EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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://wwws.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.

ESRF	**Experiment title:** Disentangling geometric and spin state changes in multinuclear spin cross-over compounds: X-ray emission and spin (site)-selective X-ray absorption spectroscopy	**Experiment number:** **CH-4413**
Beamline: ID26	**Date of experiment:** from: 15.04.2015 to: 21.04.2015	**Date of report:** 17.10.2016
Shifts: 18	**Local contact(s):** Sara Lafuerza	*Received at ESRF:*

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Report:

Spin-crossover (SCO) is a representative example of molecular bistability, in which the high-spin (HS) and low-spin (LS) states are interconvertible by physical perturbation such as temperature. [1] Since the first discovery of the SCO phenomenon it has attracted much attention from chemists, biochemists, and physicists, because it offers an understanding of ligand field theory. But despite the tremendous insights that have been gained over the past decades into the underlying electronic principles responsible for the occurrence and the specific behaviour of spin transition processes, the study of spin crossover complexes is still a highly attractive research field due to their potential application in developing electronic devices. [2]

Especially the molecular mechanisms leading to specific spin crossover behaviour are still not well understood, since usually structural (by XRD) and spin state changes (by SQUID and Mößbauer) are measured in two separate experiments.

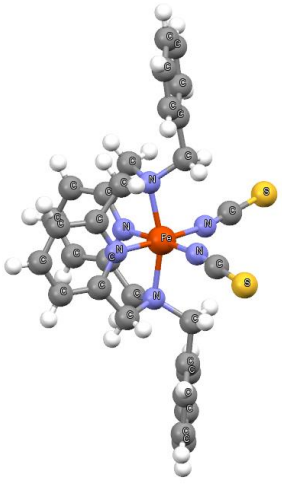

Figure 1: Structure of [Fe(L-N_4Bn_2)$(NCS)_2$]

In the experiment CH-4431 we applied K$\beta_{1,3}$- and K$\beta_{2,5}$-XES, as well as HERFD-XAS and 3p-1s(Kβ)-RIXS to study the electronic (K$\beta_{1,3}$-XES, HERFD-XANES) and structural (K$\beta_{2,5}$-XES) changes of SCO complexes during the temperature dependent spin transition in a quasi-simultaneous experiment.

Since we aimed at a close correlation between the spectral features and the spin state of the system it was mandatory to collect a large number of data points. Therefore spectra at more than 20 temperatures have been collected. The background corrected and normalized K$\beta_{2,5}$ spectra of [Fe(L-N_4Bn_2)$(NCS)_2$] (Figure 1) are displayed top left in Figure 2. The spectra show only one broad signal, which shows only slight changes in intensity and FWHM with increasing temperature. As mentioned by Vankó and de Groot [3] the features loose intensity with increasing high spin fraction because of the longer Fe-N bonds, which cause a smaller overlap with the N 2p orbitals. Since the signal to noise of the spectra is not very good, it was not possible to pick the maximum intensity for a correlation with the spin state. Instead the intensity at the emission energy 7110.627 eV (indicated

with arrow in Figure 2, top left) was read out and correlated with the spin state (Figure 2, top right). Using this approach we disagree with the conclusion of Vankó and de Groot that the $K\beta_{2,5}$ spectra are not an appropriate probe for the spin state, since we obtained a good correlation of the spectral features with the spin state (Figure 2, top right).

The normalized and background corrected HERFD-XANES prepeak region is displayed bottom left in Figure 2 for all temperatures. In the low spin case one asymmetric signal with a maximum at 7113.6 eV is observable, whereas the high spin spectrum shows two maxima at 7113.6 eV and 7112.0 eV. The signal at 7112.0 eV obviously increases with rising temperature and therefore with increasing high spin fraction. For the correlation of the changes in the prepeak region with the spin state the two features were deconvoluted with two Gaussian type functions and the intensity of the signal at lower emission energies, corresponding to the high spin fraction, was determined. Figure 2 (bottom right) shows the comparison of the Boltzmann fit functions of the intensity (red) and the magnetization obtained by SQUID (black). As can be seen the correlation of the intensity of the high spin signal with the spin state is quite good, even despite the poor signal to noise ratio.

Thes results obtained at beamline ID26 will now be connected to conventional XAS measurements in order to gain an exhaustive view on the topic and to prepare a high quality publication.

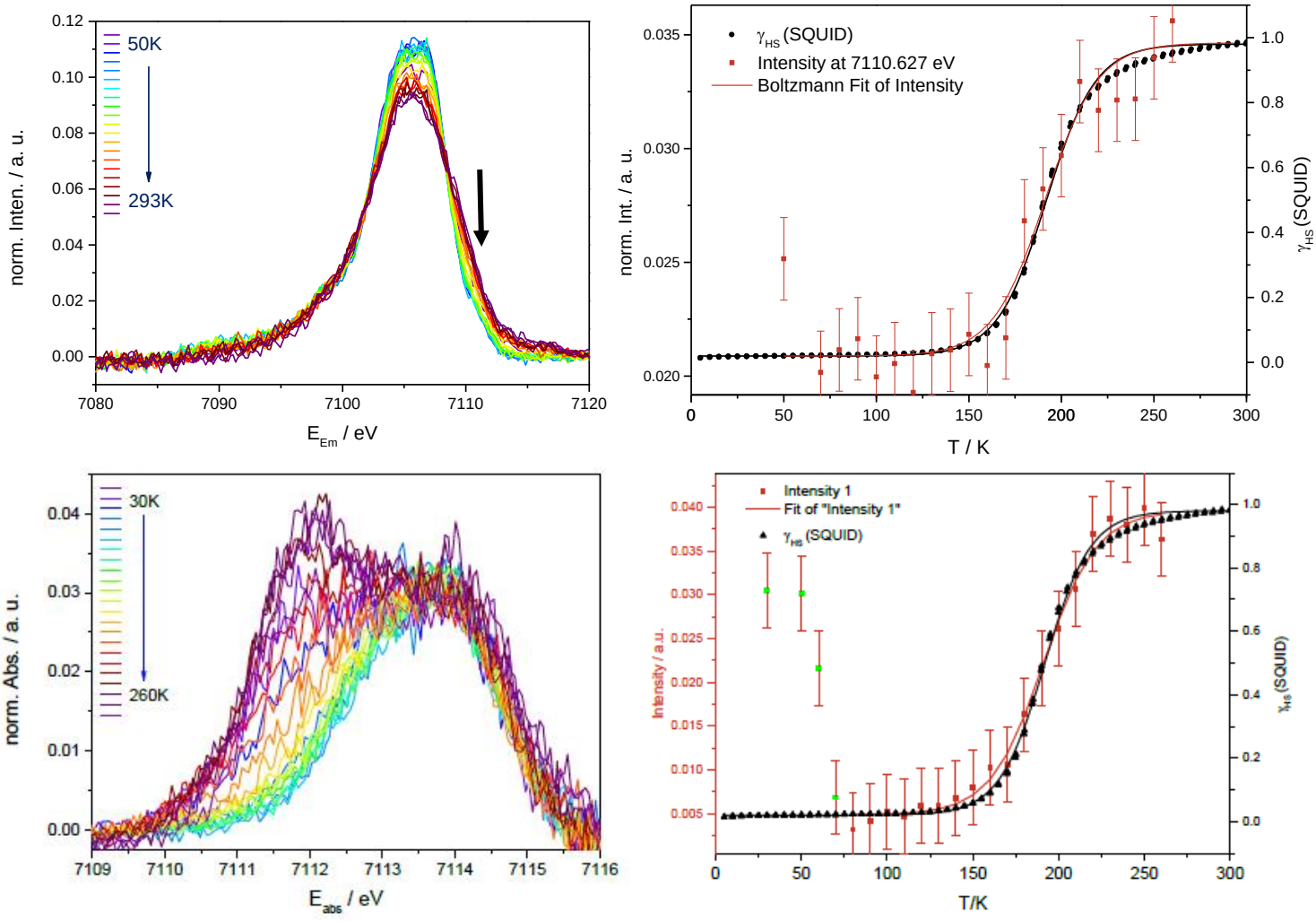

Figure 2: Background corrected and normalized $K\beta_{2,5}$ spectra in the temperature region from 50 to 293 K (top left); comparison of magnetization curve obtained by analysis of $K\beta_{2,5}$-XES and SQUID (top right); background corrected and normalized HERFD-XANES prepeak in the temperature range from 30 to 260 K (bottom left); comparison of magnetization curve obtained by analysis of HERFD-prepeak and SQUID

[1] P. Gütlich, H. A. Goodwin in *Topics in Current Chemistry*, *Vol. 233* (Eds.: P. Gütlich, H. A. Goodwin), Springer, Berlin/Heidelberg, **2004**. [2] J.-F. Létard, P. Guionneau, L. Goux-Capes in *Topics in Current Chemistry*, *Vol. 235* (Eds.: P. Gütlich, H. A. Goodwin), Springer, Berlin/Heidelberg, **2004**. [3] G. Vankó, T. Neisius, G. Molnar, F. Renz, S. Karpati, A. Shukla, F. M. F. de Groot, *J. Phys. Chem. B* **2006**, *110*, 11647–11653.