

**Materials Modelling Day,  
12 September 2025,  
Tartu, Estonia**



# Exploring Local Atomic Environments with Advanced EXAFS Tools



LATVIJAS UNIVERSITĀTES  
CIETVIELU FIZIKAS INSTITŪTS

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





## SCIENTIFIC STAFF:

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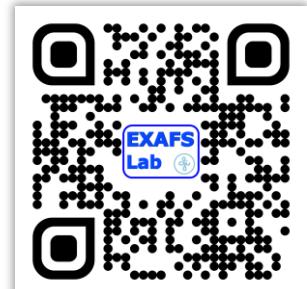
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Leons STANKEVIČS, Mg., Laboratory Assistant

Daria ZANDBERGA, Laboratory Assistant





# Talk Outline

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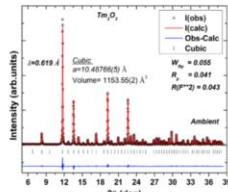
- X-ray Absorption Spectroscopy (XAS)
  - Experiment
  - Theory
  - Advanced Methods of Data Analysis (MD/RMC/ANN-EXAFS)
- Applications to Functional Materials
  - Thermochromic Copper Molybdate and its Solid Solutions
  - Polaronic Centers in Proton-intercalated Scheelite-type Tungstates
  - Photochromic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

# Non-destructive Direct Structural Experimental Methods



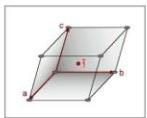
## Powder Diffraction

Long range order  
 $> 20 \text{ \AA}$  (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:**

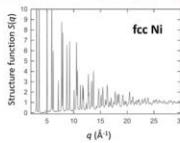
$$a, b, c, \alpha, \beta, \gamma$$

$$x_p, y_p, z_p + B_i$$

## Total Scattering or PDF Analysis

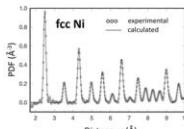
Short and medium range order  
 $< 100 \text{ \AA}$  (10 nm)

The total scattering structure function  $S(Q)$ :



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

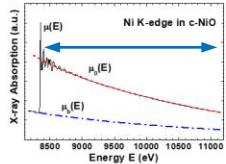
Experimental pair distribution function (PDF)  $G(r)$ :



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

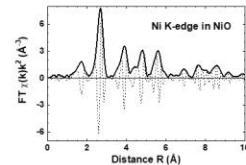
## X-ray Absorption Spectroscopy

Short range order  
 $< 6-10 \text{ \AA}$  (0.6-1 nm)



EXAFS  $\chi(E)$

$$\text{EXAFS } \chi(E): \quad \chi(E) = \frac{\mu(E) - \mu_b(E) - \mu_0(E)}{\mu_0(E)}$$

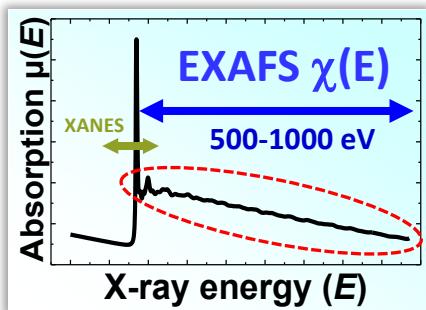
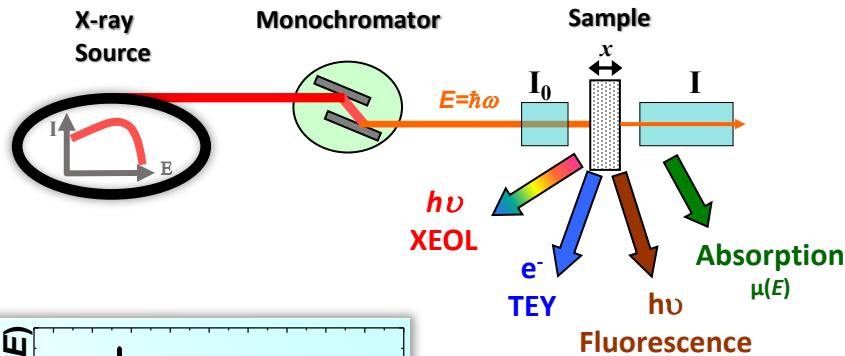
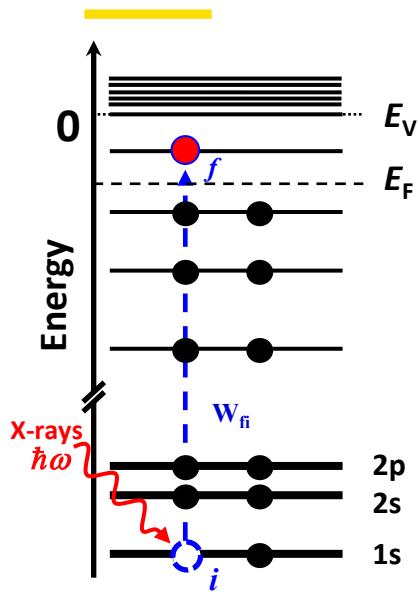


**N-body distribution functions**

$$\begin{aligned} \chi(k) &= \int 4\pi R^2 \rho_0 g_2(R) (\chi^{oiio}_2(k) + \chi^{oiio}_4(k) + \dots) dR \\ &+ \iiint 8\pi^2 R_1^2 R_2^2 \sin(\theta) \rho_0^2 g_3(R_1, R_2, \theta) \\ &\times (2\chi^{oiio}_3(k) + 2\chi^{oiijo}_4(k) + \chi^{oiijo}_4(k) + \chi^{oiijo}_4(k) + \dots) dR_1 dR_2 d\theta \\ &+ \iiint 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta) \rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega) \\ &\times (2\chi^{oiiko}_4(k) + 2\chi^{oiiko}_4(k) + 2\chi^{oiiko}_4(k) + \dots) dR_1 dR_2 d\theta dR_3 d\Omega \\ &+ \dots \end{aligned}$$

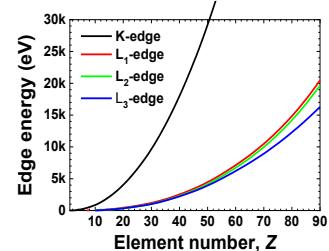


# Basics of X-ray Absorption Spectroscopy (XANES/EXAFS)



Fermi's Golden Rule:

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



X-ray absorption coefficient  $\mu(E)$ :

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

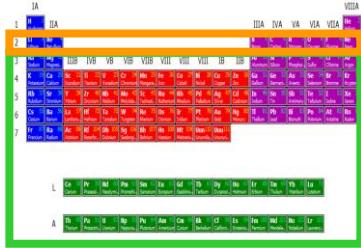
$$\mu(E) \propto \frac{I_{\text{fluo}}(E)}{I_0(E)}$$

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

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

# What can EXAFS Spectroscopy do?

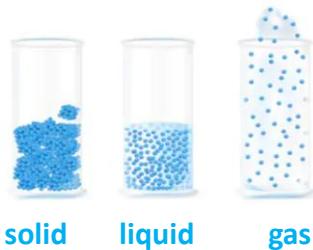
Most elements



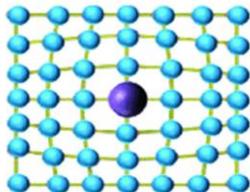
Extreme conditions  
pressure & temperature  
electric & magnetic fields



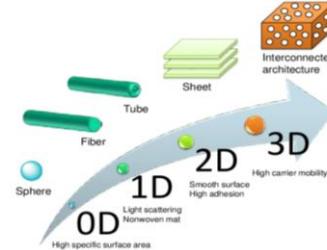
Any aggregation states



Diluted samples  
down to ~1 mmol/L

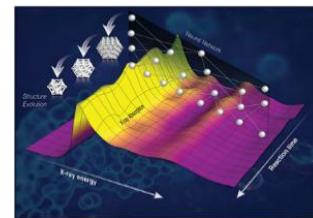


Any dimensionality

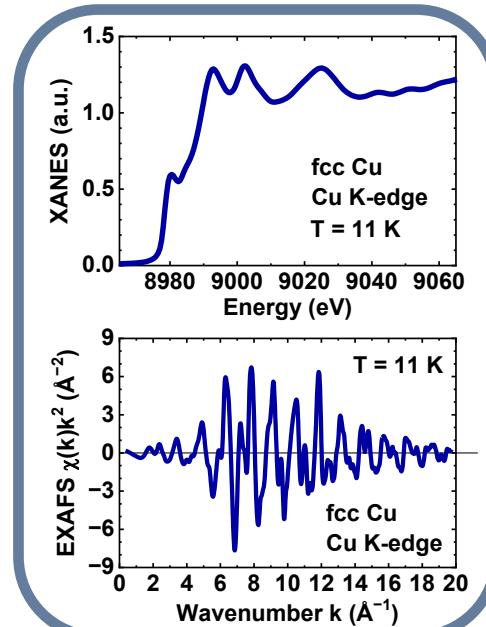
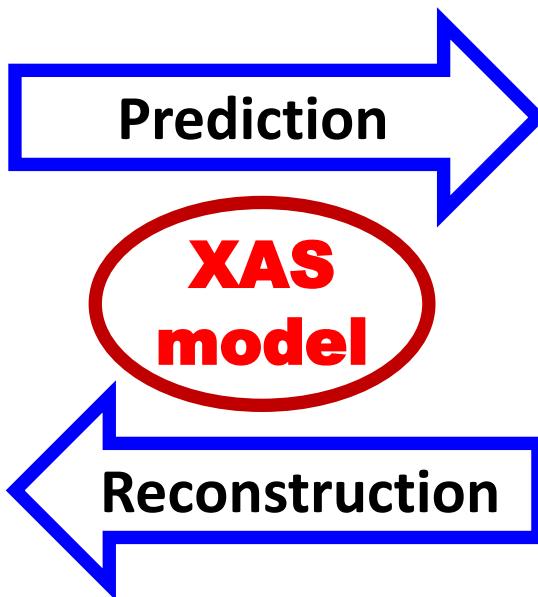
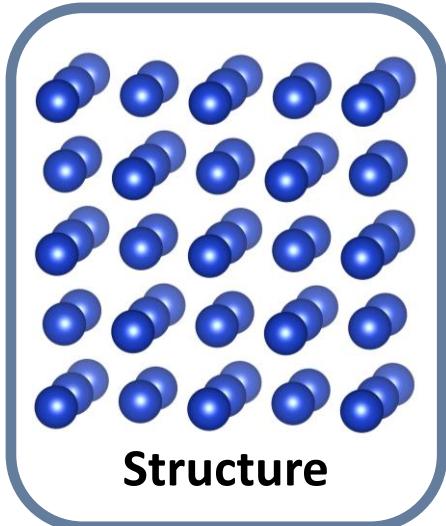


Time-dependent studies

- minutes
- ms
- down to ps (XFEL)



# Typical uses of X-ray Absorption Spectroscopy





# Basics of EXAFS Theory

## N-body expansion:

$$\begin{aligned}\chi(k) = & \int 4\pi R^2 \rho_0 g_2(R) (\chi_2^{oio}(k) + \chi_4^{oioio}(k) + \dots) dR \\ & + \iiint 8\pi^2 R_1^2 R_2^2 \sin(\theta) \rho_0^2 g_3(R_1, R_2, \theta) \\ & \times (2\chi_3^{oijo}(k) + 2\chi_4^{oijo}(k) + \chi_4^{oijio}(k) + \chi_4^{ojijo}(k) + \dots) dR_1 dR_2 d\theta \\ & + \iiint 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta) \rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega) \\ & \times (2\chi_4^{oikjo}(k) + 2\chi_4^{oikjo}(k) + 2\chi_4^{ojiko}(k) + \dots) dR_1 dR_2 d\theta dR_3 d\Omega \\ & + \dots\end{aligned}$$

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

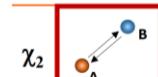
## Gaussian model:

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

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

## Multiple-scattering (MS) paths

### Single-scattering



### Double-scattering



### Triple-scattering

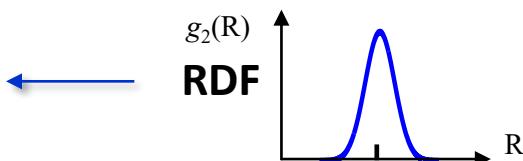


Conventional analysis

Advanced analysis

## N-body distribution functions

$\chi_2$	$\chi_3$	$\chi_4$
$g_2$	$g_3$	$g_4$





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

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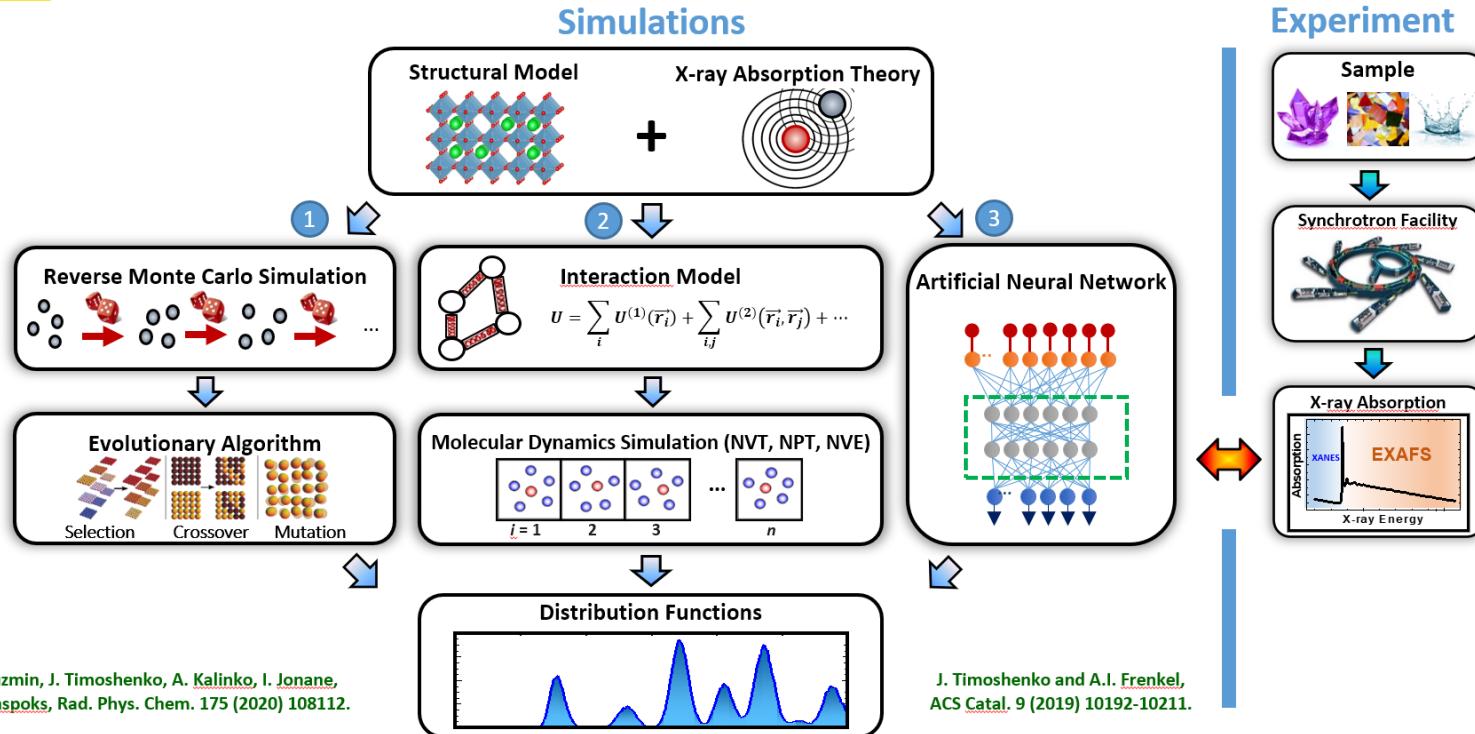
## Conventional analysis:

- Interatomic distances ( $\pm 0.02 \text{ \AA}$ )
- Coordination numbers ( $\pm 10\%$ )
- Mean square relative displacements (MSRD) ( $\pm 0.0005\text{--}0.002 \text{ \AA}^2$ )
- 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



# Computer Codes for XAS Analysis

## XAESA

SOFTWARE FOR X-RAY ABSORPTION AND EMISSION SPECTROSCOPY ANALYTICS

- Conventional XANES/EXAFS/RXES data treatment
- Analysis of the experimental EXAFS spectra using a multi-shell model or regularization-like method

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

## EDACA

SIMULATION-BASED MD-EXAFS ANALYSIS

- Based on Molecular Dynamics (MD) simulation of material's 3D structure
- Accounts for multiple-scattering effects and thermal disorder
- Ideally suited to validate theoretical models of interatomic potentials (force-fields/MLIPs/ab initio)

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

## EvAX

SIMULATION-BASED EXAFS ANALYSIS

- Based on reverse Monte Carlo (RMC) modeling of material's 3D structure
- Probes the local structural and thermal disorder in crystalline and nanocrystalline materials
- Fits the experimental EXAFS spectra in  $k$ - and  $R$ -spaces simultaneously using Morlet wavelet transform
- Accounts for multiple-scattering effects
- Ideally suited for multicomponent compounds

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

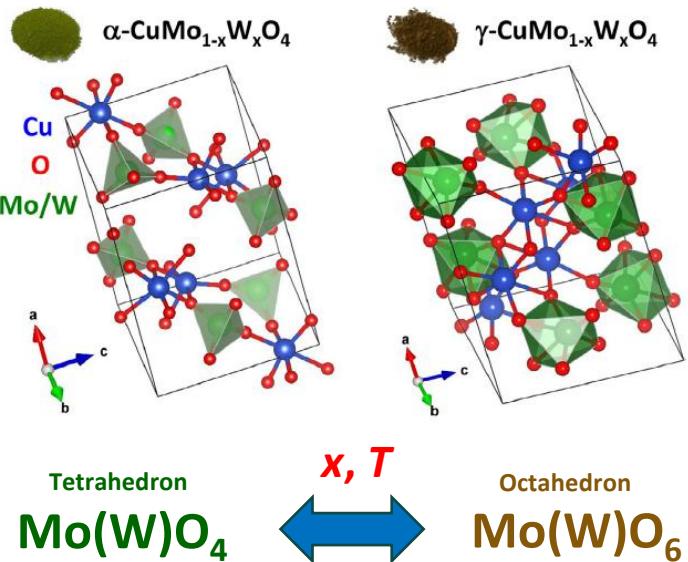


# X-ray Absorption Spectroscopy of Chromogenic Materials

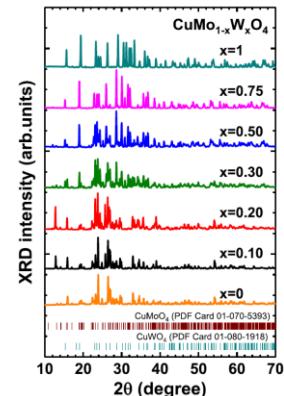
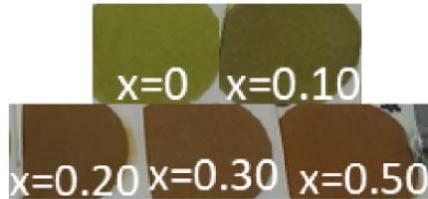
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1. Thermochromic copper molybdate and its solid solutions.
2. Structure of polaronic centers in proton-intercalated  $\text{AWO}_4$  scheelite-type tungstates.
3. Local structural distortions in photochromic yttrium oxyhydride.

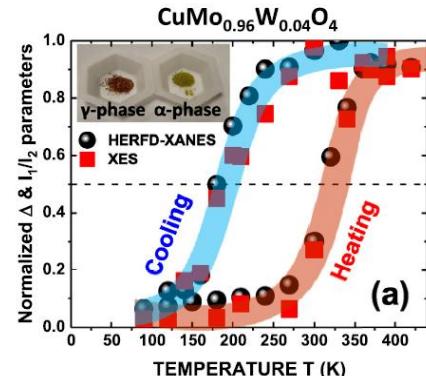
# Thermochromic Copper Molybdate and its Solid Solutions



## Effect of composition



## Effect of temperature



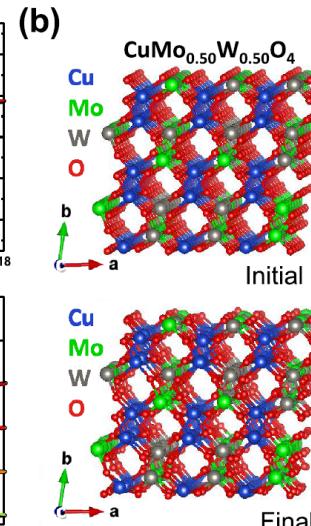
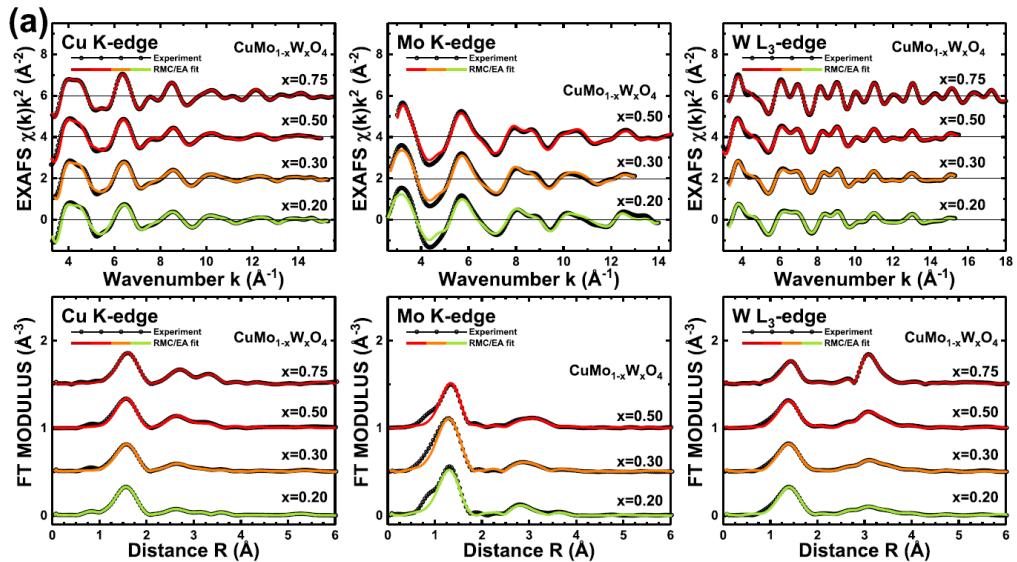
## Hysteretic phase transition

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<sub>3</sub>-W) RMC simulations

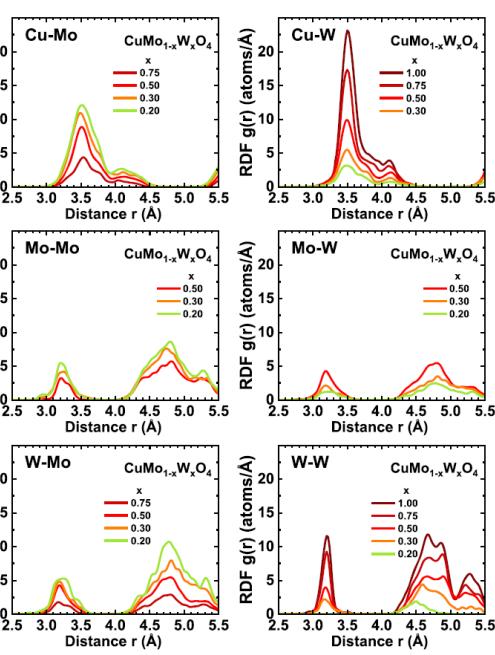
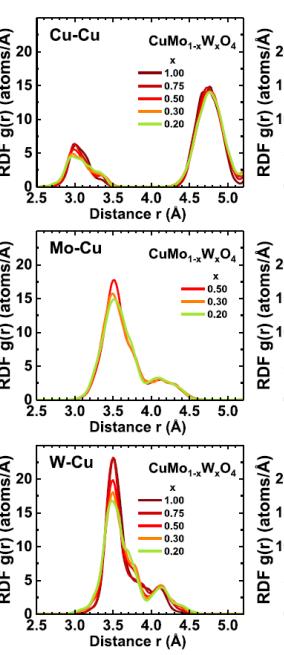
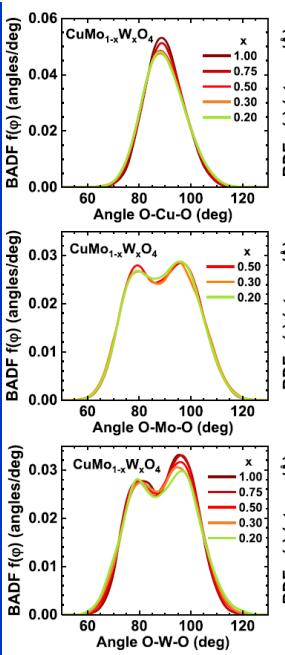
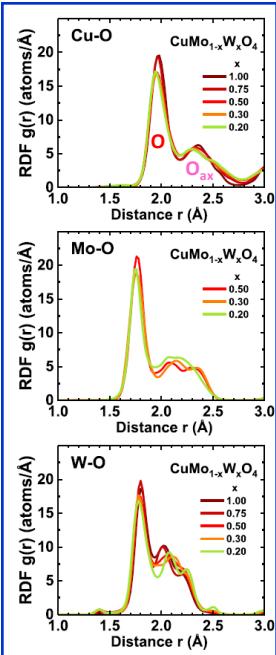
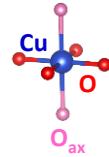


Single structural model!

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  $\text{Cu}^{2+}\text{O}_6$



Distorted  $\text{MoO}_6$

Distorted  $\text{WO}_6$

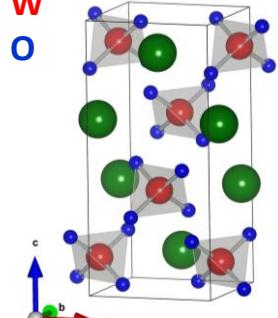
I. Pudza, A. Anspoks, G. Aquilanti, A. Kuzmin, Mater. Res. Bull. 153 (2022) 111910.

# Polaronic Centers in Proton-intercalated $\text{AW}^{6+}\text{O}_4$ Scheelite-type Tungstates



$\text{Ca/Sr/Ba}$

$\text{W}$   
 $\text{O}$



Tetragonal  $I4_1/a$  (no. 88)

Absorption edges:

$\text{L}_3\text{-W}$

$\text{K-Sr}$

$\text{L}_3\text{-Ba}$

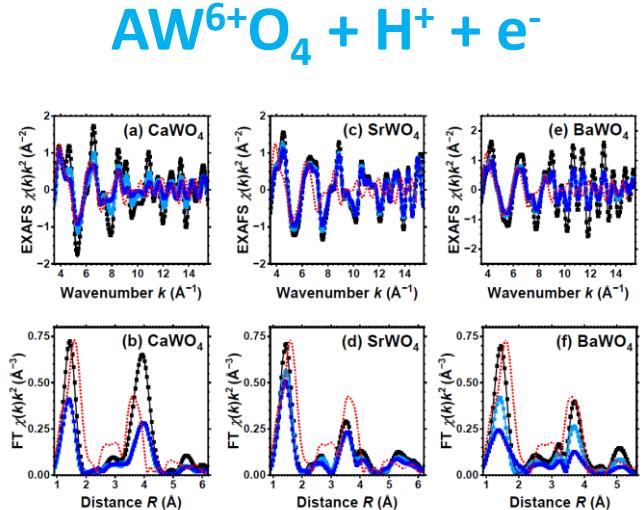
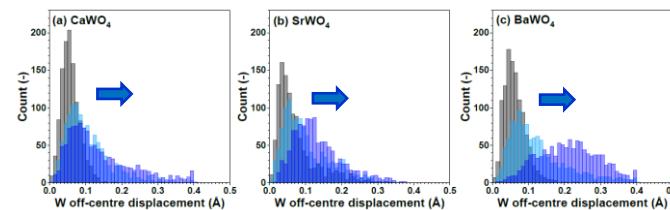
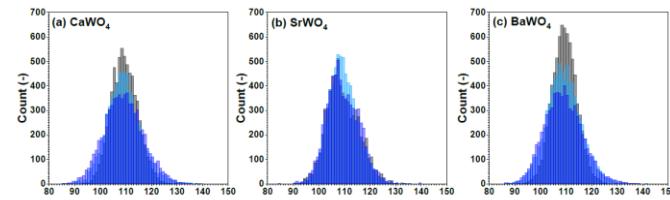
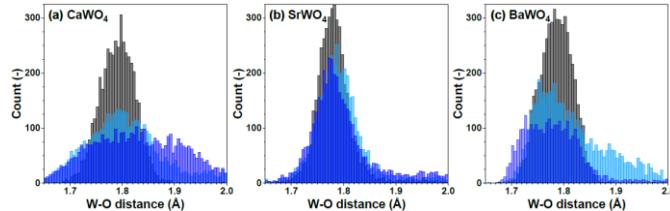


Figure 1. Experimental (symbols) and RMC/EA-simulated (solid lines) W  $\text{L}_3$ -edge EXAFS spectra  $\chi(k)k^2$  (upper panels) and their Fourier transforms (FTs) (lower panels) at 10 K for  $\text{CaWO}_4$  (a,b),  $\text{SrWO}_4$  (c,d), and  $\text{BaWO}_4$  (e,f). Black, light blue, and blue 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  $\text{L}_3$ -edge in  $\text{WO}_3 \cdot \text{H}_2\text{O}$ . See text for details.

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

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(Multi-edge) RMC simulations



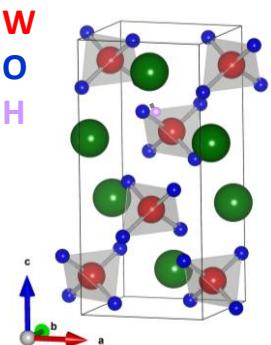
Tetrahedron  
 $\text{WO}_4$

W  
off-center

# Polaronic Centers in Proton-intercalated $\text{AWO}_4$ Scheelite-type Tungstates

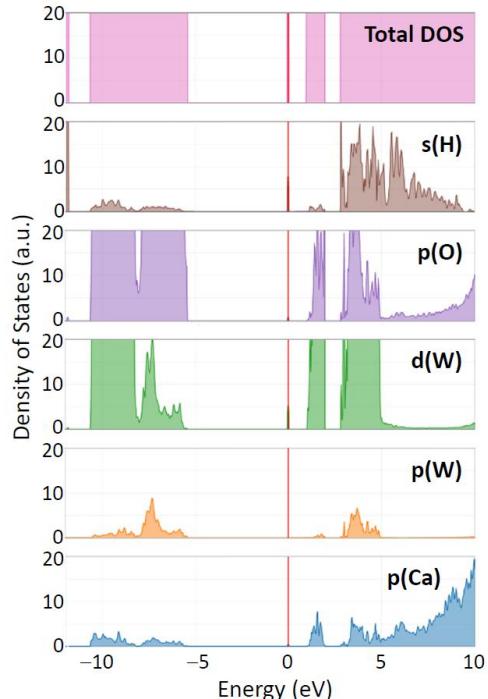


Ca/Sr/Ba



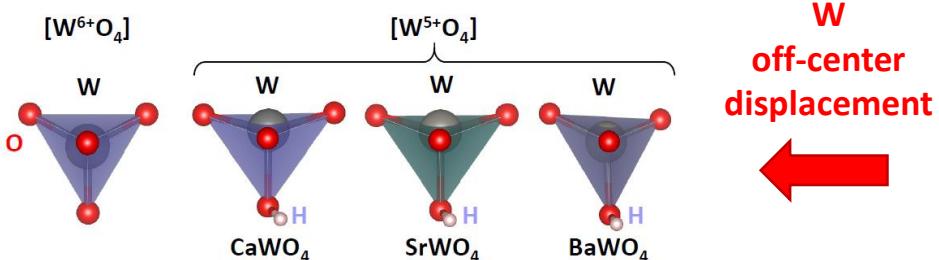
CRYSTAL17

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



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

	$\text{CaWO}_4$		$\text{SrWO}_4$		$\text{BaWO}_4$	
	Experiment	LCAO	Experiment	LCAO	Experiment	LCAO
$a$ ( $\text{\AA}$ )	5.2429	5.27	5.4168	5.47	5.6149	5.64
$c$ ( $\text{\AA}$ )	11.3737	11.34	11.951	11.88	12.7326	12.48
$x(\text{O})$	0.1507	0.157	0.2497	0.231	0.2295	0.226
$y(\text{O})$	0.0086	0.012	0.3425	0.105	0.1294	0.116
$z(\text{O})$	0.2106	0.211	0.1671	0.042	0.05024	0.045
$R(\text{W-O})$ ( $\text{\AA}$ )	1.78	1.79	1.78	1.79	1.78	1.79
$q(\text{A}^{2+})$		1.67		1.95		1.32
$q(\text{W}^{6+})$		2.79		2.77		2.75
$q(\text{O}^{2-})$		-1.11		-1.18		-1.02
$E_g$ (eV)	4.94	6.6	5.08	7.1	5.26	7.3



Regular  $[\text{W}^{6+}\text{O}_4]$  and distorted  $[\text{W}^{5+}\text{O}_4]$  tetrahedra in  $\text{CaWO}_4$ ,  $\text{SrWO}_4$ , and  $\text{BaWO}_4$  according to the DFT LCAO calculations.

Hydrogen (H) bound to the one of oxygen atoms is also shown.

# Photochromic Yttrium Oxyhydride (YHO)

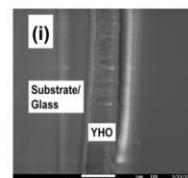
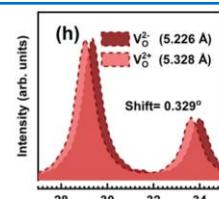
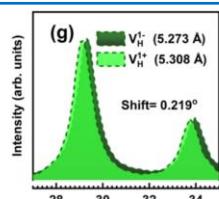
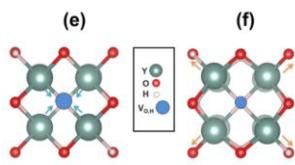
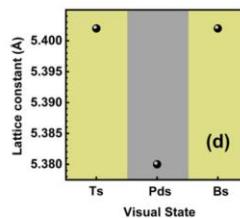
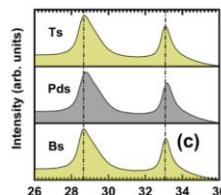
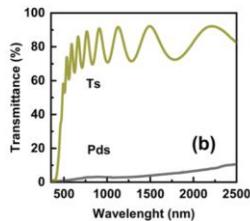
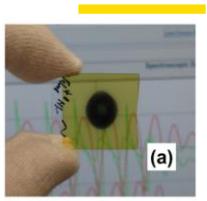
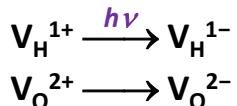


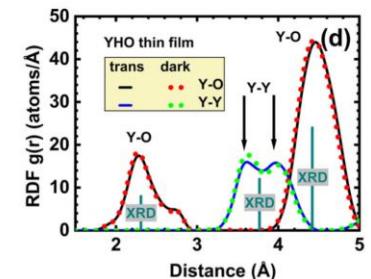
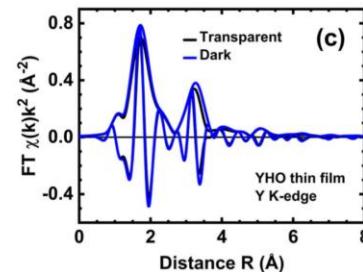
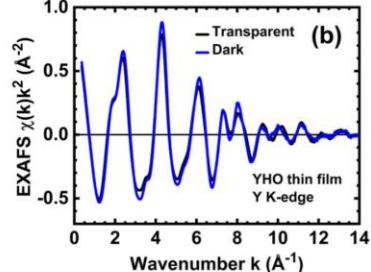
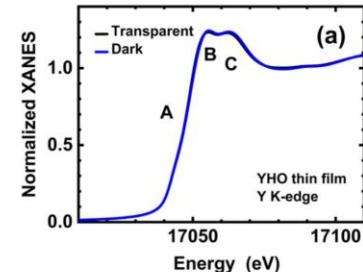
TABLE I. Refined structure parameters for yttrium oxyhydride powder from x-ray powder diffraction. Standard deviations are in parentheses. The cubic [space group  $Fm\bar{3}m$  (225)] lattice parameter  $a = 5.404(3)$  Å. Crystallite size  $d = 16(2)$  nm.

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



H. Arslan, I. Pudza, A. Kuzmin, S. Karazhanov, Appl. Phys. Lett. 124 (2024) 151901.

H. Arslan, A. Kuzmin, V. Kumar Kasi, I. Aulika, D. Moldarev, D. Primetzhofer, M. Wolff, I. Pudza, Ø. Nordseth, S. Karazhanov, Commun. Mater. 6 (2025) 154.

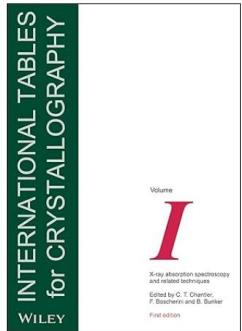




# CONCLUSIONS

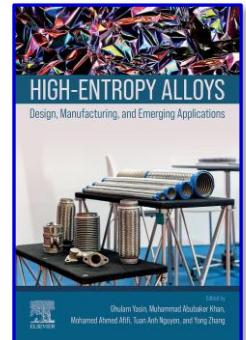
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- X-ray absorption spectroscopy is a versatile experimental method to study local atomic structure and its distortions in functional materials.
- Extraction of structural information remains challenging but can be handled based on advanced simulation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



J. Timoshenko and A. Kuzmin, *Reverse Monte Carlo and molecular-dynamics approaches to EXAFS analysis*, in International Tables for Crystallography, Volume I: X-ray Absorption Spectroscopy and Related Techniques, Eds. C. Chantler, F. Boscherini and B. Bunker (IUCr) (Wiley-Blackwell, 2024).

A. Kuzmin, *X-ray absorption spectroscopy in high-entropy material research*, in High-Entropy Alloys: Design, Manufacturing, and Emerging Applications, G. Yasin, M. Abubaker Khan, M. Afifi, T. Anh Nguyen, Y. Zhang (Eds.) (Elsevier, 2024).



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

The screenshot shows the homepage of the EXAFS Spectroscopy Lab website. At the top left is the logo 'EXAFS Lab' with a small globe icon. To its right is the text 'Institute of Solid State Physics, University of Latvia' and social media links for Facebook, LinkedIn, and YouTube. A QR code is also present. The main content area features a large blue banner with white wavy lines representing data analysis. Below the banner is a section titled 'About' with a detailed description of the lab's mission and research focus. On the left side, there is a sidebar with various navigation links and a central content area showing a grid of icons related to Structure, Modeling, Simulations, Spectroscopy, and Environments.

<https://www.facebook.com/EXAFSLab/>

The screenshot shows the Facebook page for 'EXAFS Spectroscopy Laboratory'. The cover photo features a blue wavy background with white data peaks. The page header includes the lab's logo and name. Below the header, it says '91 likes • 101 followers'. There are buttons for 'Professional dashboard' and 'Edit'. The sidebar on the left shows the page's profile picture, a list of posts, and other standard Facebook page controls.



# Thank you for your attention!



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INSTITUTE OF SOLID STATE PHYSICS  
UNIVERSITY OF LATVIA

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of Science project No. LZP-2023/1-0476.

