Photoinduced Ferrimagnetic Systems in Prussian Blue Analogues $C^{I}_{x}Co_4[Fe(CN)_6]_y$ (C^{I} = Alkali Cation). 4. Characterization of the Ferrimagnetism of the Photoinduced Metastable State in $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$ by K Edges X-ray Magnetic Circular Dichroism

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Abstract: In Part 2 of this work, the electronic and local structure of the photoinduced metastable magnetic state of the Prussian blue analogue $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$ were characterized. To determine directly the relative orientation of the magnetic moments of Co^{II} and Fe^{III} ions in the metastable state, and the nature of the exchange interaction between them, we performed X-ray magnetic circular dichroism (XMCD) experiments at the cobalt and iron K edges. We present the first direct experimental evidence of the antiferromagnetic interaction between the cobalt and the iron ions, leading to the ferrimagnetism of the photoinduced metastable state.

Introduction

After the pioneering work of Hashimoto on photomagnetic cobalt−iron Prussian blues,[1−3] we undertook a systematic study of a series of analogues to try to understand the scope and the mechanism of the phenomenon.[4−6] In part 1 of these studies,[7] we synthesized and characterized a Prussian blue analogue of chemical formula $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$ exhibiting a large photoinduced magnetization. Before irradiation, it can be described as a paramagnet in which a small fraction of high-spin Co^{II} is diluted in a diamagnetic matrix of Co^{III}(d^6, low spin, LS)−Fe^{II}(d^6, LS) pairs. Its magnetization at 5 K is multiplied by 10 after 2 h of irradiation (10 K, $\lambda = 750$ nm $\pm$ 50 nm), and it presents a Curie temperature $T_C = 21$ K.[6−8] In part 2,[9] we demonstrated the increase of Co^{II}(d^7, high spin, HS) and Fe^{III}(d^5, LS) species to the detriment of Co^{III}(LS) and Fe^{II}(LS) ones upon irradiation, which corresponds to the photoinduced electron-transfer $Co^{III}-Fe^{II} \rightarrow Co^{II}-Fe^{III}$ initially postulated by Hashimoto.[1−4] We also showed the similarity between the electronic structure and the local structure of the cobalt ions of the photoinduced metastable state and those of the Co^{II}(HS) ions existing at 300 K in the cobalt−iron Prussian blue analogue $K_{0.1}Co_4[Fe(CN)_6]_{2.7}\cdot 18H_2O$. This compound is known to be a ferrimagnet below its Curie temperature ($T_C = 16$ K).[4] According to these structural and magnetic observations, we, and other authors in studies on similar compounds, implicitly assumed an antiferromagnetic interaction between the cobalt and iron ions in the excited metastable state, leading to ferrimagnetism below 21 K. The Curie temperatures of the two compounds are consistent with this assumption: the excited metastable state is composed of magnetic pairs in interaction in three-dimensional magnetic arrays, since T_C is proportional to the number of magnetic neighbors. The character of the magnetic order in the metastable state of similar compounds has recently been discussed on the basis of dynamic studies.[10] However, until now, there has been no direct experimental evidence of the ferrimagnetism in the photoinduced metastable magnetic state.

The direct determination of the coupling between paramagnetic ions is often trivial for stable bimetallic magnetic A−B compounds with known structure, stoichiometry and mass: a minimum in the $\chi_M T$ vs T curve shows ferrimagnetism and the magnetization at saturation S_T allows the confirmation of the

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nature of the coupling ($S_T = |S_A - S_B|$). In the photoinduced metastable sample, this clear-cut macroscopic characterization proves impossible for three reasons:

(a) The irradiation of the sample is not necessarily complete and the mass of the phototransformed phase is therefore unknown. This precludes any quantitative determination of the molar magnetization of the phase.

(b) The relaxation of the photoinduced magnetic phase to the diamagnetic ground state occurs at a temperature low enough ($T = 105$ K) to impede the observation of the minimum of the $\chi_M T$ vs T curve, expected in the case of ferrimagnetism.

(c) In these conditions, even if a quantitative measurement was possible, it would be impossible to distinguish macroscopically between the two kinds of magnetic pairs: antiferromagnetic pairs Co^{II}(HS) and Fe^{III}(LS) [$S_T = {}^3/_2 - {}^1/_2 = 1$] and ferromagnetic Co^{II}(LS) Fe^{III}(LS) pairs [$S_T = {}^1/_2 + {}^1/_2 = 1$]. In the two cases, the resulting spin S_T is the same.

To determine the sign of J, we chose therefore to determine the relative orientations of the magnetic moments of the two cations, Co^{II} and Fe^{III}, by X-ray magnetic circular dichroism (XMCD).

X-ray absorption spectroscopy (XAS) is an element and orbital selective magnetic probe that has developed recently with synchrotron radiation.[11] It has already been used to investigate the local magnetic moments in magnets of the Prussian blue family.[12] We report here XMCD results at the K edges of cobalt and iron for two compounds: $K_{0.1}Co_4[Fe(CN)_6]_{2.7}\cdot 18H_2O$ (abbreviated CoFe), where the exchange interaction between the cobalt and iron ions is known to be antiferromagnetic[12] leading to ferrimagnetism, and $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$ (abbreviated RbCoFe), which presents a large photomagnetic effect.

Experimental Section

Materials. The compounds can be formulated as $K_{0.1}Co_4[Fe(CN)_6]_{2.7}\square_{1.3}\cdot 18H_2O$ (CoFe) ($\square$ stands for the $[Fe(CN)_6]$ vacancies) and $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\square_{0.7}\cdot 13H_2O$ (RbCoFe). They were synthesized as described in Part 1.[7] CoFe contains a few potassium cations in the tetrahedral sites of the cubic structure, a negligible number of diamagnetic pairs and 33% $[Fe(CN)_6]$ vacancies $\square$. RbCoFe has 82.5% Co^{III} engaged in diamagnetic $Fe^{II}-CN-Co^{III}$ pairs and 17.5% Co^{II} associated with the $[Fe(CN)_6]$ vacancies $\square$.[9]

XAS Data Collection and Processing. X-ray absorption near edge structures and XMCD spectra were recorded at the energy dispersive absorption line of the DCI ring at LURE (Orsay).[9] The recording temperature was $T = 10$ K, that is below the T_C of CoFe and that of the photoinduced phase of RbCoFe. Right-circularly polarized photons were selected by positioning a 1 mm wide slit 5.5 mm below the positron orbit plane. The circular polarization was 70%. Thin samples were used (4 mg of product dispersed on a 1 cm^2 graphite sheet) to improve the surface/bulk ratio to increase the fraction of the phototransformed phase. The sample RbCoFe was irradiated with an optical fiber (light source: $h\nu = 750$ nm $\pm$ 50 nm; $P = 60$ mW cm^{-2}) during 12 h. Total saturation was not reached.[9]

To record the XMCD spectra, the magnetic field ($H = 1$ T) was applied alternatively parallel and antiparallel to the direction of the photon beam. A first spectrum labeled $\sigma_{\uparrow\uparrow}$ was registered with the magnetic field parallel to the propagation vector of the photons. Then a second spectrum, labeled $\sigma_{\uparrow\downarrow}$, was recorded with the magnetic field applied in the opposite direction. The XMCD signal is the difference ($\sigma_{\uparrow\uparrow} - \sigma_{\uparrow\downarrow}$) between the two spectra. The area of the XMCD signal is directly proportional to the local magnetic moment carried by the absorber atom.[11]

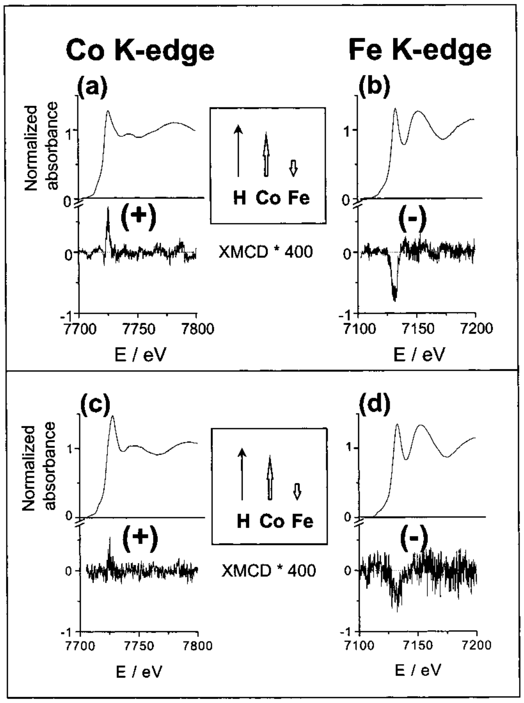

Figure 1. Isotropic and dichroic (×400) absorption spectra: (a) cobalt K edge in CoFe; (b) iron K edge in CoFe; (c) cobalt K edge in RbCoFe; (d) iron K edge in RbCoFe.

The X-ray absorption spectra were normalized at the atomic absorbance. The edge energies of the metals were fixed at the first inflection point of the metallic foils at 7709 eV for the cobalt and at 7112 eV for the iron.

Results and Discussion

The isotropic X-ray absorption near-edge spectra (XANES) and the dichroic signal (XMCD, ×400) at the K edges of cobalt and iron are displayed in Figure 1a,b for CoFe and in Figure 1c,d for RbCoFe. The inserts display the orientation of the local magnetic moments of the metallic centers in the applied magnetic field as discussed below. The isotropic X-ray absorption spectra have already been discussed in Part 2;[9] we repeat here only what is useful for the interpretation of the XMCD signals.

In the cobalt K edge absorption spectrum of CoFe, the energies of the absorption maximum at 7725 eV [allowed 1s (a_{1g}) $\rightarrow$ 4p (t_{1u})] transitions and the weak preedge at 7709 eV [forbidden 1s (a_{1g}) $\rightarrow$ 3d (t_{2g}, e_g)] corresponds to Co^{II} species.[9] For the irradiated RbCoFe sample, the edge maximum is shifted by 3 eV to higher energy (7728 eV) compared to that of CoFe and fits the energy of the absorption maximum of a Co^{III} species.[7,9] The shoulder at 7725 eV nevertheless indicates the presence of Co^{II} species in RbCoFe (known to be 17.5% before irradiation and increasing under irradiation).[9] The high-energy shift of the first EXAFS oscillations (7778 eV for CoFe and 7788 eV for RbCoFe) clearly demonstrates the presence of Co^{III}-ligand short bonds in RbCoFe.

The iron K edge spectra of the two compounds are characteristic of the $[Fe(CN)_6]$ entity.[14] The similarity of the iron K edge spectra is not surprising, given the similarity of the

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crystallographic and electronic structures of [Fe^{III}(CN)$_6$] and [Fe^{II}(CN)$_6$] entities.[15] For CoFe, the energy of the absorption maximum (7131.0 eV) indicates that the oxidation state of iron ions is +3. The spectrum of irradiated RbCoFe is similar to that of CoFe, indicating a high proportion of Fe^{III}.

A weak dichroic signal is present at the Co and Fe edges in both compounds. The energy of the signal corresponds to the allowed transition to the p-symmetry levels of the metal (7725 eV at the Co K edge, 7130 eV at the Fe K edge). All the XMCD signals present a single peak, either positive or negative. The shapes of the signals differ from those of the XMCD signals previously measured in magnetic Prussian blue analogues at the vanadium and at the chromium K edges, which were found to present successively a positive and a negative lobe, or vice versa.[12] The presence of a dichroic signal at the K edges is due to the presence of spin−orbit coupling in the metallic p levels in the excited states ($1s^1 3d^n 4p^1$ electronic configuration), and the exchange interaction of the p excited electrons with the 3d electrons. The small intensity of the signals (0.2% of the isotropic spectra for CoFe, ~0.1% for RbCoFe) is due to the absence of spin−orbit coupling in the 1s level and the weakness of the spin−orbit coupling in the final state.[16]

For CoFe, the macroscopic magnetization data are well-known and show clearly that the spins of cobalt(II) (d^7, high spin, $S = {}^3/_2$) and iron(III) (d^5, low spin, $S = {}^1/_2$) are antiferromagnetically coupled, as shown in the insert of Figure 1a,b.[13] This macroscopic observation finds its local counterpart in the dichroic signals: at the cobalt K edge, the dichroic signal is positive whereas at the iron K edge, it is the opposite. The inversion of the dichroic signal from cobalt to iron is a local characterization of the antiferromagnetic coupling between cobalt and iron ions. In the photoinduced metastable state of RbCoFe, below the Curie temperature, the dichroic signal is positive at the cobalt K edge and negative at the iron K edge, as in CoFe. These two XMCD observations mean that in the photoinduced magnetic state:

(i) there is an antiferromagnetic coupling between Co^{II} and Fe^{III} ions;

(ii) the largest magnetic moment parallel to the magnetic field is born by the cobalt ions;

(iii) the situation is the same as in the ferrimagnetic CoFe where the Co^{II}(HS) present an antiferromagnetic coupling with the iron ions, as predicted by the Kahn's model,[17] in perfect agreement with the similarity of the electronic structure for the cobalt ions previously shown by classical X-ray absorption measurements at the Co L$_{2,3}$ edges.[9] The cobalt in the photoinduced pairs is indeed high spin (HS).

This is the first experimental evidence of the ferrimagnetic nature of the magnetic metastable state for the RbCoFe.

The lower intensity of the XMCD signals and the noisy spectra reflect the smaller number of ferrimagnetic pairs in the phototransformed RbCoFe, compared to CoFe in which practically all the pairs are ferrimagnetic. The result is in agreement with previous isotropic XANES results obtained under the same experimental conditions, which showed that 30% of the pairs remains diamagnetic after irradiation.[9] The cobalt and the iron ions of the diamagnetic pairs contribute to the edge isotropic signal but not to the dichroic signal. Moreover, the bulk of the sample was not fully phototransformed due to the thickness of the sample and the insufficient penetration depth of the visible light.

Conclusions

We have used XMCD measurements to characterize the relative orientation of the local magnetic moments of the metallic ions in the photoinduced metastable state of the Prussian blue analogue $Rb_{1.8}Co_4[Fe(CN)_6]_{3.3}\cdot 13H_2O$. In this way, we propose the first direct experimental evidence of the ferrimagnetic nature of the photoinduced metastable state in this material.

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