Investigation of Prussian Blue Analogs by XMCD at the K-edge of transition metals

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Abstract. Despite transition metal (TM) K-edge x-ray magnetic circular dichroism (XMCD) seems an interesting tool to get magnetic and structural information at the atomic scale, the effects originating this signal are still poorly understood. We thus initiated a deep investigation of the TM K-edge XMCD using Prussian Blue analogs (PBA) as model-compounds. In a recent study of the NiFe PBA family, we demonstrated that the XMCD signals at the TM K-edges strongly vary with external (mechanical) or internal (chemical) pressure and so that they are highly sensitive to small structural distortions. Following these first results, we extended this approach to the MnFe and CoFe families to evaluate the effect of electronic parameters (number of unpaired electrons of the \( M^{II} \) TM) on the XMCD signal. All the results set milestones in the disentanglement of the components originating the XMCD signals at the K-edge of TM and will eventually help in a better understanding of the photomagnetic properties of PBAs.

1. Introduction

Transition metals (TM) \( L_{2,3} \)-edges X-ray Magnetic Circular Dichroism (XMCD) is a well-known and widely used technique to characterize magnetic compounds [1, 2, 3, 4, 5, 6] but only very few studies were conducted at the TM K-edges [7, 8, 9]. This technique has been used for instance to characterize under pressure Co [10], magnetite [11] or the structural \( \alpha - \epsilon \) phase transition in iron [12, 13]. In the case of molecular magnets, TM K-edge XMCD was used in two cases. Verduguer et al. first investigated three molecule-based magnets from the Prussian Blue Analogs (PBA) family (Cs\(^I\)Mn\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)], Cs\(^I\)Ni\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)] and Ni\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_2\)) and observed at each metal edge (Ni, Mn and Cr) a dichroic signal in the energy range corresponding to the allowed transitions to the metal 4\( p \) levels [14]. Champion et al. then concentrated on the Rb\(_{1.8}\)Co\(_4\)[Fe(CN)\(_6\)]\(_3\).\(_3\) PBA at both the Co and Fe K-edges for the \{Co\(^{II}\)Fe\(^{III}\)\} photoexcited states [15]. They characterized the relative orientation of the local magnetic moments of the metallic ions in the photoinduced metastable state and proposed the first direct experimental evidence of the ferrimagnetic behavior of the photoinduced metastable state in this PBA.

However, TM K-edge XMCD is still poorly understood and the effects giving rise to a signal and their influence on its spectral shape have still to be disentangled. PBA are ideal candidates as model-compounds for such an investigation. Their general formula is \( C_xA_y[B(CN)\(_6\)]_y\Box(4-y) \), where A and B are transition metals, C an alkali cation and \( \Box \) [B(CN)\(_6\)] unit vacancies. The nature of the alkali cation and of the two transition metals as well as the number of alkali cation can indeed be varied while most often conserving a face-centered cubic structure.
These characteristics offer the unique possibility to independently vary chemical, structural and electronic parameters and then evaluate their impact on the XMCD signal at the TM K-edge.

We present here the latest results obtained by TM K-edge XMCD on several PBAs (NiFe, CoFe and MnFe families). All the measurements were performed on the ODE beamline (SOLEIL synchrotron, Saint Aubin, France) \[16\]. The XMCD signals were recorded for a 1.3T magnetic field, at 10K for the NiFe PBAs and at 4.2K for the CoFe and MnFe PBAs in order to be below the Curie temperature of the compounds.

2. XMCD and structural deformation

The NiFe PBAs family was the first investigated by TM K-edge XMCD to understand the impact of structural deformation on the XMCD signals, since they never present a pressure-induced charge transfer between the Ni\(^{II}\) and Fe\(^{III}\) ions. Four NiFe PBAs were investigated: Ni\(_4\)Fe(CN)\(_6\)\(_{2.7}\) (called NiFe), CsNi\(_4\)Fe(CN)\(_6\)\(_{1.3}\) (called CsNiFe), Cs\(_2\)Ni\(_4\)Fe(CN)\(_6\)\(_{3.3}\) (called Cs\(_2\)NiFe) and Rb\(_2\)Ni\(_4\)Fe(CN)\(_6\)\(_{3.3}\) (called Rb\(_2\)NiFe). The synthesis of these compounds and the experimental details are given in Ref.\[17\], and we remind here the main results of this study.

The Ni and Fe K-edges XMCD signals of NiFe for variable pressure (0-7 GPa) are presented in figure 1. At ambient pressure, both signals are mainly characterized by an intense peak corresponding to the absorption edge (at 7128 eV in the case of Fe and at 8348 eV in the case of Ni). The relative sign of the XMCD signals at both edges indicates a ferromagnetic 3d-3d exchange interaction between the magnetic moments borne by the Ni and Fe ions. When applying a pressure (up to 7 GPa), the sign and shape of the XMCD signals remain unchanged but a significant variation of the intensity is observed: it first increases and then decreases until the signal completely disappears at 7 GPa (resp. 1.6 GPa) in the case of Fe (resp. Ni). Consistently with the variations observed on the x-ray absorption spectra for the different pressures, this pressure dependence of the XMCD signal indicates that its intensity is strongly related to the 3d-4p and 4p-4p orbital overlapping and exchange interactions, as well as to symmetry changes of the TM sites (progressive tilt of the rigid [Fe(CN)] entities around the Fe\(^{III}\) ions crystallographic positions or/and the departure of the Ni coordination polyhedra from the \(O_h\) symmetry), as explained in detail in Ref.\[17\].

The insertion of alkali cation inside the structure enables to induce an internal chemical pressure on the structure, and consequently better understand the results obtained in the opposite case of an external mechanical pressure. Figure 2 thus compares the Fe K-edge XMCD signals for the four NiFe PBAs (NiFe, CsNiFe, Cs\(_2\)NiFe and Rb\(_2\)NiFe). Here also, only the intensity of the peak corresponding to the absorption edge (7128 eV) varies with the number of alkali cation present inside the PBA unit cell. The highest intensity is observed for NiFe, which presents the structure with the highest number of vacancies and distortion since no alkali cation is present. The intensity then decreases for CsNiFe by almost a factor of 2 and the two compounds with two cations per unit cell (Cs\(_2\)NiFe and Rb\(_2\)NiFe) display the lowest intensity. These changes are consistent with those observed for NiFe for low pressures below 1 GPa (Figure 1): the higher the pressure, the more the Ni coordination polyhedra departs from the \(O_h\) symmetry and the higher the intensity of the XMCD signal at the TM K-edge. It is to be noted that the nature of the alkali cation seems to be of little influence, since the intensity is similar for Cs\(_2\)NiFe and Rb\(_2\)NiFe despite their quite different ionic radii (1.72 Å in the case of Rb\(^+\) and 1.88 Å in the case of Cs\(^+\)). This may suggest that for a given number of alkali cation in the unit cell, the size of the alkali cation induces only a weak dilatation/contraction of the structure.

3. Influence of the number of unpaired 3d electrons at the divalent site

We present now the first results on the K\(_4\)Co\(_4\)Fe(CN)\(_6\)\(_{2.7}\) and Mn\(_4\)Fe(CN)\(_6\)\(_{2.7}\) PBAs (respectively called CoFe and MnFe). If including NiFe, this Mn-Co-Ni serie illustrates the
Figure 1. Variable pressure normalized XMCD signals at the Ni (left) and Fe (right) K-edges of NiFe (recorded at 10K).

Figure 2. Normalized XMCD signals at the Fe K-edge of a series of NiFe PBA at ambient pressure (recorded at 10K).

effect of the number of unpaired 3d electrons of the divalent transition metal on the XMCD signal at the corresponding TM K-edge. Indeed, MnFe has a spin \( S=5/2 \), CoFe \( S=1/2 \) and NiFe \( S=1 \).

The normalized XMCD signals at the Fe K-edge and the M\text{II} (M=Mn, Co, Ni) edges are presented in figure 3. The relative sign of the Fe K-edge signal and the M\text{II} K-edge one are consistent with the Fe-M\text{II} 3d-3d exchange interactions. In the case of CoFe (resp. NiFe), the opposite (resp. identical) sign of the signals is the signature of a ferrimagnetic (resp. ferromagnetic) coupling of the Co\text{2+} (resp. Ni\text{2+}) and Fe\text{3+} sublattices. The case of MnFe is more complicated, since the XMCD signal at the Mn K-edge presents both a negative and positive contributions; the positive contribution clearly relates to the ferrimagnetic coupling between the Mn\text{2+} and Fe\text{3+} sublattices, but the origin of the negative contribution is still unclear. This difference between Co\text{2+} and Ni\text{2+} on the one side and Mn\text{2+} on the other side probably originates from the different filling of the 3d orbitals between these three M\text{II} cations (insets in figure 3). Indeed, in the cases of Co\text{2+} and Ni\text{2+}, each \( e_g \) orbital contains an unpaired electron and only one (resp. zero) unpaired electron is present in the \( t_{2g} \) orbital in the case of Co\text{2+} (resp. Ni\text{2+}). The opposite situation is observed in the case of Mn\text{2+} : three unpaired electrons fill the \( t_{2g} \) orbital while only two in the \( e_g \) orbital. Finally, at the Fe K-edge, the less intense broader peak at 7145.9 eV observed in the case of NiFe was attributed to the multiple-scattering contribution [17]. Despite a lower signal-to-noise ratio, this feature is also visible in the case of MnFe; we can also expect this feature to be present for CoFe but measurements with a better statistics are still required to confirm it.

4. Conclusion

We summarized here recent results obtained by XMCD at the TM K-edges of several PBAs. We undertook the comparison of the XMCD signals at different metallic edges for three M\text{II}Fe\text{III} PBAs (M = Mn, Co, Ni). We could conclude from these first preliminary results that the number of unpaired 3d electrons of the divalent transition metal in a M\text{II}Fe\text{III} PBA and the repartition of these unpaired electrons between the \( t_{2g} \) and \( e_g \) orbitals have a strong influence on the XMCD signal at the M\text{II} K-edge, whereas at the Fe K-edge, the dominant influence is the 3d-3d exchange interaction. The investigation of NiFe PBAs also demonstrated the potential for the XMCD signals at the TM K-edges as a sensitive probe of small structural distortions, induced either by an external or internal (via the insertion of alkali cation) pressure. All these
Figure 3. Normalized XMCD signals of the $M^{II}$-Fe$^{III}$ (M = Mn, Co, Ni) PBA series at the Fe and M K-edges recorded at 4K ($\text{MnFe}$ and $\text{CoFe}$) or 10K ($\text{NiFe}$) The electronic configuration of each cation (Fe$^{3+}$/low-spin, Mn$^{2+}$/Co$^{2+}$/Ni$^{2+}$/high spin) are illustrated in the insets.

results eventually indicate that the deep investigation of PBA by XMCD at the TM K-edge will bring new insights into the versatile properties of PBAs, in particular photomagnetism [18, 19, 20], and therefore shed a new light on these compounds for their use in new high-density data-storage systems.

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References
[1] Van der Laan G and Figueroa A I 2014 Coord. Chem. Rev. 277-278 95
[2] De Groot F and Kotani A 2008 Core Level Spectroscopy of Solids (Taylor & Francis, New York)
[3] Funk T, Deb A, George S J, Wang H and Cramer S P 2005 Coord. Chem. Rev. 249 3
[4] Goering E, Will J, Geissler J, Justen M, Weigand F and Schuetz G 2001 Journal of Alloys and Compounds 328 14
[5] Thole T, Carra P, Sette F and Van der Laan G 1992 Physical Review Letters 68 1943
[6] Brouder Ch and Haitak M 1991 Physical review B 43 3809
[7] Torchio R, Mathon O and Pascarelli S 2014 Coord. Chem. Rev. 277-278 80
[8] Brouder Ch, Alouani M and Bennemann K H 1996 Physical review B 54 7334
[9] Guo G Y 1996 J. Phys.: Condens. Matter 8 L747
[10] Torchio R, Monza A, Baudelet F, Pascarelli S, Mathon O, Pugh E, Antonangeli D and Itié J-P 2011 Physical review B 84 060403(R)
[11] Baudelet F, Pascarelli S, Mathon O, Itié J-P, Polian A and Chervin J-C 2010 Physical review B 82 140412(R)
[12] Baudelet F, Pascarelli S, Mathon O, Itié J-P, Polian A, d’Astuto M and Chervin J-C 2005 J. Phys.:Condens. Matter 17 S957
[13] Mathon O, Baudelet F, Itié J-P, Polian A, d’Astuto M, Chervin J-C and Pascarelli S 2004 Physical review Letters 93 255503
[14] Verdaguer M, Mallah T, Helary C, L’Hermitte F, Sainctavit Ph, Arrio M-A, Babel D, Baudelet F, Dartyge E and Fontaine 1995 Physica B 208-209 765
[15] Champion G, Escax V, Cartier dit Moulin C, Bleuzen A, Villain F, Baudelet F, Dartyge E and Verdaguer M 2001 J. Am. Chem. Soc. 123 12544
[16] Baudelet F, Kong Q, Nataf L, Cafun J-D, Congeduti A, Monza A, Chagnot S and Itié J-P 2011 High Pressure Research 31 136
[17] Cafun J-D, Lejeune J, Itié J-P, Baudelet F and Bleuzen A 2013 The Journal of Physical Chemistry C 117 19645
[18] Sato O, Iyoda T, Fujishima A, Hasimoto K 1996 Science 272 704
[19] Ohkoshi S, Tokoro H, Hashimoto K 2005 Coord. Chem. Rev. 249 1830
[20] Cafun J-D, Lejeune J, Baudelet F, Dumas P, Itié J-P and Bleuzen A 2012 Angew. Chem. Int. Ed. 51 9146