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Role of resonant inelastic X-ray scattering in high-resolution core-level spectroscopy of actinide materials

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ABSTRACT

This paper provides a brief overview of applications of advanced X-ray spectroscopic techniques that take advantage of the resonant inelastic X-ray scattering (RIXS) in the hard and tender X-ray range and have recently become available for studying the electronic structure of actinides. We focus here on the high-energy-resolution X-ray absorption near edge structure (XANES) and core-to-core and core-to-valence RIXS spectroscopies at the U L and M edges of uranium compounds. The spectral features are analyzed using a number of theoretical methods, such as the Anderson impurity model, density functional theory in the local density approximation with an added Coulomb interaction (LDA + U), and full multiple scattering (FEFF) and ab initio finite difference method near-edge structure (FDMNES) codes. In connection with presented results, the capabilities and limitations of the experimental techniques and theoretical methods are discussed.

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1. Introduction

For many years, actinides were a fascinating topic of research but were of little practical interest. This situation has changed since nuclear power was re-evaluated as an attractive carbon-free energy source [1]. The new generation of nuclear reactors is designed to supply more electricity than previous technologies, but produce radioactive waste, which must be safely handled. This provides motivation for scientists to study the fundamental and applied properties of actinide systems in connection with their synthesis [2,3], oxidation [4], corrosion [5], reprocessing [6] and migration [7], stability at extreme conditions [8,9], environmental impact [10] and disposal of nuclear waste [11]. Obviously, the development of new and beneficial use of depleted uranium may extend the application beyond the nuclear industry [6,7,12]. Characterization of U in different materials is essential for the future management of such substances.

Diverse properties of uranium systems come from the complexity of their electronic structure, in particular unfilled U 6d and U 5f valence shells. Theoretical modeling and predictions of changes in the electronic structure are difficult due to the complex crystal structure and the competition between different types of interactions: Coulomb and exchange, crystal field, spin-orbit coupling and

orbital hybridization. Experimental observations of properties of U systems involve their own challenges including toxicity, radioactivity, and other safety issues. Thus, any method that can show the capability of discovering more information about changes in the electronic structure in different U systems is of great interest.

An element-selective probe to study the electronic structure is provided by inner-shell X-ray spectroscopy. Especially, hard X-ray spectroscopy is the ideal candidate for the actinide systems, since it does not require high-vacuum environment around the sample as, for example, in the case of soft X-ray spectroscopy. For the moment, X-ray absorption near edge spectroscopy (XANES) at the U L₃ edge (~17.166 keV) has been the most commonly reported in the literature (see e.g. Refs. [13–15]). Nevertheless, the large lifetime broadening of the 2p_{3/2} level (estimations vary between 8.4 eV [16] and 7.4 eV [17] for U) renders the technique less sensitive to the fine distribution of the unoccupied electronic states.

Features in XANES spectra at the U L₃ edge can be studied in more detail due to recent advances in employing an X-ray emission spectrometer [18,19]. The emission spectrometer is tuned to the maximum of the Lα₁ (3d_{5/2}–2p_{3/2}) transition and the XANES spectrum is recorded by monitoring the maximum of the Lα₁ intensity as a function of the incident energy. The technique based on this setup has been named as partial fluorescence yield (PFY) or high-energy-resolution fluorescence detected (HERFD) X-ray absorption spectroscopy. Obviously, the technique takes advantage of the varying cross-section of core-to-core resonant inelastic X-ray scattering (RIXS) upon sweeping the incident photon energy throughout the edges. The advantage of such a setup is that the width of the spectral features is no longer limited by the 2p_{3/2} core

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Table 1
Reflections of the crystal analysers used in the detection of U X-ray emission lines, together with the corresponding Bragg angles and energy resolutions estimated.

Emission energy	Crystal analyzer	Bragg angle (°)	Resolution (eV)
HERFD at the U L ₃ edge at Lα ₁ (2p _{3/2} –3d _{5/2}) = 13.616 keV	Ge <777>	77	2.2
HERFD at the U L ₃ edge at Lβ ₂ (2p _{3/2} –4d _{5/2}) = 16.388 keV	Si <10 10 0>	81	2.0
HERFD at the U L ₃ edge at Lβ ₅ (2p _{3/2} –5d _{5/2}) = 17.063 keV	Si <10 10 0>	71	2.2
Valence band RIXS at the U L ₃ edge, E = 17.166 keV	Ge <999>	84	1.6
HERFD at the U M ₂ edge at (3p _{1/2} –5d _{3/2}) = 5079 eV	Ge <331>	71	1.2
HERFD at the U M ₃ edge at (3p _{3/2} –4d _{3/2}) = 3522 eV	Si <220>	67	1.2
HERFD at the U M ₄ edge at Mβ (4f _{5/2} –3d _{3/2}) = 3336 eV	Si <220>	75	0.7
Valence band RIXS at the U M ₅ edge, E ~ 3552 eV	Si <220>	65	1.1
HERFD at the U M ₅ edge at Mα ₁ (4f _{7/2} –3d _{5/2}) = 3171 eV	Ge <220>	78	0.9

hole lifetime but by the sharper 3d_{5/2} core hole width in the final state. This method was introduced by Hämäläinen and co-workers [18] and has been widely used for the transition metal systems (see e.g. Ref. [19]) but not so commonly for actinides [8,20]. Here we present recent results obtained for U compounds using this setup at the U L and M edges. The information about the crystal field splitting and distribution of the U 6d and U 5f states, oxidation state of uranium during oxidation reactions are analyzed by using a number of theoretical methods. We will discuss the capabilities and limitations of the experimental techniques and theoretical methods and areas of their application.

2. Experimental details

The experiments were performed at beamline ID26 of the European Synchrotron Radiation Facilities (ESRF) in Grenoble [21]. The incident energy was selected using the <3 1 1> reflection from a double Si crystal monochromator during the measurements at the U L₃, M_{2,3} edge and using the <1 1 1> reflection during experiments at the U M_{4,5} edges. Rejection of higher harmonics was achieved by three Si mirrors working under total reflection for the measurements at the U M edges and three Cr/Pd mirrors for the U L₃ edge measurements. The beam size was estimated to be ~0.3 mm vertically and 1 mm horizontally. XANES spectra were simultaneously measured in total fluorescence yield (TFY) mode using a photodiode and in HERFD mode using an X-ray emission spectrometer. The sample, analyzer crystal and photon detector (avalanche photodiode) were arranged in a vertical Rowland geometry. The core-to-valence RIXS spectra were recorded at a scattering angle of 90° in the horizontal plane using only one crystal analyzer. All HERFD-XANES measurements were performed using four Si <2 2 0> or four Ge <1 1 1> or four Ge <2 2 0> crystal analyzers in different reflections (summarized in Table 1). The difference in the energy resolution arises from the different Bragg angles of the crystal analyzer and different monochromator crystals. The intensity was normalized to the incident flux.

RIXS data are shown here as a contour map in a plane of incident and transferred photon energies, where the vertical axis represents the energy difference between the incident and emitted energies. Variations of the color on the plot correspond to the different scattering intensities. Experiments reported here were performed at room temperature in air without any additional environment around the sample. The paths of the incident and emitted X-rays through the air during the experiment at the U M edges were minimized in order to avoid losses in intensity due to absorption in the air. The polycrystalline materials UO₂, U₃O₈, and U₄O₉, uranyl nitrate hexahydrate UO₂(NO₃)₂(H₂O)₆, and torbernite mineral Cu(UO₂)₂(PO₄)₂(H₂O)₁₂ were covered by 50 μm Kapton film and did not show any radiation damage.

The U₄O₉ powder was prepared by heat treatment of a mixture of UO₂ and U₃O₈ powders. The relative mass fraction of UO₂ and U₃O₈ was chosen in order to get, on average, a UO_{2,23}

composition. The powders were mixed carefully, placed in an air-tight closed quartz tube and underwent a heat treatment at 1050 °C for 30 days. After that they were slowly cooled down to room temperature over 12 h. The powder obtained had a dark color. The quality was checked by X-ray diffraction and contained less than 1% U₃O₈, assuming that the U₄O₉ phase in the sample had an oxygen composition that was very close to the phase stability limit in the phase diagram. The U₃O₈ powder was obtained via isothermal annealing at 900 K of a sintered UO₂ pellet in dry air. The X-ray diffraction pattern showed the expected structure. For the HERFD-XANES experiment, 10 mg of U₄O₉ or U₃O₈ were diluted in 200 mg of boron nitride and then pressed to obtain a solid pellet. To avoid any further oxidation of these two samples, after preparation each pellet was immediately put in a sealed copper sample holder with a 5 μm Kapton window and once more covered by 50 μm Kapton film.

3. Computational details

3.1. FDMNES calculations

The XANES spectrum at the U L₃ edge of UO₂ was simulated by the finite difference method for near-edge structure (FDMNES) [22]. The code allows the calculation of the occupied and unoccupied projected density of states (DOS) in relation to the X-ray absorption and emission processes. Simulations were performed using an atomic cluster with 4.6 Å radius for UO₂ using Cartesian coordinates listed in the Inorganic Crystal Structure Database (ICSD). UO₂ has a fluorite-type structure (*Fm-3m*) with lattice parameter $a = 0.571$ nm, where each U atom is surrounded by eight O atoms. Relativistic self-consistent field calculations using the Dirac-Slater approach have been performed for each atom in the considered cluster. From the superposed self-consistent atomic densities in the selected cluster, the Poisson equation was solved to obtain the Coulomb potential. The energy-dependent exchange correlation potential was evaluated using the local-density approximation. The exchange-correlation potential was constructed using both the real Hedin-Lundquist and the Von Barth formulations [20].

3.2. LDA + U calculations

The first-principles calculations of UO₂ and UO₂(NO₃)₂·6H₂O were performed using the linearized muffin-tin orbitals method LMTO-ASA [23] in the atomic sphere approximation. The radii of muffin-tin spheres were set to R(U) = 1.73 a.u. and R(O) = 1.6 a.u. Interstitial space was filled with empty spheres. Structural relaxation effects were neglected. In the calculations of UO₂ the lattice parameter of 0.5371 nm was used, which corresponds to the minimum of the energy of the system [24]. In order to reproduce the antiferromagnetic order observed in earlier experiments [25] a $\sqrt{2} \times \sqrt{2} \times 1$ supercell dimension was selected. In the calculations of UO₂(NO₃)₂·6H₂O the atomic positions and crystal structure

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