a Si(440) and a Si(531) crystal) for all the samples, as well as RIXS planes at the Fe K-edge for 3 macroscopic PBA.

In the case of the size reduction effect, the comparison of the polymer, the nanoparticles and the molecule show significant differences in the speciation of both the Co and Fe ions. For

instance, at the Fe K-edge, the single pre-edge peak for the 3 compounds is consistent with the expected low-spin state of the Fe^{II} ions but for the molecule, the intensity of this pre-edge peak is more intense, indicating a more important distortion of the Fe site for the molecule with respect to the polymer and the nanoparticles. At the Co K-edge, the most significant differences arise between the nanoparticles and the 2 other compounds (polymer/molecule) : the white line is splitted, indicating two oxidation states for the Co ions in the nanoparticles, while both the molecule and the polymer contain only Co^{III} ions. Nevertheless, the energy of the 1st exafs feature is different for the 3 compounds, indicating a different Co-to-1st neighbors distance.

In the case of the variation of the nature of the alkali cation inserted in the polymer PBA, the Fe K-edge spectra reveals an identical local environment for the Fe ions (also with a linear Co-NC-Fe linkage) whatever the alkali cation; the oxidation state is however different, with a +II oxidation state for the free- and Na-bearing PBAs and a +III one for the Cs and Rb-bearing PBAs. At the Co K-edge, the differences are much more pronounced. The oxidation state is consistent with those of the Fe ions, with Fe^{II}-Co^{III} pairs for the free- and Na-bearing alkali cation PBAs and Fe^{II}-Co^{III} pairs for the Cs and Rb-bearing PBAs. The energy of the 1st EXAFS peak also reveals longer Co-1st neighbor distances for the Cs and Rb-bearing PBAs. The number of pre-edge features observed for this set of PBAs is consistent with the information deduced from the main edge. Interestingly, in the case of Rb and Cs alkali-cations in the polymer, the spectra at both edges are almost superimposed; this similarity is also observed for the molecules : the two Rb and Cs-bearing molecules display an identical speciation of both the Fe and Co ions in the two compounds.

To conclude, we have efficiently used this beamtime to investigate (i) the effect of size reduction on the electronic structure and local environment of the Fe and Co ions in macroscopic PBAs (polymer), nanoparticles and molecules, and (ii) the effect of the nature of the alkali cation (in polymer and molecule PBA). The stability of the beamline as well as the high quality of the spectrometer enables to record high-quality data. The initial measurements plan had to be adapted due to technical constraints (no space to combine the microcryostat with the 1 crystal spectrometer), but it enabled to record data on molecular PBA, which will enable to get a clearer picture of the size reduction effect on crystallographic and electronic structure.

First results were presented at a poster at the ESRF Users' meeting 2018*, and an abstract was submitted to present more complete results at the XAFS conference in July 2018.

* The poster does not appear in the conference booklet because of deadline delay but it was displayed on a spare panel. It is however recorded in the database of the Users' meeting and is entitled "The Co and Fe speciation in PBAs and their derivatives: Evolution from the polymer down to the molecule"

The Co and Fe speciation in PBAs and their derivatives : Evolution from the polymer down to the molecule

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Introduction

Prussian Blue Analogs (PBA) are well-known for their photomagnetic properties, which depend on the nature of the transition metals and on the number/nature of the inserted alkali cation. Their very rich chemistry also enables to shape them at a nano- or molecular scale, which is priceless for a potential use in real devices. Nevertheless, two big questions remain open :

(i) What is the effect of size reduction on photomagnetic properties?
(ii) Why the nature of the alkali cation has such a drastic effect?

HERFD-XAS on BM20
Kvashnina and Schenstov (2019) J. Synch. Rad. 23:305-347

- Co and Fe K-edge High-Resolution Fluorescence-Detected X-ray Absorption
- Use of the new 1-crystal spectrometer (since 01/2018 : 5 crystals available)
 - Co Ka : Si (531) - d = 1m
 - Fe Ka : Ge(220) - d = 1m

Polymer (100 - 200 nm particles)
Catin et al. (2016) JACS 138:11552-11559

- Dropswise precipitation in aqueous solution of the precursors (K₂[M(CN)₆] and (NO₃)₂ (+)NO₂ if needed)
- Photomagnetic properties depending on the alkali cation

$X_n[M(CN)_6]_n \cdot nH_2O$
n: Alkali cation
M, n: Transition metal

Nanoparticle (5 nm)
Moun et al. (2017) EJCIC 2017:1303-1313

- Impregnation of a mesoporous silica monolith containing Co ions (obtained by sol-gel chemistry) with the K₂[Fe(CN)₆] (+RbNO₃) precursor (soluble solvent method).
- Core-shell structure (induced by the confined growth)
- Conservation of the photomagnetic properties of the RbCoFe polymer but a different ground state

Molecule
Jimenez et al. (2017) Dalton Trans. 46:15549-15557

- Self-assembly of preformed complexes (Rb₄[Fe(CN)₆] and CoCl₂ with L = tridentate blocking ligand) in presence of alkali cation.
- Cubic molecular complex
- Photomagnetic properties less dependent on the alkali cation than in polymers.

Size reduction effect
The case of the photomagnetic RbCoFe PBA

- Speciation of Fe : +II oxidation state, octahedral symmetry whatever the size
- Identical Fe-C distances
- Identical Co-NC-Fe linkage in the polymer and the 5nm particle
- Only 1 pre-edge peak, consistent with the low-spin state of the Fe^{II} ions
- Significant change in the pre-edge intensity for the molecule : the Fe site is more distorted than in the polymer and the 5nm-particle

Impact of the alkali cation nature

- 2 sets of PBAs : CoFeNaCoFe with Co^{II}Fe^{II} pairs and RbCoFeCsCoFe with Co^{III}Fe^{II} pairs
- Number of features in the pre-edge consistent with Fe(LS) Fe^{II}(LS) and Co(HS)Co^{II}(LS) ions
- Different local environment for Co
- Longer Co-N distances for RbCoCs

Conclusion

First results

- Co and Fe K-edge XAS on the same PBA but at 3 different scales (polymer, 5nm-particle, molecule)
- Information on the ground state of the photomagnetic compounds with a 1st evaluation of the size effect
- 1st evaluation of the effect of the alkali cation nature at different scales

Next steps

- Investigation of the photomagnetic properties (measurements at low temperature under irradiation)
- A coupled analysis of the spectra with conventional XAS data
- DFT calculations of the spectra (including the pre-edge)

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