



## 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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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

Reports can now 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.



**Experiment title:** Nature of magnetic ordering of Fe-porphyrin molecules on ferromagnetic and non-magnetic substrates

**Experiment number:**  
HE-2700

**Beamline:**  
ID08

**Date of experiment:**  
from: 23/07/2008 to: 30/07/2008

**Date of report:**  
31/08/2010

**Shifts:**  
21

**Local contact(s):**  
Dr. Carsten TIEG

*Received at ESRF:*

**Names and affiliations of applicants (\* indicates experimentalists):**

Dr. Carolin Antoniak, Dr. Claudia Weis, Dietger Bovenschen, and Prof. Dr. Heiko Wende  
Fachbereich Physik, Experimentalphysik–AG Wende and Center for Nanointegration  
Duisburg-Essen (CeNIDE), Universität Duisburg-Essen, Lotharstrasse 1, 47048 Duisburg,  
Germany

Dr. Jorge Miguel, Matthias Bernien, and Prof. Dr. Wolfgang Kuch  
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin,  
Germany

**Report:**

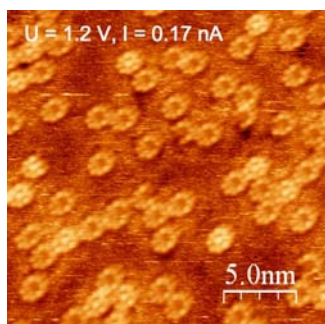


Fig. 1

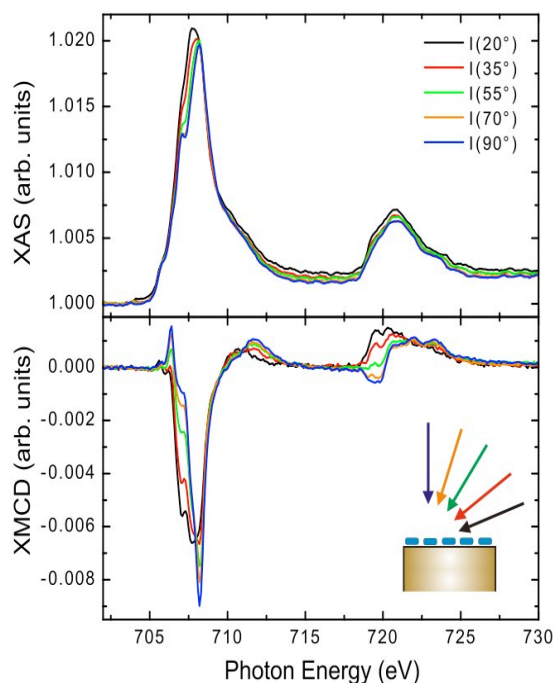


Fig. 2

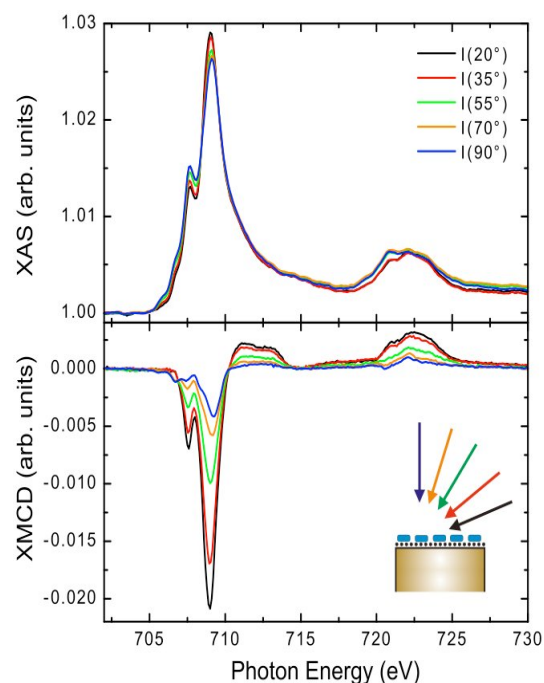


Fig. 3

We investigated the electronic structure and the magnetic properties of oriented Fe octaethyl-porphyrin (OEP) molecules adsorbed onto bare and oxygen-covered Cu(100) single crystals. Since these molecules are paramagnetic the measurements had to be carried out in a high magnetic field and at low temperatures in order to align the magnetic moment of the Fe center. The hybridization of the orbitals of the central metal ion with the substrate modifies the ligand field experienced by the ion and the ion's oxidation state. Thereby basic magnetic properties may be altered, such as the magnetic moment and magnetic anisotropy. The modifications of the electronic structure of the ion and its magnetic properties were studied by means of angle dependent NEXAFS and XMCD measurements at the Fe-L<sub>2,3</sub> edges, respectively. The samples are prepared by evaporation of the molecules from a Knudsen cell at 485 K onto the substrates held at room temperature.

Figure 1 shows an STM image of Fe OEP on Cu(100) at room temperature. The intramolecular structure of the porphyrin molecules is resolved. It is directly evident that the Fe-porphyrin molecules adsorb flat on Cu(100). The mobility of the molecules is quite low since they do not agglomerate and hardly change their position between successive images. A coverage of 0.4 monomolecular layers is deduced from the evaluation of several images.

Angle-dependent X-ray absorption measurements were carried out to study the anisotropy of charge and spin densities of the individual electronic levels of the metal center. Figure 2 shows the Fe-L<sub>2,3</sub> edges for different X-ray incidence angles measured at a temperature of T = 8 K in an applied magnetic field of B = 5 T along the X-ray incidence directions. The upper panel shows the helicity-averaged spectra using left and right circularly polarized X rays. The lower panel shows the difference between the two helicities, i.e., the XMCD spectra, reflecting the unoccupied spin density at the Fe site. A sizable XMCD signal is found for all measured incidence angles, evidencing the presence of an Fe magnetic moment. Four resonances can be identified in the XMCD and XAS signals, best visible for normal incidence. Since the applied magnetic field and the temperature were not sufficient to magnetically saturate the molecules, their magnetization might change when varying the direction of the magnetic field due to a magnetic anisotropy of the Fe center. Although the XMCD line shape varies strongly with the incidence angle, the integrated XMCD signal is constant within 10% indicating a negligible magnetic anisotropy of the Fe ion. The L<sub>3</sub> peak position of Fe OEP on Cu(100) is red-shifted by about 1 eV with respect to the one of the Fe(III) OEP Cl bulk sample indicating that the oxidation state of the Fe center on the surface is reduced.

In a subsequent experiment, we deposited Fe OEP molecules onto a pre-oxidized Cu(100) single crystal, which was prepared by dosing 1200 L of O<sub>2</sub> onto the substrate held at 500 K. As a result, the surface is covered by half a monolayer of atomic oxygen forming a well-known ( $\sqrt{2} \times 2\sqrt{2}$ )R45°, so-called missing row, reconstruction. We deposited 0.4 ML of Fe OEP molecules, after cooling the crystal down to room temperature. The Fe- L<sub>3</sub> peak position coincides within 0.2

eV with that of the Fe(III) OEP Cl bulk sample, suggesting an Fe 3+ oxidation state. Figure 3 shows the Fe-L<sub>2,3</sub> XAS and XMCD signals which were measured at different X-ray incidence angles and at a temperature of T = 8 K in an applied magnetic field of B = 5 T along the X-ray incidence directions. The most prominent effect is a 5-fold decrease of the XMCD signal when comparing the spectrum at normal incidence to the one at 20°. This decrease can only be explained by the presence of a strong magnetic anisotropy, with the easy axis of the Fe magnetic moment oriented in-plane, as a result of an interaction of the iron centers and the oxygen atoms. This very pronounced effect is astonishing since the coordination of the oxygen atom to the Fe center as a fifth ligand should reduce the tetragonal distortion of the ligand field as it is also reflected by the reduced angular dependence of the line shape of the XAS and XMCD signal. This should lead to a reduction of the orbital moment, which is the driving force of the magnetic anisotropy. Indeed, the orbital to spin moment ratio is in the range of 10% for both samples as evaluated by applying the sum rules. The origin of the strong magnetic anisotropy is currently investigated by means of DFT calculations.