

Electronic structure of actinide compounds by high-resolution x-ray absorption spectroscopy

Sergei M. Butorin

Department of Physics and Astronomy, Uppsala University, Sweden

sergei.butorin@physics.uu.se

Actinides (An) are essential materials for nuclear power plants, but their long-term storage safety has always been a serious concern. Even a simple issue such as oxidation becomes a problem in the storage of radioactive materials. A thorough understanding and control of the reactions and the phases of actinide compounds is therefore very important. It is crucial to establish the spectroscopic signatures of different oxidation states of An in various crystal symmetries.

The conversion of U(VI) released into the environment may cause a creation of the U(IV) species in the form of nanoparticles (NPs). For example, the abiotic reduction of U(VI) by green rust or the microbial activity can produce the UO₂ nanocrystals. The created U(IV) nano-species might be relatively mobile in the environment. Furthermore, the possibility of formation of the UO₂ nanostructure in the fuel during irradiation at high-burn-up has been also identified. The knowledge about UO₂ NPs and their reactivity is scarce compared to NPs of semiconductors and metals and therefore requires further research. X-ray spectroscopy turns to be an efficient tool for that.

The x-ray absorption spectra (XAS) at An shallow edges can be obtained using electron-energy-loss spectroscopy and can be used for quantitative analysis of An species. This facilitates in-house experiments and helps to avoid additional safety problems and restrictions in case of measurements at synchrotron radiation facilities. However, the interpretation of the data such as spectra at the actinide 5d edges is hampered by so-called giant resonances governed by autoionization processes, thus requiring the model calculations.

We applied an advanced technique such as HERFD-XAS at An L₃, M_{4,5} edges [1-3] as well as An 5d XAS to study the electronic structure in Th, U, Am, and Cm compounds. The HERFD-XAS measurements were performed at ID26, ESRF and 5d XAS were recorded at beamline I511, MAX-lab and beamline 7.0, ALS. The experiments were supported the Anderson impurity model (AIM) and DFT+U calculations.

The following obtained results will be discussed:

- signatures of U(V) and U(VI) in different environments/crystal symmetries were established for the U M₄ HERFD-XAS and enforced by model calculations;
- while the U L₃ and M₄ HERFD-XAS of the UO₂ NPs revealed the presence of U(V) as the surface contribution, the spectra of the ThO₂ NPs showed a clear change in the local symmetry of Th(IV) on the surface which was analyzed by AIM and DFT+U calculations;
- while the 5d XAS of early An (example of ThO₂) was found to be sensitive to the crystal-field interaction and An 5f – ligand 2p hybridization effects, the 5d XAS of Am and Cm only depends on the nominal oxidation state.

[1] SM Butorin et al., Chem. Commun. 53, 115 (2017); SM Butorin et al., PNAS 113, 8093 (2016).

[2] SM Butorin et al., Chem. Eur. J. 22, 9693 (2016).

[3] KO Kvashnina, YO Kvashnin, JR Vegelius, A Bosak, P Martin, SM Butorin, Anal. Chem. 87, 8772 (2015).