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Experiment Report Form

ESRF	**Experiment title:** Photo-induced phase transition in Prussian blue analogues	**Experiment number**: HE-1721
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Names and affiliations of applicants (* indicates experimentalists):

- Dr. Isabelle MAURIN*, Laboratoire de Magnétisme et d'Optique, UMR8634, CNRS-Université de Versailles. 45, avenue des Etats Unis, 78035 Versailles Cedex. France
- Dr. Antoine GOUJON*, Laboratoire Léon Brillouin, CNRS-CEA. Saclay, 91191 Gif sur Yvette. France
- Pr. Anne BLEUZEN, Laboratoire de Chimie Inorganique, UMR 8613, CNRS-Université d'Orsay. Bat. 420, 91405 Orsay Cedex. France (previous address: LCIMM, CNRS-Université Pierre et Marie Curie. 4, place Jussieu 75257 Paris Cedex 5)
- Pr. François VARRET, Laboratoire de Magnétisme et d'Optique, UMR8634, CNRS-Université de Versailles. 45, avenue des Etats Unis, 78035 Versailles Cedex. France

Experiment report:

Photo-control of the magnetic properties is an emerging field that would open the way to novel materials functionalities with potential applications in opto-electronics (optical memories, optical isolators…)[1,2,3]. For a more fundamental point of view, it offers the possibility to control magnetic dilution, *e.g.* by combination of photo-excitation and thermal relaxation. Of particular interest are Prussian blue analogues (PBAs) which have already provided a wealth of attractive results: high-T_C magnet, photo-induced ferrimagnetism [1], photo-controlled pole inversion [2], photo- and thermo-chromism, magnetisation-induced second harmonic generation [3]…

Cobalt hexacyanoferrates, $A_xCo_4[Fe(CN)_6]_{(x+8)/3}.zH_2O$, exhibit a charge transfer-induced spin state transition (CTISST) as a function of temperature or, at low temperature (< 160K), under red light irradiation. Photo-efficiency depends on several factors related to the chemical environment, namely the amount of Co^{III}(LS)-Fe^{II}(LS) diamagnetic pairs[#], leading to Co^{II}(HS)-Fe^{III}(LS) magnetic pairs by optical electron transfer, and the lattice flexibility. The latter factor is primarily due to the presence of $[Fe(CN)_6]$ vacancies but also to the size of the alkali metal counter ion, A.

[#] LS= low spin, HS= high spin

We have recently undertaken a thorough investigation of the equilibrium and photo-induced properties of various cobalt hexacyanoferrates. In particular, owing the ease in trapping the high temperature (HT) phase by rapid cooling, we have compared the properties of the quenched HT phase with those of the photo-excited phase in terms of magnetic behaviour, thermal decay and relaxation mechanism. We have evidenced a depressed Curie temperature for the quenched state, in addition with a higher decay temperature and a slower relaxation at short times [4]. Up to now, it was conjectured that the high temperature stable state and the photo-induced metastable state present a same electronic fine structure, as exemplified in [5].

We thought that such differences might originate from subtle structural changes that were very little studied according to the literature. Only recent low-resolution synchrotron X-ray powder diffraction experiments performed on the BL02B2 workstation (Spring8, Japan) on a $Na_{0.42}Co[Fe(CN)_6]_{0.78}$ sample [6] suggested a strongly reduced structural coherence length and a decreased lattice parameter for the quenched phase with respect to the photo-excited phase. However, both effects could also be interpreted as due to a partial relaxation of the quenched state (ca. 40%) leading to rather small nuclei of the low temperature (LT) stable state (*a*-cubic parameter~ 10.00Å) in a matrix which lattice constant has an average value of 10.19Å in-between those of the LT and HT (*a*~ 10.30Å) phases. EXAFS measurements on a caesium analogue have also evidenced a change in the Co-NC-Fe arrangement upon cooling, from bended to linear, which was attributed to a displacement of the large Cs ions within the tetrahedral sites of the *fcc* structure [7]. However, this latter result is deduced from measurements at the Cs L_3-edge, so that this distortion might be local and not coherent within the crystal. Note that those structural changes would be of particular importance since the magnetic interactions proceed via superexchange coupling through the cyanide bridges.

First results:

The samples which were studied were provided by the group of K. Hashimoto and S. Ohkoshi (RCAST, University of Tokyo, Japan) and the group of A. Bleuzen (LCIMM, Université Pierre et Marie Curie, France). The powder diffraction experiments were performed on BM01a using the fast data acquisition capabilities of the image plate set-up. The wavelength was tuned to 0.82Å to be comparable to [6]. Both static and dynamic structural changes were followed in the (i) stable, (ii) photo-excited and (iii) HT quenched states. Comparison was made with reference compounds, namely $Co_3[Fe(CN)_6]_2.14H_2O$ and $Rb_{0.45}Co[Fe(CN)_6]_{0.83}.3.3H_2O$, which retain the HT and LT structures respectively, over the whole temperature range (10K-300K).

1. for the **alkali-free** reference sample $Co_3[Fe(CN)_6]_2.14H_2O$ showing no spin transition, we have observed a large thermal expansion indicative of a soft crystal structure (Fig.1a) together with a slight anisotropic line broadening that could be ascribed to micro-strains or to an unresolved structural distortion. Using an empirical model of uniaxial strain along the 111 direction, we could reproduce the various line shapes. This anisotropic broadening is partly suppressed when the temperature decreases. However, the fact that the intensity of the narrowest (*h*00) lines also decreases might better reflect an increased lattice distortion (Fig.1b). Further studies, including high resolution powder diffraction measurements, are clearly needed to understand the peculiar temperature dependence observed for this sample.

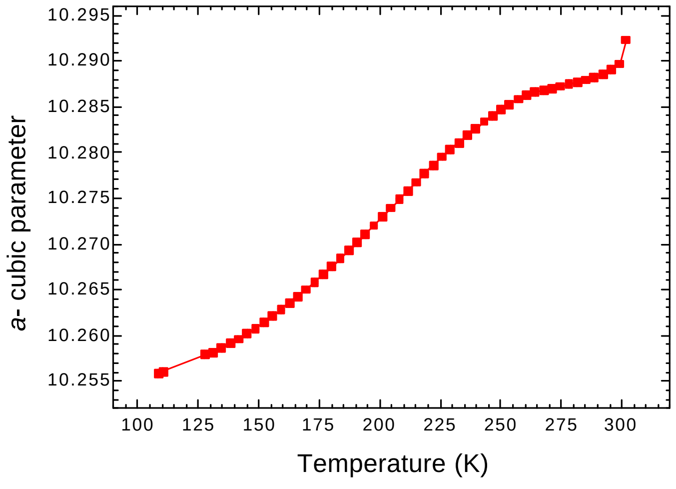

Fig.1a Cubic lattice parameter as a function of temperature for $Co_3[Fe(CN)_6]_2.14H_2O$.

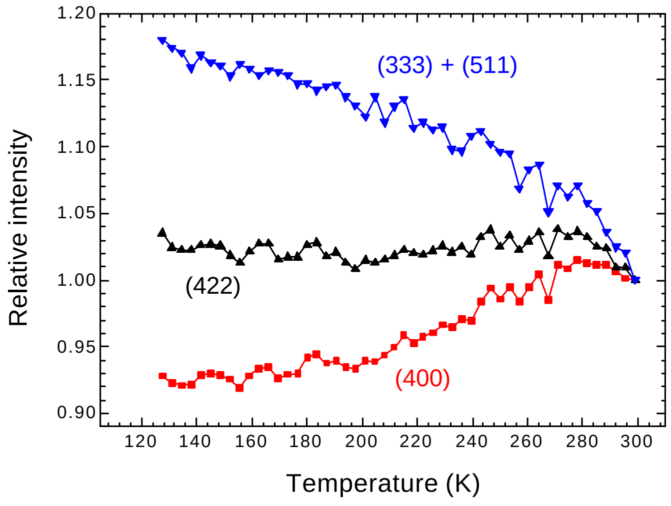

Fig.1b Relative intensity as a function of temperature for the (400), (422) and (333) lines, assuming a *fcc* crystal structure.

On the contrary, the thermal dependence for $Rb_{0.45}Co[Fe(CN)_6]_{0.83}.3.3H_2O$ is consistent with a harder structure with a contraction of ca. 0.008Å on the temperature range studied.

2. For the **alkali-doped sample** $Na_{0.32}Co[Fe(CN)_6]_{0.74}.3.4H_2O$ showing a discontinuous spin transition, Fig. 2 shows the diffraction patterns recorded: (i) at 300K, (ii) after slow cooling at 110K and (iii) after subsequent photo-excitation at 110K. Irradiation was carried out with a laser diode (collimated beam of ca. 1mm in diameter, λ= 690nm, power: 20mWatt). The residual LT phase after irradiation might be attributed to: (i) a slight misalignment of the laser with the part of the sample probed by the X-ray beam or else to (ii) bulk absorption effects that limits the penetration depth of the red light despite of the rather small sample thickness (0.1mmØ capillary).

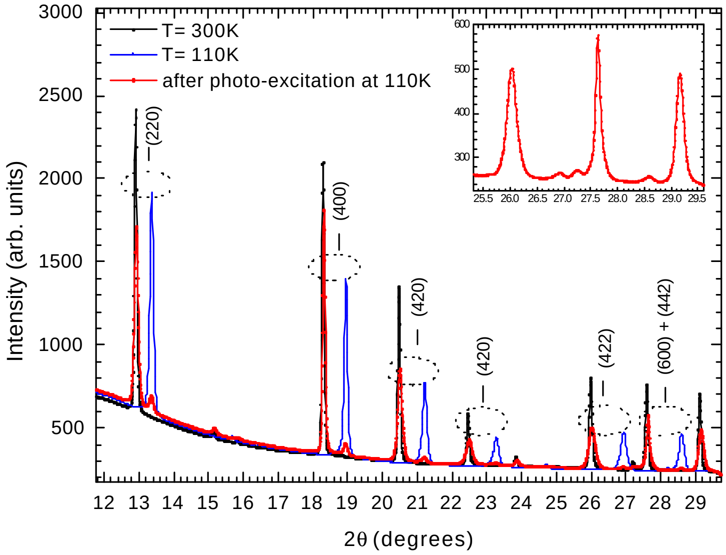

Fig.2 Synchrotron X-ray diffraction profiles for $Na_{0.32}Co[Fe(CN)_6]_{0.74}.3.4H_2O$. Peaks were indexed according to the *fcc* crystal structure proposed for Prussian blue, $Fe_4[Fe(CN)_6]_3$, by Buser and col. (Inorg. Chem. **1977**, 16, 2704). In inset, anisotropic peak broadening in the photo-excited phase.

Both HT and LT phases could be indexed using the same *Fm3m* structural model. The LT phase is characterised by a large volume contraction (~90Å^3 per *fcc* unit cell) preliminary due to the Co-N bond shortening (~0.18Å from EXAFS studies) which accompanies the $Co^{II}(HS)\rightarrow Co^{III}(LS)$ electron transfer. Large (and reversible) "strain" effects are evident in the LT phase. Its slightly asymetric line shape could account for a residual Co^{II} fraction (Co/Fe ratio larger than 1 in the sample studied) and as-related displacement disorder effects. Nevertheless, the large peak broadening at low temperature is probably not only due to strains. Indeed, despite of the rather low instrumental resolution, a small peak splitting has been observed for the (600)+(442) line.

As expected, irradiation gives rise to a new phase with an increased lattice parameter value (due to the spin transition). The striking result is the **strong anisotropic peak broadening** apparent for the photo-excited phase, which results from some kind of "strain release" along the <*h*00> directions (see for instance the inset of Fig. 2). Such narrowing of the (*h*00) lines is similar to the case study of the alkali-free sample, but the effect is much larger. Again high-resolution diffraction data would help understanding the origin of this anisotropic line shape.

3. Comparison between quenched and photo-excited states. The present experiments allow to draw more definite conclusions compared to previous studies [6]. Indeed, the decrease in lattice parameter and the peak broadening reported in [6] for the quenched phase must be ascribed to an uncomplete quenching procedure. For an efficient trapping, one needs to minimize the temperature interval between the thermal decay of the metastable state and the cooling branch of the thermal hysteresis loop. It is hence strongly dependent on the sample composition. This criterium was fullfilled for the sample studied [see 8 for instance] and only a small peak broadening could be observed, after quenching.

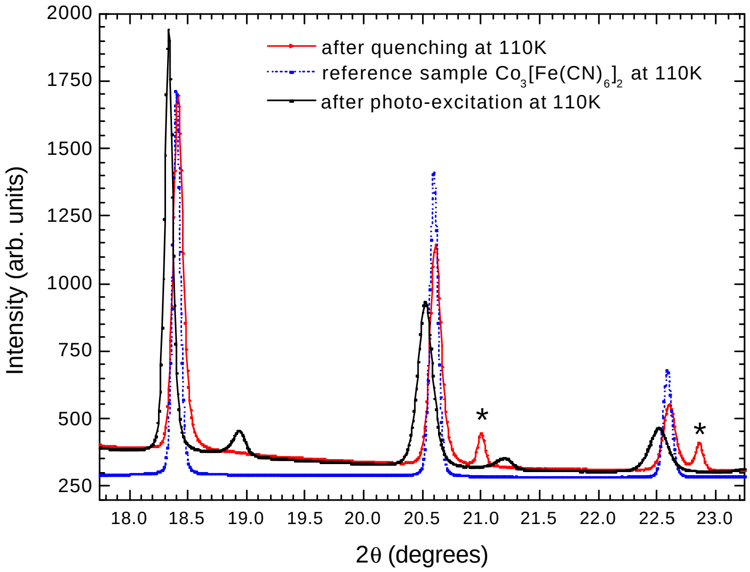

Fig. 2 Diffraction profiles recorded after quenching at 110K and after photo-excitation at 110K for $Na_{0.32}Co[Fe(CN)_6]_{0.74}.3.4H_2O$. Comparison is made with the reference sample $Co_3[Fe(CN)_6]_2.14H_2O$ measured after slow cooling down to 110K. Peaks marked with * correspond to ice.

Fig. 2 show the comparison between the diffraction patterns measured at 110K for the photo-excited phase, the HT quenched phase and the reference compound $Co^{II}_3[Fe^{III}(CN)_6]_2$. The two latter profiles are comparable, while the photo-excited phase shows a larger lattice parameter. More detailed analyses are in progress. However, both the larger lattice parameter value and the larger strain effects observed for the photo-excited phase are in apparent contradiction with the larger Curie temperature compared to that of the quenched phase.

Relaxation measurements performed as a function of temperature (or time at a given temperature) confirmed that the decay of the HT quenched phase occurs at higher temperature, and hence implies a larger barrier energy. In addition, shifts and broadenings of the diffraction peaks seem to show that the relaxation proceeds inhomogeneously throughout the sample, either via spinodal decomposition or because of a distribution of barrier energies. Such a distribution has already been invoked and estimated through the analyses of relaxation curves obtained from macroscopic magnetic susceptibility data [8]. Yet such a distribution should be associated with the presence of point defects [8]. Not only the $[Fe(CN)_6]$ vacancies but also the alkali metal ions could participate to the building up of such distributions as claimed by [7]. New structural analyses, for different sample compositions (nature and concentration of alkali metal), will be performed (exp. HE1956).

References

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