


Experiment Report Form

	Experiment title: High resolution powder X-ray diffraction on photomagnetic Prussian blue analogues: search for possible structural distortion	Experiment number: HE-2193
	Beamline: ID31	Date of experiment: from: 10/03/06 to: 13/03/06
Shifts: 9	Local contact(s): Dr. Irene MARGIOLAKI	<i>Received at ESRF:</i> 11/10/07
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Experiment report:

The present report refers to structural issues related to thermally- and photo-induced phase transitions in Prussian blue derivatives. The magnetic properties of some of these compounds can be controlled optically. Various photo-magnetisation effects have been reported, such as light-induced ferrimagnetism¹ or photo-controlled pole inversion², that would open the way to applications in opto-electronics (optical memories, optical isolators...). For a more fundamental point of view, such effects would allow to continuously tune the magnetic dilution, *e.g.* by a combination of photo-excitation and thermal relaxation.³

In this respect, cobalt hexacyanoferrate samples, $A_xCo_4[Fe(CN)_6]_{(x+8)/3} \cdot zH_2O$, have been extensively studied. These compounds exhibit a charge transfer-induced spin transition (CTIST) as a function of temperature or, at low temperature ($< 160K$), under red light irradiation. We have recently undertaken a thorough investigation of their equilibrium and photo-induced properties. In particular, owing the ease in trapping the high-temperature (HT) phase by rapid cooling, we have compared the properties of the HT quenched phase with those of the photo-excited phase in terms of magnetic behaviour, thermal decay and

¹ Sato, O. et al. *Science* **1996**, 272, 704.

² Ohkoshi, S. et al. *Appl. Phys. Lett.* **1997**, 70, 1040.

³ Goujon, A. et al. *Polyhedron* **2001**, 20, 1347.

relaxation mechanism. Despite an analogy in their formal electronic configuration, we have evidenced a depressed Curie temperature for the quenched phase, in addition with a higher decay temperature and a slower relaxation at short times.⁴ It is thus necessary to assume a structural deformation that differentiates the two metastable phases. As the symmetrical Bragg reflections, the peak positions and the systematic absences are consistent with a *fcc* cubic cell for the two phases (expt. HE-1956), we propose local and incoherent tiltings of the [Fe(CN)₆] polyhedral units as a structural model for the high-temperature phase, which only results in a slight decrease of the mean lattice constant. Such tilts weaken the magnetic superexchange interactions and tend to localize the Co e_g electrons responsible for the thermally- and photo-induced phase transitions. Departures in the temperature evolution of the two metastable phases were also observed. In particular, we have evidenced a new secondary phase which is formed during the decay of the HT quenched phase. High-resolution synchrotron data were required to clarify the structural models for the various intermediate phases.

Experimental part:

The samples were provided by the group of K. Hashimoto and S.I. Ohkoshi (Dept. of Applied Chemistry, The University of Tokyo, Japan) and the group of A. Bleuzen (LCI, Université Paris-Sud, France). The wavelength was tuned to 0.8017(6)Å to be comparable to that used for the low-resolution diffraction measurements performed on the BM1a workstation (expt. HE-1956).

The major difficulty was related to **radiation damage**, the origin of which being unclear yet as it may involve several processes: merely photonic effects (formation of radicals, isomerism and flipping of the cyano bridge⁵...) or photo-thermal processes associated with X-ray absorption and subsequent sample heating (for instance, dehydration). Radiation damage was here evidenced by a shift of the diffraction lines, usually (but not systematically) towards high 2θ-angles. This shift was found to be continuous over long periods, well above 1h 30min. A broadening of the Bragg reflections was also observed in a second stage. We checked that these changes were not reversible, at least after 1-hour rest without X-rays.

Attempts to overcome this effect by an attenuation of the X-ray beam (using filters or a reduced number of IDs) did not lead to satisfactory results because the sample-to-noise ratio was then too low to monitor the radiation damage. We thus used the translation stage developed on-site, which allows fresh parts of the sample to be sequentially probed. Fast acquisition conditions were chosen, and only superimposable patterns were summed and rebinned. In these conditions, the characteristic time for radiation damage was estimated to be of the order of **10 mins** at 100K and **60 mins** at 180K. X-ray absorption was tentatively reduced using shorter X-rays in following runs: HE-2198 (0.6379Å) and HS-3096 on BM1a (0.7271Å). If a decrease of the sample heating was confirmed (HS-3096), the time for radiation damage was almost unchanged (HE-2198), again suggesting that mere photonic effects also take place under X-ray illumination.

All measurements were then performed at low temperatures (below 180K) to limit sample heating and dehydration. Indeed, we have observed by Mössbauer spectroscopy that the thermal spin transition is sizeably shifted toward high temperatures after sample dehydration. It also turns out that the transition becomes incomplete (persistence at low temperature of unconverted Co^{II}-Fe^{III} pairs). The extreme situation of a complete inhibition of the Fe^{III}→Fe^{II} electron transfer was obtained by a three-day treatment at 340K under dynamic vacuum.

Preliminary results:

For a Na_{0.32}Co[Fe(CN)₆]_{0.74}·3.4H₂O sample composition, we reported that different metastable phases can be produced depending on the photo-thermal history of the sample, from combined magnetic and low-resolution powder X-ray diffraction data (expt. HE-1956). The aim of these new measurements was to thoroughly characterise the various (meta)-stable phases. Similarly to Bleuzen *et al.*⁶ and Margadonna *et al.*,⁷ we have observed a photo-excitation under the X-ray beam, which begins within the first 3 mins of irradiation

⁴ Maurin I. et al. in preparation for submission.

⁵ Coronado E. et al. *J. Am. Chem. Soc.* **2005**, *127*, 4580.

⁶ Bleuzen et al., *J. Phys. Chem. B* **2003**, *107*, 4763.

⁷ Margadonna S. et al. *Ang. Chem. Int. Ed.* **2004**, *43*, 6316.

at 100K. It is noteworthy that this effect was not detected, even after several hours, on BM1a and thus could strongly depend on the X-ray photon flux. The structural characterisation of the low-temperature (LT) phase (obtained after slow cooling) and that of the Q-relaxed phase (obtained after the thermal decay of the HT quenched phase) were therefore carried out at 180K. At this temperature, the relaxation of the X ray-induced phase is much faster than its conversion rate.

The diffraction patterns of these two phases show split Bragg reflections (see Fig. 1 for instance), in agreement with the former low-resolution diffraction measurements. These split lines cannot be assigned to two phases of cubic symmetry. Therefore, if a phase separation is present, the majority phase can be considered as cubic, whereas the minority phase has to adopt a less symmetrical unit cell. Such a symmetry reduction cannot arise from a slight variation in the Na or $[\text{Fe}(\text{CN})_6]$ vacancy content because similar results (main cubic phase and secondary phase of lower symmetry, roughly in the same proportion as in the sample investigated here) were also encountered for another sample of nominal composition $\text{Na}_{0.45}\text{Co}[\text{Fe}(\text{CN})_6]_{0.78} \cdot 3.3\text{H}_2\text{O}$. Thus, we believe that if phase separation occurs it has an intrinsic origin and accounts for a multi-valley free energy landscape which origin involves a flexibility of the Co-NC-Fe network or (dis)-ordered orientational states of the water molecules that affect the crystal symmetry. Several authors already mentioned that, in hydrated Prussian blue derivatives, the H-bonding backbone could have an important role in stabilizing the structure.⁸

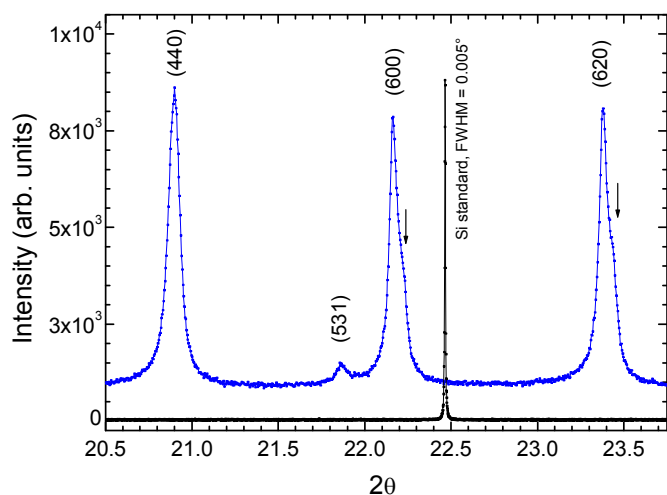


Fig.1 Synchrotron diffraction profile of the $\text{Na}_{0.32}\text{Co}[\text{Fe}(\text{CN})_6]_{0.74} \cdot 3.4\text{H}_2\text{O}$ sample, quenched at 80K and then heated up to 180K (Q-relaxed phase), $\lambda = 0.6379\text{\AA}$. Results of the HE-2198 experiments are presented here as they show better statistics. Indexation corresponds to the *fcc* crystal structure proposed for Prussian blue by Buser and col. (*Inorg. Chem.* **1977**, *16*, 2704). Arrows mark the split lines. The instrumental resolution function is given for comparison (Silicon standard).

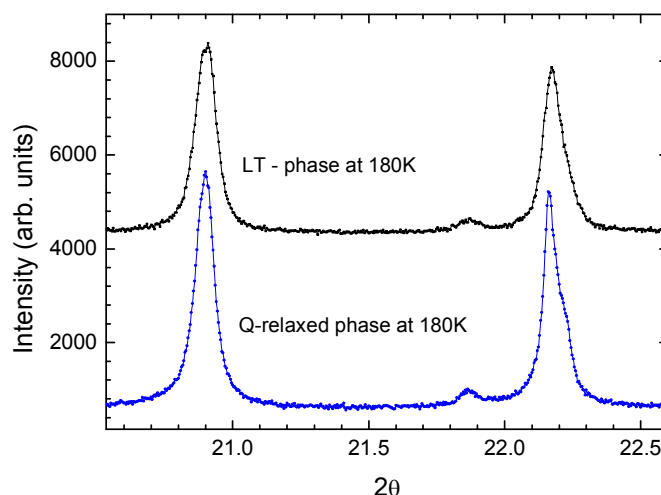


Fig.2 Synchrotron diffraction profiles of the Q-relaxed phase and of the slowly-cooled phase at 180K, $\lambda = 0.6379\text{\AA}$. Results of the HE-2198 run.

The two phases mainly differ by the linewidth, but even in the case of the Q-relaxed phase which presents the narrowest Bragg reflections, the peak width is much larger than the instrumental resolution function. For this latter phase and in the assumption of a single-phase sample, preliminary indexation attempts give a rhombohedral or an orthorhombic distortion of the double-perovskite structure with equal goodness. Further analyses are now in progress.

Difficulties also arose in the characterisation of the photo-excited phase because of the large sample heating induced by the simultaneous absorption of the X-ray beam and of the excitation light ($\lambda = 690\text{ nm}$, $0.1\text{ W}\cdot\text{cm}^{-2}$). At 100K, the relaxation process was then efficiently competing with photo-excitation, leading to a two-phase diffraction pattern with a large residual LT-phase. Results of the photo-excitation experiments will be further described in the HE-2198 experimental report.

⁸ Gravereau P. *Acta Cryst. C* **1984**, *40*, 1306. Beall G.W. *Inorg. Chem.* **1977**, *16*, 2715.