Interplay between Transition-Metal K-edge XMCD and Magnetism in Prussian Blue Analogs

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ABSTRACT: To disentangle the information contained in transition-metal K-edge X-ray magnetic circular dichroism (XMCD), two series of Prussian blue analogs (PBAs) were investigated as model compounds. The number of 3d electrons and the magnetic orbitals have been varied on both sites of the bimetallic cyanide polymer by combining with the hexacyanoferrate or the hexacyanochromate entities’ various divalent metal ions $A^{2+}$ ($\text{Mn}^{2+}$, $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, and $\text{Cu}^{2+}$). These PBA were studied by Fe and Cr X-ray absorption spectroscopy and XMCD. The results, compared to those obtained at the A K-edges in a previous work, show that transition-metal K-edge XMCD is very sensitive to orbital symmetry and can therefore give valuable information on the local structure of the magnetic centers. Expressions of the intensity of the main $1s \rightarrow 4p$ contribution to the signal are proposed for all K-edges and all compounds. The results pave the way toward a new tool for molecular materials able to give access to valuable information on the local orientation of the magnetic moments or to better understand the role of 4p orbitals involved in their magnetic properties.

1. INTRODUCTION

Improvement and discovery of new magnetic properties are major challenges to enable novel technological applications in several fields. In this context, a strong interest has grown for techniques able to probe at a local scale the magnetic properties of matter such as X-ray magnetic circular dichroism (XMCD). XMCD, derived from X-ray absorption spectroscopy, has indeed the great advantage to present both a chemical and an orbital selectivity. This technique has rapidly become over the past few decades of major importance for several scientific communities, especially physics, chemistry, or biochemistry. Nevertheless, if the element selectivity has been largely explored, the full exploitation of orbital selectivity has been impeded by the lack of satisfactory interpretation of the XMCD signal at some metal edges. Thus, in the case of first-row transition metals (TMs), which are of first importance in the fields of magnetometry and magnetic materials, XMCD at the $L_{2,3}$ edges has become a reference technique. Due to the sum rules, quantitative information about the spin and orbital momenta can be extracted from the XMCD signals and crystal field multiplet calculations well reproduce the signals. On the contrary, the interpretation of TM K-edges XMCD signals is still widely debated, despite the first spin-dependent absorption in the X-ray range was observed at the K-edge of iron. And yet this technique offers many advantages, among them (i) compatibility with demanding sample environments, which made it the preferred technique to probe magnetism under pressure, and (ii) bulk sensitivity without limitation to surface species. However, a clear interpretation of these signals is still missing, in spite of the many efforts devoted to apply the sum rule at the K-edges, and to understand and reproduce the signals, especially by using different calculation approaches.

So, we are engaged in the development and implementation of an original experimental approach, so that the processes at the origin of these TM K-edges XMCD signals can be disentangled. Most of the works on TM K-edges in the literature deal with the investigation of metal oxides and especially metals, metal alloys, and intermetallics, the electronic properties of which are well described in terms of the band structure. Works dealing with molecular compounds, in which the electrons are localized and the electronic properties are well described in terms of molecular orbitals, are scarcer. And yet, molecular orbital approaches have proved fruitful to describe and anticipate some electronic properties of molecular compounds. Our work belongs within this kind of less developed approach and invites us to take a fresh look at this long-standing issue. Our strategy, presented in a previous work, uses the versatile chemistry of a family of isostructural coordination compounds, the Prussian blue
anals (PBAs). Briefly, PBAs with the chemical formula \( A_p[B(CN)_{6q}] \cdot xH_2O \), where A and B mostly are first-row TM ions, form a large family of compounds exhibiting the well-known face-centered cubic structure.\(^{35-37}\) Figure 1a presents

![Diagram](attachment://figure1a.png)

**Figure 1.** (a) Scheme of the unit cell of a Prussian blue analog with the chemical formula \( A_p[B(CN)_{6q}] \cdot xH_2O \). Yellow circles stand for the B\(^6\) ion (Cr\(^{3+}\) or Fe\(^{3+}\)), light gray circles for the A\(^2+\) ions (Mn\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\)), dark gray circles for the carbon atoms, blue circles for the nitrogen atoms, and red circles for the oxygen atoms. The zeolitic water molecules are omitted for clarity. (b) Spin quantum number and expected orientation of the magnetic moments carried by the A\(^2+\) and B\(^6\) (Cr\(^{3+}\), Fe\(^{3+}\)) TM ions in an external magnetic field for the AFe (left) and ACr (right) series.

one unit cell of PBA. The charges of the \([B(CN)_{6}]^q\) entities and of the A\(^{2+}\) ions are generally different so that the electroneutrality of the solid is ensured by \([B(CN)_{6}]^p\) vacancies. A large variety of A and B TM ions can thus be combined in isostructural compounds, allowing for the independent variation of the magnetic orbitals on both A and B sites and consequently for the analysis of their effect on the XMCD signal at both TM K-edges. Nevertheless, it has to be noticed that PBAs are usually obtained in powder form and crystals having a size big enough to be analyzed by single-crystal diffraction are scarce.\(^{38,39}\) Given this lack of big enough crystals and the intrinsic structural disorder of the compounds due to the presence of vacancies and water molecules as well as possible distortions of the B–CN–A linkages, the crystallographic position of all atoms (with the exception of the TM ions) is generally not exactly known. These structural features make also tricky the implementation of theoretical calculations or the use of some techniques such as neutron diffraction for instance. Regarding the TM sites, the two A and B sites are different from a chemical and a structural point of view. In the alkali cation-free PBAs made of A\(^{2+}\) and B\(^6\) cations, the A cation is linked to an average of four cyanide ligands linked by the N side and two water molecules. The ratio of −NC and OH\(_2\) ligands in the coordination sphere of the A\(^2+\) cation can also vary from one A\(^2+\) cation to another depending on the distribution of the B(CN)\(_6\) vacancies. Thus, the symmetry at the A site departs from the centro-symmetric octahedral one. The cation at the B site is six-fold coordinated, linked to the C side of six same cyanide ligands. The B–CN covalent bonds are linear and the cyanide exerts a strong ligand field. The hexacyanometallate entities are thus stable, rigid, and, usually assumed to have a perfect O\(_h\) symmetry.\(^{40,41}\)

In our previous work mentioned above,\(^{28}\) we focused on the XMCD signal at the A K-edges of two series of PBAs of the chemical formula \( A_p[Fe(CN)_{6q}] \cdot nH_2O \) (A\(^{2+}\) = Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\)) and \( A_p[Cr(CN)_{6q}] \cdot nH_2O \) (A\(^{2+}\) = Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\)). In the following, we call AFe and ACr these two series of model PBAs. The characterization of their chemical composition and structure as well as of their macroscopic magnetic properties are presented in reference 28. The magnetic information needed for the present study can be summed up as follows. In the AFe series, NiFe and CuFe are ferrimagnetic with a magnetic ordering temperature of 22 and 19 K, respectively, while MnFe and CoFe are ferrimagnetic below 12 and 14 K, respectively. In the ACr series, FeCr, CoCr, and NiCr are ferrimagnetic with a magnetic ordering temperature of 16, 25, and 65 K, respectively, while MnCr is ferrimagnetic below 64 K. The spin quantum number (S) and the expected direction of the magnetic moment carried by each A\(^{2+}\) and B\(^6\) TM ion of the coordination polymer in an external magnetic field are given in Figure 1b.\(^{28}\) We showed in reference 28 that the 1s → 4p contribution to the A K-edge XMCD signal can be related to the magnetic behavior of the probed A\(^2+\) ion: the shape of the signal to the filling of the 3d orbitals, the sign of the XMCD signal to the direction of the magnetic moment with respect to the applied magnetic field, and the intensity of the signal and the area under the curve to the total spin number S and the Curie constant C\(_A\) of the absorber atom, respectively.

In this work, we focus on the XMCD signal at the K-edges of the B site of the coordination polymer. The \( Cr^{3+}(CN)_6 \) and \( Fe^{3+}(CN)_6 \) entities have nondegenerate \( ^4A_2 \) and degenerate \( ^2T_{2g} \) electronic ground states, respectively. Like at the A K-edge, the contributions to the XMCD signals are compared to the XANES spectra to assign the different contributions and then extract qualitative and quantitative data from the variation of the XMCD signals along the series of compounds. We can thus compare the characteristics of the XMCD signals at the A and B K-edges and particularly the intensity of the XMCD signal to get a better insight into the information contained in these signals. The new data obtained at the Cr and Fe K-edges allow us (i) to clearly evidence different local magnetic behaviors of the A and B sites of the coordination polymer and (ii) to go deeper in the interpretation of the intensity of the
XMCD signal. In return, this information combined with macroscopic magnetometry measurements and local X-ray absorption data can be used to get new insight into the macroscopic magnetic properties of the compounds.

2. EXPERIMENTAL SECTION

The syntheses and macroscopic characterizations of the four A[Fe(CN)]$\text{6}_{2-}$ (AFe series) and four A[Cr(CN)]$\text{6}_{2-}$ (ACr series) PBAs are presented in reference 28.

**TM K-edge XAS.** Cr (5989 eV) and Fe (7112 eV) K-edge X-ray absorption spectra were recorded for, respectively, the ACr and AFe series on the SAMBA beamline$^{12}$ at SOLEIL synchrotron (Gif sur Yvette, France). Room-temperature spectra were recorded up to 500–1000 eV above the edge (depending on the PBA) on pellets in the transmission mode, using the continuous mode of the Si(220) monochromator. No radiation damage occurred. We used the ATHENA software$^{27}$ to perform the energy calibration and conventionally normalize the spectra.

**TM K-edge XMCD.** Cr and Fe K-edges X-ray absorption near-edge structure (XANES) spectra and XMCD signals were recorded in the transmission mode using the dispersive setup of the ODE$^{44}$ beamline at SOLEIL synchrotron (Gif sur Yvette, France). Detailed information is given about the measurements and normalization procedure in ref 27, so only the main ones are reminded here. The circular polarization rate is the same for all of the edges. The Si(311) polychromator was chosen to reach the highest possible resolution in the white line region of the spectra. Then, it is critical (i) to be well below the Curie temperature of the eight investigated PBAs and (ii) to avoid any artifact in the intensity related to a change in the temperature, so we were careful to perform the measurements at 4 K. The largest external magnetic field (1.3 T) that can be reached when the cryostat is used was applied alternatively parallel and antiparallel to the direction of the photon beam. For the AFe series, the samples were placed in a diamond anvil cell (DAC) (with no pressure-transmitting medium), which ensures an optimized homogeneity of the sample. In the case of the ACr series, an experimental challenge was to minimize the absorption of the beam while retaining a brilliant enough flux to be able to perform the measurements; this was achieved by replacing the diamonds of the DAC with a Plexiglas strip. No radiation damage occurred due to attenuators of appropriate thickness. A metallic foil was recorded at both edges for energy calibration. We normalized the XANES spectra and XMCD signals using the procedure described in ref 27.

3. RESULTS

### 3.1. Cr K-edge XMCD Signals

Figure 2a shows the normalized XMCD signals at the Cr K-edge of MnCr, FeCr, CoCr, and NiCr. The different contributions were clearly assigned due to the comparison of the XMCD signals with the corresponding XANES spectra (S1), which are very similar from one compound to another along the ACr series. This reflects a very similar electronic structure of the Cr$^{3+}$ ion and a very similar local structure around the absorber atom along the series. One can notice the intense multiple scattering contribution just above the absorption edge characteristic of the linear Cr–CN linkages. The XMCD signals are compared to the XANES spectrum of CoCr in Figure 2b.

The XMCD signal is different from one compound to another along the series, whereas the Cr K-edge XANES spectra are almost exactly the same (S1). The differences among the XMCD signals therefore arise from different magnetic environments of the Cr ion. Nevertheless, even though the contributions exhibit variable signs and intensities, the XMCD signals all exhibit the same shape with the same number of contributions located at the same energies: one main contribution (δ) and two other contributions with significantly smaller intensity (β and γ). The γ contribution will not be discussed here.

The main contribution to the XMCD signal (δ) is at the energy of the XANES white line and can therefore be assigned to the electric dipole-allowed $1s \rightarrow 4p$ transitions. We already discussed the shape of this main δ contribution to the XMCD signal in reference 28. The derivative shape of the signal is associated with the same spin quantum number for all electrons in the 3d orbitals, which is the case for the $(t_{2g})^3(e_g)^0$ electronic configuration of the Cr$^{3+}$ ion.

The β contribution to the XMCD signal is located at the same energy as the main structure in the rising edge of the XANES spectra. This structure is assigned to the $1s \rightarrow t_{2g}$ CNR$^a$ transitions, having the same symmetry as the 4p orbitals in the O$_h$ symmetry. K-edge XMCD gaining intensity from the $1s \rightarrow 4p$ transition, a contribution to the XMCD signal at this energy, is therefore expected.

Over the pre-edge energy range (below 5995 eV), no contribution to the XMCD signal is detectable (Figure 2b). Over this energy range, the Cr K-edge XANES spectra exhibit two peaks (S1) assignable to the electric quadrupole $1s \rightarrow 3d$ transitions. This indicates that XMCD at the TM K-edges does not gain intensity from such electric quadrupole transitions in the centro-symmetric environment, for which no contribution...
from the electric dipole-allowed 1s → 4p transitions is expected over this energy range.

3.2. Fe K-edge XMCD Signals. Figure 3a shows the normalized XMCD signals at the Fe K-edge of MnFe, CoFe, NiFe, and CuFe. The different contributions were clearly assigned due to the comparison of the XMCD signals with the corresponding XANES spectra (S2). All XANES spectra are almost exactly the same, showing that, like at the Cr K-edge, the electronic structure and the local structure around the Fe ions are very close from one compound to the other. These spectra are characteristic of the Fe(CN)$_6$ entity. As at the Cr K-edge, the intense multiple scattering contribution above the edge is characteristic of the linear Fe–CN linkages. We can observe that the profile of the Fe K-edge spectra along the AFe series is very close to that of the Cr K-edge spectra along the ACr series, showing that the local structure around the absorber atom and therefore the local structures of both Fe(CN)$_6$ and Cr(CN)$_6$ entities are very close in both series. The XMCD signals are compared to the XANES spectrum of CoFe in Figure 3b.

As at the Cr K-edge, the XMCD signal is different from one compound to the other along the series, whereas the Fe K-edge XANES spectra are almost exactly the same (S2). One can again conclude that the differences among the XMCD signals arise from different magnetic environments of the Fe$^{3+}$ ion. All Fe K-edge signals exhibit the same contributions: one main (δ) and two smaller ones (α and γ). These contributions have the same shape, only their sign and intensity vary. The γ contribution will not be discussed here.

As at the Cr K-edge, the main contribution to the XMCD signal (δ) is at the energy of the XANES white line and can be assigned to the electric dipole-allowed 1s → 4p transitions. The shape of the contribution with one dominant lobe is in line with the presence of one electron pair in the t$_{2g}$ orbitals of the Fe$^{3+}$ low spin ion.

Surprisingly, the low-energy contribution to the XMCD signal (α peak) is located over the pre-edge energy range of the XANES spectra (below 7115 eV). At the Fe K-edge, the XANES spectra of the AFe series (S2) exhibit two weak pre-edge peaks located at 7112 and 7115 eV (peaks α$_1$ and α$_2$ on S2), which can be assigned to 1s → 3d transitions. The α XMCD peak is situated at the same energy as the α$_1$ peak on the XANES spectrum, whereas XMCD gains no intensity at the energy corresponding to the α$_2$ peak of the XANES spectra. It is noticeable that the intensity of the α XMCD peak varies as one of the main δ peaks, as confirmed by the plot of the intensity of the α peak as a function of that of the δ peak (S3). The observed linear variation shows that the α XMCD peak gains intensity from the 1s → 4p transition, which reflects some 3d-4p orbital mixing that can be assigned to a slight departure of the Fe(CN)$_6$ entities from the pure O$_6$ centrosymmetric geometry. The linear variation between the intensities of the α and δ XMCD peaks also indicates that the structural distortion is the same for all Fe(CN)$_6$ entities of the AFe series and is therefore inherent to the Fe(CN)$_6$ entity and independent of the nature of the other ion on the A site. A configuration mixing in the ground configuration of the Fe(CN)$_6$ entity in the pure O$_6$ symmetry can be ruled out due to the important energy gap between the ground and excited states in the strong ligand field exerted by the cyanide ions linked by the C side, as it is also the case for the Cr(CN)$_6$ entity.

At last, the XMCD signal at the Fe K-edge gains no intensity over the energy range corresponding to the rising edge of the XANES spectra. This observation, which is again not expected for a pure centro-symmetric O$_6$ geometry, is probably associated with the slight structural distortion of the Fe(CN)$_6$ entities clearly highlighted by the presence and the behavior of the α XMCD peak.

3.3. Pre-edge Contribution to the XMCD Signals. Over the pre-edge energy range, the XMCD signals at the Cr and Fe K-edges of the ACr and AFe series are very different (Figures 2 and 3). They are also different from the XMCD signals at the A K-edge of both series presented in ref 28 and reminded in S4. Nevertheless, for all compounds and all edges, when XMCD gains intensity over this energy range, the contribution always has an opposite sign but the same shape as the main contribution. Its intensity is also linked to that of the main contribution, indicating that over this energy range, XMCD gains intensity from the 1s → 4p transitions. The absolute value of the intensity of the pre-edge contributions and its relative intensity with regard to the main contribution (in %) are gathered in Table S1.

For both the ACr and AFe series, the A K-edges XANES spectra and XMCD signals are presented in ref 28 and are reminded here in S4. The XANES spectra of all compounds exhibit one single pre-edge peak with variable broadness and intensity, assigned to the 1s → 3d transitions. At all A K-edges, XMCD gains intensity at the energy of the XANES pre-edge peak, whatever the population of the 3d orbitals (from d$^3$ to d$^5$). From a molecular point of view, the coordination sphere of the A$^{2+}$ ion is mainly made of four −NC and two −OH$_2$ ligands. For this chemical composition, the cis-configuration with two adjacent water molecules, belonging to the C$_{2v}$ point group, is expected to be the main species. Nevertheless, given the random distribution of B(CN)$_6$
vacancies in the coordination polymer, the trans-conformation of the A(NC)_6(OH)_2, coordination polyhedron can also be found, as well as coordination polyhedra with chemical composition A(NC)_6(OH)_2 and A(NC)_6(OH)_2. From a solid-state point of view, the symmetry of the A site is therefore very low and can rather be considered to belong to the C1 point group with generalized- or multiple-pathway 3d-4p orbital mixing, explaining the XMCD contribution over the pre-edge energy range of the XANES spectra.

In the ACr series, the absence of contribution to the XMCD signal over the pre-edge energy range at the Cr K-edge can be assigned, as mentioned above, to the centro-symmetric O₆ geometry of the Cr(CN)₆ entities in the coordination polymer. Without 3d-4p orbital mixing associated with a contribution of the electric dipole-allowed 1s → 4p transitions over this energy range, XMCD gains no intensity from the electric quadrupole 1s → 3d transitions, whatever the population of the 3d orbitals.

In the AFe series, the Fe K-edge XMCD contribution at the energy of the α, XANES peak reveals some 3d-4p orbital mixing and the departure of the Fe(CN)₆ entities from the pure O₆ centro-symmetric geometry. Nevertheless, the lack of XMCD contribution at the energy of the α, XANES peak also indicates that 3d-4p orbital mixing associated with the symmetry lowering is restricted to one or few 3d orbitals involved in the transitions originating in the α, XANES peak.

The fact that the same α peak appears on all Fe K-edge XMCD signals of the AFe series and that its intensity varies as that of the main contribution shows that the Fe(CN)₆ entities undergo the same slight structural distortion in all compounds of the AFe series, independently of the associated A²⁺ ion. Such a structural distortion specific to the Fe(CN)₆ entity is not surprising and can be related to the degenerate electronic ²T₂g state of the Fe(III)CN₆ entity likely to undergo a spontaneous Jahn–Teller distortion,⁵⁰,⁵¹ which is not expected for the nondegenerate ⁴A₂g ground state of the Cr(III)CN₆ moiety. Thus, a DFT-based study on the Jahn–Teller effect in 3d hexacyanomelates with orbitally degenerate ground states⁵² predicts a compressed trigonal geometry for the Fe(III)CN₆ entity, with a D₃d point group as the highest possible symmetry. This is in agreement with the room-temperature crystal structures of K₃[Fe(CN)₆] in its monoclinic and orthorhombic forms, showing a trigonal geometry of the hexacyanometalate unit with the C3 axis approximately parallel to the crystallographic axis (a), superimposed by an additional orthorhombic distortion.⁵³ Such a distortion can explain our observation. In our case, the symmetry is obviously noncentrosymmetric, i.e., lower than D₃d.

In summary, the TM K-edge XMCD signal is very sensitive to slight structural distortions, hardly detectable on the XANES spectra. The observed pre-edge contributions are in line with (i) a low symmetry of the A site surrounded by randomly distributed M(CN)₆ vacancies in the two ACr and AFe series, (ii) a pure centro-symmetric O₆ geometry for the nondegenerate ⁴A₂g ground state of the Cr(III)CN₆ entities in the ACr series, and (iii) a slight departure from the centro-symmetric O₆ geometry in the degenerate electronic ²T₂g state of the Fe(III)CN₆ moieties in the AFe series, which can be assigned to a Jahn–Teller effect.

3.4. Main δ Contribution to the XMCD Signal. Sign of the Signal. The sign of the high-energy lobe of the main δ contribution to the XMCD signal of molecular compounds is assigned in the literature to the direction of the magnetic moment carried by the absorber atom with regard to that of the applied magnetic field.⁵⁴ This can be verified here too. The magnetic moments borne by the A²⁺ ions point in the same direction as the applied magnetic field for all compounds (Figure 1b). We choose as a convention to define the positive sign of the high-energy lobe of the XMCD signal when the magnetic moment of the absorbing atom points in the same direction as the external magnetic field. The A K-edge XMCD signals of all compounds of both AFe and ACr series are thus all positive (S₄, Figure 1b).⁶ At the B K-edges of the two AB series, the XMCD signals also have the expected sign with respect to this convention. In the ferromagnetic NiFe, CuFe, FeCr, CoCr, and NiCr compounds, the XMCD signals are positive (Figures 2 and 3), in agreement with a magnetic moment carried by the Fe²⁺(Cr³⁺) ions pointing, as that of the A²⁺ ion, in the same direction as the applied magnetic field (Figure 1b). In contrast, the XMCD signal is negative in the ferrimagnetic MnFe, CoFe, and MnCr compounds (Figures 2 and 3), in agreement with a magnetic moment carried by the Fe²⁺(Cr³⁺) ions pointing in the opposite direction as that of both the A²⁺ ion and applied magnetic field (Figure 1b).⁶

Peak Area under the Curve. We showed at the A K-edge of both ACr and AFe series that the absolute intensity and the integrated intensity, i.e., the peak area under the curve, of the XMCD signal can bring information: the intensity of the signal and the peak area under the curve are linear functions of the total spin quantum number and of the Curie constant of the A²⁺ ion, respectively.⁶ However, at the Fe K-edge, the peak area under the curve for the main δ peak is a linear function of its intensity with a slope of 3 (S5). At the Cr K-edge, the peak areas under each lobe of the curve of the XMCD signal, as well as the difference between the peak areas under the two lobes, are, respectively, linear functions of the intensity of each lobe and of the difference between their intensities, with a slope of 1.95 (S6). As the peak areas under curves and the intensities are proportional, only the intensity of the main peak at the Fe K-edge and the difference between the intensities of the two lobes at the Cr K-edge are considered in the following; they are called IFe and IΔ, respectively. Work is in progress to understand this different behavior of the main contribution to the XMCD signal between the two A and B sites of the coordination polymers. The differences between the intensities of the two lobes at the Cr K-edge have been considered because we showed that, at the Mn K-edge of MnCr, this value follows the same trend as the intensity of the main lobe when the XMCD main contribution exhibits one predominant lobe.⁶

Expression of the Intensity. In both the ACr and AFe series, the intensity of the main peak as defined above (IFe and IΔ) depends on the nature of the magnetic neighbor of the absorber ion. No variation trend of the maximum intensity with any magnetic parameters such as the magnetization value at 1.3 T and 4 K, Sₐ, the total spin quantum number of the A²⁺ ion,..., emerges at first glance. Nevertheless, we showed in our previous work on the A K-edges²⁸ that the intensity of the main contribution to the A K-edges XMCD signal is the sum of a constant term and an Sₐ-dependent term. So, we also tried to add or subtract a constant term to the XMCD intensity at the Fe and Cr K-edges, and we plotted the result as well as its absolute value as a function of Sₐ.

At the Fe K-edge of the AFe compounds, we found, after trials and errors, a linear trend when plotting as a function of Sₐ the absolute value of the difference between IΔ²⁸ and 0.0036;
this plot is presented in Figure 4. The point corresponding to MnFe slightly deviates from the trend. As this compound exhibits a peculiar behavior in its magnetic properties and at the Mn K-edge, it has not been taken into account in the first step. It is striking that within the error bar (±0.001), (i) the correlation line passes through the origin and (ii) the value of the slope (0.004) is very close to the value subtracted from the XMCD intensity of the MnFe (black circle), CoFe, NiFe, and CuFe (black square). Difference between the intensity of the main XMCD signal at the Cr K-edge and 0.023 versus the total spin quantum number \( S_A \) of the \( A^{2+} \) ion for MnFe, FeCr, CoCr, and NiCr (white square).

\[
I_{Fe} = (1 \pm S_A) \times 0.004 \tag{1}
\]

where the sign (+(-)) depends on the F(AF) exchange interaction between the magnetic moments carried by the \( A^{2+} \) and \( Fe^{3+} \) ions (Figure 1b).

The same treatment was performed for the signal intensity \( I_{Fe} \) at the Cr K-edge \( (I_{Fe} \) is the difference between the intensity of the two lobes). After trials and errors, we found a linear trend when plotting as a function of \( S_A \) the difference between \( I_{Fe} \) and 0.023; this plot is presented in Figure 4. As at the Fe K-edge, it is striking that, within the error bar (±0.002), (i) the correlation line passes through the origin and (ii) the value of the slope (−0.012) is very close to the value subtracted from the XMCD intensity (−0.023). The XMCD intensity at the Cr K-edge can hence be expressed as

\[
I_{Cr} = (2 - S_A) \times 0.012 \tag{2}
\]

These expressions (eqs 1 and 2) have to be compared to the ones obtained at the A K-edges for CoFe, NiFe, CuFe, MnCr, FeCr, CoCr, NiCr (eq 3), and MnFe (eq 4) in ref 28 and recalled below

\[
I_A = (S_A - 1/2) \times 0.0115 \tag{3}
\]

\[
I_{MnFe} = (S_A - 1/2) \times 0.0038 \tag{4}
\]

Within the error bar, the proportional coefficients are the same in eqs 1 and 4 on the one hand and in eqs 2 and 3 on the other hand. If we define this proportional coefficient in eq 3 as \( P_{exp} (P_{lu} \ in \ ref \ 28) \), eqs 1–4 can be rewritten as follows

\[
I_{Fe} = (1 \pm S_A) \times \left(\frac{1}{3}\right) \times P_{exp} \tag{5}
\]

\[
I_{Cr} = (2 - S_A) \times P_{exp} \tag{6}
\]

\[
I_A = (S_A - 1/2) \times P_{exp} \tag{7}
\]

\[
I_{MnFe} = (S_A - 1/2) \times \left(\frac{1}{3}\right) \times P_{exp} \tag{8}
\]

For all compounds at both A and B K-edges, the calculated intensity using eqs 5–8 with \( P_{exp} = 0.012 \) is plotted as a function of the experimental intensity in Figure 5.

The linear variation with a correlation coefficient close to 1 shows that eqs 5–8 very well reproduce the intensity of the XMCD signal for all compounds. It is also satisfying to see that the four equations are made of comparable terms. They will be further discussed later.

4. DISCUSSION

The knowledge of the information contained in the TM K-edge XMCD signals is essential to make the technique become a widely used tool for the study of molecular magnetic materials. The establishment of the expressions of the intensity of the main contribution to the XMCD signal is the first promising step. In the first part of the discussion, we will try to go a bit further in our understanding of these expressions. In the second part, we will try to use the data extracted from the technique to better understand the magnetic properties of the model compounds.

4.1. Intensity of the Main \( \delta \) Contribution to the XMCD Signal

A magnetic dichroic signal appears at the K-edge of TM in the presence of spin–orbit coupling in the 4p orbitals in the excited state. Information on the magnetic properties then derives from exchange interactions between the photoelectron in the 4p orbital and the 3d unpaired electrons.
Equations 5–8 are a product of three terms: the first one depending on \( S_A \), the total spin quantum number of the \( A^2+ \) ion, the second one taking the value of 1 or 1/3 depending on the sample and on the K-edge and called \( \Omega \) in the following, and the third one is the \( P_{\text{exp}} \) coefficient. These three terms are further discussed in the following:

**\( P_{\text{exp}} \) coefficient.** The \( P_{\text{exp}} \) coefficient depends neither on the sample nor on the K-edge. It must therefore depend on experimental parameters, such as the temperature, the magnetic field, and the rate of circular polarization of light, as suggested in this study and our previous works.\(^7,24\) We indeed showed in ref 27 that, for a given position of the slits used to select the circular polarization of the X-ray beam, the rate of circular polarization does not change over the energy range for our experiments. So, this parameter is the same for all measurements. As the intensity of the XMCD signal strongly depends on the magnetic field and even more on the temperature (even below the magnetic ordering temperature of the compounds),\(^7,27\) it was therefore of prime importance to have fixed them at exactly the same values for the whole study, an experimental constraint we strictly respected.

**\( S_A \)-Dependent Term.** The \( S_A \)-dependent term (eqs 5–8) has the form of a sum or a difference between \( S_A \) and a constant. At the A K-edge, this term is thus composed of the total spin quantum number of the absorbing atom (\( S_A \)) and the 1/2 value, which we proposed to assign to the spin of the photoelectron:\(^7,28\) eqs 5 and 6 can be reformulated to make appear the total spin quantum number of the absorbing atom (\( S_{\text{Fe}} = 1/2 \) and \( S_{\text{Cr}} = 3/2 \)), which also induces the presence of the 1/2 value

\[
I^{\text{Fe}} = ( (S_{\text{Fe}} + 1/2) \pm S_A ) \times \left( \frac{1}{3} \right) \times P_{\text{exp}}
\]

\[
I^{\text{Cr}} = ( (S_{\text{Cr}} + 1/2) - S_A ) \times P_{\text{exp}}
\]

This shows that the constant term that was added or subtracted to the experimental intensity of the XMCD signal to get eqs 1 and 2 and then eqs 5 and 6 is directly linked to the spin of the absorbing atom and the 1/2 value and has therefore a physical meaning. Thus, the \( S_A \)-dependent terms in eqs 7–9 all contain the spin of the absorbing atom (\( S_A \) in eq 7, \( S_{\text{Mn}} \) in \( I_{\text{Mn}} \) in eq 8, \( S_{\text{Fe}} \) in \( I^{\text{Fe}} \) in eq 9, and \( S_{\text{Cr}} \) in \( I^{\text{Cr}} \) in eq 10). In addition to the spin of the absorbing atom, the \( S_A \)-dependent term can contain the spin of the other TM ion (\( S_A \) in eqs 9 and 10). At last, the \( S_A \)-dependent terms always contain the 1/2 value in addition to the other spin value(s). It is therefore appealing to assign this value of 1/2 to a spin value, which would be the same for all K-edges and which we propose to assign to the spin of the photoelectron. Nevertheless, this assignment remains to be demonstrated.

In what follows, we concentrate on better understanding the origin of the elements of this \( S_A \)-dependent term.

**Intrasite Spin Polarization.** At all K-edges of the TM ions, the spin-dependent term contains the total spin of the absorber ion (\( S_I \) in eqs 7 and 8, \( S_{\text{Fe}} \) in eq 9, and \( S_{\text{Cr}} \) in eq 10), indicating that the 4p orbitals of the absorber atom are always spin-polarized by the unpaired electrons in the 3d orbitals in the same atom through intra-atomic 3d\(_{\text{A}}\)-4p\(_{\text{A}}\) or 3d\(_{\text{B}}\)-4p\(_{\text{B}}\) interactions. One can notice that the sign in front of the spin of the absorber atom is always positive and does not depend on the direction of the magnetic moment with regard to that of the applied magnetic field, although the overall sign of the signal directly depends on it.

**Intersite Spin Polarization.** The presence of \( S_A \) in the expression of the intensity of the signal at the Fe and Cr K-edges (eqs 9 and 10) shows that the 4p\(_{\text{B}}\) orbitals are also spin-polarized by the 3d\(_{\text{A}}\) electrons of the A site for the two AFe and ACr series. A direct interaction between electrons in 4p\(_{\text{B}}\) and 3d\(_{\text{A}}\) orbitals is expected to be very small, too small to be involved in such a polarization process. Besides, if such interactions would be involved, an intersite spin polarization by the 3d electrons would be expected for both A and B sites, which is not the case. Therefore, the interaction between the photoelectron in the 4p\(_{\text{B}}\) orbitals and the 3d\(_{\text{A}}\) electrons goes through either (i) the 4p\(_{\text{B}}\)-4p\(_{\text{A}}\)-3d\(_{\text{A}}\) three-orbital pathway or (ii) the 4p\(_{\text{B}}\)-3d\(_{\text{B}}\)-3d\(_{\text{A}}\) one. This 4p\(_{\text{B}}\)-3d\(_{\text{B}}\)-3d\(_{\text{A}}\) pathway can be excluded as such a pathway implies that \( I^B \) should also contain a contribution from the B\(^{3+} \) ion through the 4p\(_{\text{B}}\)-3d\(_{\text{B}}\)-3d\(_{\text{A}}\) pathway, which is not the case. Therefore, the interaction originating in the \( S_A \) term in eqs 9 and 10 goes through the empty 4p\(_{\text{A}}\) orbitals, i.e., intra-atomic 3d\(_{\text{A}}\)-4p\(_{\text{A}}\) mixing on the A site with low symmetry and interatomic 4p\(_{\text{A}}\)-4p\(_{\text{B}}\) orbital mixing between both sites. This suggests that spin polarization propagates through many-orbital mixing also involving empty 4p orbitals (4p\(_{\text{A}}\)). The delocalized 4p\(_{\text{A}}\) and 4p\(_{\text{B}}\) orbitals of the A\(^{2+} \) and B\(^{3+} \) ions, having relatively close energy levels as well as the same symmetry and strong overlapping along one axis out of three, significantly mix along this axis. Thus, the presence of the \( S_A \) term in eqs 9 and 10 can be explained by the combination of 3d\(_{\text{A}}\)-4p\(_{\text{A}}\) intrasite and 4p\(_{\text{A}}\)-4p\(_{\text{B}}\) intersite orbital mixing. Without overlap or without enough overlap pathways between the 3d\(_{\text{B}}\) and 4p\(_{\text{B}}\) orbitals, the 4p\(_{\text{A}}\) orbitals are not spin-polarized by the 3d\(_{\text{B}}\) unpaired electrons, so that eqs 7 and 8 do not contain any \( S_B \) term.

The proposed explanation for intersite spin polarization can thus be summarized as follows and schematized in Figure 6.

![Figure 6. Scheme illustrating the proposed explanation for intersite spin polarization.](https://doi.org/10.1021/acs.omegaz.2c04049)
orbitals are empty. Thus, at the A K-edge, the 3d\text{A}→4p\text{B} interaction pathway is switched off and the expression of the intensity of the XMCD main contribution only contains S\text{A}.

The sign in front of the S\text{A} term in eqs 9 and 10 remains intriguing. In the expression of the intensity of the signal at the Fe K-edge, it seems to be linked to the relative orientation of the magnetic moment on the A and B sites (i.e., to the nature of the exchange interaction between both sites), whereas in the expression of the intensity of the signal at the Cr K-edge, it is always negative whatever the relative orientation of the magnetic moments on the A and B sites. This difference is probably once again related to the different electronic and local structures of both Cr(CN)\text{6} and Fe(CN)\text{6} entities. Work is in progress to better understand the origin of this sign.

Conclusions. It appears from the discussion on the S\text{A} dependent term in the intensity of the main contribution to the XMCD signal that:

(i) the 4p\text{B} orbitals of the absorber atom are always spin-polarized by the unpaired electrons on the 3d\text{A} orbitals on the same site and the sign in front of the associated term S\text{A} is always positive,

(ii) the 4p\text{B} orbitals of the absorber atom can be spin-polarized by the 3d\text{A} unpaired electrons on the neighboring site through a combination of intrasite and intersite orbital mixing, and the sign in front of the corresponding term remains to be understood.

It is remarkable that empty 4p orbitals can propagate exchange interactions between intersite 3d and 4p orbitals. One can thus foresee that they could even do so between 3d orbitals when the sites of the magnetic centers are non-centrosymmetric. This suggests that empty 4p orbitals could play a noninnocent role in the magnetic properties of molecular materials.

The Ω coefficient. The Ω coefficient takes the values of 1 or 1/3 for all samples and all K-edges (eqs 7–10). With doubt about neither the magnetic moment borne by the ions nor the measurement conditions, we proposed in our previous work focused on the A K-edges\textsuperscript{28} to assign these different values (1 and 1/3) to different orientations of the magnetic moment borne by the absorber atom with regard to the (100) crystallographic axes, which are also the axes of the probed 4p orbitals. The same assignment for Ω can be proposed at the Cr and Fe K-edges. The local environments around the Cr\textsuperscript{3+} and the Fe\textsuperscript{3+} ions are different, octahedral in the former and slightly departing from centro-symmetric O\textsubscript{h} in the latter. This difference can generate different magnetocrystalline anisotropy for the two sublattices with possible different easy axes of magnetization. Thus, in the O\textsubscript{h} Cr(CN)\textsubscript{6} units, an alignment of the magnetic moment along the (100) crystallographic axes through spin–orbit coupling can be anticipated. In contrast, in the distorted Fe(CN)\textsubscript{6} units, assuming a trigonal distortion like in the K\textsubscript{3}[Fe(CN)\textsubscript{6}] crystals mentioned above,\textsuperscript{52} an alignment of the magnetic moments along the (111) directions, which are also the C\textsubscript{3} axes of the distorted coordination polyhedra, can be foreseen like in K\textsubscript{3}[Fe(CN)\textsubscript{6}].\textsuperscript{52} Such an assignment is supported by the fact that the 1 and 1/3 values correspond to the value of \(\cos^3(\theta)\), where \(\theta\) is the angle between the proposed direction for the magnetic moments and the axes of the probed 4p orbitals. A scheme of the proposed orientations for all of the magnetic moments along the A\text{Cr} and A\text{Fe} series is shown in Figure 7. With the same Ω value in the expression of the intensity of the XMCD signal at the Mn K-edge of Mn\text{Fe} and

the intensity of the XMCD at the Fe K-edge in the A\text{Fe} series, the same orientation of the magnetic moment carried by the Mn\textsuperscript{2+} ion in Mn\text{Fe} as that borne by the Fe\textsuperscript{3+} ions along the A\text{Fe} series is proposed. The direction of the magnetic moments was deduced from the nature of the exchange interaction between both TM obtained from the sign of the Weiss temperature in the Curie–Weiss law and the magnetization value under a high magnetic field.\textsuperscript{28}

4.2. Complementarity of Macroscopic SQUID and Local TM K-edge XAS and XMCD Data Toward a Better Understanding of the Magnetic Properties of PBAs. The investigation of the macroscopic magnetic properties of the A\text{Cr} and A\text{Fe} series of PBAs is presented in reference \textsuperscript{28}. The magnetic ordering temperatures were determined from the derivative of the FC magnetization curves. The Curie constant and the Weiss temperature were determined from the temperature dependence of the inverse of the molar magnetic susceptibility.\textsuperscript{28} The magnetic ordering temperature and the sign of the Weiss temperature have already been well explained by an orbital approach,\textsuperscript{55} and the Curie constant can be related to the total spin of the ions with possible orbital contribution depending on the ground state.\textsuperscript{28} If these magnetic data are well understood,\textsuperscript{55} questions remain on the magnetic field dependence of the magnetization curves below the magnetic ordering temperature. These curves recorded at 4 K, temperatures at which the XMCD measurements were performed, are shown in S7, and the main magnetic parameters deduced from these curves (magnetization at 1.3 T (temperature of the XMCD measurements), magnetization at 4 T (highest magnetic field reached by the magnetometer used for the magnetic measurements)), calculated saturation magnetization, and coercive field) are gathered in Table 1. Assuming that the Ω values (1 or 1/3) characterize the local orientation of the magnetic moments as proposed above, one can propose a further interpretation of these curves.

Magnetization Value at 1.3 T. It is striking to note that the macroscopic magnetization value measured by SQUID magnetometry at the magnetic field applied for the XMCD measurements (1.3 T) does not reach the saturation magnetization for most of the compounds (Table 1, S7), with various gaps between the magnetization at 1.3 T and the
Our experimental results clearly show that the intensity of the XMCD signal would not be proportional to the spin of the error). If this were the case, the experimental intensity of the magnetization by 53 saturation magnetization (departure from the saturation exchange interaction between both Fe ions is 1/3 in eq 8 indicates that the magnetic moments carried by the Mn ion sublattice suggests that the magnetic anisotropy is often much more important for ions, for which the ground state has a first-order orbital momentum. As the magneto-crystalline anisotropy energy is expected (Fe³⁺ in MnFe, Fe²⁺ in FeCr and Co²⁺ in CoCr). This can explain the higher coercive field value. In FeCr and CoCr, it is not surprising that the easy magnetization axes are the (100) directions in the two sublattices (Ω = 1 in eqs 7 and 10). In contrast, in the case of MnFe, the Fe³⁺ ions in distorted octahedral geometry have the highest magneto-crystalline anisotropy energy with magnetic moments oriented along the ⟨111⟩ directions. This also indicates that the orientation of the magnetic moments carried by the Mn²⁺ ion sublattice is dictated by that of the Fe³⁺ ion sublattice, suggesting that the exchange interaction between both Fe³⁺ and Mn²⁺ ions is stronger than the magneto-crystalline anisotropy on the Mn²⁺ ion. This can also explain the specific behavior of MnFe, for

| Compound | \( M_{\text{sat}} \) | \( \langle \mu_B \rangle \) | \( H_1 \) | \( H_{\text{Coercive}} \) |
|----------|-----------------|-----------------|--------|-----------------|
| MnFe     | 17.3            | 14.1 (81%)      | 9.1    | 16 (53%)        | 246  |
| CoFe     | 9.3             | 8.3 (89%)       | 6.2    | 6.2 (67%)       | 1240 |
| NiFe     | 10.7            | 10.1 (94%)      | 8.5    | 7.9 (79%)       | 2000 |
| CoCr     | 6.7             | 6.3 (94%)       | 5.3    | 5.3 (79%)       | 2350 |
| MnCr     | 11.9            | 11.7 (100%)     | 11.7   | 11.7 (100%)     | 10   |
| FeCr     | 24.1            | 18.4 (76%)      | 16     | 16 (66%)        | 175  |
| CoCr     | 20.1            | 17.1 (85%)      | 16.3   | 16.3 (81%)      | 550  |
| NiCr     | 16.1            | 16 (100%)       | 16     | 16 (100%)       | 67   |
which the magnetization value departs the most from saturation in both the AFe and ACr series.

Finally, in the compounds of the third group (CoFe, NiFe and CuFe), both sites are occupied by ions having different Ω values (1 at the A site and 1/3 at the Fe site, eqs 7 and 9) and therefore different orientations of the magnetic moments. This would mean that the easy magnetization axes are different on both sites and the magneto-crystalline anisotropy energy is high on both sites (higher than the exchange interaction energy). As discussed above, the magneto-crystalline anisotropy energy of the Fe2+ ions is high and, due to the peculiar distortion of the coordination polyhedron, their magnetic moments are oriented along the ⟨111⟩ directions. The easy magnetization axes of the A2+ ions (six-fold coordinated ions with metal-to-ligand axes oriented along the ⟨100⟩ directions) are the ⟨100⟩ directions. The Co2+ ion in CoFe has a first-order orbital momentum so that the magnetic anisotropy energy can indeed be expected to be important, higher than the exchange interaction energy (which is not the case for MnFe). Contrary to the Co2+ ion, the Cu2+ and Ni2+ ions have no first-order orbital momentum. In the case of the Cu2+ ion, a significant magnetic anisotropy can arise from a slight axial distortion due to the Jahn–Teller effect. Such a distortion is hardly detectable in the alkali cation-free CuFe PBA. Indeed, the Cu2+ ion being neighbored by an average of two randomly distributed Fe(CN)6 vacancies acting as strain relaxation points in the lattice, the elongated axes develop in all ⟨100⟩ directions, while keeping a cubic structure. The Jahn–Teller effect exhibited by the Cu2+ ions can nevertheless be revealed in CuFe PBAs containing enough alkali cations, for which a collective distortion is clearly detectable on the powder X-ray diffraction pattern (S8). The case of the Ni2+ ion is again different. Associated with Cr(CN)6 entities in the PBA structure, the macroscopic magnetic behavior is in line with a low magneto-crystalline anisotropy energy of the Ni2+ complexes (see above). One possible explanation for the different behavior of the Ni2+ ion in NiFe can be found in the comparison of the XANES spectra at the Ni K-edge of NiFe and NiCr. If the overall spectra show that the electronic structure and the local structure of the Ni2+ ions are very close in both compounds in agreement with the location in the same octahedral site of the PBA cubic structure, the pre-edge regions of the spectra are clearly different (S9). These differences reveal slightly different geometries of the Ni2+ coordination polyhedra in both compounds with an expected impact on the magnetic behavior of the Ni2+ sublattice and its magnetic anisotropy. Work is in progress to better characterize the local structure difference around the Ni2+ ion and to better understand the different magnetic behavior of this ion in both compounds.

5. CONCLUSIONS

This study shows, like our previous work at the A K-edges of the same series of compounds,28 that the Prussian blue analog family is particularly well suited to gain insight into XMCD at the transition-metal K-edges in molecular compounds. And in turn, XMCD at the transition-metal K-edges can provide valuable and original information on the electronic and local structure as well as on the magnetic properties of those compounds.

TM K-edge XMCD gains intensity from the dipole-allowed 1s → 4p transitions. Therefore, this technique is particularly well suited to evidence orbital mixing with 4p orbitals. In the pre-edge region, XMCD gains intensity for non-centro-symmetric sites and it is proving to be very sensitive to slight structural distortions.

An expression for the intensity of the main contribution of the TM K-edge XMCD signal has been proposed for all K-edges of the TM ions of all compounds of both series. The intensity is a product of three components. The first component depends on experimental parameters (temperature, magnetic field, rate of circular polarization of light). It is constant in our case since the measurement conditions have been strictly kept the same all along the experiments. The second component is assigned to the local orientation of the magnetic moment carried by the absorber atom.

The third component is a function of spin quantum numbers. In all cases, the intensity of the XMCD signal depends on the total spin of the absorber atom (S). The intensity of TM K-edge XMCD can also contain an intersite contribution reflecting the spin polarization of the probed 4p orbitals by the spin of the other sublattice. This spin polarization originates from three-orbital interactions going through intrasite 3d-4p and intersite 4p-4p orbital mixing. The existence of such magnetic interaction spreading through empty 4p orbitals suggests that 4p orbitals could play a significant role in the magnetic properties of molecular materials made of 3d magnetic centers and that TM K-edge XMCD is a particularly appropriate technique to tackle such a question.

The whole study shows that the expressions of the intensity of the TM K-edge XMCD signals are very different at the A and B sites of the coordination polymers and that these differences are related to the different local symmetry of the sites. It also shows that TM K-edge XMCD can provide new local magnetic information, which, combined with magnetic macroscopic data and local structure data, can provide a new tool, which should be able to tackle tricky magnetic anisotropy issues or to better understand the role of the 4p orbitals in the magnetic properties of TM ions.

To our knowledge, this is the first time that a systematic study of molecular compounds allows for establishing relationships between experimental TM K-edge XMCD signals and some magnetic parameters of the compounds. In this context, the proposition of expressions that fairly reproduce the intensity of the XMCD signals at the two TM K-edges of eight PBAs opens new perspectives toward a better understanding of such signals, toward the possible extension of such an approach to the study of other molecular compounds, and as a consequence toward an increased use and general understanding of the technique. We also hope that this work could be the starting point for further experimental systematic work to better understand TM K-edge XMCD for molecular compounds. Neutron diffraction57,58 on model compounds or the investigation of molecular compounds with well-known easy axes of magnetization could for instance provide complementary information on the orientation of the local magnetic moments. All of these experimental data could also be confronted with theoretical studies.

ASSOCIATED CONTENT

+ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04049.
S1 Cr K-edge XANES spectra; S2 Fe K-edge XANES spectra; S3 Intensities of the XMCD $\alpha$ and $\gamma$ peaks as a function of the intensity of the $\delta$ peak; S4 XMCD signal compared to the XANES spectrum at the A K-edge; S5 and S6 Area under the curve versus intensity for the main $\delta$ peak of the XMCD signal; S7 Magnetic field dependence of the magnetization at 4 K; S8 Powder X-ray diffraction of CuFe PBAs containing an increasing amount of Cs$^+$ cations inserted in interstitial sites; S9 XANES spectra of NiFe and NiCr (PDF)

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**ABBREVIATIONS USED**

PBA, Prussian blue analog; XANES, X-ray absorption near-edge structure; XAS, X-ray absorption spectroscopy; MT, transition metal; ZFC, zero field cooled; FC, field cooled; XMCD, X-ray magnetic circular dichroism; DAC, diamond anvil cell
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