



<b>Experiment title:</b> Resonant inelastic X-ray scattering studies of thorium compounds		<b>Experiment number:</b> 20-01-800
<b>Beamline:</b> <b>BM20</b>	<b>Date of experiment:</b> from: 01.10.2017 to: 04.10.2017	<b>Date of report:</b> 05.03.2018
<b>Shifts:</b> 18	<b>Local contact(s):</b> Kristina Kvashnina, BM20, ESRF	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Kristina Kvashnina</b> , ESRF, Grenoble <b>Jurij Galanzew</b> , ESRF, Grenoble		

Our understanding of actinide chemistry lags behind that of the remainder of the periodic table [2-5]. There are some knowledge gaps in fields controlling the chemical reactivity and bonding mechanisms between Th and ligands in complex actinide systems. We report here, the results of HERFD and RIXS experiment at the Th L<sub>3</sub> edge for different Th systems, performed at Rossendorf Beamline (BM20) of ESRF [1].

The content of thorium (Th) on the earth's crust is three to four times higher than that of the uranium, so the idea of using thorium as the main component of nuclear fuel is currently developing.<sup>[2]</sup>

In recent years High Energy Resolution Fluorescence Detected (HERFD) and Resonant Inelastic X-ray Scattering (RIXS) were shown to be a highly valuable tool for investigation of the electronic structure of actinides. Also methods for *ab initio* codes like FEFF9.6 underwent drastical improvement, especially for the *f*-element systems.

## EXPERIMENT

Th L<sub>3</sub> HERFD spectra and RIXS maps of ThO<sub>2</sub>, Th(NO<sub>3</sub>)<sub>4</sub> • 5 H<sub>2</sub>O and [Th<sub>2</sub>(μ<sub>2</sub>-OH)<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>]Cl<sub>2</sub> were measured at ROBL

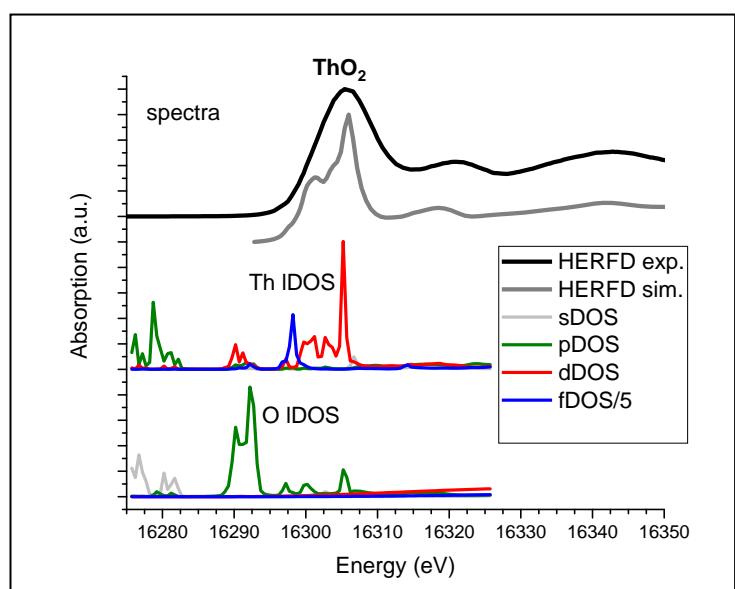


Fig. 1: Experimental and simulated Th L<sub>3</sub> HERFD spectrum of ThO<sub>2</sub>.

beamline (BM20) of ESRF in a HERFD setup (0.5 m radius) with one Si (8 8 0) stripped analyzer crystal (0.5 m bending radius). For the incident beam a Si (1 1 1) double crystal monochromator and a vertical slit of 100  $\mu$ m were used [1]. *Ab initio* calculations for Th L<sub>3</sub> XANES were performed using the FEFF 9.6 code with tabulated crystal structures.

## RESULTS

FEFF9.6 calculations suggest a different crystal field splitting of the 6d states (ranging over few eV) for several thorium compounds (cf. Fig. 1). HERFD spectra show a broader absorption edge for ThO<sub>2</sub> compared to Th(NO<sub>3</sub>)<sub>4</sub> in agreement to the simulated spectra (sf. Fig. 2). Evaluation of the RIXS maps (cf. Fig 3) showed an increased absorption broadening for ThO<sub>2</sub> compared to Th(NO<sub>3</sub>)<sub>4</sub> - 9.6 eV versus 5.8 eV respectively.

A surprising result was obtained during further evaluation of the RIXS maps (cf. Fig 3). A emission broadening of ThO<sub>2</sub> for compare to Th(NO<sub>3</sub>)<sub>4</sub> of 6.4 eV to 5.0 eV respectively was observed. The resonant emission depends on the 3d core states. Most probable explanation is a multiplet splitting of the excited states.

Additionally Th 4f XPS spectra show a shift of 1.4 eV to lower binding energy for ThO<sub>2</sub> compared to Th(NO<sub>3</sub>)<sub>4</sub>. The shake-up satellite for the leading edge in ThO<sub>2</sub> shows a much lower intensity than the same signal in Th(NO<sub>3</sub>)<sub>4</sub>.

XPS results indicate a covalent contribution to bond formation in ThO<sub>2</sub> [5], a covalent contribution could interact with one electron in the resonant excited state and explain the result obtained from investigation of RIXS maps. The possibility to use RIXS maps as a tool to investigate covalence will be an interesting field for future study.

## REFERENCES

- [1] Kvashnina, K. O. et al. (2016) *J. Synchrotron Rad* **23**, 836–841. [2] International Atomic Energy Agency (2005) *Thorium fuel cycle. Potential benefits and challenges*. International Atomic Energy Agency, Vienna. [3] Butorin, S. M. et al. (2016) *Chem. Eur. J.* **22**, 9693–9698. [4] Butorin, S. M. et al. (2016) *J. Phys. Chem. C* **113**, 8093–8097. [5] Butorin, S. M. et al. (2016) *PNAS* **22**, 9693–9698. [6] Rehr, J. J. et al. (2010) *Phys. Chem. Chem. Phys.* **12**, 5503–5513.

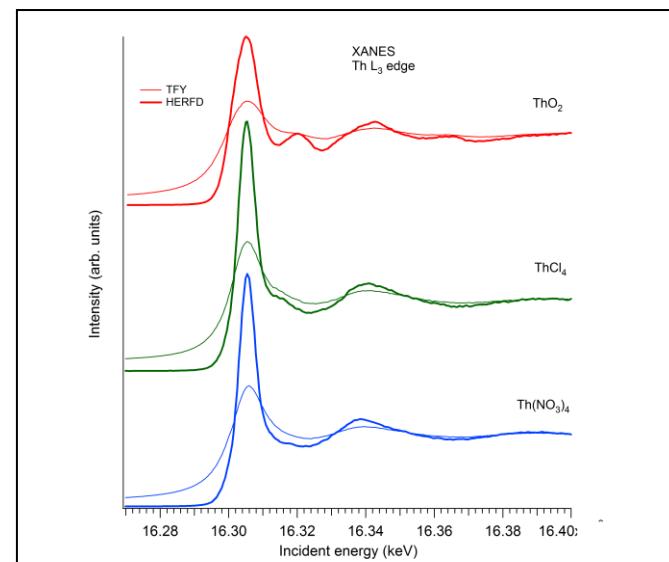
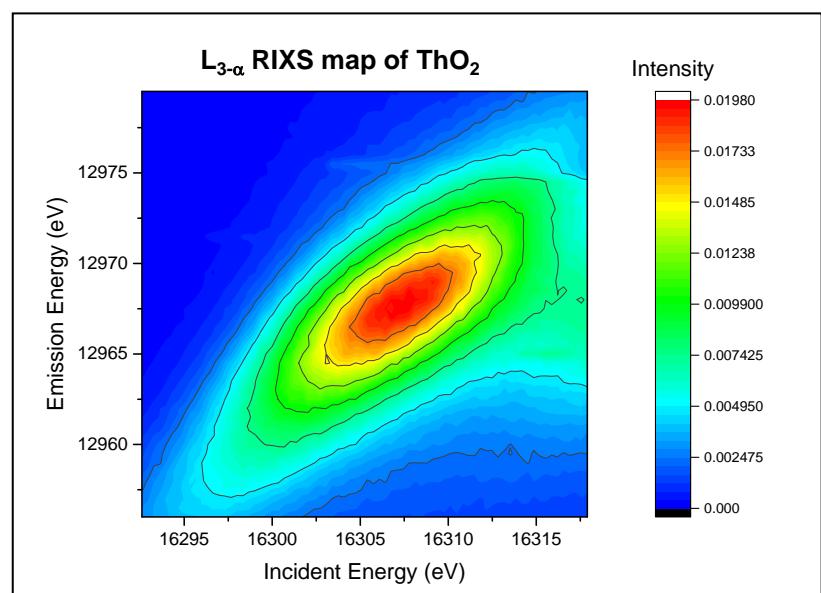


Fig.2. The Th L<sub>3</sub> edge TFY and HERFD spectra for the different Th compounds.



RIXS intensities displayed as a contour map with axes corresponding to incident and emission energies over the Th L<sub>3</sub> absorption edge and Th La<sub>1</sub> emission line of ThO<sub>2</sub>.