Materials Modelling Day,
12 September 2025,
Tartu, Estonia

Exploring Local Atomic Environments with Advanced EXAFS Tools

LATVIJAS UNIVERSITĀTES
CIETVIELU FIZIKAS INSTITŪTS
INSTITUTE OF SOLID STATE PHYSICS
UNIVERSITY OF LATVIA

Dr.phys. Alexei Kuzmin

Head of the EXAFS Spectroscopy Laboratory

E-mail: a.kuzmin@cfi.lu.lv

https://www.dragon.lv/exafs

Team

SCIENTIFIC STAFF:

Alexei KUZMIN, Dr.phys., Head of the Laboratory, Leading Researcher

Andris ANSPOKS, Dr.phys., Leading Researcher

Inga PUDZA (ex. JONANE), Ph.D., Researcher

Pjotrs ŽGUNS, Ph.D., Researcher

Aleksandr KALINKO, Dr.phys., Leading Researcher (on leave at DESY P64 beamline, Germany)

Janis TIMOSHENKO, Dr.phys., Researcher (on leave at Fritz Haber Institute of the Max Planck Society, Germany)

STUDENTS:

Vitalijs DIMITRIJEVS, Mg., Research Assistant

Julija LUKASEVICA, Mg., Research Assistant

Leons STANKEVIČS, Mg., Laboratory Assistant

Daria ZANDBERGA, Laboratory Assistant

Talk Outline

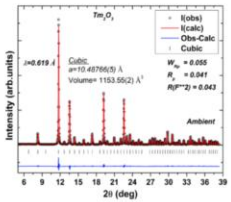
- **X-ray Absorption Spectroscopy (XAS)**
  - **Experiment**
  - **Theory**
  - **Advanced Methods of Data Analysis (MD/RMC/ANN-EXAFS)**
- **Applications to Functional Materials**
  - **Thermochromic Copper Molybdate and its Solid Solutions**
  - **Polaronic Centers in Proton-intercalated Scheelite-type Tungstates**
  - **Photochromic Yttrium Oxyhydride**
- **Conclusions**

Non-destructive Direct Structural Experimental Methods

Scattering

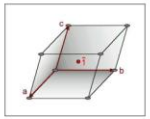
Powder Diffraction

Long range order
> 20 Å (2 nm)



Rietveld refinement:

$$I(\theta) = Ap\left(\frac{1+\cos^2(2\theta)}{\sin^2(\theta)\cos(\theta)}\right)|F|^2 e^{-B\sin^2(\theta)/\lambda^2}$$



Unit cell parameters:

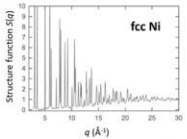
$a, b, c, \ \alpha, \beta, \gamma$

$x_i, y_i, z_i \ + B_i$

Total Scattering or PDF Analysis

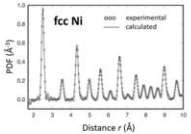
Short and medium range order
< 100 Å (10 nm)

The total scattering structure function S(Q):



$$S(Q) = \frac{I^{coh}(Q) - \sum c_i |f_i(Q)|^2}{\left|\sum c_i f_i(Q)\right|^2} + 1$$

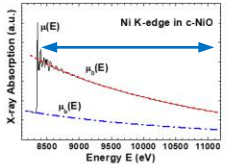
Experimental pair distribution function (PDF) G(r):



$$G(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} Q[S(Q)-1]\sin(Qr)dQ$$

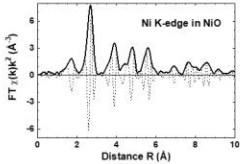
X-ray Absorption Spectroscopy

Short range order
< 6-10 Å (0.6-1 nm)



EXAFS χ(E)

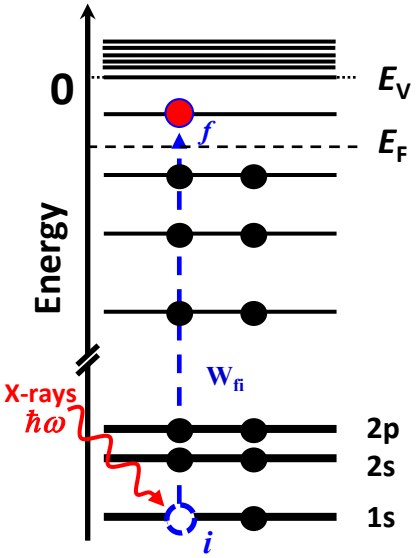
EXAFS χ(E): $\chi(E) = \dfrac{\mu(E) - \mu_b(E) - \mu_0(E)}{\mu_0(E)}$

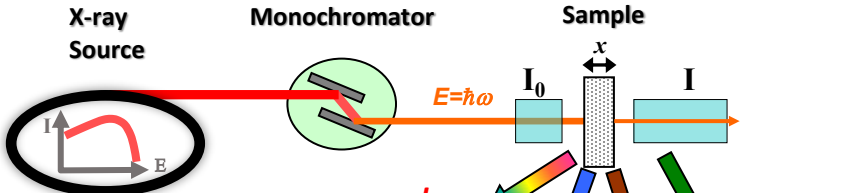


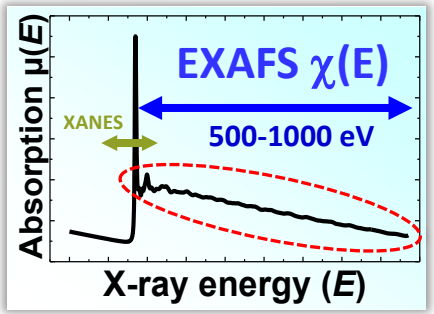
$$\begin{aligned}\chi(k) \;=\; & \int 4\pi R^2 \rho_0 g_2(R)(\chi_2^{aio}(k) + \chi_4^{aioio}(k) + \ldots)\mathrm{d}R \\ & + \iint 8\pi^2 R_1^2 R_2^2 \sin(\theta)\rho_0^2 g_3(R_1, R_2, \theta) \\ & \times(2\chi_3^{aijo}(k) + 2\chi_4^{aiojo}(k) + \chi_4^{aijio}(k) + \chi_4^{aijio}(k) + \ldots)\mathrm{d}R_1\mathrm{d}R_2\mathrm{d}\theta \\ & + \iiint 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta)\rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega) \\ & \times(2\chi_4^{aijko}(k) + 2\chi_4^{aikjo}(k) + 2\chi_4^{aijko}(k) + \ldots)\mathrm{d}R_1\mathrm{d}R_2\mathrm{d}\theta\mathrm{d}R_3\mathrm{d}\Omega \\ & + \ldots\end{aligned}$$

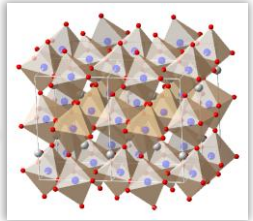
N-body distribution functions

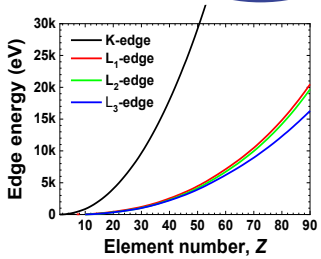
Basics of X-ray Absorption Spectroscopy (XANES/EXAFS)











Fermi's Golden Rule:

$$\mu(E) \propto \sum_f |\langle f|\hat{\mathbf{H}}|i\rangle|^2 \delta(E_f - E_i - \hbar\omega) = \mu_0(E)[1 + \chi(E)]$$

X-ray absorption coefficient μ(*E*):

$$\mu(E) = \frac{1}{x}\ln\left(\frac{I_0(E)}{I(E)}\right)$$

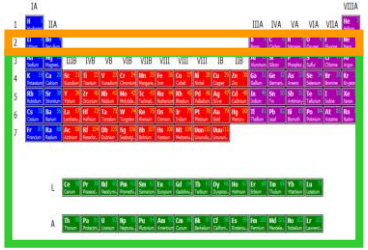
$$\mu(E) \propto \frac{I_{fluo}(E)}{I_0(E)}$$

$$\mu(E) \propto \frac{I_{TEY}(E)}{I_0(E)}$$

$$\mu(E) \propto \frac{I_{XEOL}(E)}{I_0(E)}$$

What can EXAFS Spectroscopy do?

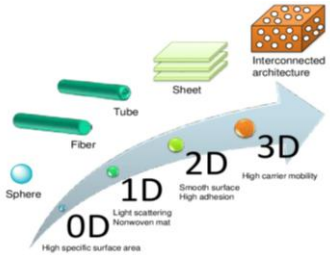
Most elements



Any aggregation states

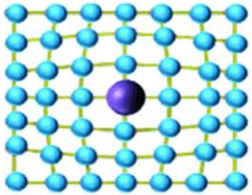
solid liquid gas

Any dimensionality



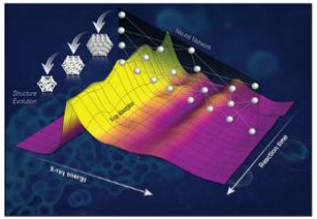
Extreme conditions
pressure & temperature
electric & magnetic fields

Diluted samples
down to ~1 mmol/L

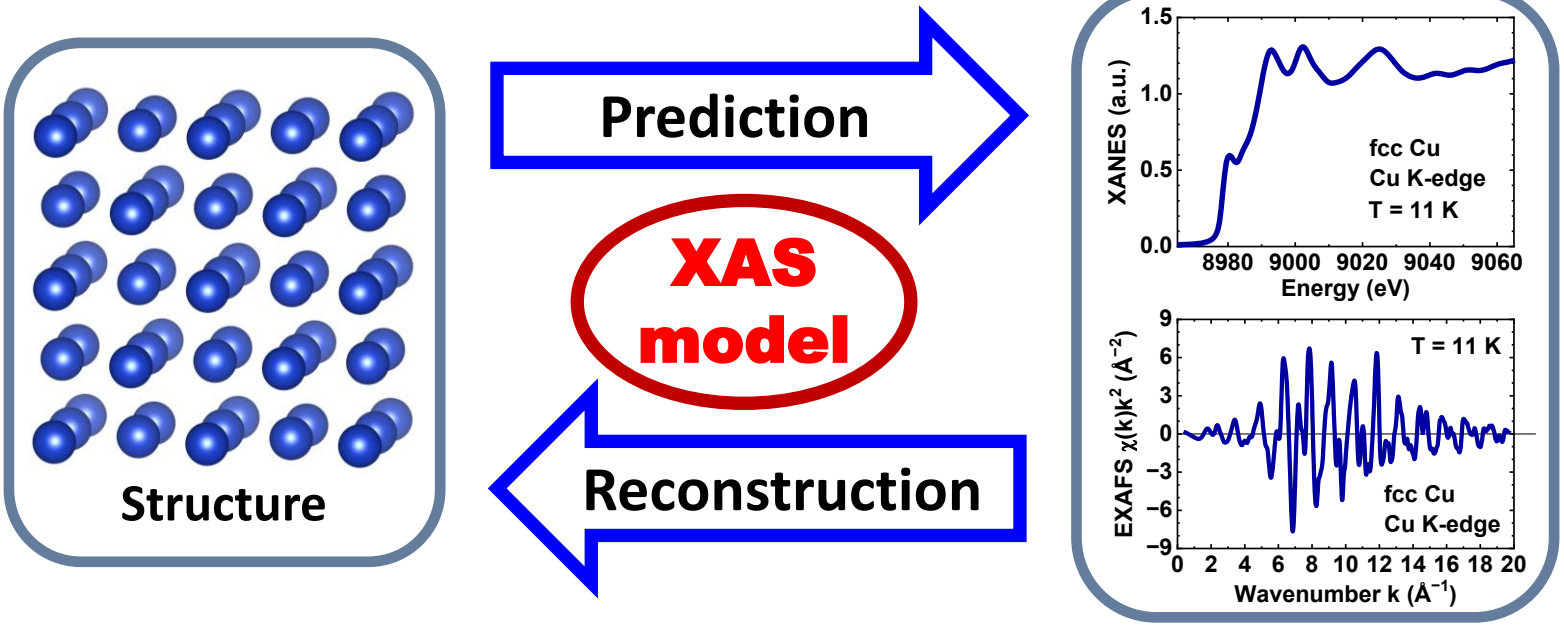


Time-dependent studies

- minutes
- ms
- down to ps (XFEL)



Typical uses of X-ray Absorption Spectroscopy

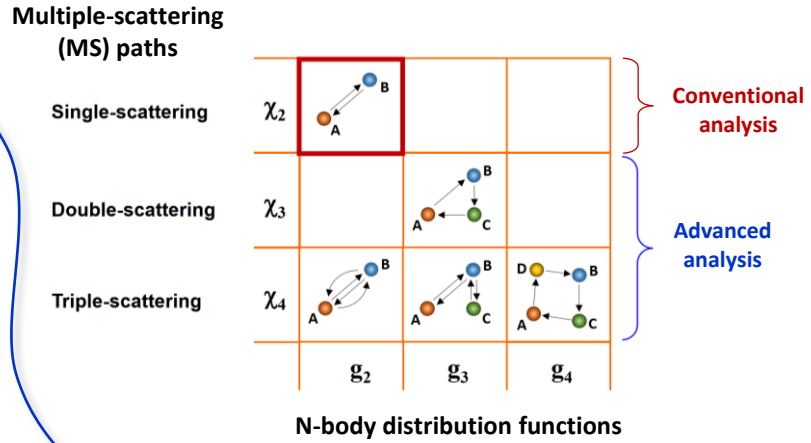


Basics of EXAFS Theory

N-body expansion:

$$\chi(k) = \int 4\pi R^2 \rho_0 g_2(R)(\chi_2^{oio}(k) + \chi_4^{oioio}(k) + \ldots)\mathrm{d}R$$
$$+ \iiint 8\pi^2 R_1^2 R_2^2 \sin(\theta)\rho_0^2 g_3(R_1, R_2, \theta)$$
$$\times(2\chi_3^{oijo}(k) + 2\chi_4^{oiojo}(k) + \chi_4^{oijio}(k) + \chi_4^{ojijo}(k) + \ldots)\mathrm{d}R_1\mathrm{d}R_2\mathrm{d}\theta$$
$$+ \iiiint 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta)\rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega)$$
$$\times(2\chi_4^{oijko}(k) + 2\chi_4^{oikjo}(k) + 2\chi_4^{ojiko}(k) + \ldots)\mathrm{d}R_1\mathrm{d}R_2\mathrm{d}\theta\mathrm{d}R_3\mathrm{d}\Omega$$
$$+ \ldots$$

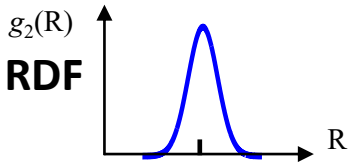
A. Filipponi, A. Di Cicco, C. R. Natoli, Phys. Rev. B 52 (1995) 15122.



Gaussian model:

$$\chi(k) = S_0^2 \boldsymbol{N} \frac{|f_{eff}(k,R)|}{k\boldsymbol{R}^2} e^{-2\boldsymbol{R}/\lambda(k)} \sin(2k\boldsymbol{R} + \phi(k,R)) e^{-2k^2\boldsymbol{\sigma}^2}$$

D.E. Sayers, E.A. Stern, F.W. Lytle, Phys. Bev. Lett. 27 (1971) 1204.



What Information (Shortlist) can be obtained from XAS Spectra?

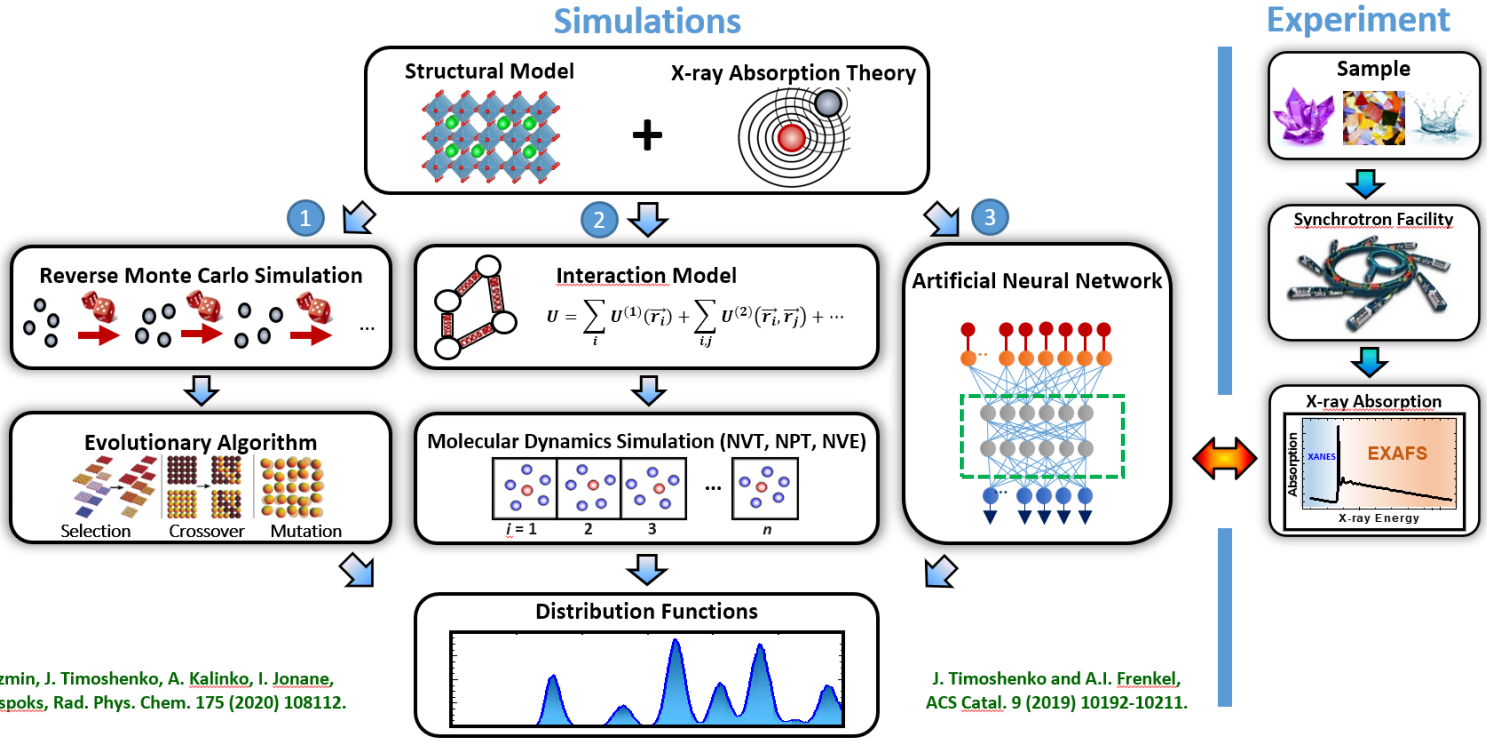
Conventional analysis:

- Interatomic distances (±0.02 Å)
- Coordination numbers (± 10%)
- Mean square relative displacements (MSRD) (±0.0005-0.002 $Å^2$)
- Oxidation states (from the absorption edge shift)

Advanced analysis:

- Radial distribution functions (RDF)
- Bond-angle distribution functions (BADF)
- Mean square displacements (MSD)
- Nanoparticle size
- Theory validation

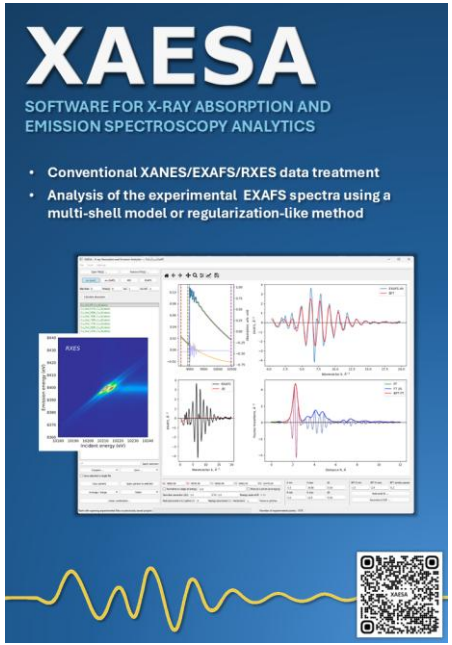
Advanced Methods of XAS Analysis using Atomistic Simulations



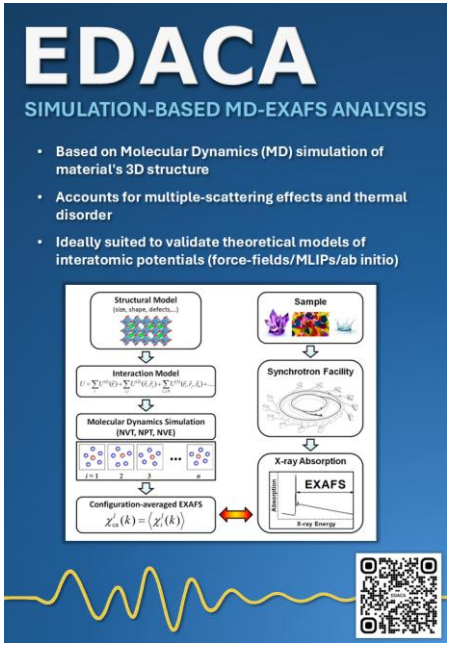
A. Kuzmin, J. Timoshenko, A. Kalinko, I. Jonane, A. Anspoks, Rad. Phys. Chem. 175 (2020) 108112.

J. Timoshenko and A.I. Frenkel, ACS Catal. 9 (2019) 10192-10211.

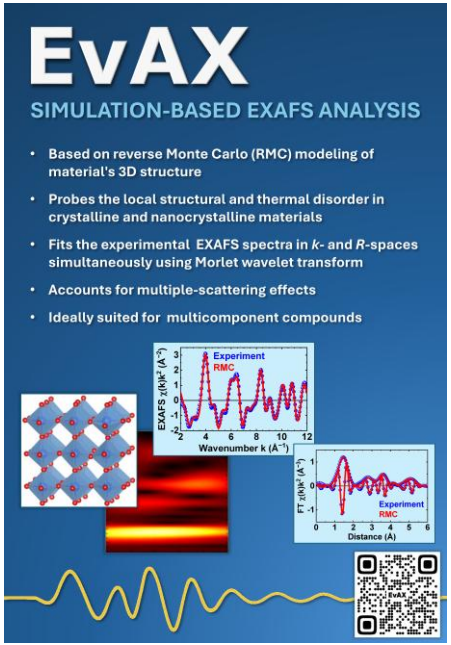
Computer Codes for XAS Analysis



https://gitlab.desy.de/aleksandr.kalinko/xaesa



https://www.dragon.lv/edaca/

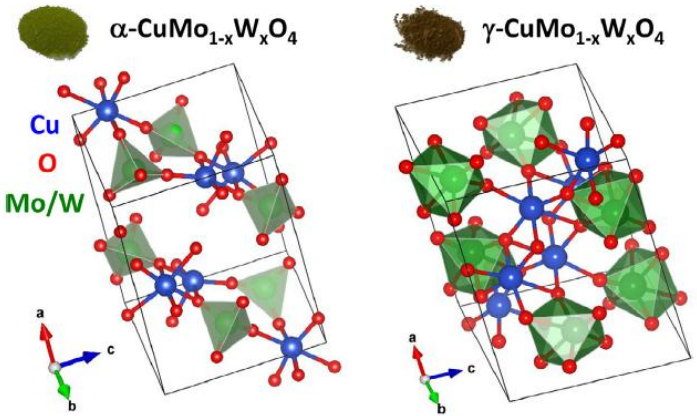


https://www.dragon.lv/evax/

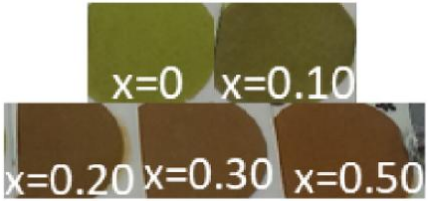
X-ray Absorption Spectroscopy of Chromogenic Materials

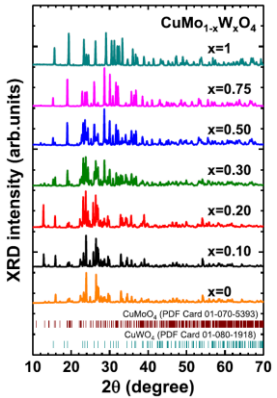
1. Thermochromic copper molybdate and its solid solutions.
2. Structure of polaronic centers in proton-intercalated AWO_4 scheelite-type tungstates.
3. Local structural distortions in photochromic yttrium oxyhydride.

Thermochromic Copper Molybdate and its Solid Solutions

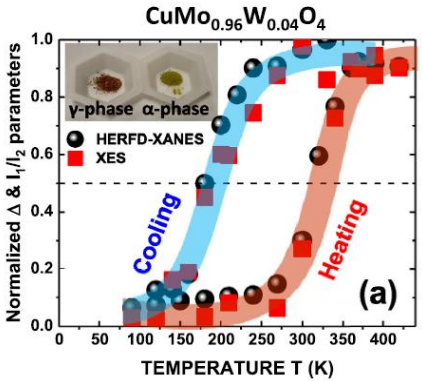


Effect of composition





Effect of temperature

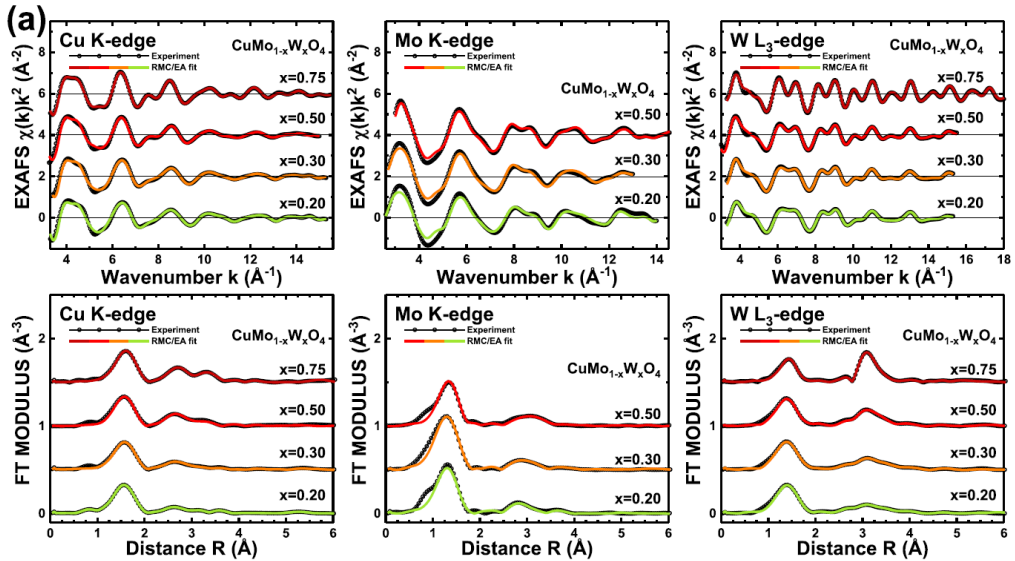


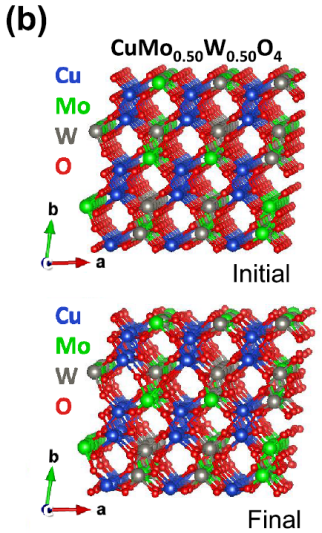
Hysteretic phase transition

I. Pudza, A. Kalinko, A. Cintins, A. Kuzmin, Acta Mater. 205 (2021) 116581.
I. Pudza, A. Anspoks, G. Aquilanti, A. Kuzmin, Mater. Res. Bull. 153 (2022) 111910.

Thermochromic Copper Molybdate and its Solid Solutions

Multi-edge (K-Cu, K-Mo, L_3-W) RMC simulations



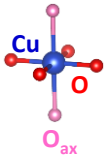


Single structural model!

I. Pudza, A. Anspoks, G. Aquilanti, A. Kuzmin, Mater. Res. Bull. 153 (2022) 111910.

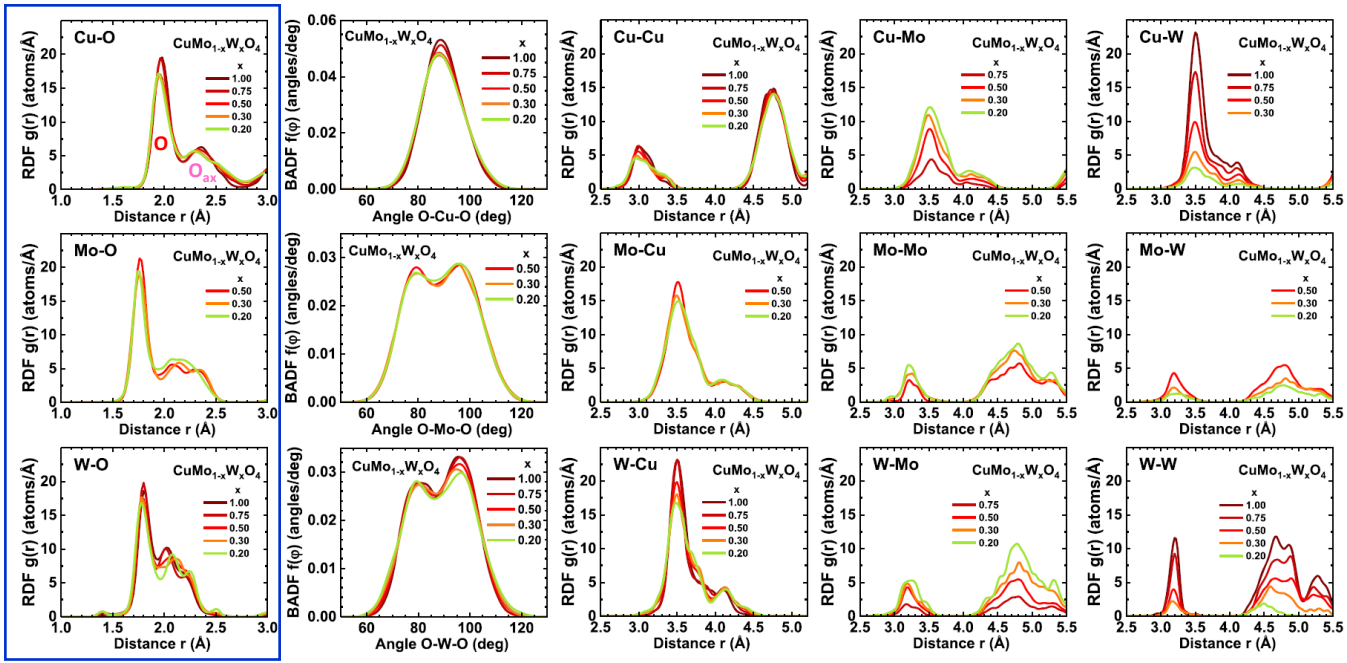
Thermochromic Copper Molybdate and its Solid Solutions

Jahn-Teller distortion of $Cu^{2+}O_6$



Distorted MoO_6

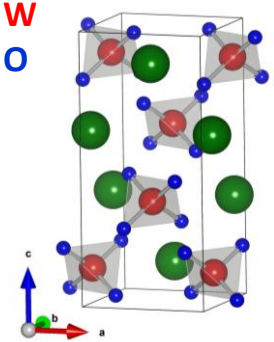
Distorted WO_6



I. Pudza, A. Anspoks, G. Aquilanti, A. Kuzmin, Mater. Res. Bull. 153 (2022) 111910.

Polaronic Centers in Proton-intercalated AWO_4 Scheelite-type Tungstates

Ca/Sr/Ba
W
O



Tetragonal $I4_1/a$ (no. 88)

Absorption edges:
L_3-W
K-Sr
L_3-Ba

$AW^{6+}O_4 + H^+ + e^-$

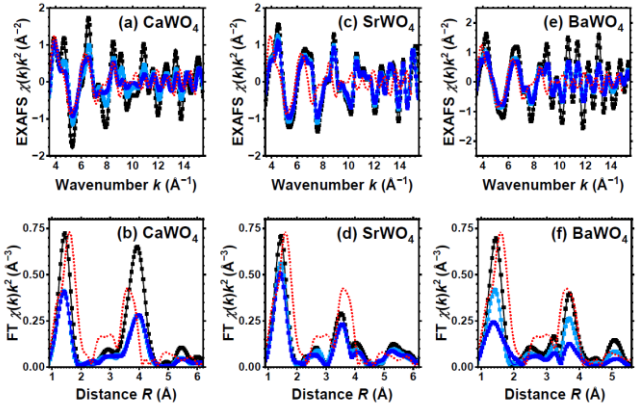
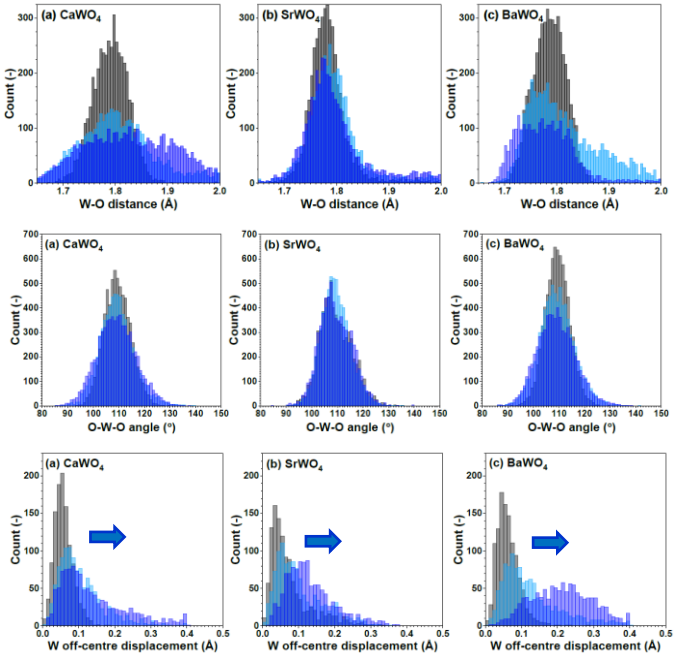


Figure 1. Experimental (symbols) and RMC/EA-simulated (solid lines) W L_3-edge EXAFS spectra $\chi(k)k^2$ (**upper** panels) and their Fourier transforms (FTs) (**lower** panels) at 10 K for $CaWO_4$ (**a**,**b**), $SrWO_4$ (**c**,**d**), and $BaWO_4$ (**e**,**f**). Black, light blue, and blue curves correspond to pristine (white), light-blue colored, and dark blue-purple colored samples, respectively. Only moduli of FTs are shown. Red dotted lines show experimental data for the W L_3-edge in $WO_3 \cdot H_2O$. See text for details.

(Multi-edge) RMC simulations



Tetrahedron WO_4

W off-center

G. Bakradze, E. Welter, A. Kuzmin, Materials 17 (2024) 3071.

Polaronic Centers in Proton-intercalated AWO_4 Scheelite-type Tungstates

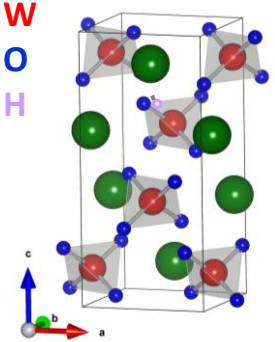
$AW^{6+}O_4 + H^+ + e^-$

Ca/Sr/Ba

W

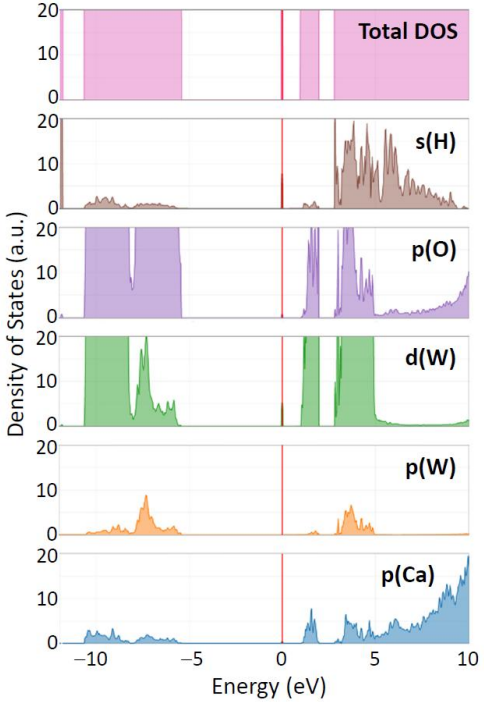
O

H

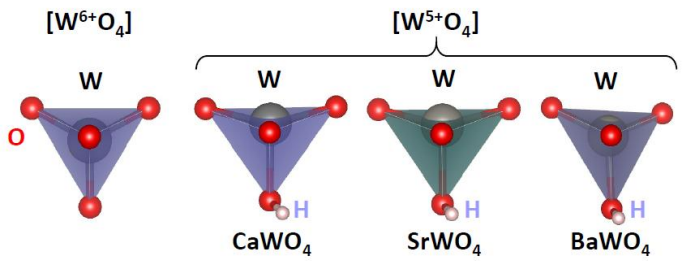


CRYSTAL17

DFT LCAO calculations with hybrid M06 functional, 2x2x2 supercell with 97 atoms: 16 Ca (Sr/Ba), 16 W, 64 O, 1 H.



	$CaWO_4$		$SrWO_4$		$BaWO_4$	
	Experiment	LCAO	Experiment	LCAO	Experiment	LCAO
a (Å)	5.2429	5.27	5.4168	5.47	5.6149	5.64
c (Å)	11.3737	11.34	11.951	11.88	12.7326	12.48
x(O)	0.1507	0.157	0.2497	0.231	0.2295	0.226
y(O)	0.0086	0.012	0.3425	0.105	0.1294	0.116
z(O)	0.2106	0.211	0.1671	0.042	0.05024	0.045
R(W–O) (Å)	1.78	1.79	1.78	1.79	1.78	1.79
$q(A^{2+})$		1.67		1.95		1.32
$q(W^{6+})$		2.79		2.77		2.75
$q(O^{2-})$		−1.11		−1.18		−1.02
E_g (eV)	4.94	6.6	5.08	7.1	5.26	7.3

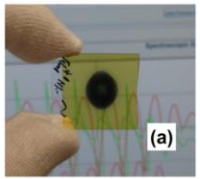


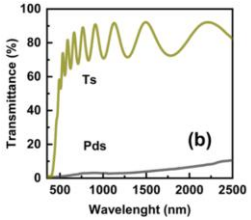
W off-center displacement

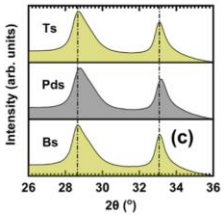
Regular $[W^{6+}O_4]$ and distorted $[W^{5+}O_4]$ tetrahedra in $CaWO_4$, $SrWO_4$, and $BaWO_4$ according to the DFT LCAO calculations.
Hydrogen (H) bound to the one of oxygen atoms is also shown.

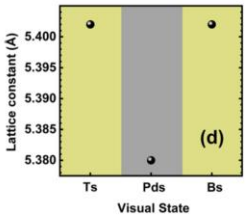
G. Bakradze, E. Welter, A. Kuzmin, Materials 17 (2024) 3071.

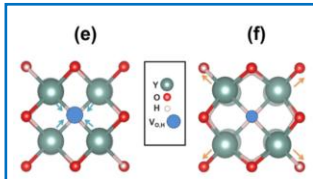
Photochromic Yttrium Oxyhydride (YHO)

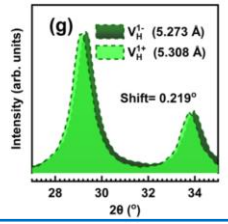


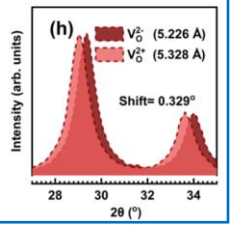


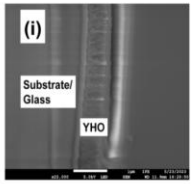








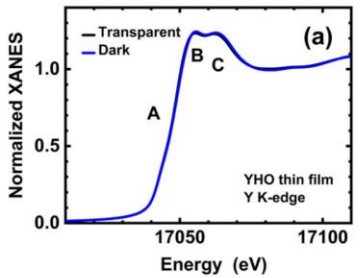


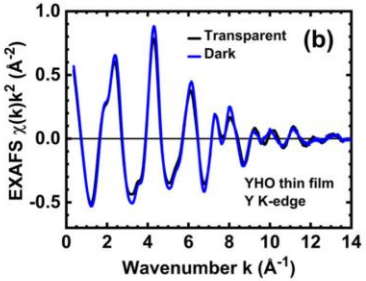


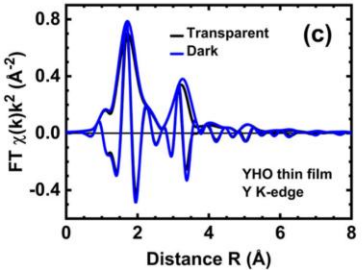
$$V_H^{1+} \xrightarrow{h\nu} V_H^{1-}$$
$$V_O^{2+} \longrightarrow V_O^{2-}$$

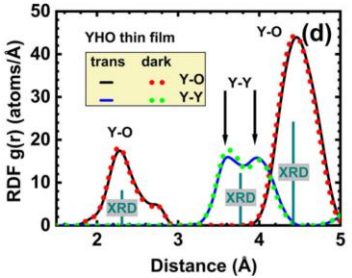
TABLE I. Refined structure parameters for yttrium oxyhydride powder from x-ray powder diffraction. Standard deviations are in parentheses. The cubic [space group *Fm*-3*m* (225)] lattice parameter $a = 5.404(3)$ Å. Crystallite size $d = 16(2)$ nm.

Element	Wyckoff position	Atomic coordinates	Occupation	B_{iso} (Å^2)
Y	4*a*	0, 0, 0	1	1.5(1)
O	8*c*	0.25, 0.25, 0.25	0.40(2)	5.2(3)









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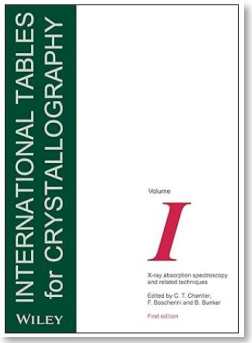
CONCLUSIONS

- **X-ray absorption spectroscopy is a versatile experimental method to study local atomic structure and its distortions in functional materials.**
- **Extraction of structural information remains challenging but can be handled based on advanced simulation methods.**



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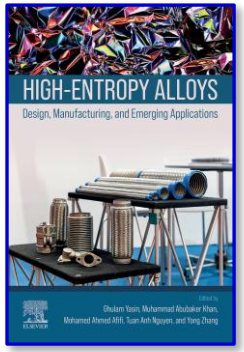
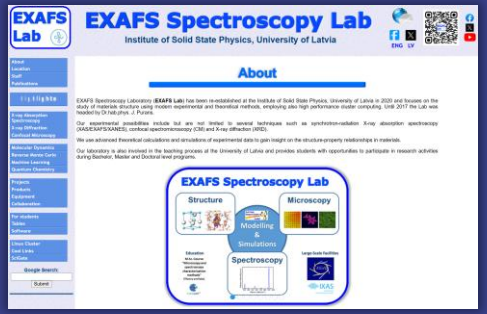


https://www.dragon.lv/exafs/



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Thank you for your attention!

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