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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: Magnetic properties of pyridin-based metalorganic networks	**Experiment number**: HE-3537
Beamline: ID08	**Date of experiment**: from: 13/04/2011 to: 18/04/2011	**Date of report**: 31/08/2011
Shifts: 18	**Local contact(s)**: Dr. Violetta Sessi	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of the experiment HE-3537 was the investigation of the fundamental magnetic properties (anisotropy, ratio between spin and orbital moments, spin and oxidation state, and superexchange interactions) of 3d metal atoms interacting with pyridine organic endgroups in two-dimensional metal-organic networks. During the beamtime we focussed on Fe and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (t4pt in the following) on Au(111). The preparation was carried out in-situ at the ESRF taking advantage of the dedicated STM chamber connected to the high-field magnet of the ID08 beamline. Before studying the samples by x-ray absorption spectroscopy, they were characterized by STM. Figure 1 shows a typical STM image taken during the beamtime. The 2-dimensional metal organic network of t4pt and Fe consists of ordered arrays of triangular shaped domains, where the side length of one triangle is about 9 nm.

Temperature and magnetic field-dependent XAS and XMCD spectra were recorded at the Fe $L_{2,3}$ edges and the N K edge in total electron yield mode using circularly and linearly p-polarized light at normal (0°) and grazing (70°) incidence angles.

The coordination of the Fe atoms and the t4pt molecules is evident not only in the STM images, but also in the N K-edge NEXAFS. Fig. 2 shows spectra of two different preparations, measured at room temperature under grazing incidence. In pure t4pt, the π* peaks of the triazene and the pyridine nitrogen atoms coincide in photon energy. Coordination with Fe leads to a shift in energy of the NEXAFS signal of the pyridine nitrogen atoms of about 0.5 eV to higher photon energies, pointing towards a net charge transfer away from the nitrogen atoms, while the signal of the nitrogen atoms in the triazene remains at constant energy. The blue dotted line in Fig. 2 was measured on a sample containing the stoichiometric amount of Fe and t4pt (less than one full monolayer coverage). The spectrum exhibits a double-peak structure with about equal intensity of the two peaks. The black line was measured at a sample with a deliberately reduced amount of Fe. Here the peak at higher photon energy from the

coordinated nitrogen is visible just as a shoulder. The angle dependence of the N K edge NEXAFS (not shown here) confirms that the molecules are all lying flat on the surface. From the shape and the energetic position of the Fe $L_{2,3}$ absorption spectra we conclude that Fe is in a 2+ oxidation state in our networks.

Fig. 3 shows the XAS and XMCD measured at 8 K in a magnetic field of 5 T at grazing and normal incidence and field direction. Under these conditions, the XMCD signal in normal geometry is nearly a factor of two larger than in grazing geometry, while the line shape is very similar. The rather large XMCD signal points towards an S=2 high-spin state of the Fe, however, multiplet calculations are needed to fully confirm that the Fe is not in the S=1 intermediate spin state.

Field- and temperature-dependent XMCD data have been taken for several samples of different coverages and Fe-to-t4pt ratios. The detailed analysis is still ongoing at the time of the writing of this report. Fig. 4 shows the field-dependence of the Fe L_3 XMCD maximum of a near-full monolayer stoichiometric sample at 8 K. The stronger curvature of the magnetization curves at normal incidence together with the higher XMCD signal indicates that there is a strong anisotropy in the system with the easy axis pointing out of the film plane.
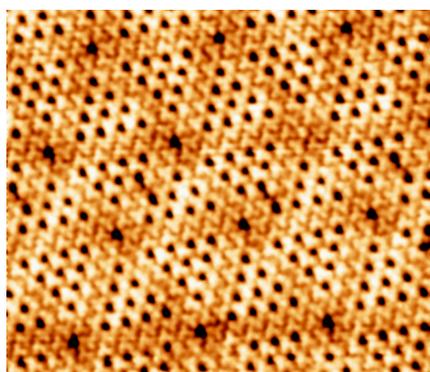

Fig. 1: STM image (30 × 30 nm), of a regular 2-dimensional Fe–t4pt network on Au(111), taken at the ESRF at room temperature.
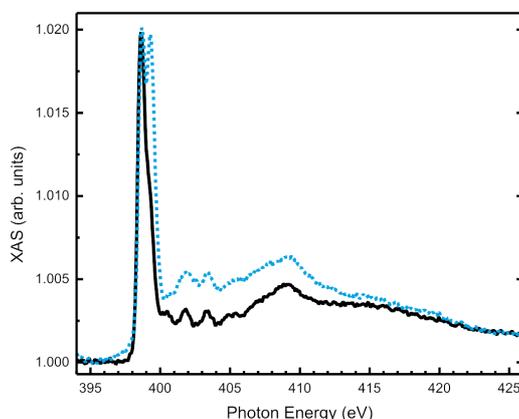

Fig. 2: N K NEXAFS at grazing incidence of a stoichoimetic Fe–t4pt sample (blue dotted line) and a sample with Fe deficiency (black solid line).
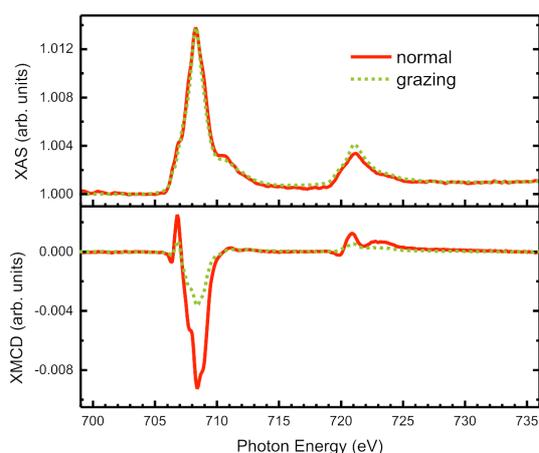

Fig. 3: Fe $L_{2,3}$ absorption spectra (top) and XMCD difference spectra (bottom), acquired in normal (red solid line) and grazing geometry (green dotted line) in a 5 T magnetic field at 8 K temperature.
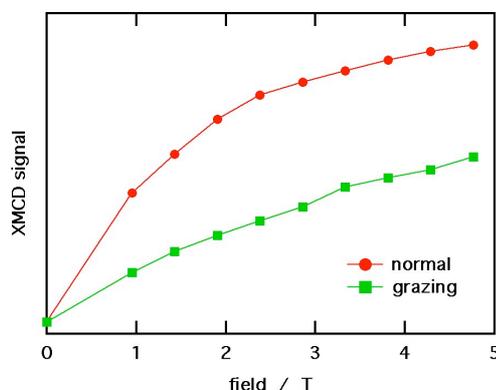

Fig. 4: Field-dependence of the Fe L_3 XMCD signal for normal (red circles) and grazing incidence (green squares), measured at 8 K.