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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:** **Determination of uranium valence state in URu2Si2 using HERFD**	**Experiment number**: **HC–1543**
Beamline: ID26	**Date of experiment**: from: 11–Dec–2014 to: 17–Dec–2014	**Date of report**:
Shifts: 18	**Local contact(s)**: K. Kvashnina	*Received at ESRF:*

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Report:

The object of these experiments was to test whether the high-energy resolution fluorescence detection (HERFD) method at the 5*f* M_4 and M_5 edges, where a core-hole is formed in the 3*d* shell and electron promoted to the 5*f* valence band, would shed some light on the valence of *intermetallic* uranium 5*f* materials, as it has been successful with *insulating* uranium oxides [1]. The principal motivation was to examine samples of URu_2Si_2, which has been one of the most enigmatic materials in actinide physics and about which there has been much speculation as to the ground state of the 5*f* electrons.

Fig. 1 shows the HEFRD spectra at the M_4 edge for 5 different samples, two of URu_2Si_2 (one cleaved and the other exposed to air), and single crystals of UO_2, UPd_3, and USb. From a body of earlier work, the nominal valencies of the last 3 samples are UO_2 – $5f^2$, UPd_3 – $5f^2$, and USb – $5f^3$. On the basis of the work on UO_2 and higher oxides [1] we would expect a shift of ~ 1 eV for a valence change of 1, i.e. the peak should shift by –1 eV for U(IV) $5f^2 \rightarrow$ U(III) $5f^3$. Although USb spectrum does have more weight to the lower energy side, the peak has clearly not shifted significantly. An examination of the HERFD spectra at the M_5 edge showed similar curves.

In Fig. 2, we show some of the resonent emission x-ray spectra (REXS) spectra of URu_2Si_2. Clearly there are no significant features away from the line relating $E_{transfer}$ to $E_{incident}$. However, as shown in the right-hand side of Fig. 2, we did find an interesting "forbidden" peak just below the main M_β flourescence line associated with the hole transferring from the $3d_{3/2} \rightarrow 4f_{5/2}$ shell, and this can be associated with transfer of the hole to the $4f_{7/2}$ shell, which is normally dipole forbidden. This peak existed in all the materials, and was about 1% in intensity of the main M_β intensity. One reason for this occurrence could be that the assumption of no *J*-mixing is not fully justified.

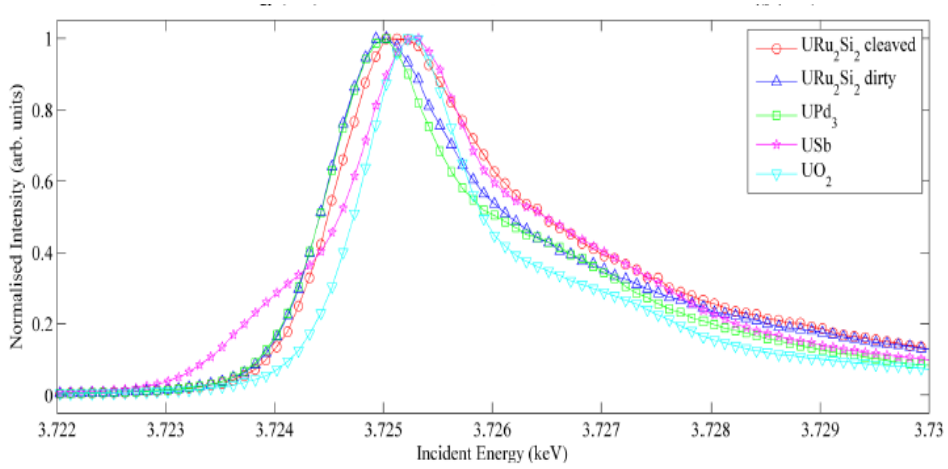

Fig. 1 HERFD spectra of 5 different samples at T = 300 K and at the U M_4 edge. Analaysis of the peak positions shows that there are differences, but they are at most ~ 0.3 eV. The widths are all between 4.3 and 4.7 eV.

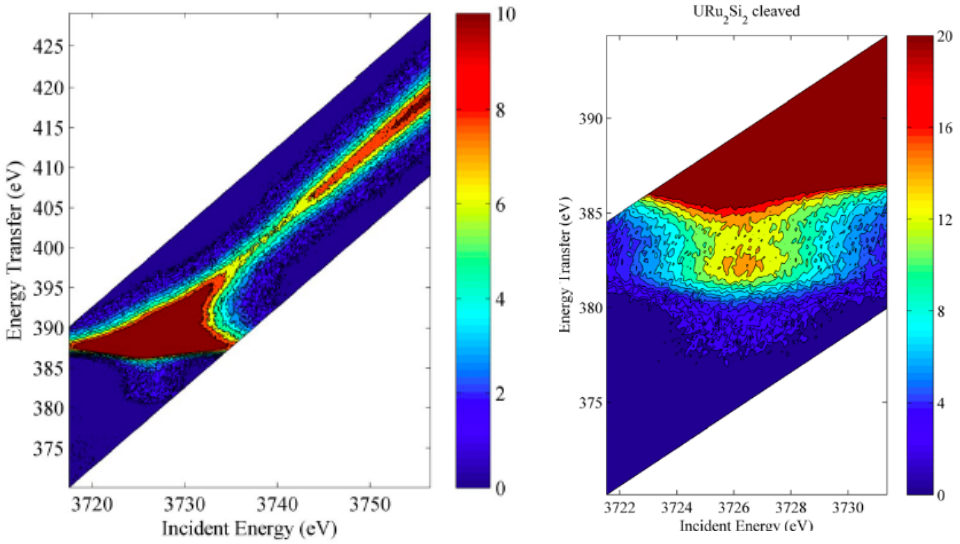

Figure 2

Left: Full REXS spectra through the M_4 resonance transition for URu_2Si_2.

Right: Details of the spectra involving transitions from the hole in the $3d_{3/2}$ to the $4f_{7/2}$ state, which is dipole forbidden. This intensity is about 1% of the main peak showing a transfer from $3d_{3/2} \rightarrow 4f_{5/2}$.

Conclusions:

It appears that examining *intermetallic* compounds, where there is hybridization between the 5*f* and conduction states (which is not the case in UO_2), makes the interpretation of the M_4 and M_5 REXS spectra more complicated than we previously thought. At the moment, such differences of less than 1 eV are beyond the scope of theory [3]. These measurements raise some doubt over the interpretation of similar measurements reported by Booth *et al* [4] at the actinide L_3 edges, where they have made assignments of the 5*f* occupation based on interpretation of similar HEFRD data. However, their experiments initially produce the core-hole in the 2*p* shell with the electron promoted to the 6*d* valence shell, so our experiments promoting the additional electron in the 5*f* shell should be more sensitive to the 5*f* ground state.

References

[1] K. Kvashnina et al., Phys. Rev. Lett. **111**, 253002 (2013)
[2] J. Mydosh & P. Oppeneer, Rev. Mod. Phys. **83**, 1301 (2011)
[3] J. Kolerenc, private communication, Prague, April 2015
[4] C. H. Booth *et al.,* Proc. Nat. Academy USA **109**, 10205 (2012)