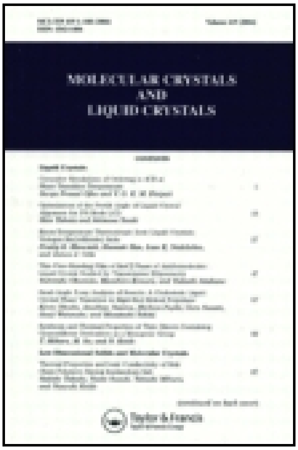

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Photo-Induced Electron Transfer and Magnetic Switching in CoFe Cyanides: Study of the Metastable State

Anne Bleuzen [a] , Claire Lomenech [a] , Anne Dolbecq [a] , Francoise Villain [a] , Antoine Goujon [b] , Olivier Roubeau [b] , Marc Nogues [b] , Francois Varret [b] , Francois Baudelet [c] , Elisabeth Dartyge [c] , Christine Giorgetti [c] , Jean-Jacques Gallet [c] , Christophe Cartier Dit Moulin [c] [a] & Michel Verdaguer [c]

[a] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, ESA CNRS 7071, Université Pierre et Marie Curie, 4 place Jussieu, 75252, Paris, cedex, 05, FRANCE

[b] Laboratoire de Magnétisme et d'Optique, Université de Versailles, 45 avenue des Etats-Unis, 78035, Versailles, Cedex, FRANCE

[c] Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bat. 209 D, BP 34, 91898, Orsay, cedex, FRANCE

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Photo-Induced Electron Transfer and Magnetic Switching in CoFe Cyanides: Study of the Metastable State

ANNE BLEUZEN[a], CLAIRE LOMENECH[a], ANNE DOLBECQ[a],
FRANCOISE VILLAIN[a], ANTOINE GOUJON[b],
OLIVIER ROUBEAU[b], MARC NOGUES[b], FRANCOIS VARRET[b],
FRANCOIS BAUDELET[c], ELISABETH DARTYGE[c],
CHRISTINE GIORGETTI[c], JEAN-JACQUES GALLET[c],
CHRISTOPHE CARTIER Dit MOULIN[ca] and MICHEL VERDAGUER[a]

[a]*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, ESA CNRS 7071, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris cedex 05, FRANCE,* [b]*Laboratoire de Magnétisme et d'Optique, Université de Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex, FRANCE and* [c]*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bat. 209 D, BP 34, 91898 Orsay cedex, FRANCE*

Photo-induced magnetisation has been recently evidenced by Hashimoto *et al.* in CoFe cyanide[1]. We synthesized a diamagnetic RbFeCo cyanide able to present the same photomagnetic effect. The magnetic properties of the excited state, the electronic structure and the local structure of the ground and the excited states have been investigated. The conditions required to observe the phenomenon and the mechanism of the electron transfer are discussed.

Keywords: CoFe Prussian blue; photomagnetism; X-ray absorption spectroscopy

INTRODUCTION

In 1996, Hashimoto and coworkers evidenced a new phenomenon in Prussian blue analogs. Starting from aqueous solutions of Co^{II} and hexacyanoferrate(III), they got a powder which exhibits spectacular photo-induced magnetisation at low temperature[1]. The proposed explanation of this phenomenon was the presence of isolated diamagnetic pairs Co^{III} -Fe^{II} in the compound mainly built of Co^{II}-CN-Fe^{III} units and a photo-induced electron transfer from Fe^{II} to Co^{III} through the cyanide bridge[1,2]. The key of the phenomenon would then be the presence of diamagnetic pairs in the compound.

The synthesis of these powders involves the substitution of water molecules of $[Co^{II}(H_2O)_6]$ by $[Fe^{III}(CN)_6]$. This means a progressive increase of the Co ligand field, oxygen atoms are replaced by nitrogen ones from NC ligands. For a sufficient amount of nitrogen atoms around the Co^{II} ion, Co^{II} can become low spin and its reducing power is drastically increased (stabilisation of the Co^{III} state). A very stable pair Co^{III}-Fe^{II} is then quick formed through a chemically-induced electron transfer. In order to increase the number of diamagnetic pairs responsible for the photo-induced effect, one has then to increase the number of nitrogen atoms around Co.

Once the diamagnetic pairs are obtained, the photo-induced electron transfer should occur, leading to two hypothetical excited states: low spin or high spin Co^{II}- low spin Fe^{III}.

In order to understand the mechanism of the photo-induced electron transfer, we increased the number of diamagnetic pairs in the compounds. We evidenced the conditions required to observe the photo-induced phenomenon and finally we characterized the photo-induced electron transfer at a microscopic level by studying the electronic structure and the local structure of the ground and the excited state.

EXPERIMENTAL

Synthesis

Compound **1** was synthesized by addition of a 10^{-2} mol l^{-1} aqueous solution of Co^{II} nitrate to a 10^{-2} mol l^{-1} solution of hexacyanoferrate(III) in the presence of an excess of potassium cations. Compounds **2** and **3** were prepared by addition of a 10^{-2} mol l^{-1} aqueous solution of hexacyanoferrate(III) to a 10^{-2} mol l^{-1} Co^{II} nitrate in the presence of an excess of rubidium for compound **2** and an excess of caesium for compound **3**. Elemental analysis of Co, Fe, C, N, H, K, Rb or Cs were performed at the analysis facility of the CNRS in Vérnaison (the oxygen was assumed to be the only other element and its content was obtained by difference to 100%). Infra-red spectra were recorded with a Biorad Fourier transform spectrometer. Powder X ray diffraction was performed with a Philipps diffractometer.

Magnetic measurements

Magnetisation measurements were performed in a SQUID magnetometer equipped with an optical fiber (light source : hν=750 nm±50 nm, P = $60 mWcm^{-2}$).

Electronic and structural studies

X-ray absorption spectra were recorded at the french synchrotron radiation facility, DCI (XAS10 beamline for the Co K edge) and Super-ACO (SU23 beamline for the Co and Fe $L_{2,3}$ edges).

RESULTS AND DISCUSSION

Characterization of the compounds

The formula of the compounds, calculated from elemental analysis, are in table 1.

TABLE 1 Formula of compounds **1**, **2**, **3**

Compound	Formula
compound **1**	$K_{0.1}Co_4[Fe(CN)_6]_{2.8},18.4H_2O$
compound **2**	$Rb_{1.8}Co_4[Fe(CN)_6]_{3.30},13H_2O$
compound **3**	$Cs_{3.7}Co_4[Fe(CN)_6]_{3.7},9.2H_2O$

In each case the structure is face centered cubic. The cell parameter a is 10.36±0.05Å for compound **1** and 10.04±0.05Å for compounds **2** and **3**.

The oxidation state of cobalt, obtained by X ray absorption spectroscopy at the Co K edge is mainly +II for compound **1** and +III for compounds **2** and **3**.

The larger the alkali cation is, the more it remains trapped in the structure. Potassium does not remain in the structure so that a lacunary structure $Co^{II}_3Fe^{III}_2.xH_2O$(figure 1a), in agreement with the electroneutrality of the solid, is obtained. In average, cobalt is surrounded by 4 nitrogen atoms and 2 oxygen atoms. In this environment, Co^{II} is still high spin. The rubidium cations fill about a quarter of the tetrahedral sites of the fcc structure, leading to a structure where, in average, cobalt is surrounded by 5 N and 1O. In this case, the Co ligand field appears strong enough to induce a spin transition followed by the spontaneous electron transfer from Co^{II} to Fe^{III}. Finally in **3**, the caesium cations fill nearly half of the tetrahedral sites. Co is surrounded by nearly 6 nitrogen atoms (figure 1b). The same structurally-induced electron transfer as above leads to Co^{III}.

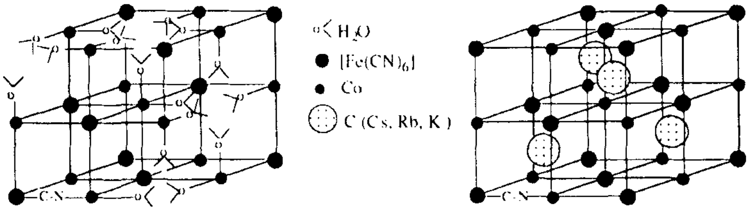

FIGURE 1 Structure of a compound containing a) no alkali cation (compound **1**), b) a maximum of alkali cations (compound **3**).

The cell parameters of **2** and **3** are smaller by ≈ 0.3 Å than the cell parameter of **1** due to the change of cobalt from high spin Co^{II} to low spin Co^{III}.

The number of diamagnetic pairs in the compounds strongly depends on the ability of the alkali cation to be trapped in the structure. Compound **1** contains very few diamagnetic pairs, compound **2** contains about 80% of diamagnetic pairs and 20% of Co-defect pairs, compound **3** is mainly composed of diamagnetic pairs.

Photo-induced Magnetisation of the Compounds

Magnetisation as a function of temperature was recorded before and after an irradiation (15 min, 750±50 nm) for the three compounds.

Compound **1** is already ferrimagnetic before irradiation with a T_c at 16K (figure 2a). Magnetisation exhibits no effect of light. Compound **2**, essentially diamagnetic before irradiation, exhibits spectacular photo-induced magnetisation (figure 2b). Compound **3**, also diamagnetic before irradiation, exhibits a very small effect of light.

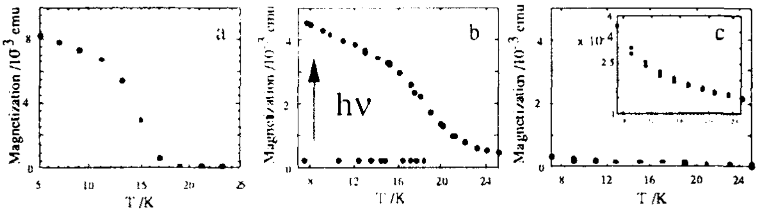

FIGURE 2 Magnetisation and photo-induced magnetisation of a) compound **1**, b) compound **2** and c) compound **3** (Insert: y scaled x 10).

The behaviour of compound **1** is not surprising since it is made mainly of paramagnetic Co^{II} - Fe^{III} pairs. The behaviour of compound **2** is in agreement with an important amount of diamagnetic pairs. The magnetic properties of the excited state have been studied elsewhere[13]. The behaviour of compound **3** is surprising since it is mainly composed of diamagnetic pairs. The result shows that the presence of diamagnetic pairs in the compound is required to observe the photo-induced phenomenon but this is not a sufficient condition.

Compound **2** which exhibits the most important photo-induced effect was chosen for the study of the metastable state.

Characterization of the photo-induced metastable state at Co and Fe $L_{2,3}$ edges

$L_{2,3}$ edges of 3d transition metals involve symmetry allowed electric dipole transitions from 2p core electrons to incompletly filled 3d and 4s levels ($2p^6 4s^0$

$\rightarrow 2p^5 4s^1$ transitions can be neglected due to their low intensity relative to the $2p^6 3d^n \rightarrow 2p^5 3d^{n+1}$ ones). They consist of complex structures due to the $2p^5 3d^{n+1}$ configurations. The positions of the $L_{2,3}$ edges multiplet structures depend on the final state energies arising from Coulomb and exchange interactions within the 3d shell and between 2p and 3d shells, from spin-orbit interaction on the 2p and 3d shells and from crystal field on the 3d shell. So, X-ray absorption spectroscopy is sensitive to the local environment (symmetry, nature of the ligands, metal-ligand distances and bonding), the oxidation and spin states of the metal.

To better understand XAS data, we recorded $L_{2,3}$ edges of four relevant model compounds: $Co^{II}Cl_2.6H_2O$ [HS, $t_{2g}^5 e_g^2$], $K_3Co^{III}(CN)_6$ [LS, $t_{2g}^6 e_g^0$], $K_4Fe^{II}(CN)_6$ [LS, $t_{2g}^6 e_g^0$], $K_3Fe^{III}(CN)_6$ [LS, $t_{2g}^5 e_g^0$], which have the same electronic configurations that we want to evidence.

The Co $L_{2,3}$ edges of the model compounds are reported on FIGURE 3. The detection is a total yield detection mode, hence the measure is surface sensitive (a few tens Å), due to the escape depth of the electrons.

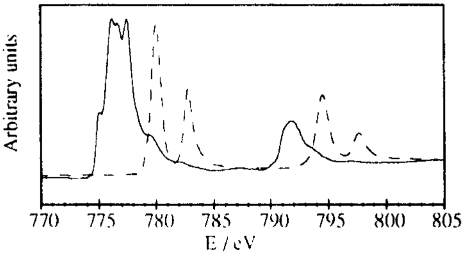

FIGURE 3 Co $L_{2,3}$ edges of ( ) $Co^{II}Cl_2.6H_2O$ and (---) $K_3Co^{III}(CN)_6$.

The spectra of the two compounds are completly different : the spectrum of $Co^{II}Cl_2.6H_2O$ is characteristic of a Co^{II}HS in octahedral symmetry[4]. The spectrum of $K_3Co^{III}(CN)_6$ is characteristic of a Co^{III}LS in octahedral symmetry[4]. All the features observed in $K_3Co^{III}(CN)_6$ are shifted at high energies. This is due to the increase of the oxidation state and the shortening of the Co-ligand distances. The less structured spectrum compared to the Co^{II}HS one is due to the lower number of multiplets expected for the $2p^5t_{2g}^6e_g^1$ configuration. The very intense band at 783 eV is the signature of the presence of the CN π^* orbitals. The high intensity of the L_2 peak compared to the L_3 is the signature of the S=0 spin state[5]. This technique is therefore *a priori* able to distinguish clearly between the two electronic structures expected in compound 2.

In FIGURE 4 are reported the Co $L_{2,3}$ edges of compound 2 measured before and after irradiation (hν=750nm during 15 min, T=20K).

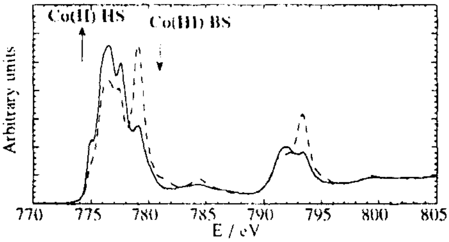

FIGURE 4 Co $L_{2,3}$ edges (---) before and ( ) after irradiation for compound 2.

The ground state of the material is a mixing of the two Co^{III} [LS, $t_{2g}^6e_g^0$] and Co^{II} [HS, $t_{2g}^5e_g^2$] species. It is impossible to extract from the spectrum a quantitative information relative to the percentage of each one. Due to the detection mode, we observe the surface of the particles, which is different from the bulk structure and richer of defects.

The spectrum obtained after irradiation displays a decrease of the signal of the Co^{III} LS species and simultaneously, an increase of the Co^{II}HS species. The light induces the transformation of Co^{III} in Co^{II}, accompanied by a spin change of the Co ions. Indeed, a Co^{II}LS species would have a completely different signature not observed here.[4]

The Fe $L_{2,3}$ edges are reported in FIGURE 5. The comparison of the spectra with the spectra of the two models not reported here allows us to attribute the origin of the peaks. For the spectra of 2 before irradiation, the feature at 705 eV, not observed in the $K_4Fe^{II}(CN)_6$ spectrum, is the Fe^{III} LS signature corresponding to the singlet $2p_{3/2}t_{2g}^{5} \rightarrow 2p_{3/2}t_{2g}^{6}$.[6] Its presence in the spectrum of 2 shows that the surface of the particles presents a mixture of Fe^{II} LS and Fe^{III} LS entities. The result is in line with the presence of Co^{II} and Co^{III} entities evidenced at the Co $L_{2,3}$ edges.

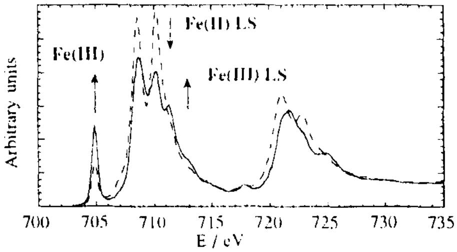

FIGURE 5 Fe $L_{2,3}$ edges (---) before and ( ) after irradiation for compound 2.

After irradiation, the intensity of the 705 eV peak increases, related to the Fe^{II} LS to Fe^{III} LS transformation. This observation confirms those at the Co $L_{2,3}$ edges.

Our data give, for the first time, a clear evidence of the light induced electronic transfer $Co^{III}Fe^{II} \rightarrow Co^{II}Fe^{III}$, postulated to explain the changes in macroscopic magnetic properties of the material.

Charactarization of the metastable state at Co K edge

Co K edge EXAFS spectra were recorded in transmission mode using the energy dispersive absorption beamline. In this experimental geometry, thin samples are needed (4 mg of product dispersed on a 1 cm^2 millipore membrane): in this way, we increase the percentage of transformed compound, by increasing the penetration depth of visible light. The disadvantage of this recording mode is the reduced energy range scanned (up to 8 Å^{-1} in k), compared to a step by step EXAFS beamline (14 Å^{-1}). The results shown here have been confirmed recently by classical EXAFS results obtained in fluorescence detection mode in grazing incidence.

On FIGURE 6 are reported the Fourier transform moduli of EXAFS signals measured at the Co K edge before and after irradiation for compound **2** (hν=750 nm during 12 hours, T=10 K).

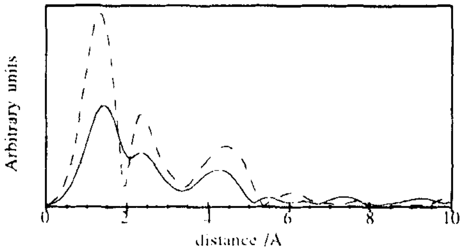

FIGURE 6 Fourier transform moduli of EXAFS signals measured at the Co K edge (---) before and ( ) after irradiation for compound 2.

In the ground state, the spectrum presents three peaks attributed to the three first shells around the cobalt, O and N, C from CN ligands, Fe and Rb atoms. After irradiation, we observe important changes in the spectrum which are difficult to interpret, since the linear geometry of the Co-NC-Fe entities introduces strong multiple scattering phenomena in the EXAFS signal. The quantitative analysis of the second and third peaks are underway. The first peak and its changes are more easy to analyse. It corresponds to the mean Co-L_6 (L=N,O) distances.

In the ground state, the best fit is obtained with a two shells fitting procedure with two Co-L_6 distances. We found 90% of d_{Co-L} = 1.90 Å distances and 10% of d_{Co-L} = 2.08 Å. The short distance is characteristic of Co^{III} low spin entities, the second one is close to the ones obtained in Co^{II} high spin species. That means that before irradiation, we observe about 10% of HS Co^{II}. After irradiation, the two distances remain the same but we have now 60% of Co atoms with long Co-L_6 distances: 50% of Co^{III}-Fe^{II} pairs have been transformed in Co^{II}-Fe^{III} pairs. The increase $\Delta\ d_{Co-L} = 0.18$ Å induced by irradiation is in agreement with the 0.32 Å increase of the a cristallographic parameter, evidenced by XRD.

CONCLUSION

Our study confirms the explanation of the photo-induced magnetisation proposed by Sato and coworkers. To our knowledge this is the first experimental local spectroscopic evidence of a photo-induced metal to metal electron transfer in a three dimensional compound:

$Co^{III}(LS)\text{-}NC\text{-}Fe^{II}(LS) \rightarrow Co^{II}(HS)\text{-}NC\text{-}Fe^{III}(LS)$.

The condition required to observe the phenomenon is not only the presence of diamagnetic excitable pairs Co^{III}-Fe^{II} in the compound, but also the presence of a certain amount of defects in the cubic structure. This is probably due to the important expansion of the network accompanying the photo-induced electron transfer. In a perfect structure, without defects, strains in the bulk are strong so that only diamagnetic pairs at the surface of the compound are transformable.

In the structure with vacancies, the steric contraints are weaker, the network is more flexible and the photo-induced metastable state is able to propagate in the bulk. We are now engaged in the study of this phenomenon.

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