Investigation of the structure-property relationship in Prussian Bleu analogs by a coupled laboratory/multi-beamlines synchrotron approach

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Prussian Blue Analogs (PBA) of general formula YxA4[B(CN)6](8+x)/3 (Y = alkali cation; A,B = transition metal (TM); x = 0-4) are studied for their (photo)magnetic property, which are interesting for high-density information storage. For some stoichiometry, a reversible metal-metal charge transfer along the A—NC—B cyanide bridge can indeed be photoinduced, but it is observed at a temperature that is too low to be used in real applications. The cyanide bridge structural distortion appears to be the key to control and adjust this property. As they are too small to be quantified with classical structure-characterization techniques, we are working on the development of a methodology based on X-ray Magnetic Circular Dichroism (XMCD) at the TM K-edge, which is a derived technique from X-ray Absorption Spectroscopy (XAS). First measurements for NiFe PBAs indeed showed significant variations of the Fe and Ni K-edges signals related to pressure-induced structural distorsion1,2. Nevertheless, the XMCD signals at the TM K-edge are not well understood yet, and it is mandatory (i) to develop a methodology to quantify small structural distortions from these signals and (ii) to disentangle the physical effects originating TM K-edge XMCD.

To develop this methodology, we are conducting a systematic XMCD investigation of non-photomagnetic PBAs (A4[B(CN)6]2.7) at the K-edge of the A and B transition metals (ODE@SOLEIL, St Aubin). Classical XAS measurements are also performed to characterize in details the electronic structure and local environment of the transition metals in the model PBAs (FAME-UHD@ESRF, Grenoble; SAMBA@SOLEIL). By combining the information obtained thanks to this multibeamlines approach, we will (i) get a deep knowledge of our model PBAs and hence (ii) relate the variations observed on the XMCD signals to variations in the electronic and structural parameters.

We will present our first results on the A4[Fe(CN)6]2.7 (A = Mn, Co, Ni, Cu) series, with a particular emphasis on (i) the interest of combining several synchrotron techniques to get a wider picture and (ii) the priceless complementarity of laboratory (X-ray diffraction, SQUID magnetometry) and synchrotron (TM K-edge XAS and XMCD) techniques to better understand and so constraint structure-property relationship.

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