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 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.

ESRF	**Experiment title:** An XAS study of the graphite intercalation compounds, XC_6 (X=Ca, Sr, Ba, Yb) and XLD, XMCD measurements in the superconducting state of CaC_6	**Experiment number**: HE- 3300
Beamline: ID12	**Date of experiment**: from: 30 March 2010 to: 06 April 2010	**Date of report**:
Shifts: 24	**Local contact(s)**: Andrei Rogalev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Ross Springell* Laboratory London Centre for Nanotechnology 17-19 Gordon Street WC1H 0AH LONDON UK

Dr Chris Howard* Laboratory London Centre for Nanotechnology 17-19 Gordon Street WC1H 0AH LONDON UK

Dr Mark Dean* Brookhaven National Lab P.O. Box 5000 Upton, NY 11973-5000

Report:

Sample	**Measurement**
CaC_6	Ca K edge
YbC_6	Yb L_2 edge
	Yb L_3 edge
EuC_6	Eu L_2 edge
	Eu L_3 edge

Table 1: A summary of measurements performed in this experiment. CaC_6 and YbC_6 were mounted in normal incidence. EuC_6 was canted to ensure sensitivity of the absorption cross-section to the in-plane moment.

The discovery of superconductivity in CaC_6 and YbC_6 , at temperatures below 11.5 K and 6.5 K respectively, has initiated a resurgence of interest in graphite intercalation compounds (GICs). Advances in intercalation chemistry have allowed synthesis of bulk samples, facilitating deeper exploration into the physics of the superconducting state. Additionally, europium based GICs are of interest on account of their frustrated magnetic behaviour. At low temperatures EuC_6 exhibits ferrimagnetism when a magnetic field is applied parallel to the graphene sheets. The underlying mechanism is thought to be an RKKY interaction between the Eu^{2+} moments mediated via π-band electrons. The instrumentation on ID12 permits extensive coverage of the phase diagram and enables shell specific detection of the local europium moment.

We report here the first measurements of XANES (x-ray absorption near-edge spectra) and XMCD (x-ray magnetic circular dichroism) from the superconductors CaC_6 and YbC_6 and the magnetic donor GIC EuC_6. A summary of the measurements is given in Table 1. The polarization of the incident photons was manipulated using a HELIOS-II undulator. A magnetic field was applied using a 6 Tesla superconducting cryomagnet. The signal was detected in the fluorescence channel. XMCD spectra were obtained through reversing the field direction and the photon helicity.

The samples were prepared at University College London using vapour transport techniques (YbC_6 and EuC_6) and a molten alloy method (CaC_6). The samples were characterised using in-house XRD and sealed and transported under argon atmosphere to prevent oxidation.

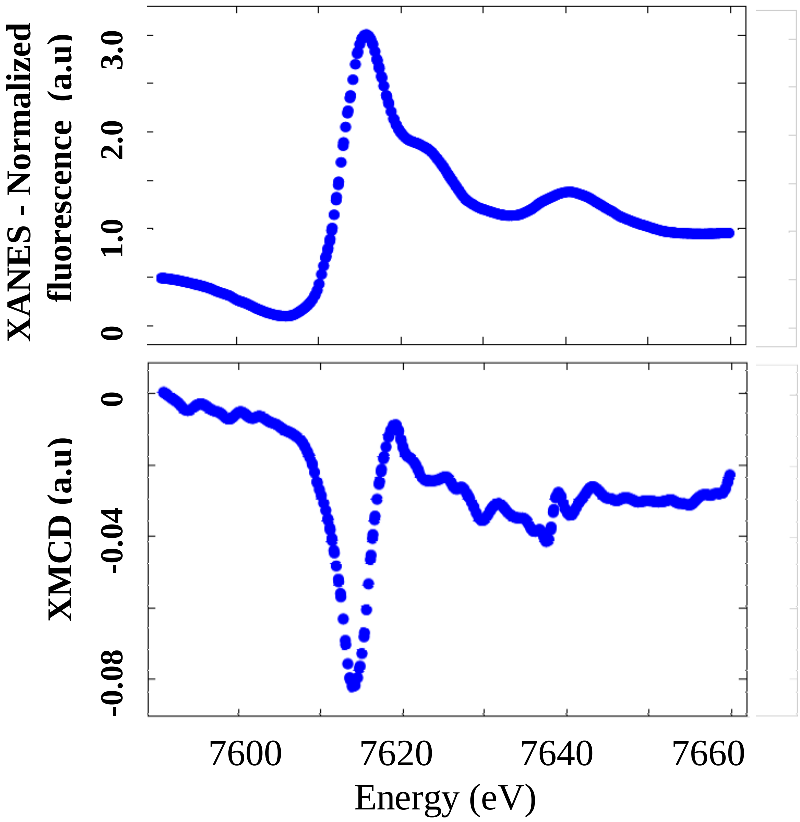

Figure 1: XANES and XMCD spectra of the Eu L_2 edge in EuC_6. Data were taken at T= 8 K and in magnetic fields of B= ± 6 T.

We initially investigated the absorption spectra from EuC_6 at the Eu L_2 and L_3 edges. To ensure that the absorption coefficient was sensitive to the in-plane magnetism the sample was canted with respect to the incident beam. A measurable XMCD signal was detected at the L_2 and L_3 edges (the L_2 edge is shown in Figure 1). The XMCD signal is given by $\Delta\mu(E)=(\mu^+ - \mu^-)$ and the XANES by $(\mu^+ + \mu^-)/2$ where $\mu^+$and μ^- are the x-ray absorption coefficients measured with positive and negative photon helicities respectively. The presence of an XMCD signal demonstrates a non-zero polarization of the Eu 5*d* shell. This polarization may be attributed to an exchange interaction between the 5*d* shell and the magnetic 4*f* electrons.

The post-edge shoulder, approximately 8 eV above the main peak, is associated with the minority Eu^{3+} state, most probably due to a surface oxide layer of Eu_2O_3. The dominance of the divalent state from the data is consistent with Mössbauer and paramagnetic susceptibilty measurements.

Difficulties arise with the standard sum rule analysis due to the spin dependence of the transition matrix elements. This means that the XMCD is no longer proportional to the difference in the spin dependent density of states. This hinders a deconstruction of the total magnetic moment into spin and orbital components. Soft x-ray absorption measurements at the Eu M edges are being considered as these constitute a direct probe of the europium 4*f* magnetic moments.

We also report XANES and XMCD measurements at the calcium K-edge of the superconductor CaC_6. Hints from SQUID magnetometry data motivated us to probe the calcium K shell to search for signs of interplay between superconductivity and magnetism within this compound. We find that the XMCD from this compound is negligible. The situation was very similar in the analagous layered superconductor YbC_6. The XANES and XMCD for this material were measured at the L_2 and L_3 edges. No detectable dichroism was found implying no net polarization of the Yb 5*d* shell.