



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> First evidence of photomagnetism in solution	<b>Experiment number:</b> CH-5012
<b>Beamline:</b> ID12	<b>Date of experiment:</b> from: 4/04/2017 to: 11/04/2017	<b>Date of report:</b>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Andrei Rogalev, Fabrice Wilhelm	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Corine Mathonière (ICMCB, University of Bordeaux, France)</b> <b>Panagiota Perlepe (CRPP - ICMCB, University of Bordeaux, France)</b> <b>Amélie Juhin (IPCMC, Université Paris P. M. Curie, Paris, France)</b>		

## Report:

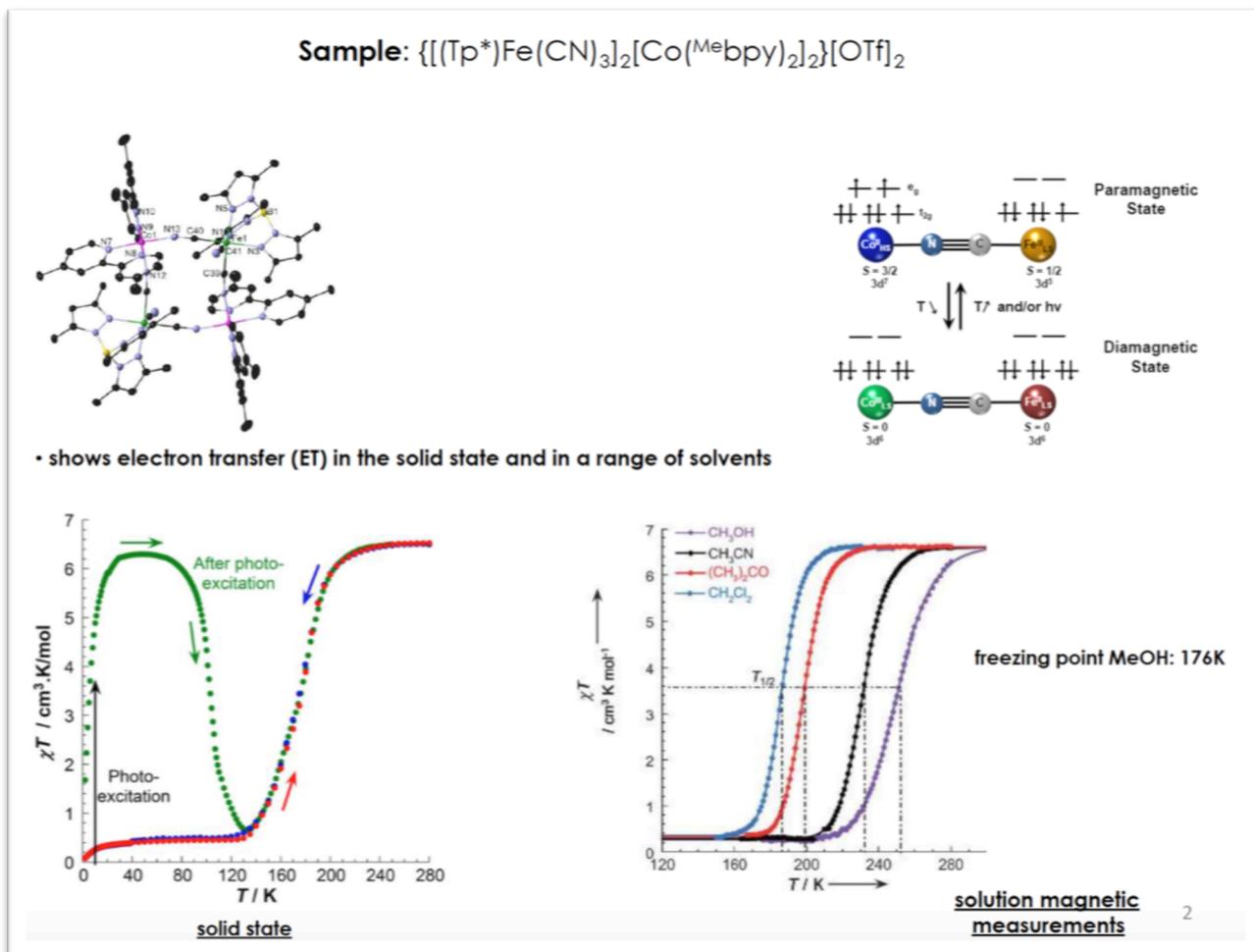
The objective of the experiment is to study the metal-to-metal electron transfer in cyanido-bridged FeCo squares in solutions.

This mechanism has been studied in solid state for this compound during previous beam times (CH-4036 and CH-4330). Some tests have been done in solutions. The main conclusions were :

- the thermal-induced ET on Co and Fe K-edges have been confirmed in solid state and in solutions.
- the photo-induced ET on Co and Fe K-edges have been confirmed only in solid state.
- in solutions, the X-ray flow must be reduced to avoid the X-ray induced Co(II) reduction.

The purpose of this new beamtime is to investigate in detail the photo-induced ET in solutions as this experiment is not possible with other techniques used to characterize the ET as magnetometry. The beamline scientists designed a new set-up on ID12 for photoexcitations experiments. This set-up allows the light to be focused on the sample with a power of 4 mW/cm<sup>2</sup> from an external source.

The selected compound is the square of formula  $\{[(Tp^*)Fe(CN)_3]_2[Co(Me-bipy)_2]\}(OTf)_2$  / Its properties in solid state and in solutions are given in Figure 1.



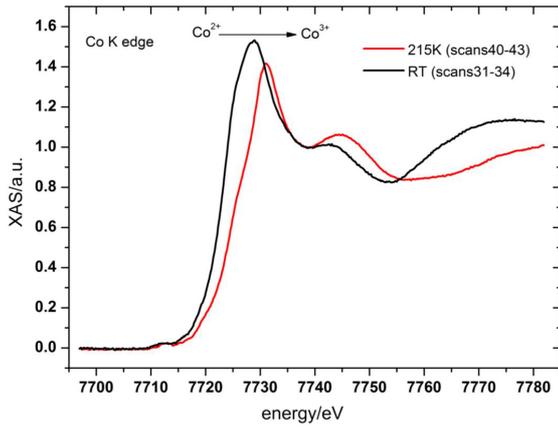
**Figure 1** : Molecular structure of the electron transfer square (top left). Electron transfer (ET) mechanism (top right). Magnetic properties in solid state (bottom left) and in solution (bottom right) showing the thermal-induced ET above 120 K and the photo-induced ET in solid state below 120 K.

For this compound, we prepared a solution of the concentration of  $1.5 \cdot 10^{-3}$  mol/L (ie. 19.5 mg dissolved in 6 mL of MeOH). This solution is then inserted in a specific glass cell adapted for the solution measurements.

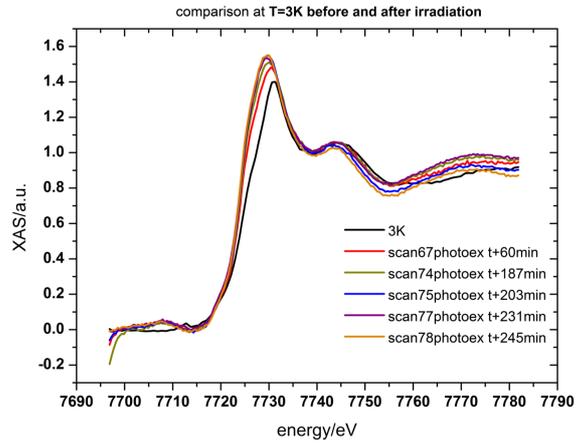
We measured:

- the XAS spectra for the Co and Fe K-edges at room temperature
- the XAS spectra for the Co and Fe K-edges at 215 K and 3 K
- the light irradiation with a LED at 940 nm at 3 K on the Co edges.

The results are given in the next figures.

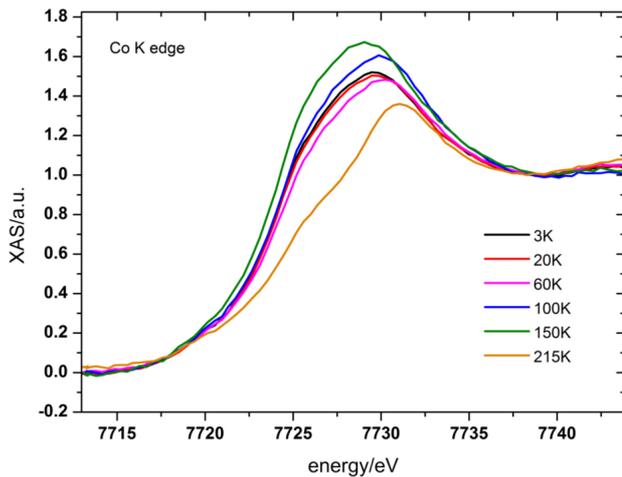


**Figure 2 :** XAS of the Co K-edge in temperature in the liquid phase.



**Figure 3 :** XAS of the Co K-edge at 3 K after 940 nm irradiation in frozen solution

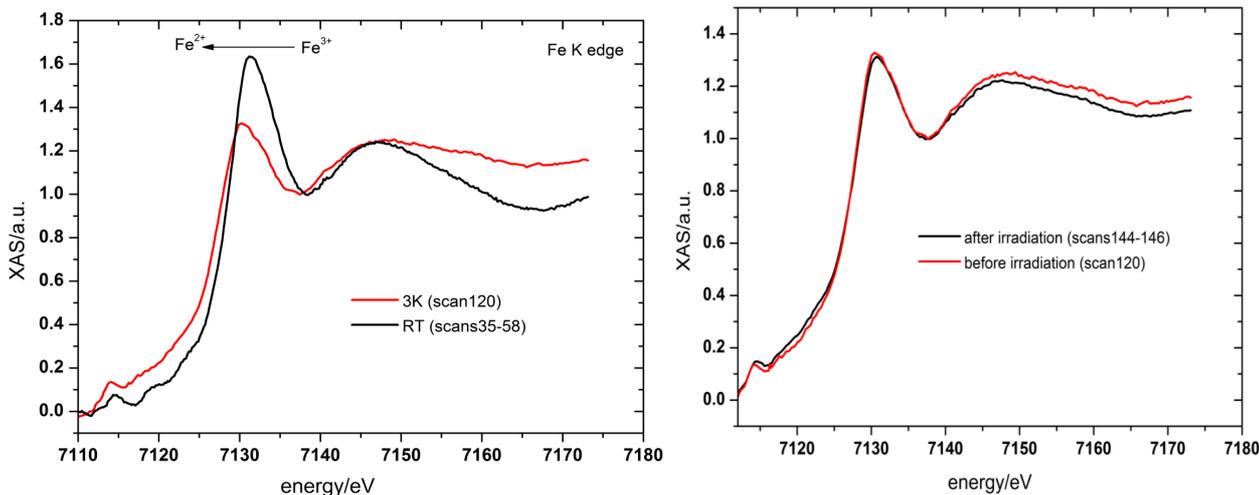
The figure 2 confirms the ET in solution on the Co K-edge (and also Fe K-edge but not shown here). The figure 3 shows the XAS measured at 3 K in frozen solution after 1 h, 3 h, and 4 hours of irradiation. We have estimated the conversion at 52 % of  $\text{Co}^{3+}$  in  $\text{Co}^{2+}$  after one hour and 83 % after 4 hours. After these photoexcitation, we also followed the relaxation when the temperature is increasing. These measurements are shown in Figure 4.



**Figure 4 :** XAS of the Co K-edge after photoexcitation with temperature increase.

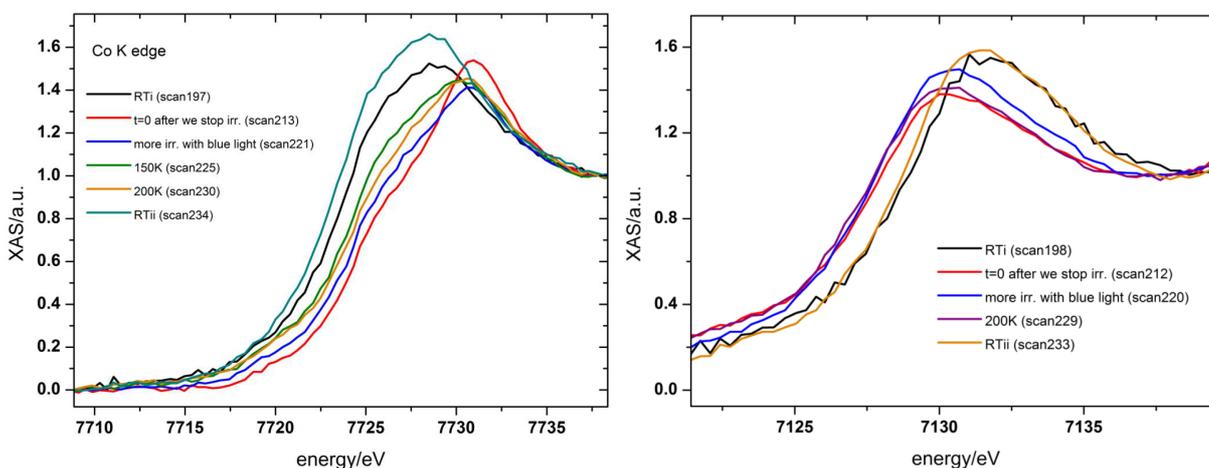
Two important informations can be retained from Figure 4. First the  $\text{Co}^{2+}$  is still increasing even when the 940 nm-irradiation is stopped. That means that X-ray irradiation has a role in the  $\text{Co}^{2+}$  generation. When the temperature is back at 215 K, the sample is again liquid and we observed a clear  $\text{Co}^{3+}$  signature. This can not be associated undoubtedly to the reversibility of the ET process as the point measured in the frozen point is probably not the same than the point measured in solution.

In parallel, we follow the XAS of the Fe K edges (Figure 5). The  $\text{Fe}^{3+}$  is reduced in liquid state in  $\text{Fe}^{2+}$ , in full agreement of the thermal-induced ET process. To follow the XAS of the Fe in the frozen solution, it was necessary to modify the position of the X-ray beam on the sample because the crystallized frozen ethanol creates a background diffusion. This is why the spectra at 3 K and 300 K have different baselines. But the information of the oxidation state of the Fe remains correct. It has been possible to conclude that the irradiation is not changing the Fe oxidation state in the frozen solution.



**Figure 5** : XAS of the Fe K-edges. (Left) At room temperature and at 3 K showing the oxidation state change of the Fe. (Right) Before and after irradiation with 940 nm LED.

With the objective to discriminate the role of X-ray irradiation and 940-nm irradiation we performed an other experiment. We measured the spectra at room temperature (scans Co K-edge #197 and Fe K-edge #198) and went directly at 3 K and irradiated the sample for 3 hours. The XAS of first Fe and then Co K-edges have been measured and correspond mainly to  $\text{Fe}^{2+}$  and  $\text{Co}^{3+}$  (spectra #212 and #213 respectively). These spectra are shown on figure 6.



**Figure 6** : XAS of the Co (left) Fe K-edges (right). at room temperature (black), after 3 hours of 940 nm irradiation at 3 K (red) and after irradiation at different temperatures.

In conclusion from these experiments, it was possible to follow the thermal-induced ET in solution, for both Co and Fe K-edges. At low temperature, it has been complicated to discriminate the effect of the X-ray irradiation and the 940-nm irradiation of the Co edge as the X-ray irradiation is able to photo-reduce the Co. On the other side the Fe is mainly unchanged by light or X-ray irradiation in frozen solution. We conclude that the frozen MeOH can generate electrons that can reduce the Co This is in agreement with papers published several years ago (Moan et al., 1975 J. Phys. Chem., 21, 2220; Palumbo et al., Astron. Astrophys. 1999, 342, 551).

**Perspectives :** The MeOH frozen solution forms a crystalline diffusing phase at low temperature which renders the XAS analysis difficult, in particular on the Fe K-edge. Moreover, the frozen MeOH is sensitive to X-ray irradiation by creating radicals and electrons that destroys partially the ET squares. To avoid these problems, an alternative would be the use of a frozen "transparent" and neutral medium to solubilize our compound and create a homogeneous film. We identified the O-terphenyl compound to form a transparent frozen matrix even at low temperature. Further tests of solubility of the square compounds are in progress in our team.

