

## EXAFS as a tool for bond-length determination in the environment of heavy atoms

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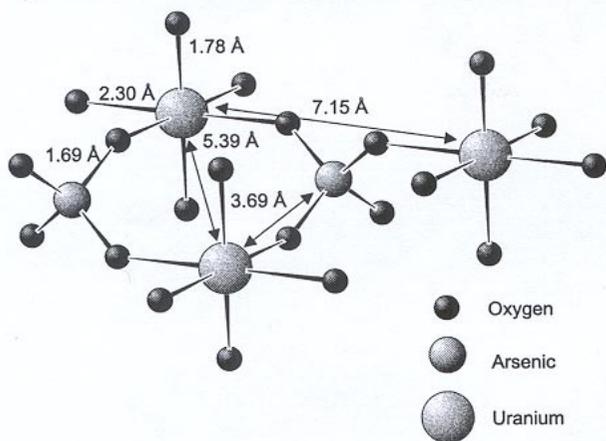
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Single crystal X-ray diffraction measurements are complicated in the presence of heavy atoms. In these cases the structure factors are mainly influenced by the heavy scatterers and the error in determination of atomic coordinates increases for light atoms. The difficulties grow if the unit cell dimensions or the space group symmetry remain uncertain. If the structure model is similar to the correct structure, it is difficult to find an independent criterion for the accuracy of the bond-length determination. We demonstrate that extended X-ray absorption fine structure (EXAFS) spectroscopy is a useful tool for the investigation of local bond lengths in the environment of heavy atoms.

**Keywords:** heavy atoms, uranyl arsenate, EXAFS, XRD

### 1. Introduction

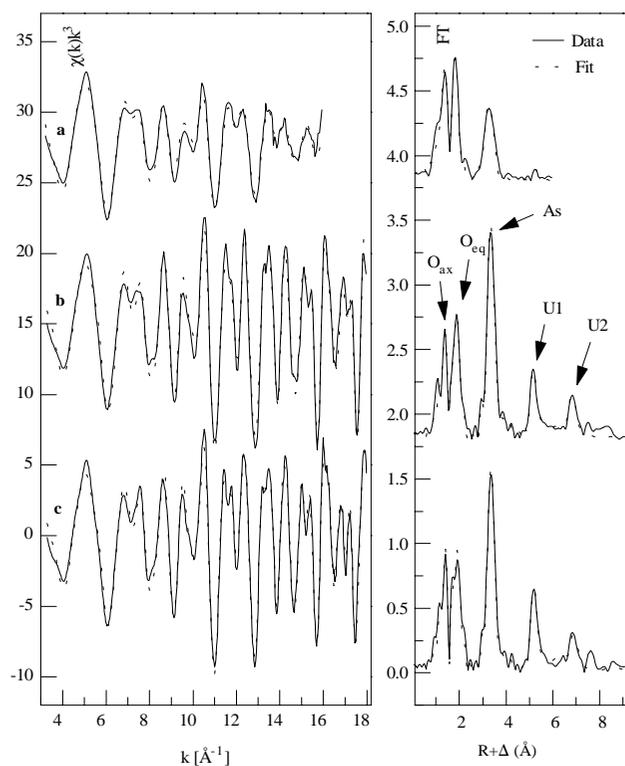
EXAFS allows a direct measurement of bond lengths and avoids, therefore, problems caused by incorrect determined lattice parameters. A determination of local bond lengths by EXAFS is reliable within an error limit of 0.02 Å. As an example, the atomic distances of meta-zeunerite,  $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ , and trögerite,  $\text{H}_2[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$  were determined by EXAFS measurements. The measured atomic distances were compared to X-ray diffraction and neutron diffraction literature data.



**Figure 1**

Detail of the uranyl arsenate layer  $[\text{UO}_2\text{AsO}_4]_\infty$  in meta-zeunerite and trögerite. Distances are given for meta-zeunerite determined by EXAFS measurements.

Meta-zeunerite and trögerite belong to the structure family with the chemical formula  $\text{A}[\text{UO}_2\text{XO}_4]_2 \cdot n\text{H}_2\text{O}$ , where  $\text{XO}_4$  appears as phosphate or arsenate and A is a hydrated monovalent or divalent cation. Each  $[\text{UO}_2]^{2+}$  unit is built up by uranium with two double bonded oxygen atoms in axial direction ( $\text{O}_{\text{ax}}$ ). This uranyl unit is surrounded equatorially by four oxygen atoms ( $\text{O}_{\text{eq}}$ ) in a square planar arrangement. Tetrahedra of  $[\text{XO}_4]^{3-}$  and tetragonal dipyramidal coordinated uranyl ions  $[\text{UO}_2]^{2+}$  built up stable two-dimensional layers. These  $[\text{UO}_2\text{XO}_4]_\infty$  layers are connected together forming a tetragonal or pseudotetragonal crystal morphology and a platy (001) habit. 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. The interlayer water content varies depending on vapour pressure and temperature.



**Figure 2**

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

### 2. Experimental

A natural meta-zeunerite mineral,  $\text{Cu}[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$ , from Wheal Basset, Cornwall/England and a synthetic compound of  $\text{H}_2[\text{UO}_2\text{AsO}_4]_2 \cdot 8\text{H}_2\text{O}$  were used for EXAFS measurements. The sample was ground, mixed with boron nitride and pressed as 1.3 cm diameter pellet.

EXAFS measurements were carried out on the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) under dedicated ring conditions (6.0 GeV, 100–200 mA). The monochromator equipped with a water cooled

Si(111) double-crystal system was used in fixed-exit measuring mode. Higher harmonics were rejected by two Pt coated mirrors. Energy steps were calculated giving corresponding k-space steps of 0.05 Å<sup>-1</sup>. Uranium L<sub>III</sub>-edge and arsenic K-edge EXAFS were collected in transmission geometry using argon-filled ionization chambers. First inflection points at the Zr K-edge at 17995.9 eV and at the Au L<sub>III</sub>-edge at 11919.7 eV were used for energy calibration, respectively. The measurements were performed at room temperature. In addition a closed-cycle He cryostat was used to reduce thermal oscillations. EXAFS data were extracted from the raw absorption spectra by standard methods using the computer program EXAFSPAK [George & Pickering (1995)]. Backscattering phase and amplitude functions were calculated using the FEFF8 code [Ankudinov (1998)]. The amplitude reduction factor, S<sub>0</sub><sup>2</sup>, was held constant at 1.0 during the fit procedures. Phase and amplitude functions for the scattering pairs were calculated using clusters build up by atomic coordinates of D<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8D<sub>2</sub>O [Fitch et al. (1982)] and our own crystal structure data from X-ray diffraction measurements on Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O [Hennig et al. (2000)].

### 3. Results and discussion

Uranium k<sup>3</sup>-weighted EXAFS spectra of meta-zeunerite, Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O, and trögerite, H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O at T = 298 K and T = 15 K are shown in figure 2. The first shell in both compounds represents the axial oxygen atoms, O<sub>ax</sub>, at a distance of 1.77-1.78 Å and a coordination number of 1.6 (tab. 1).

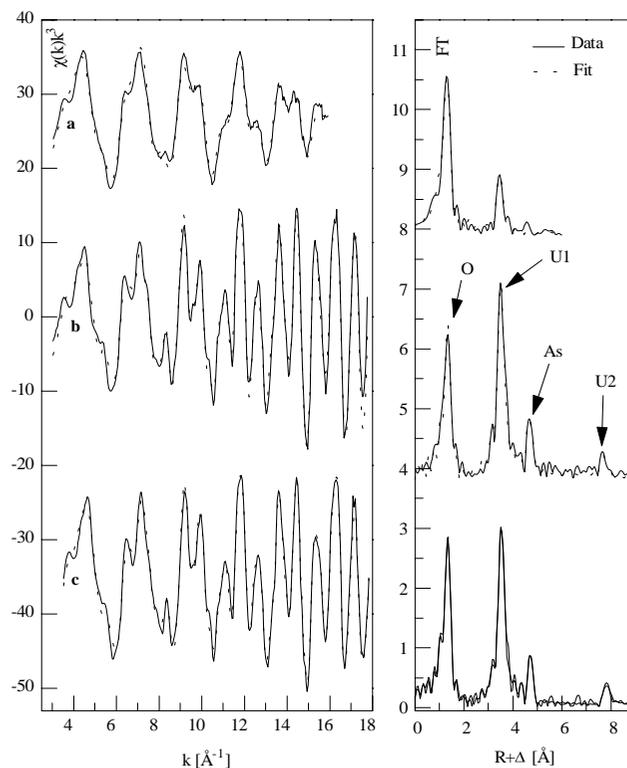
**Table 1**  
EXAFS structural parameters for Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O (**1**) and H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O (**2**) at T = 298 K and T = 15 K at the U L<sub>III</sub>-edge.

Sample	Shell	R [Å] <sup>a</sup>	N <sup>b</sup>	σ <sup>2</sup> [Å <sup>2</sup> ]	ΔE [eV]
<b>1</b> 298 K	U-O <sub>ax</sub>	1.77	1.6(1)	0.0021	0.1
	U-O <sub>eq</sub>	2.29	4.5(1)	0.0035	
	U-As	3.70	2.7(2)	0.0039	
<b>1</b> 15 K	U-O <sub>ax</sub>	1.78	1.6(1)	0.0028	5.5
	U-O <sub>eq</sub>	2.30	4.3(2)	0.0021	2.1
	U-As	3.69	3.5(2)	0.0012	0.2
	U-U1	5.39	3.7(6)	0.0027	-1.4
	U-U2	7.15	3.1(9)	0.0012	-10.8
<b>2</b> 15 K	U-O <sub>ax</sub>	1.78	1.6(1)	0.0016	6.2
	U-O <sub>eq</sub>	2.30	4.6(1)	0.0020	2.4
	U-As	3.70	4.1(2)	0.0015	0.7
	U-U1	5.40	5.4(5)	0.0029	1.7
	U-U2	7.21	6.3(2)	0.0023	-9.1

<sup>a</sup>Errors in distances R are ± 0.02 Å, <sup>b</sup>errors in coordination numbers N are ± 25 % with standard deviations in parentheses, σ<sup>2</sup> Debye-Waller factor.

The second shell correspond to the bond distance of four symmetry-equivalent equatorial atoms (O<sub>eq</sub>) with a bond length of 2.29-2.30 Å and a determined coordination number of 4.3 and 4.6. Deviations between expected coordination numbers (N<sub>O<sub>ax</sub></sub>=2, N<sub>O<sub>eq</sub></sub>=4) and measured values arise from significant polarization effects originating from preferred orientation of the uranyl

arsenate layers in the sample [Hennig et al. (1999)]. The arsenic scattering contribution gives a significant third Fourier transform peak with a calculated distance of 3.69-3.70 Å. At T = 298 K the U-U scattering contribution generates only a weak peak. To analyse higher shells, low temperature measurements were performed. At a temperature of 15 K, the scattering contributions of uranium appear in a U-U1 distance of 5.39 Å and a U-U2 distance of 7.15 Å for Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O. EXAFS measurements on H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O show within the error limits the same distances except for the U-U2 shell. The values are calculated using Fourier filter procedures and used as start parameters for the fit procedure. Multiple scattering (MS) effects were analyzed using FEFF8 program package. Because of their weak amplitude ratio, the U-O<sub>ax1</sub>-U-O<sub>ax2</sub>-U MS contributions could be neglected. The energy shift ΔE, used as free parameter for low temperature measurements, differs widely from each other. A subtraction of the U-U2-O<sub>eq</sub>-U and U-O<sub>eq</sub>-U2-O<sub>eq</sub>-U MS contributions from the spectra reduces the energy shift of the U-U2 shell without significantly changing distance determined. The atomic distance U-U2 corresponds to the **a** lattice constant. At low temperature the crystal symmetry of D<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8D<sub>2</sub>O changes from the tetragonal space group P4/ncc at 305 K to orthorhombic and triclinic symmetry at low temperature [Fitch et al. (1982)]. But the calculated average atomic distances are only weakly influenced. For Cu<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O a similar phase transition is expected. At 298 K the space group of the ordered state is also P4/ncc.



**Figure 3**  
As K-edge k<sup>3</sup>-weighted EXAFS spectra and the corresponding Fourier transform (right) for Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O at T = 298 K (a), Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O at T = 15 K (b), H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O at T = 43 K (c)

EXAFS measurements with As as absorbing atom are shown for meta-zeunerite at 298 K and 15 K in figure 3. The calculated values are given in table 2. The arsenate tetrahedra is characterized by the As-O<sub>eq</sub> distance of 1.68-1.69 Å with a calculated coordination number of 5.1 at room temperature and 3.7 at 15 K. The As-U1 distance is determined to 3.68-3.69 Å with coordination number of 2.8 at room temperature and 4.2 at 15K. At low temperature the fit procedure gives for the As-As shell a distance of 5.02 Å and for the As-U2 shell a distance of 8.01 Å. The measurements on H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O show within the error limits the same distances. Similar to the U L<sub>III</sub>-edge, the energy shift ΔE differ particular for the largest shell. FEFF8 simulation showed that MS contributions are negligible for the As K edge.

**Table 2**

EXAFS structural parameters for Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O (**1**) at T = 298 K and T = 15 K and H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O (**2**) at T=43K at the As K-edge

Sample	Shell	R [Å] <sup>a</sup>	N <sup>b</sup>	σ <sup>2</sup> [Å <sup>2</sup> ]	ΔE [eV]
<b>1</b> 298 K	As-O <sub>eq</sub>	1.68	5.1(1)	0.0025	-7.2
	As-U1	3.68	2.8(13)	0.0042	
<b>1</b> 15 K	As-O <sub>eq</sub>	1.69	3.7(1)	0.0014	-1.7
	As-U1	3.69	4.2(2)	0.0016	-7.1
	As-As	5.02	3.1(5)	0.0013	-9.7
	As-U2	8.01	6.5(9)	0.0030 <sup>c</sup>	-13.9
<b>2</b> 43 K	As-O <sub>eq</sub>	1.69	4.1(1)	0.0018	0.6
	As-U1	3.70	3.9(2)	0.0018	-3.9
	As-As	5.06	4.9(6)	0.0036	-0.8
	As-U2	8.04	8.3(8)	0.0035 <sup>c</sup>	-9.5

<sup>a</sup>Errors in distances R are ± 0.02 Å, <sup>b</sup>errors in coordination numbers N are ± 25 % with standard deviations in parentheses, <sup>c</sup>fixed, σ<sup>2</sup> Debye-Waller factor.

In table 3 atomic distances determined by EXAFS measurements are compared to X-ray diffraction data from literature. The EXAFS data on the H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O sample show a good agreement to the neutron diffraction literature data. The measurements on D<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8D<sub>2</sub>O, described in the literature, were taken with neutron diffraction on a powder sample using Rietveld refinement procedures at room temperature [Fitch et al. (1983)] and at 4 K [Fitch et al. (1982)]. For Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O the observed atomic distances between heavy and light scatterers deviate approximately 0.1-0.2 Å to the literature data of single crystal X-ray diffraction measurements [Hanic (1960)]. However, the atomic distances between heavy scatterers agree well with the EXAFS data. The X-ray crystal structure analysis of meta-zeunerite was performed on a single crystal using Weissenberg photographs [Hanic (1960)]. The difficulty for this single crystal structure analysis seems to be caused by stacking faults of the [UO<sub>2</sub>XO<sub>4</sub>]<sub>∞</sub> layers in the c lattice direction. As frequently observed in heavy atom structures, the position of the heavy scatterers are correctly determined, but the positions of the light atoms are incorrect. The crystal structure of meta-zeunerite was completely redetermined using single crystal

diffraction measurements [Hennig et al. (2000)]. These measurements confirmed the structural parameters given by the EXAFS measurements.

**Table 3**

Comparison of the atomic distances in Å between EXAFS measurements and XRD literature data.

Shell	Cu[UO <sub>2</sub> AsO <sub>4</sub> ] <sub>2</sub> ·8H <sub>2</sub> O		X <sub>2</sub> [UO <sub>2</sub> AsO <sub>4</sub> ] <sub>2</sub> ·8X <sub>2</sub> O	
	EXAFS	XRD [1]	EXAFS	ND [2]
U-O <sub>ax</sub>	1.78	1.94, 1.78	1.78	1.79, 1.78
U-O <sub>eq</sub>	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 <sub>eq</sub>	1.68	1.77	1.69**	1.68
As-As	5.02*	5.02	5.06**	5.06

[1] = [Hanic (1960)], [2] = [Fitch et al. (1982, 1983)]

XRD = X-ray diffraction, ND = Neutron diffraction

X=H for the EXAFS measurements, X=D in the literature [Fitch et al. (1982, 1983)] \*T = 15K, \*\*T = 43K

#### 4. Conclusion

The atomic distances between heavy and light atoms in meta-zeunerite show differences of approximately 0.1-0.2 Å in comparison to X-ray diffraction literature data [Hanic (1960)], whereas the EXAFS measurements and the neutron diffraction literature data of trögerite [Fitch et al. (1982, 1983)] are in good agreement. A revision of the Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O crystal structure shows a good agreement in the error limits of 0.02 Å between atomic distances determined by EXAFS and X-ray diffraction measurements [Hennig et al. (2000)]. This investigation demonstrates that a bond-length determination independent from crystal quality and knowledge of symmetry and lattice parameters is important. EXAFS spectroscopy has proven to be such an useful tool for determining local bond lengths in the environment of heavy atoms. The comparison between H<sub>2</sub>[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O and Cu[UO<sub>2</sub>AsO<sub>4</sub>]<sub>2</sub>·8H<sub>2</sub>O point out that no significant structural differences appear in the uranyl arsenate layers. The interlayer cation influence on structural differences is lower than expected from literature.

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