



	Experiment title: <i>Charge localization in mixed-valence uranium oxides from diffraction anomalous fine structure (DAFS)</i>	Experiment number: CH-6221
Beamline: ID22	Date of experiment: from: 05/04/2022 to: 11/04/2022	Date of report: 13/09/2022
Shifts: 18	Local contact(s): Ola Gjonnes GRENDAL	<i>Received at ESRF:</i>
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Report:

The physico-chemical properties of uranium and its oxide-derived compounds have been investigated extensively for almost a century. Uranium finds its main application as nuclear fuel in commercial power generation and research reactors, but also in other application fields such catalysis a growing interest is developing, owing to the complex coordination chemistry and the wide range of possible valence states that has been observed. We have characterized the oxide phase known as U_3O_7 (or more formally $U_{60}O_{140}$) extensively in the last 5 years, but encountered ambiguous results on the charge distribution. Datasets of X-ray absorption experiments carried out at the U M_4 -edge and at the U L_3 -edge did not indicate a substantial contribution of $U^{(VI)}$ in U_3O_7 [1,2]. However, in the structure refined from neutron scattering experiments a subset of 4 out of 60 uranium atoms, all positioned on the special Wyckoff position $4d$, were assigned a formal $U^{(VI)}$ state [3]. To bridge between the spectroscopic and structural results, we have performed DAFS around the U L_3 -edge (17.170 keV) on U_3O_7 and other mixed-valence uranium oxides (including also single-valence compounds as reference material), in order to obtain site-specific information on the chemical state of uranium. To the best of our knowledge, the application of DAFS on uranium compounds has been quite limited to certain macromolecules and our proposed experiment presented a unique opportunity to demonstrate a novel application of this characterization technique on nuclear materials, providing structural information which is inaccessible from the isolated methods.

The DAFS experiments were carried out on beamline ID22, which is equipped with a high-resolution X-ray diffractometer. Samples were loaded in glass capillaries with a kapton sleeve, and the packing factor was chosen to limit absorption effects. Sample preparation was performed at the laboratories of SCK CEN, and samples were mailed to the ESRF stores before the start of the beamtime. All samples were first screened at a more typical beamline energy of 35 keV, before shifting the monochromator to the range of interest (17 keV). Several scans were performed in order to determine the experimental approach, i.e. stepsize in energy, 2theta range of

interest, total counting time, number of repetitions, etc. in order to optimize the available beamtime. Around 8 h was needed to complete one DAFS measurement, covering a 200 eV range with steps of 2 eV. It was foreseen to measure simultaneously to the diffraction data the fluorescence yield by mounting a detector close to the sample, at an angle to the beam direction. However, it was found out that the fluorescence detector was not able to measure the absorption edge correctly at the predicted energy, while the edge could be observed from the scattered intensity arriving at one of the Eiger detector channels. It was concluded this detector system was faulty, and could not be used. Fortunately X-ray absorption data had been previously acquired on the same set of samples, during different beamtimes at the ESRF, and this data could be used for the further processing of the DAFS data. In hindsight, it would have been valuable to measure the absorption of each sample in transmission mode, during the DAFS experiment, as this data can be directly used to correct for absorption effects in the diffraction data, and to predict the anomalous scattering factors f' and f'' at the incident energies.

The prepared samples were systematically measured throughout the available beamtime. For some of the samples (most notably for β - UO_3 , but also for U_3O_8) significant instabilities (peak shifts and intensity variation other than absorption effects) in the diffraction patterns were observed during the acquisition. The origin for these instabilities are likely a result of beam damage. Different sample positions were tried to mitigate this issue, but this was not successful for the experiment on the β - UO_3 sample. During the beamtime we started with the development of Python scripts in order to process the diffraction data, with the aim to produce a spectrum of the reflected intensity, for a selection of reflections, corrected for the Lorentz factor, absorption and background. The script was further worked out in the later weeks and months, in parallel assessing also the theory of anomalous diffraction and developing a routine to extract information on the anomalous scattering factors f' and f'' . Ultimately, the goal is to compare the f'' spectrum of uranium in different chemical states ($\text{U}^{(\text{IV}/\text{V}/\text{VI})}$), and to retrieve this information also in mixed-valence compounds as a function of the contributing atomic sites. Currently, the routine is being finalized and first results on the UO_2 sample are being obtained (see Figure 1).

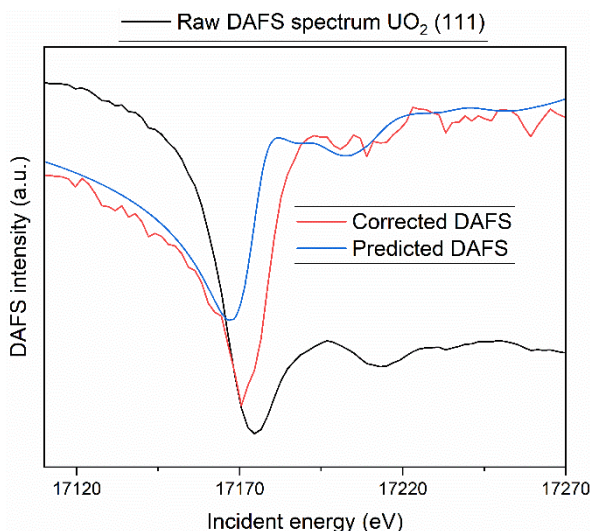


Figure 1. DAFS spectrum of the UO_2 (111) reflection. Black line: the “raw” spectrum consisting of the diffracted intensity. Red line: The DAFS spectrum obtained by applying corrections for the Lorentz factor and absorption. Blue line: The predicted DAFS spectrum from f' and f'' values derived from X-ray absorption data. The analysis routine will use the corrected DAFS spectrum and extract new f' and f'' values which match with the experimental data.

The experiment was successful in performing DAFS experiments on a set of uranium oxide samples, to the best of our knowledge still unique in its kind. With the completion of the analysis routine we will be able to report on the chemical state of uranium in mixed-valence oxides based on the anomalous scattering technique, and the analysis will further extend to provide experimentally determined f' and f'' spectra for uranium in different valence states around the U L_3 -edge. We believe this will be a significant contribution to the dissemination of important physico-chemical properties of uranium. The work will be presented at the Nuclear Materials 2022 conference (24-28 October, Ghent, Belgium) and it is intended to be reported in more detail in the open literature, in the coming months.

- [1] G. Leinders, R. Bes, J. Pakarinen, K. Kvashnina, M. Verwerft, *Inorganic Chemistry*, 56 (2017) 6784.
- [2] G. Leinders, R. Bes, K.O. Kvashnina, M. Verwerft, *Inorganic Chemistry*, 59 (2020) 4576.
- [3] G. Leinders, G. Baldinozzi, C. Ritter, R. Saniz, I. Arts, D. Lamoen, M. Verwerft, *Inorganic Chemistry*, 60 (2021) 10550.