

| | | |
|---|---|--|
| | Experiment title: Resonant inelastic X-ray scattering studies of thorium compounds | Experiment number: 20-01-800 |
| Beamline: BM20 | Date of experiment: from: 01.10.2017 to: 04.10.2017 | Date of report: 05.03.2018 |
| Shifts: 18 | Local contact(s): Kristina Kvashnina, BM20, ESRF | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Kristina Kvashnina , ESRF, Grenoble Jurij Galanzew , 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 L₃ 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 uranium, so the idea of using thorium as the main component of nuclear fuel is currently developing.^[2] 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 drastic improvement, especially for the *f*-element systems.

EXPERIMENT

Th L₃ HERFD spectra and RIXS maps of ThO₂, Th(NO₃)₄ · 5 H₂O and [Th₂(μ₂-OH)₂Cl₂(OH)₂(H₂O)₁₀]Cl₂ were measured at ROBL

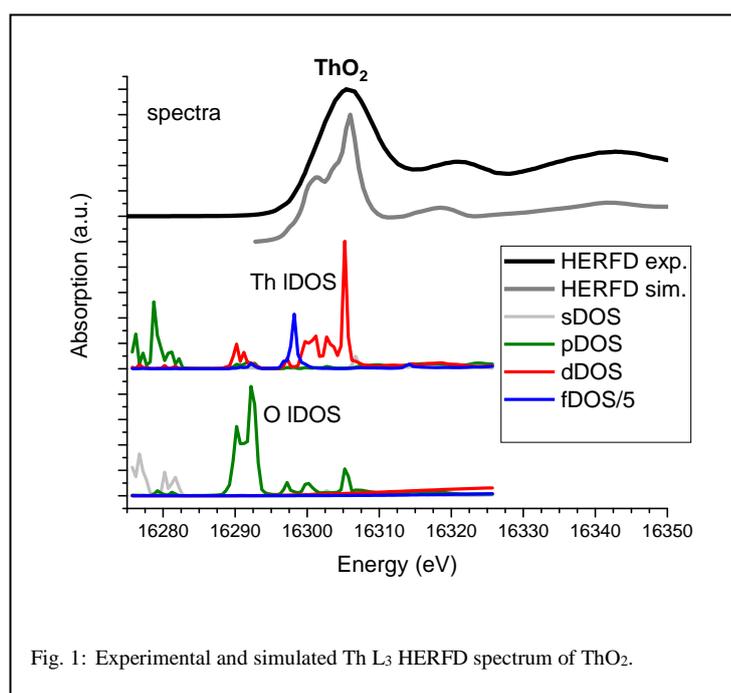


Fig. 1: Experimental and simulated Th L₃ HERFD spectrum of ThO₂.

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 μm were used [1]. *Ab initio* calculations for Th L_3 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_2 compared to $\text{Th}(\text{NO}_3)_4$ in agreement to the simulated spectra (cf. Fig. 2). Evaluation of the RIXS maps (cf. Fig 3) showed an increased absorption broadening for ThO_2 compared to $\text{Th}(\text{NO}_3)_4$ - 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_2 for compare to $\text{Th}(\text{NO}_3)_4$ 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_2 compared to $\text{Th}(\text{NO}_3)_4$. The shake-up satellite for the leading edge in ThO_2 shows a much lower intensity than the same signal in $\text{Th}(\text{NO}_3)_4$.

XPS results indicate a covalent contribution to bond formation in ThO_2 [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.

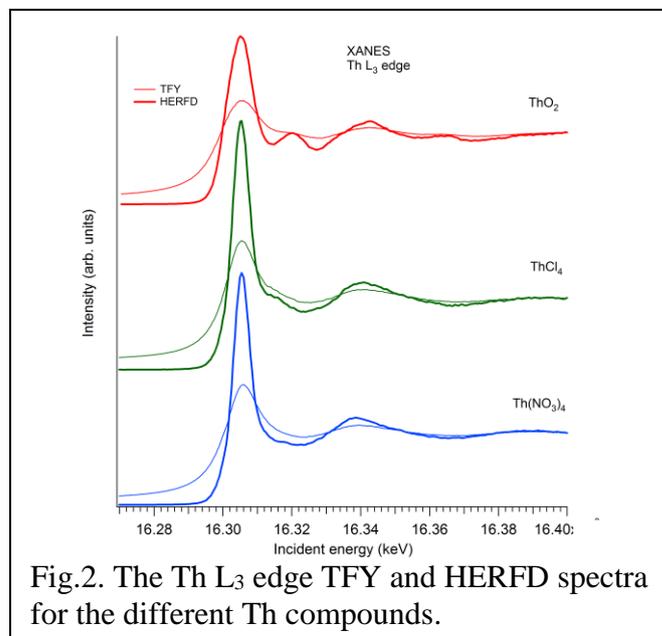
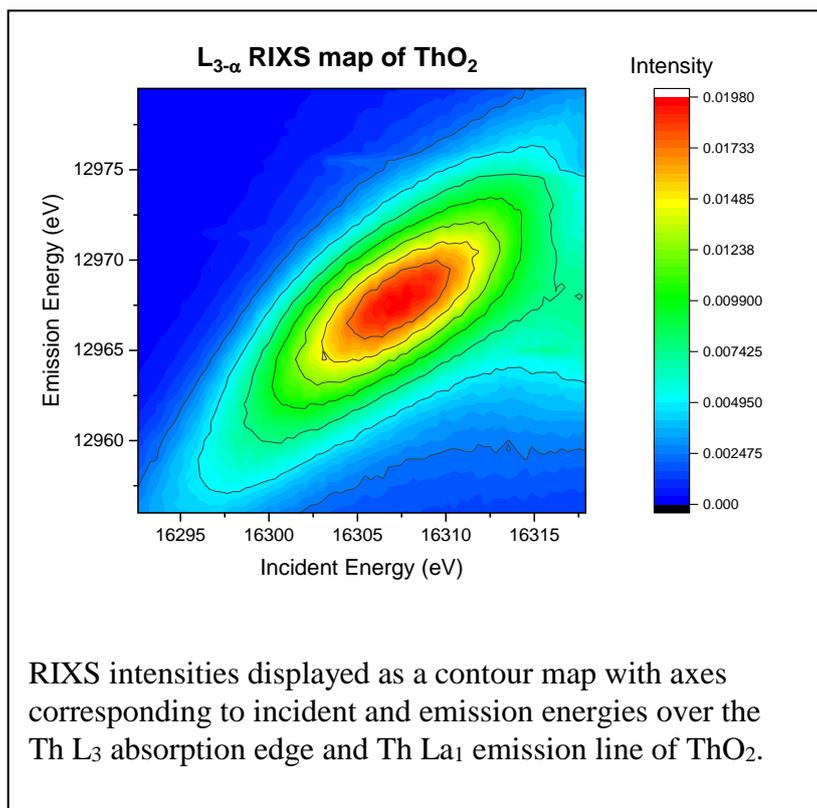


Fig.2. The Th L_3 edge TFY and HERFD spectra for the different Th compounds.



RIXS intensities displayed as a contour map with axes corresponding to incident and emission energies over the Th L_3 absorption edge and Th La_1 emission line of ThO_2 .