ROBL-CRG	**Experiment title:** EXAFS measurements at low temperature	**Experiment number:** 20-01-019
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Report:

The aim of these low temperature measurements is to obtain structural information on solid uranium compounds using EXAFS. The analysis of structural differences between $Cu[UO_2AsO_4]_2 \cdot 12H_2O$ and $Cu[UO_2AsO_4]_2 \cdot 8H_2O$ serves as an example.

Sample **1** is obtained by synthesis and consists of pure $Cu[UO_2AsO_4]_2 \cdot 12H_2O$. The structure contains two symmetry-inequivalent 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 [1]. Sample **2** is a natural meta-zeunerite mineral. This structure contains one symmetry-independent Cu atom position [1]. The powdered sample contains 14% $Cu[UO_2AsO_4]_2 \cdot 12H_2O$. However, the EXAFS is dominated by the scattering contribution of $Cu[UO_2AsO_4]_2 \cdot 8H_2O$. Due to the damping of thermal oscillations at 15K, a lot of backscattering shells occur in the Fourier transform (FT). To simplify the data analysis, the FT between $R+\Delta$=5.5-10Å was Fourier filtered, back transformed and subtracted from raw EXAFS data of each spectrum. The $[Cu(H_2O)_4]^{2+}$ group causes dominant FT peaks with Cu-O distances of 1.94Å for sample **1** and **2**. Sample **1** shows one Cu-U peak at a distance of 4.22Å. A strong Cu-U-O_{ax}-Cu MS contribution appears because

the involved atoms are arranged linearly. This observation points to a highly symmetric arrangement of the $[UO_2AsO_4]_\infty$ layers concerning Cu.

	Shell	R [Å][a]	N[b]	σ^2 [Å^2]	ΔE_0 [eV]
1	Cu-OW	1.94	3.1(2)	0.0016	-4.4
	Cu-O_{ax}	2.46	1.1(2)	0.0016**	
	Cu-U	4.22	1.3(5)	0.0013	
	Cu-U_{MS}	4.22**	2.7**	0.0026**	
2	Cu-OW	1.94	2.4(1)	0.0018	-13.9
	Cu-O_{ax}	2.46	1.2(1)**	0.0018**	
	Cu-U1	4.04	0.8(1)	0.002*	
	Cu-U2	4.52	0.7(1)*	0.002*	
	Cu-As	4.84	1.6(2)	0.002*	

Tab. 1: EXAFS structural parameters

[a]Errors in distances R are ± 0.02 Å, [b]errors in coordination numbers N are ± 25 % with standard deviations in parentheses, *value fixed during the fit, **dependent from the previous variable

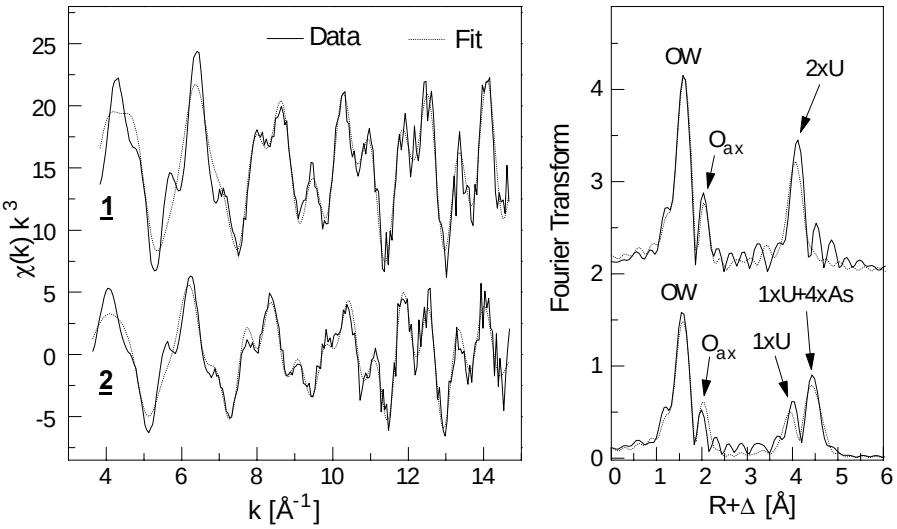

Fig. 1: Cu K-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transform (right) for sample (**1**) and (**2**) at T = 15 K.

In contrast, the spectrum of sample **2** shows two FT peaks in that region. The first peak is originated by one uranium atom in a distance of 4.04Å. The second peak consists of arsenic atoms in a distance of 4.84Å and one uranium atom in a distance of 4.52Å. These observations indicate that in meta-zeunerite one $[UO_2AsO_4]_\infty$ layer is arranged closer to the Cu atom.

References

[1] Hennig et al., unpublished