

EXAFS measurements of radioactive samples at low temperature

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1. Introduction

Thermal oscillations of atoms lead to damping effects in the EXAFS amplitude. In the EXAFS equation, the amplitude reduction factor (Debye-Waller factor) is included in the form of $\exp(-2\sigma^2k^2)$. It summarises the contribution of thermal as well as structural disorder $\sigma^2 = \sigma_{\text{therm}}^2 + \sigma_{\text{stat}}^2$. Low temperature reduces this EXAFS amplitude damping which allows the extension of measurements to a higher k range. Consequently, the Fourier transform reveals more backscattering shells. In spite of the fact that the chemical bondings are preserved for most of the phase transitions at low temperature, EXAFS spectroscopy has proven to be a reliable tool for determining local bond lengths. This contribution demonstrates the gain in short-range structural information from EXAFS measurements at low temperature using the cryostat installed recently at ROBL.

2. Apparatus design

The safety regulations for the radiochemistry hutch at ROBL prohibit a water circulation with the surroundings outside of the experimental station. Therefore, an air-cooled helium compressor (CTI-Cryogenics) was combined with a specially designed closed-cycle helium cryostat (OXFORD Instruments) to an unconventional arrangement (Fig. 1). In order to allow sample change inside the glove box, the sample holder is horizontally arranged. Based on an intelligent temperature controller module (OXFORD Instruments), a temperature control software was written and extensively tested. The device is designed to perform XAFS measurements in transmission and in fluorescence. The cooldown time from ambient to base temperature of 15 K is 120 minutes. At this temperature, the cooling power is 1.5 W and the temperature stability is ± 0.1 K. Inner and outer windows are made from clear mylar foils. The maximal sample dimension is limited by the window diameter of 10 mm.



Fig. 1:
View into the ROBL glove box:
special designed helium cryostat
(OXFORD Instruments) with
horizontally arranged sample
holder.

3. Experimental results

3.1. Analysis of atomic distances in inaccurately determined heavy-atom crystal structures: $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ and $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$

X-ray diffraction analysis in the presence of heavy atoms can be complicated because the structure factor is mainly influenced by the heavy scatterers. The error in the determination of atomic coordinates increases for light atoms. Additionally, if the heavy atoms are located at special positions, the space group can remain uncertain. EXAFS spectroscopy allows a direct determination of bond lengths in heavy-atom structures and avoids, therefore, problems caused by the coexistence of heavy and light scatterers.

EXAFS was used to determine bond lengths around heavy scatterers in meta-zeunerite, $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$, and trögerite, $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$. These compounds belong to the structure family with the chemical formula $\text{A}^{n+}[\text{UO}_2\text{XO}_4]_n \cdot m\text{H}_2\text{O}$, where $[\text{XO}_4]^{3-}$ appears as phosphate or arsenate and A^{n+} is a hydrated monovalent or divalent cation. Tetrahedra of $[\text{XO}_4]^{3-}$ and tetragonal dipyramidal coordinated uranyl ions $[\text{UO}_2]^{2+}$ built up two-dimensional layers. Charge neutrality of the uranyl arsenate layers is given by different interlayer cations like $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ in meta-zeunerite and $[\text{H}_3\text{O}]^+$ in trögerite. Uranium and the axial oxygen atoms are located at the fourfold symmetry axes. The positions of the surrounding O_{eq} and As atoms are symmetry-equivalent.

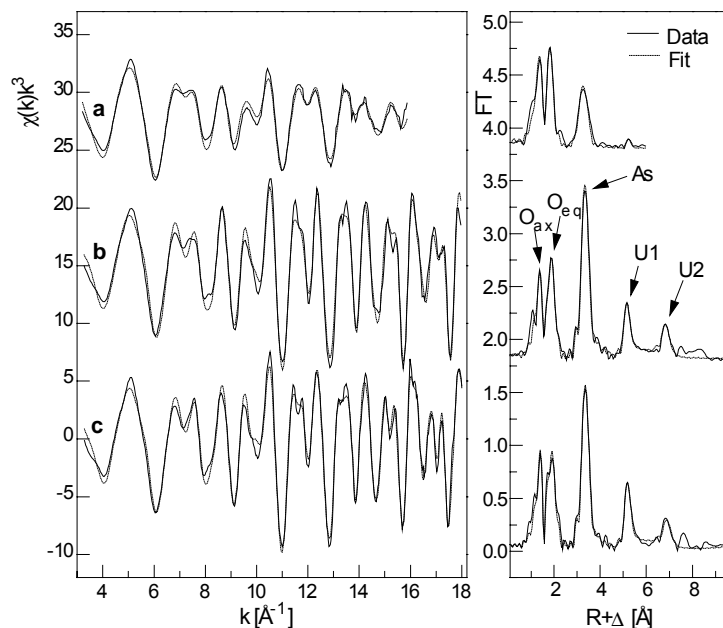


Fig. 2:
 U L_{III} -edge k^3 -weighted transmission EXAFS spectra (left) and the corresponding Fourier transforms (right) for
 (a) $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ at $T = 298 \text{ K}$,
 (b) $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ at $T = 15 \text{ K}$,
 (c) $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$ at $T = 15 \text{ K}$.

Room temperature U L_{III} -edge EXAFS measurements of both $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ (Fig. 2a) and $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$ (not depicted) show a distance between uranium and the axial oxygen atoms, O_{ax} , of 1.77-1.78 Å. The second shell corresponds to the bond distance of four symmetry-equivalent equatorial atoms (O_{eq}) with a bond length of 2.29-2.30 Å. The arsenic scattering contribution gives a significant third Fourier transform peak with a calculated distance of 3.69-3.70 Å. At $T = 298 \text{ K}$ the U-U scattering contribution generates only a very weak peak. To analyse higher shells, low temperature measurements were performed. A measurement of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ at a temperature of 15 K shows that the scattering contributions of uranium appear at an U-U1 distance of 5.39 Å and an U-U2 distance of 7.15 Å. EXAFS measurements on $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$ (Fig. 2c) show within the error limits comparable distances. The atomic distance U-U2 corresponds to the lattice constant a .

In Tab. 1 atomic distances determined by EXAFS measurements are compared to X-ray diffraction data from literature. The EXAFS data on the $\text{H}[\text{UO}_2\text{AsO}_4] \cdot 4\text{H}_2\text{O}$ sample show a good agreement with the diffraction data of the literature. The measurements on $\text{D}[\text{UO}_2\text{AsO}_4] \cdot 4\text{D}_2\text{O}$, were taken with neutron diffraction on a powder sample at room temperature [1] and at 4 K [2].

In $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ the atomic distances between heavy and light scatterers observed by EXAFS deviate approximately 0.1-0.2 Å in comparison with single crystal X-ray diffraction measurements from the literature [3]. However, the atomic distances between the heavy scatterers agree well with the EXAFS data. As sometimes observed in heavy atom structures, the position of the heavy scatterers are correctly determined, but the positions of the light atoms are incorrect. However, EXAFS measurements are restricted to atomic distance determinations in form of radial distribution functions.

Shell	$\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$		$\text{X}[\text{UO}_2\text{AsO}_4] \cdot 4\text{X}_2\text{O}$	
	EXAFS	XRD [3]	EXAFS	ND [1, 2]
U-O _{ax}	1.78	1.94, 1.78	1.78	1.78, 1.80
U-O _{eq}	2.30	2.17	2.30	2.30
U-As	3.69	3.68	3.70	3.70
U-U1	5.39*	5.38	5.40*	5.39
U-U2	7.15*	7.10	7.21*	7.16
As-O _{eq}	1.68	1.77	1.69**	1.68
As-As	5.02*	5.02	5.06**	5.06
As-U2	8.01*	8.00	8.04**	8.04

Tab. 1: Comparison of the atomic distances from EXAFS measurements with diffraction data from literature. Distances are given in Å.

XRD = X-ray diffraction, ND = Neutron diffraction

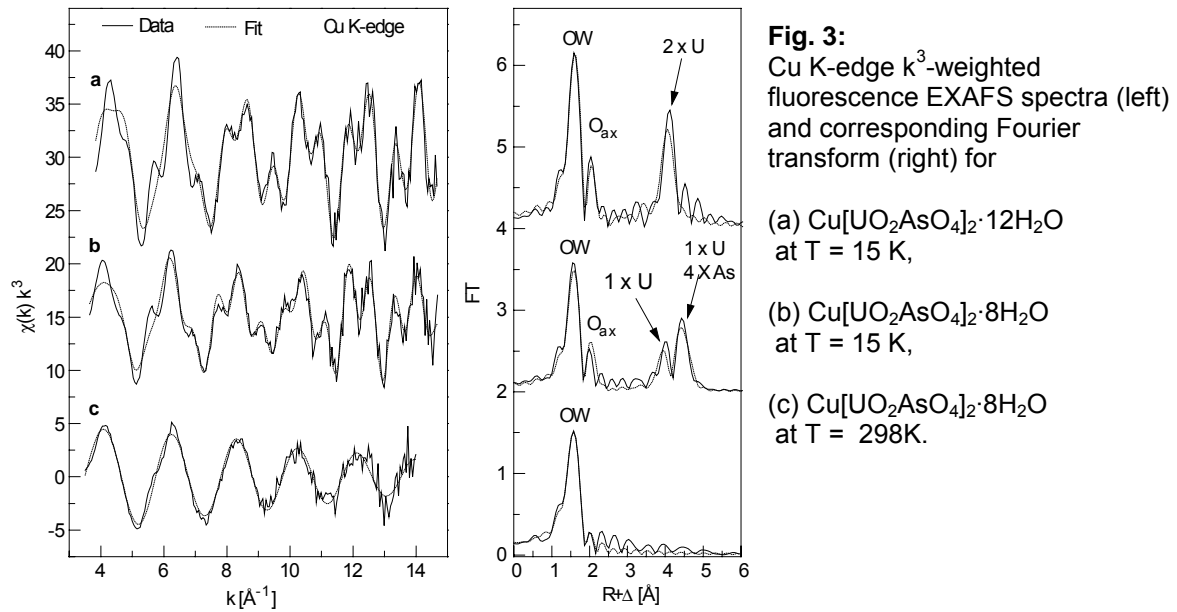
X=H for the EXAFS measurements, X=D in the literature [1, 2] *T = 15K, **T = 43K

This is connected with a loss of the bonding angle information. For this reason and taking into account that Hanic [3] could use only intensities from Weißenberg photographs for his structure analysis, the crystal structure of meta-zeunerite was completely redetermined using single crystal diffraction measurements [4]. These measurements confirmed the structural parameters given by the EXAFS measurements.

3.2. Investigation of compounds with symmetry-dependent structure modifications: $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 12\text{H}_2\text{O}$ and $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$

$\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 12\text{H}_2\text{O}$ and $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ show differences only in the crystal-water content, connected with a swap in the space group symmetry. Only one backscattering shell is visible in the Cu K-shell EXAFS Fourier transform measured at 289K (Fig. 3c). In comparison, strong differences are visible at the low temperature measurements.

The structure of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 12\text{H}_2\text{O}$ contains two non symmetry-equivalent Cu positions. In the EXAFS analysis only one Cu atom position is considered, because the second one has only an occupation factor of 0.075. The structure of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ contains one symmetry-independent Cu atom position. In addition, this powder of this sample contained 14% $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 12\text{H}_2\text{O}$. However, the EXAFS is dominated by the scattering contribution of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$. Due to the damping of thermal oscillations, a lot of backscattering shells occur in the Fourier transform (FT). For simplifying the data analysis, the FT between $R+\Delta=5.5-10$ Å was Fourier filtered, back transformed and subtracted from raw Cu K-shell EXAFS data of each spectrum. The $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ group causes dominant FT peaks with Cu-O distances of 1.94 Å for both samples. The sample of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 12\text{H}_2\text{O}$ shows one Cu-U peak at a distance of 4.22 Å. A strong Cu-U-O_{ax}-Cu multiple scattering contribution appears because the involved atoms are arranged linearly. This observation points to a highly symmetric arrangement of the $[\text{UO}_2\text{AsO}_4]_\infty$ layers concerning Cu. In contrast, the



spectrum of $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ shows two FT peaks in the region $R+\Delta = 3.5\text{-}5.0 \text{ \AA}$. The first peak originates from one uranium atom in a distance of 4.04 \AA . The second peak consists of arsenic atoms at a distance of 4.84 \AA and one uranium atom at a distance of 4.52 \AA . These observations indicate that in $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ one $[\text{UO}_2\text{AsO}_4]_\infty$ layer is arranged closer to the Cu atom.

3.3. Analysis of a structure sequence: $\text{UO}_2[\text{H}_2\text{AsO}_4]_2 \cdot \text{H}_2\text{O}$

It is no problem to determine the atomic coordinates of uranium using X-ray powder diffraction because the scattering contribution of heavy atoms dominates. Indeed it is difficult to locate the light atoms. On the other hand, a method like EXAFS, sensitive to short range order, gives reliable atomic distances in the surroundings of heavy atoms and allows to characterise the coordination polyhedra. This method allows to elucidate the main structure sequence. Including the information from EXAFS as restraints in the structure solving procedure, the probability increases to obtain the complete structure. As an example, the EXAFS interpretation of a structure sequence is demonstrated using $\text{UO}_2[\text{H}_2\text{AsO}_4]_2 \cdot \text{H}_2\text{O}$.

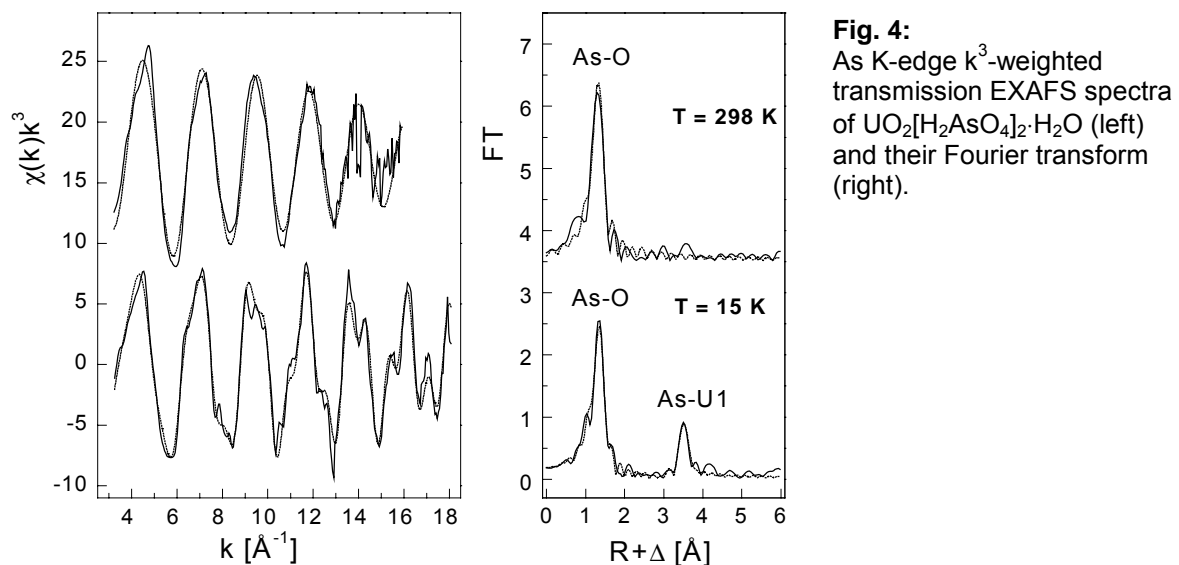


Fig. 4 depicts the As K-edge k^3 -weighted EXAFS spectra of $\text{UO}_2[\text{H}_2\text{AsO}_4]_2 \cdot \text{H}_2\text{O}$. The measurement at room temperature (298 K) shows that As is surrounded by four oxygen atoms an average distance of 1.68 Å indicating a $[\text{AsO}_4]$ tetrahedron. In order to reduce the thermal atomic movement, the same sample was measured at 15 K. This measurement shows that each $[\text{AsO}_4]$ tetrahedron is surrounded by two uranium atoms at a distance of 3.71 Å. This bond length points to a monodentate connection between arsenate and uranyl polyhedra.

EXAFS measurements of $\text{UO}_2[\text{H}_2\text{AsO}_4]_2 \cdot \text{H}_2\text{O}$ at the U L_{III} -edge are shown in Fig. 5. There are two axial oxygen atoms at a distance of 1.77 Å and five equatorial oxygen atoms are detected at an average distance of 2.38 Å. That they are not symmetry-equivalent is indicated by the high Debye-Waller factor of 0.0069 \AA^2 . The U-As distance is determined to 3.70 Å. The uranium atom is coordinated by four As atoms via oxygen atoms. Therefore, the fifth equatorial oxygen atom belongs to the H_2O molecule given in the chemical formula.

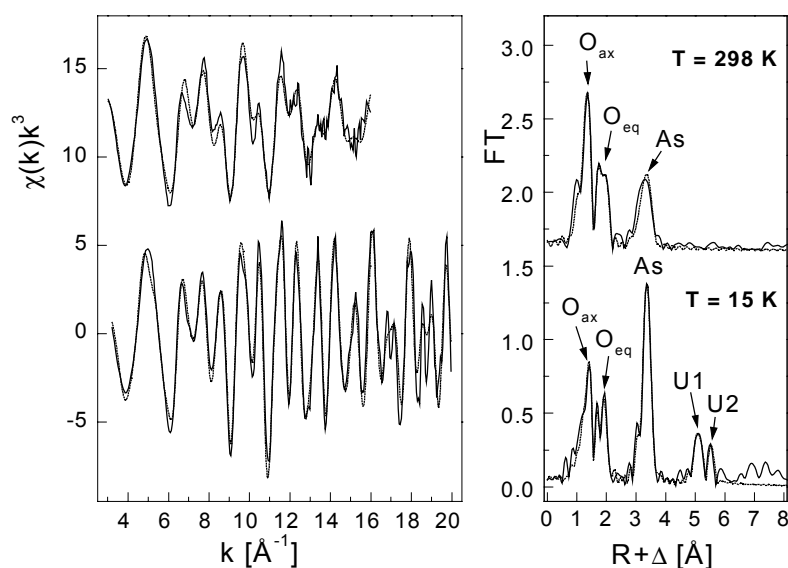


Fig. 5: U L_{III} -edge k^3 -weighted transmission EXAFS spectra of $\text{UO}_2[\text{H}_2\text{AsO}_4]_2 \cdot \text{H}_2\text{O}$ (left) and their Fourier transform (right).

In conclusion, our specially designed closed-cycle He cryostat allows to measure low-temperature (15 K) EXAFS spectra of radioactive samples both in transmission and fluorescence in excellent quality. The U L_{III} -edge and As and Cu K-edge EXAFS spectra of several uranyl arsenates showed that distant heavy backscattering atoms, i.e., U and As, that are “silent” at room temperature, become “visible” at low temperature. This greatly enhances the amount of structural information available from EXAFS measurements.

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