Interpretation of the U L$_3$-edge EXAFS in uranium dioxide using molecular dynamics and density functional theory simulations

Dmitry Bocharov[1],[2], Melanie Chollet[1], Matthias Krack[1], Johannes Bertsch[1], Daniel Grolimund[1], Matthias Martin[1], Alexei Kuzmin[2], Juris Purans[2], and Eugene Kotomin[2]

[1]Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
[2]Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063, Riga, Latvia

E-mail: `bocharov@latnet.lv, matthias.krack@psi.ch, a.kuzmin@cfi.lu.lv`

Abstract. X-ray absorption spectroscopy is employed to study the local structure of pure and Cr-doped UO$_2$ at 300 K. The U L$_3$-edge EXAFS spectrum is interpreted within the multiple-scattering (MS) theory using the results of the classical and ab initio molecular dynamics simulations, allowing us to validate the accuracy of theoretical models. The Cr K-edge XANES is simulated within the full-multiple-scattering formalism considering a substitutional model (Cr at U site). It is shown that both unrelaxed and relaxed structures, produced by ab initio density functional theory (DFT) calculations, fail to describe the experiment.

1. Introduction

Uranium dioxide (UO$_2$) is employed as a fuel material in most nuclear reactors world-wide. Its doping with small amounts of chromium sesquioxide (Cr$_2$O$_3$) is technically applied to obtain a larger average grain size after the fuel sintering process [1]. The change in grain structure results in a higher plasticity of the fuel material. The retention of fission gases inside the fuel matrix is also improved due to the larger grain size.

However, the accurate mechanism of Cr cation incorporation into the UO$_2$ matrix is still not fully identified. Indeed, Cr^{3+} ions could replace U^{4+} atom, with a charge compensation by oxygen vacancies. It could be feasible through creation of O ion vacancies. A Coulomb attraction between O vacancies and dopant cations could result in formation of defect complexes [2]. On the other side, the cubic face centered structure of UO$_2$ provides enough space to accommodate interstitial Cr^{3+} ions. In this study, we address this problem using EXAFS spectroscopy, which is well suited for the local structure investigations (e.g. first neighbour bond distances and coordination numbers) of UO$_2$ fuel matrix and Cr dopant.

The interpretation of the X-ray absorption spectra is a non-trivial task, especially for such complicated systems like doped fuel. Here we will address this challenging problem using two approaches based on molecular dynamics (MD) [3] and density functional theory (DFT) simulations [4]. The first approach [3], which combines both classical and ab initio MD using the CP2K code [5, 6] with ab initio MS EXAFS theory [7], is used to interpret the behaviour of pure UO$_2$. Alternatively, DFT simulations are performed to determine the influence of the

chromium doping on the fuel matrix. The atomic structure around the chromium impurity is relaxed, and the resulting structures are used to calculate the Cr K-edge X-ray absorption near edge (XANES) spectra within the ab initio full-multiple-scattering (FMS) formalism [7]. The comparison of the simulated XANES spectra derived from DFT results with the experimental one allows the identification of valid atomic configurations.

2. Experimental

In this study two X-ray absorption spectroscopy experiments were performed on Cr-doped and undoped UO_2 samples at 300 K using the radioactive microprobe end-station at the microXAS beamline (undulator beam line X05LA [8] at the Swiss Light Source facility, Paul Scherrer Institute, Switzerland). The Cr K-edge [9] and U L_3-edge [10] X-ray absorption spectra were measured for an irradiated Cr-doped and undoped UO_2 samples to retrieve information on the local chemical environment of chromium atoms within the UO_2 matrix. Energy is tuned with a Si(111) double crystal monochromator. In case of the irradiated, active materials, spectra are collected in the fluorescence mode using an energy dispersive solid state silicon drift detector. Additionally, pure non-irradiated UO_2 was studied as a reference. The low-activity of the non-irradiated UO_2 allows us to use an ionization chamber as detector in the transmission mode.

Finally, we also used the U L_3-edge X-ray absorption spectrum of UO_2, measured at 300 K in transmission mode at the ESRF ROBL BM-20 beamline in [11]. Three scans were collected from each sample then averaged.

3. Computational details

Classical [12, 13] and ab initio molecular dynamics (CMD and AIMD) simulations as well as static DFT calculations were performed using the CP2K code [5].

A set of atomic configurations was generated by MD runs within the canonical ensemble (NVT) with periodic boundary conditions at T=300 K using supercells of $6a_0{\times}6a_0{\times}6a_0$ (2592 atoms) and $3a_0{\times}3a_0{\times}3a_0$ (324 atoms) for the CMD and AIMD runs, respectively (a_0 is the UO_2 lattice parameter). A set of 4000 atomic configurations was collected during MD runs of 20 ps and 15 ps in classical and AIMD simulations, respectively. Two force-field models, the core-shell potential of Meis et al. [14] (a_0=5.4682 Å) and the rigid-ion potential of Karakasidis et al. [15] (a_0=5.4657 Å), were used in the CMD runs. The exchange-correlation functional PBE [16] and a fixed lattice constant of a_0=5.4682 Å were employed in the AIMD runs.

The configuration-averaged U L_3-edge EXAFS spectra were calculated using the scheme described in [3] by averaging spectra calculated independently for each atomic configuration using the ab initio real-space MS code FEFF9.64 [7, 17]. The amplitude of all theoretical EXAFS spectra was multiplied by the scale factor S_0^2=0.83, estimated from the prior analysis of the first shell U–O EXAFS signal. The obtained configuration-averaged EXAFS spectra and their Fourier transforms (FTs), calculated employing a 10%-Gaussian window function in the k-space range 0.5–18.0 Å^{-1}, are reported in Fig. 1. Substitution of uranium with chromium in the UO_2 host lattice was studied using the DFT module QUICKSTEP of the CP2K code [6]. Geometry optimised atomic configurations for Cr at a regular U site without and with structure relaxation were used to perform static FMS Cr K-edge XANES calculations by the FEFF9.64 code [7, 17]. The cluster radius around Cr was equal to 8 Å to guarantee the convergence of the FMS series. Complex Hedin-Lundqvist exchange-correlation potential was used to describe inelastic effects in both MS and FMS calculations [7]. The obtained results are compared with the experimental Cr K-edge XANES spectrum of Cr-doped UO_2 [10] in Fig. 2.

4. Results and discussions

A comparison of the experimental and calculated U L_3-edge EXAFS spectra (Fig. 1) indicates rather good overall agreement between them. All three MD simulations describe well the
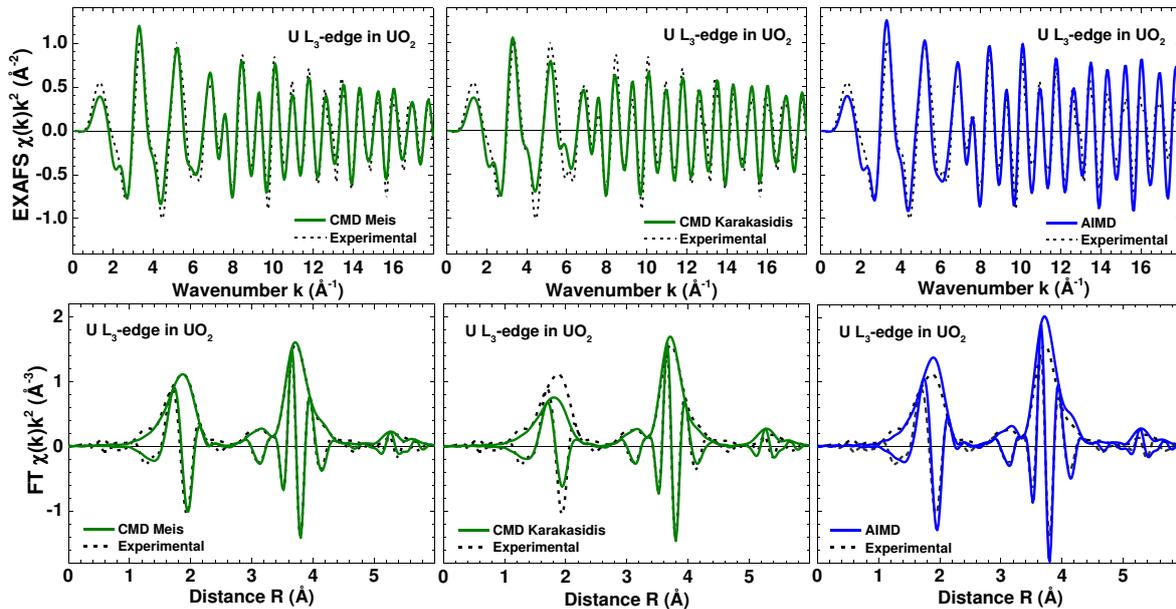
Figure 1. Comparison of the experimental (dotted lines) and calculated (solid lines) U L$_3$-edge EXAFS spectra and their Fourier transforms (FTs) (both modulus and imaginary parts are shown) for UO$_2$ at T=300 K. The experimental EXAFS spectrum was taken from [11].
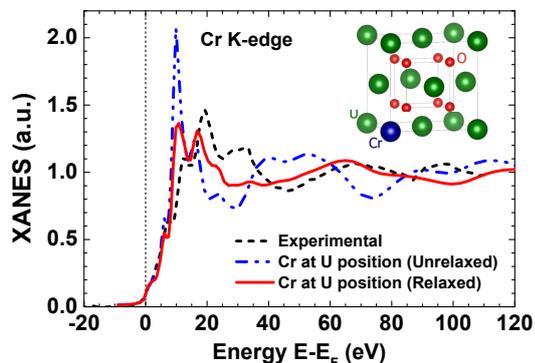

Figure 2. Comparison between the experimental [10] and FMS Cr K-edge XANES spectra of Cr-doped UO$_2$. The calculations correspond to chromium atom substituting uranium atom in UO$_2$ matrix without and with structure relaxation. The substitutional model (Cr at U site) is also shown as inset. The energy scale is relative to the Fermi level E_F.

structure of UO$_2$ at 300 K, thus reproducing well the phase of the EXAFS spectrum. However, some differences are clearly observed in the EXAFS amplitude due to a simplicity of interaction models employed in the MD simulations that resulted in an inaccurate description of thermal disorder. The best result was obtained for the core-shell potential of Meis et al. [14], which gives good agreement with the experimental data in both k and R spaces. The rigid-ion potential of Karakasidis et al. [15] underestimates the strength of the U–O interactions, resulting in a significantly reduced amplitude of the first coordination shell peak at ∼1.9 Å. On the contrary, the strength of the nearest interatomic interactions is slightly overestimated in the AIMD simulation, leading to larger amplitude of the first peak in FT. The values of the mean-squared relative displacement (MSRD) for the U–O atomic pair in the first shell are 0.0063 Å^2 for the Meis potential, 0.0120 Å^2 for the Karakasidis potential and 0.0050 Å^2 for the AIMD compared to the MSRD value 0.0060±0.0005 Å^2 determined from the best-fit analysis of the experimental EXAFS spectrum.

The simplest model for Cr-doped UO$_2$ is the substitutional one, when Cr atoms are located at U sites. Our FMS Cr K-edge XANES calculations (Fig. 2) show that such model agrees

with the experiment only within the first 6-8 eV above the Fermi level and fails to describe the fine structure at higher energies. For unrelaxed structure, the difference is dramatic, since the theoretical and experimental XANES are nearly out of phase due to overestimated Cr–O bond lengths. Upon structure relaxation, the difference decreases mainly due to a shortening of the nearest Cr–O bonds. However, also in this case, the local environment around Cr atoms is still far from the reality, that is observed as the absence of peaks at ∼30 eV and ∼100 eV. Future work will have to address alternative more complicated environments for the embedding of Cr atoms into the UO_2 matrix, e.g as proposed in the work by Desgranges et al. [18].

5. Conclusions

The experimental U L_3-edge EXAFS spectra of UO_2 were interpreted up to 6 Å in R-space using the results of both CMD and AIMD simulations taking into account the MS effects. The accuracy of the CMD method relies on the used force-field model, therefore EXAFS spectra can be employed for its validation. For UO_2 a very good agreement between theoretical and experimental EXAFS spectra was found for the Meis force-field [14], whereas the Karakasidis force-field [15] fails to describe correctly mainly U–O interactions. The advantage of the AIMD method is the absence of the adjustable parameters, except for the choice of the functional model. The exchange-correlation functional PBE [16] employed in this study predicts slightly too rigid interactions.

The analysis of the Cr K-edge XANES spectrum of Cr-doped UO_2 suggests that the substitutional model (Cr at U site) differs from the experimental data, even when structure relaxation is taken into account. Therefore, further investigations are required to shed light on the accommodation of Cr atoms and precipitates within the UO_2 host lattice.

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