Polarized EXAFS of uranium L_1 and L_3 edges - A comparison

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Introduction

Uranium(VI) consists predominantly of two double bonded oxygen atoms in axial direction (O_{ax}) and 4, 5 or 6 oxygen atoms in the equatorial plane (O_{eq}) [see figure right]. This anisotropic coordination leads to a strong polarization dependence of XAFS.

Responsible for the polarization dependence are the electron waves with different impulse-momentum at the L_1 and L_3 edges.

Here we investigated this effect by comparing experimental data with the theory.

Experimental

Polarized EXAFS spectra using a single crystal of $Ca[UO_2PO_4]_2\cdot6H_2O$ were collected at the Rossendorf Beamline in transmission mode at room temperature. Effective coordination numbers N_{eff} were extracted from these spectra by shell fitting and additionally calculated as shown below.

4 - fold rotation axis

2.29 Å   1.76 Å
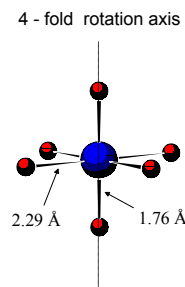
Conclusions

• Theory and experiment are in good agreement

• Polarization dependence of L_1 edge is significantly stronger that of L_3 edge

• However, the higher transition probability at the L_3 edge is responsible for a lower noise of the spectra

Uranium L_1 edge

At the L_1 edge the photoelectron is excited from s ground state into final state p. For a single-scattering process and in plane-wave approximation the angular dependence of L_1 and K edges can be written as:

$$N_{eff}(\theta) = \sum_{n=1}^{N} 3|\vec{\varepsilon}\cdot\vec{r}|^2$$

In order to relate polarization vector $\vec{\varepsilon}$ and and the vector conecting the absorbing and backscattering atom $\vec{r}$ to morphological parameters of the sample, θ is divided into two angles α and β.
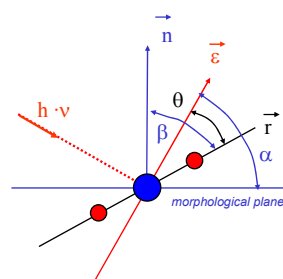
$$|\vec{\varepsilon}\cdot\vec{r}|^2 = \cos^2\beta\sin^2\alpha + (\sin^2\beta\cos^2\alpha)/2$$

The effective coordination number N_{eff} is then related to the real crystallographic coordination N_{cryst} by:

$$N_{eff}(\theta) = N_{cryst}\,3\left(\cos^2\beta\sin^2\alpha + (\sin^2\beta\cos^2\alpha)/2\right)$$

Uranium L_3 edge

At the L_2 and L_3 edges the photoelectron is excited from p ground state into final states s ($l=0$) and d ($l=2$). The EXAFS expression comprises here pure s, pure d and coupled s-d states.

Defining c as the ratio between the radial dipol matrix elements M_{01} and M_{21} coupling the initial $2p$ wave function with the s and d final states, the coordination number can be expressed as the sum of three effective partial coordination numbers [1]:
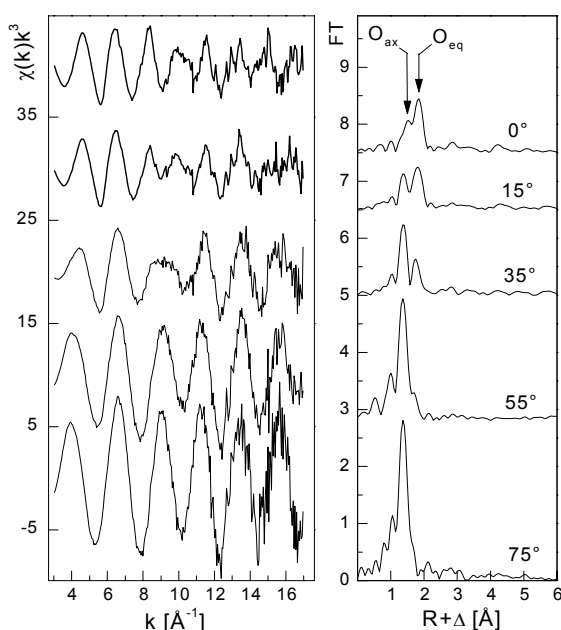
$$N_{eff}^d(\theta) = 0.5\left[\frac{2}{2+c^2}\right]\sum_{i=1}^{N}(1+3|\vec{\varepsilon}\cdot\vec{r}|^2)$$
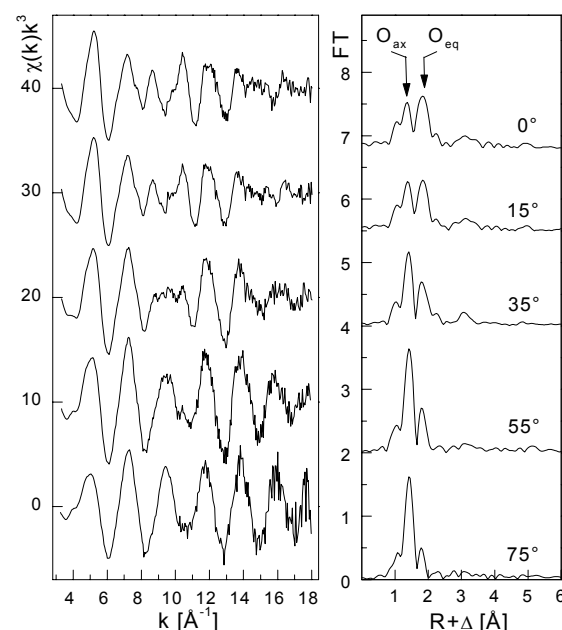
$$N_{eff}^s = 0.5\left[\frac{c^2}{2+c^2}\right]$$

$$N_{eff}^{sd}(\theta) = \left[\frac{2c}{2+c^2}\right]\sum_{i=1}^{N}(1-3|\vec{\varepsilon}\cdot\vec{r}|^2)$$

The value c depends only weakly on k and can be approximated by 0.2 for elements with $Z > 20$ [2]. Neglecting the N_{eff}^s term, the expression in then approximated according by [1]:
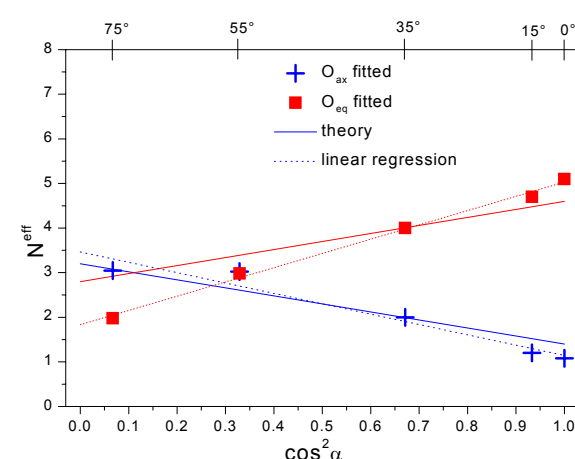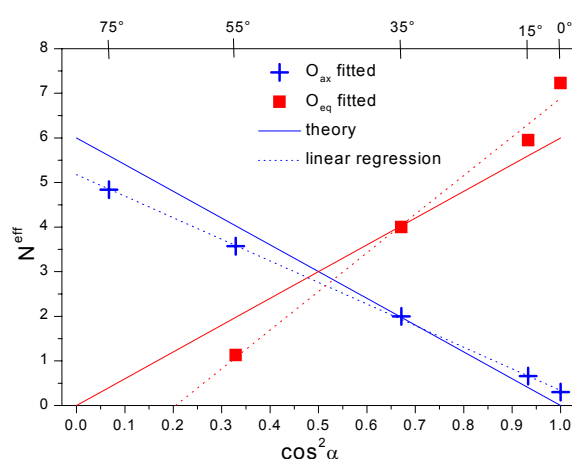
$$N_{eff}(\theta) = \sum_{i=1}^{N}(0.7 + 0.9|\vec{\varepsilon}\cdot\vec{r}|^2)$$

Coordination number

α	$N(O_{ax})$	$N(O_{eq})$
0°	0.30	7.23
15°	0.66	5.95
35°	2.00	4.00
55°	3.57	1.13
75°	4.84	

Coordination number

α	$N(O_{ax})$	$N(O_{eq})$
0°	1.08	4.60
15°	1.20	4.48
35°	2.00	4.00
55°	3.02	3.39
75°	3.05	2.92

/1/ Citrin, P.H., Phys.Rev. B **31** 700 (1985)
/2/ Teo, B.K., J. Am. Chem. Soc. **101** 2815 (1979)

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