



ROBL-CRG

Experiment title:

EXAFS investigations on uranyl arsenates

Experiment**number:**

20-01-01

Beamline:

BM 20

Date of experiment:

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35

Local contact(s):*Received at**ROBL:*

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First EXAFS measurements were taken on the new Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The monochromator, equipped with a Si(111) water cooled double-crystal system, was used in the channel-cut mode. Higher harmonics were rejected by Pt coated mirrors. U L_{III}-edge and As K-edge EXAFS spectra were collected in transmission. The Cu K-edge EXAFS spectrum was measured with a multichannel Ge fluorescence detector /1/. Two or three scans were obtained in transmission mode and 32 single accumulations were taken for the Cu K-edge fluorescence spectra. The measurements were carried out with a sample orientation of 0° and 45° to the beam direction to investigate the influence of polarization effects (not discussed here). For energy calibration of the uranium spectra we used the first inflection point of Zr at 17996eV. The samples are natural meta-zeunerite from Wheal Basset, Cornwall, and hydrogen uranyl arsenate hydrate, prepared according to the literature /2/.

Uranyl arsenates like meta-zeunerite, Cu[UO₂AsO₄]₂ · 8H₂O, and hydrogen uranyl arsenate hydrate, H[UO₂AsO₄] · 4H₂O, are built up by stable layers of [UO₂]²⁺ and [AsO₄]³⁻ units. The charge neutrality is achieved by different interlayer cations like Cu²⁺, H⁺ and H₃O⁺. We used EXAFS measurements to compare the crystal structures. The results of the curve fitting to the k³-weighted EXAFS data are shown in Figs. 1-2.

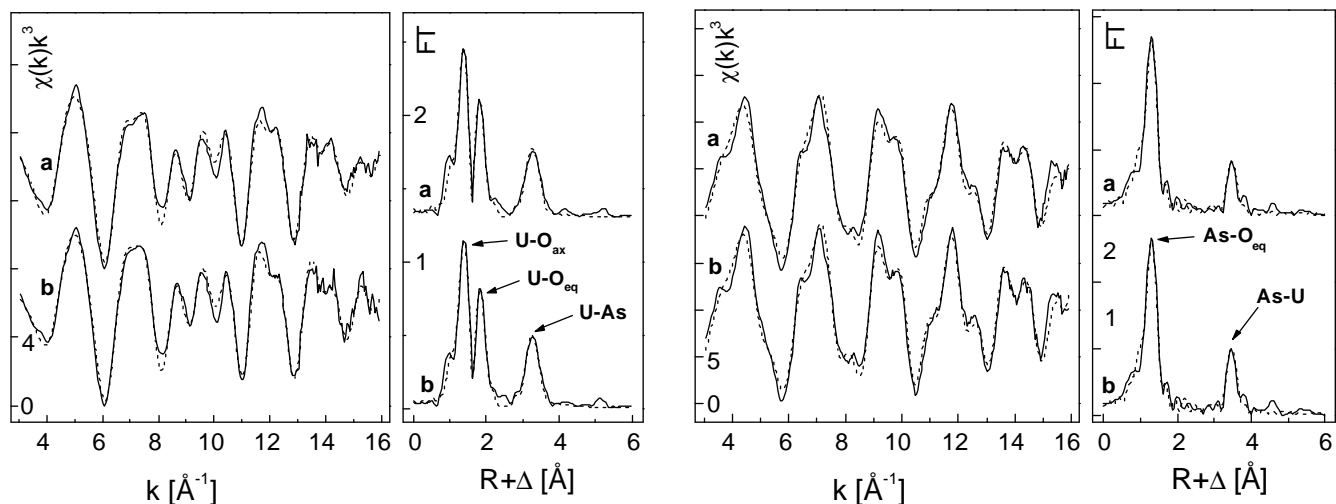


Fig. 1: U L_{III}-edge EXAFS spectra and FT of H[UO2AsO4]·4H₂O (a), and Cu[UO2AsO4]₂·8H₂O (b). Fig. 2: As K-edge EXAFS spectra and FT of H[UO2AsO4]·4H₂O (a), and Cu[UO2AsO4]₂·8H₂O (b)

All figures show left the k^3 -weighted EXAFS spectra and right the corresponding Fourier transforms, the solid lines are measured data, the dotted lines are the calculated values. In the U L_{III}-edge EXAFS of meta-zeunerite (Fig. 1), the first shell represent the axial oxygen atoms (O_{ax}) at a distance of 1.79Å. The second shell correspond to the equatorial atoms with a distance of 2.28Å and the third shell originates from the arsenic atoms with a distance of 3.67Å. Using As as absorbing atom (Fig. 2), the As-U distance was confirmed to 3.68Å and the As-O_{eq} distance was determined to 1.68Å. The measurements at two near-neighbour absorber atoms allows to calculate the bond angle U-O_{eq}-As to 135.34°. The interlayer Cu-O distance in meta-zeunerite was measured by Cu K-edge EXAFS to 1.95Å. The EXAFS data of the uranyl arsenate layer on H[UO2AsO4]·4H₂O are quite similar within the error of 0.02Å. In conclusion, the uranyl arsenate layer structure is nearly independent from the interlayer cation arrangement. Furthermore, our investigation demonstrates the possibility to compensate the lost angle information in EXAFS using the radial distribution functions at various absorption edges.

References:

- /1/ Bucher, J.J., et al., Rev. Sci. Instrum., 67, 1, 1996
- /2/ Weiss, A., et al., Z. Naturforsch., 12b, 669, 1957