EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Correlation of large orbital moment with the local structure for the organic hybrid system CoOEP/HOPG	**Experiment number**: HC-966
Beamline:	**Date of experiment**: from: 22.09.2015 to: 29.09.2015	**Date of report**:
Shifts: 18	**Local contact(s)**: F. Guillou	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

K. Ollefs*, H. Wende, D. Klar, A. Smekova and N. Rothenbach*

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Report:

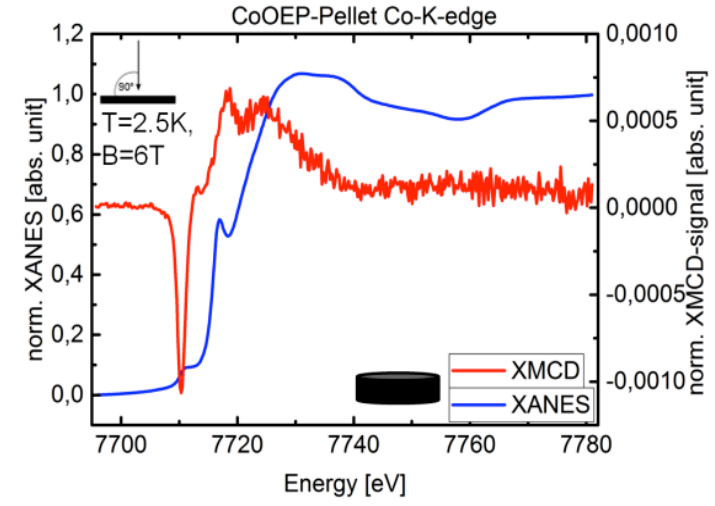

Figure 1: XANES and XMCD spectra at Co K-edge on a pressed Co OEP pellet measured at 2.5K and in 6T.

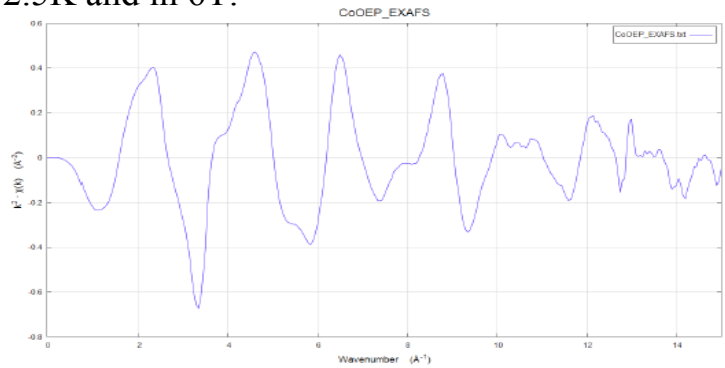

Figure 2: Exemplary EXAFS taken on the Co-OEP pellet sample at 2K in normal incidence of the x-rays

For this experiment we planned to measure Co-octaethylporphyrin (OEP) molecules on a HOPG substrate and correlate the large orbital moment which was observed in soft-x-ray XMCD measurements to the local structure of the Co by (surface) EXAFS and XMCD. For that a deposition chamber was brought to the ESRF from Duisburg and mounted to beamline ID12. Several layers of molecules were then evaporated onto HOPG which was fixed to the cold-finger of the cryostat. The cryostat was then introduced into the 6T Oxford magnet. This deposition corresponds to a submonolayer coverage of Co as every molecule contains just one Co atom, we planned to use the energy-resolved detector which was mounted on the magnet from the other side under a fixed angle. Unfortunately the geometry dictated by the experiment did not allow us to detect the Co K-edge signal because it was dominated by a diffraction peak of the HOPG substrate. Even an Fe filter did not shield the detector sufficiently as it created a large additional artefact (background?) signal in the detector. In

order to be successful for this experiment, either the measurement geometry needs to be changed or another substrate has to be used which avoids a diffraction peak in this direction. In order to measure the Co OEP molecules despite these difficulties we pressed a pellet from the molecule powder. In the following extended x-ray absorption fine structure (EXAFS), x-ray near edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) were recorded at the Co K-edge.

Analysis of the Co EXAFS (Fig. 1, bottom) allowed us to verify a planar configuration of the Co within the molecule which was also observed in the Co OEP molecules on surfaces [1].

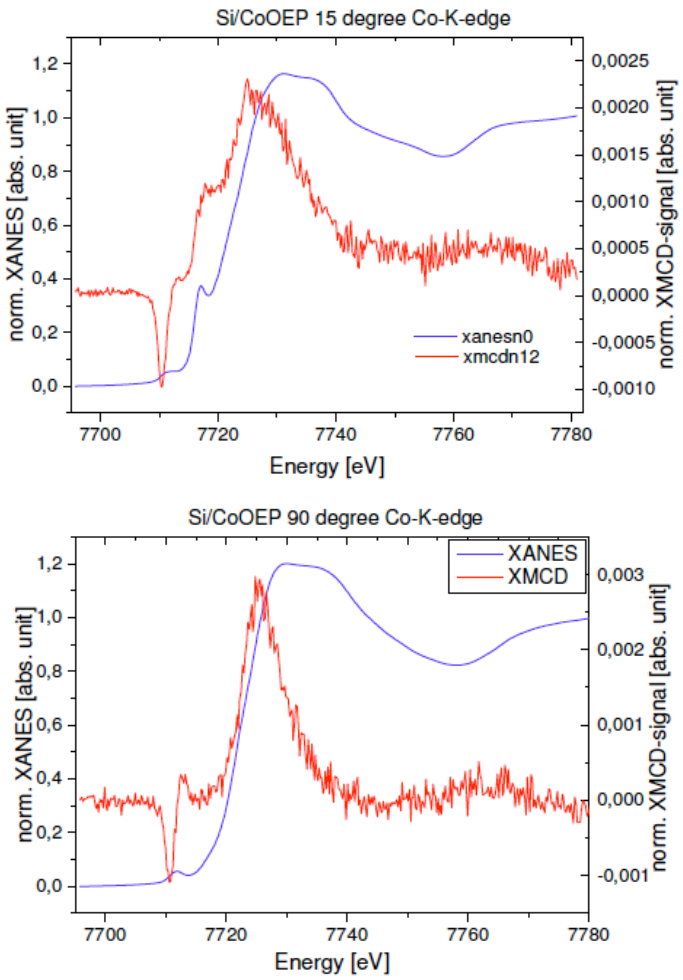

Figure 2: XANES and XMCD spectra at Co K-edge of Co OEP molecules drop-casted on Si-substrate measured at 2.5K and in 6T for 15° and 90° incident angle.

The detailed analysis of the spectra by ab initio calcuations (FEFF9 code) is currently performed.

The XANES (Fig. 1, top) reveals a very distinct structure at the pre-edge and rising edge which can be attributed to orbitals in Co along different orientations which are visible in all spectra due to the rather arbitrary orientation of the molecules in the pellet.

These distinct features are also observed in the the XMCD spectra. Magnetic field-dependent measurements have been carried out at the photon-energy of the Co pre-edge. They show a field dependence which differs from a simple Brillouin-like behavior. A detailed analysis is ongoing.

To measure the Co OEP molecules in an oriented way we, dispersed them in solution and prepared a thin layer by drop-casting. The respective XANES and XMCD spectra are shown in Fig. 2. The different spectral shape for 15° and 90° incident angle of the x-rays indicates that the molecules are oriented parallel on the Si substrate for this multilayer coverage.

Despite the multilayer coverage of the Co-OEP molecules on Si, many spectra had to be recorded in order to enhance signal-to-noise ratio of the XMCD spectra. Further careful analysis of the individual spectra is under way. For further understanding theoretical modelling and calculation of the spectra will be performed.

References:

[1] D. Klar et al. Phys. Rev. B **89**, 144411 (2014)