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Local structure studies of multifunctional $CuMoO_4$ and $CuWO_4$ solid solutions

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b DESY

http://www.dragon.lv/exafs

MOTIVATION I

M. Wiesmann, et al., J. Solid State Chem. 132 (1997) 88-97.
F. Rodríguez, et al., Phys. Rev. B 61 (2000) 16497.
M. Gaudon et al., Adv. Mater.19 (2007) 3517.
L. Robertson, et al., J. of Materials Chem. C 3 (2015) 2918-2924.
Q. Morelle, et al., Mater. Lett., 253 (2019) 140-143.

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T. G. Steiner, et al., J. Anal. Chem. 370 (2001) 731.
M. Gaudon, et al., Inorg. Chem. 46 (2007) 10200-10207.
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L. Robertson, et al., J. of Materials Chem. C 3 (2015) 2918-2924.
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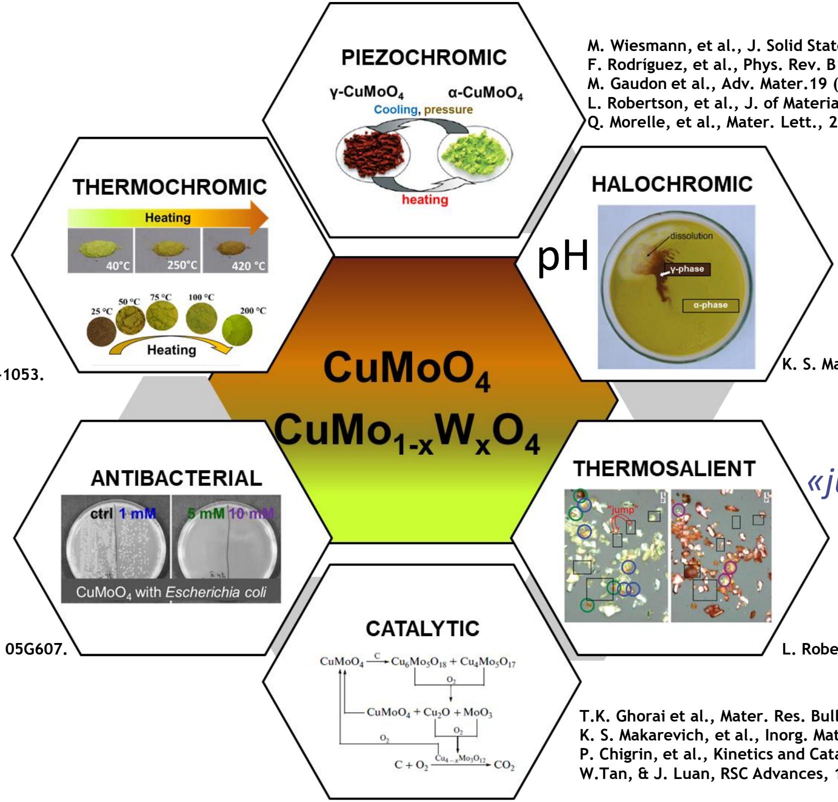

K. S. Makarevich, et al., Inorg. Mater. 46 (2010) 1359-1364.

«jumping crystal effect»

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L. Robertson, et al., J. of Materials Chem. C 3 (2015) 2918-2924.

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K. S. Makarevich, et al., Inorg. Mater. 46 (2010) 1359.
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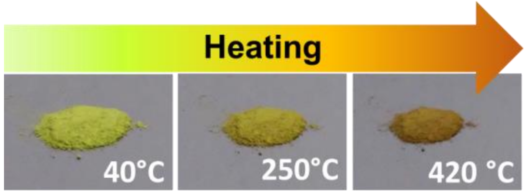
W.Tan, & J. Luan, RSC Advances, 10 (2020) 9745-9759.

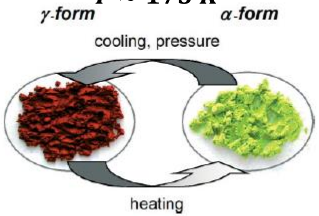
MOTIVATION II

Thermochromism

$CuMoO_4$

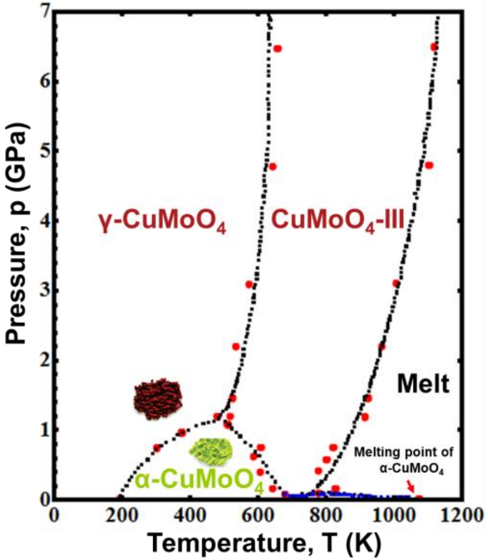


$T \approx 175\ K$



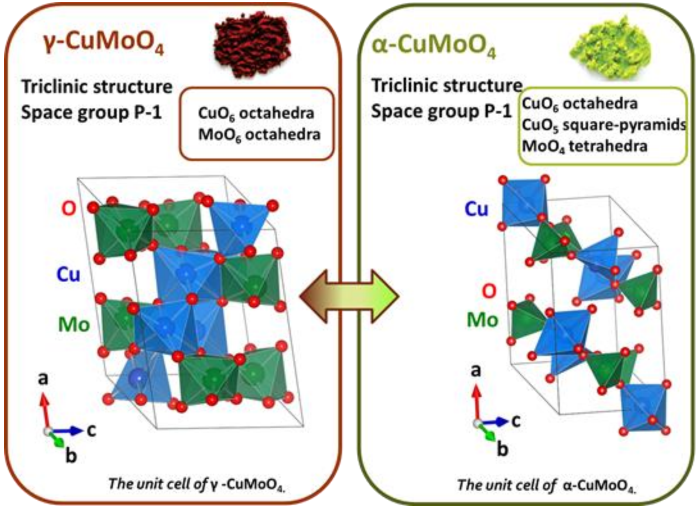
$T \approx 250\ K$

P-T diagram



M. Wiesmann, et al., J. Solid State Chem. 132 (1997) 88.

Structure



$\Delta V \approx 12 - 13\%$

MOTIVATION III

Hysteresis

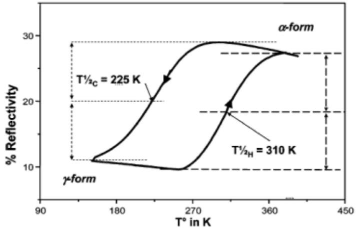


Figure 6. Evolution of the integrated reflectivity percentage in the green zone (500−550 nm) of $CuMo_{0.97}W_{0.03}O_4$ compound with temperature.

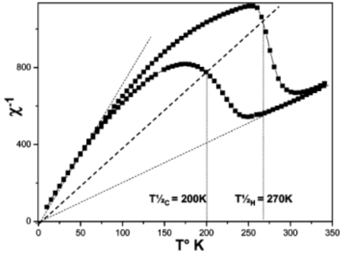


Figure 8. Evolution of the magnetic susceptibility of the $CuMo_{0.95}W_{0.05}O_4$ compound with the temperature.

M. Gaudon, et al., Inorg. Chem. 46 (2007) 10200-10207.
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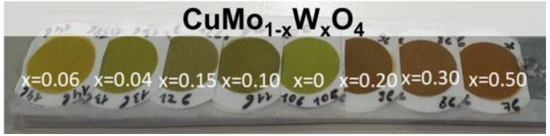
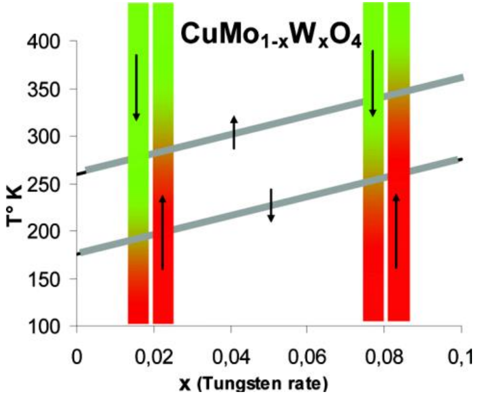
Adaptable thermochromism





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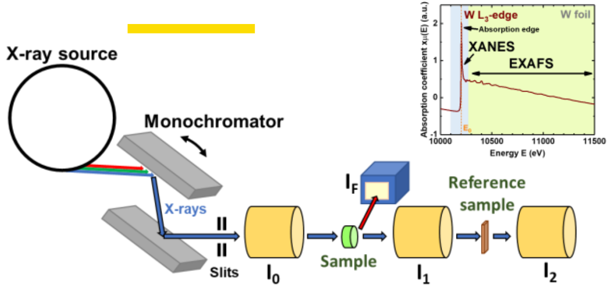
Questions

-Can we detect the hysteresis of the phase transition by probing the local structure of the material?

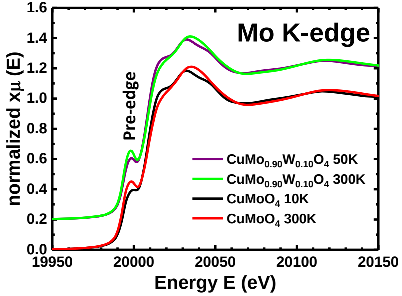
-What is the role of W in these solid solutions?

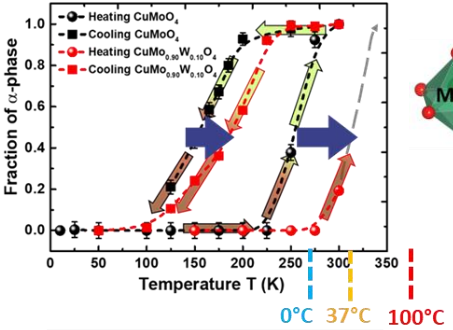
X-RAY ABSORPTION SPECTROSCOPY STUDY

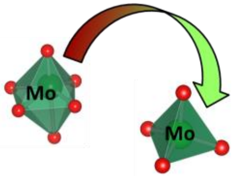


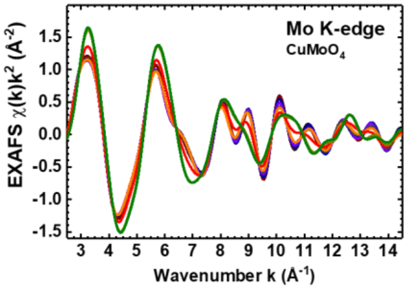
XANES – X-ray Absorption Near-Edge Structure
EXAFS – Extended X-ray Absorption Fine Structure

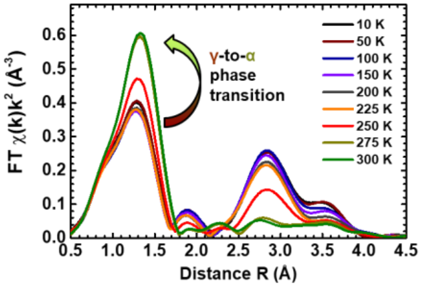
PETRA III beamline P65











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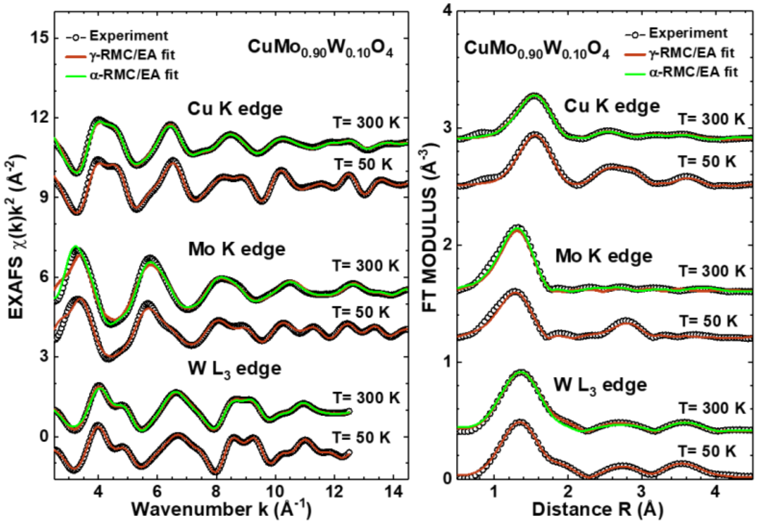
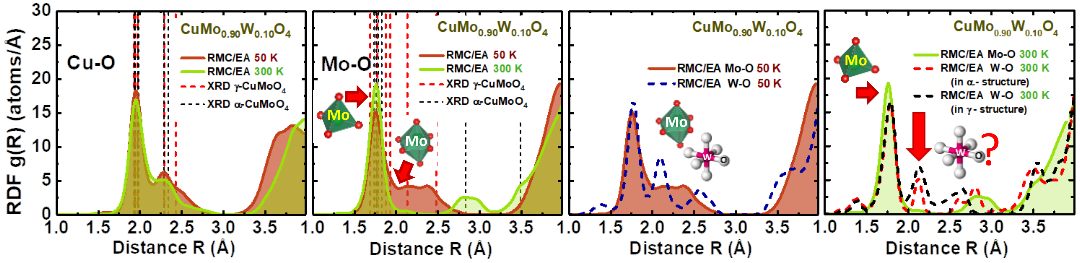
I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Rad. Phys. Chem. 175 (2020) 108411.

X-RAY ABSORPTION SPECTROSCOPY STUDY

Results from Reverse Monte Carlo (RMC) calculations





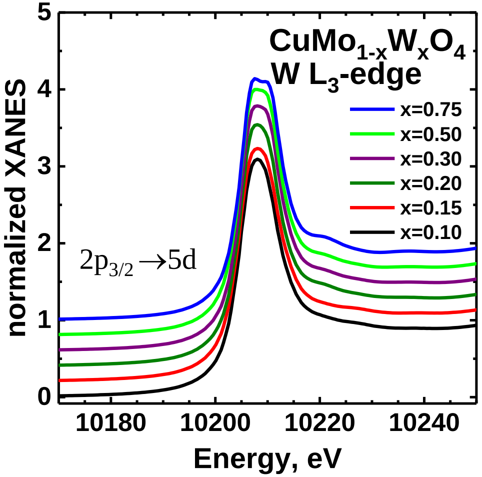
At 300 K, structural model with W initially in octahedral coordination (γ-phase) gives slightly better agreement with the experiment!

In γ phase W environment is similar to Mo and it is octahedral.
In α phase W tends to have more distorted environment than Mo.

I. Jonane, A. Anspoks, G. Aquilanti, A. Kuzmin, Acta Mater. 179 (2019) 26-35.
I. Jonane, A. Cintins, A. Kalinko, R. Chernikov, A. Kuzmin, Rad. Phys. Chem. 175 (2020) 108411.

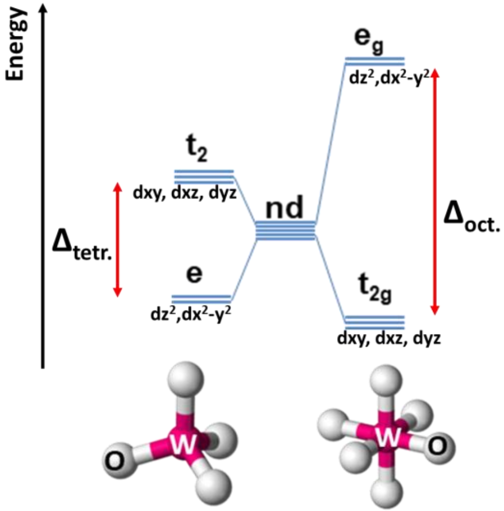
W L_3-EDGE: EXPERIMENT VS. THEORY

Experiment



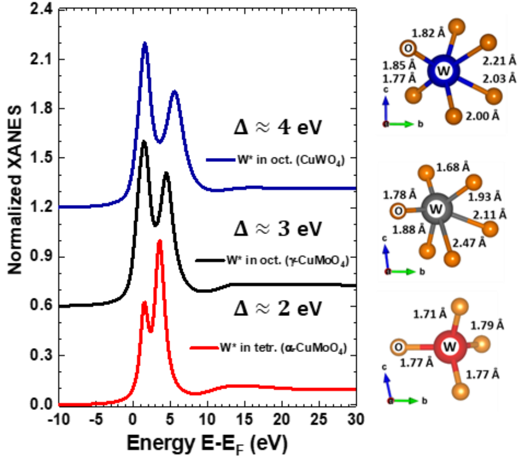
$$2p_{3/2}\ \Gamma_{hole} \approx 4.57\ eV$$

Crystal field splitting



$e:t_2 = 2:3$ $t_{2g} : e_g = 3:2$

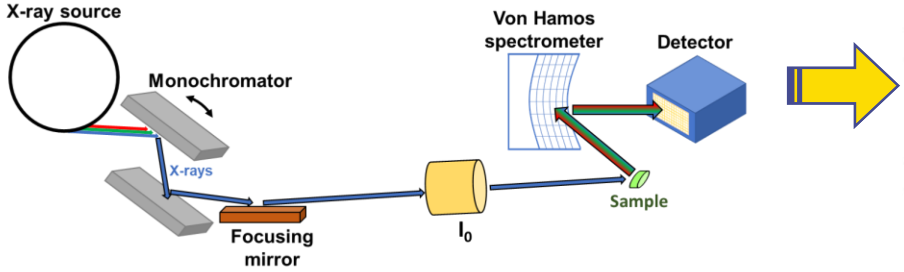
FDMNES

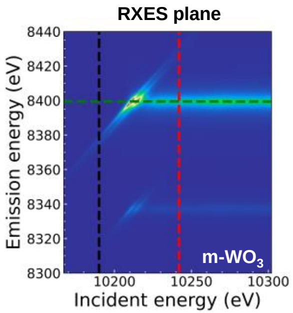


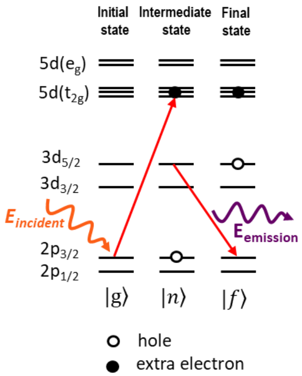
$$\Gamma_{hole} = 1\ eV$$

RESONANT X-RAY EMISSION SPECTROSCOPY EXPERIMENT

PETRA III P64 Advanced X-ray Absorption Spectroscopy beamline







Experimental details:

- High flux ($5 \cdot 10^{11}$ photons/s)
- Si(311) monochromator
- 100x240 μm focused beam
- Von Hamos-type spectrometer with Si(444) analyzer crystals
- Dectris 2D Pilatus 300 K detector (High-resolution < 1 eV)
- Liquid nitrogen cryostat Linkam THMS600 for low T measurements

$$2p_{3/2}\ \Gamma_{hole} \approx 4.57\ eV$$

$$3d_{5/2}\ \Gamma_{hole} \approx 2.01\ eV$$

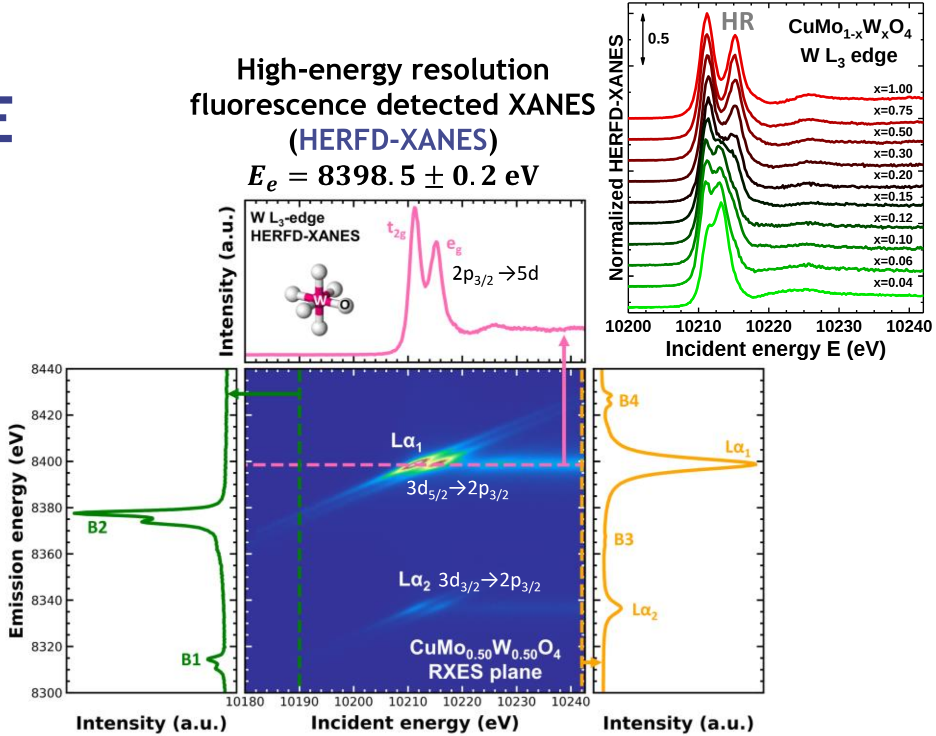
W.A. Caliebe, et al., AIP Conf. Proc. 2054 (2019) 060031.
A . Kalinko, et al., J. Synchrotron Rad. 27 (2020) 31-36.

Experimental resolution is of the order of the core hole lifetime broadening.

RXES PLANE

High-energy resolution fluorescence detected XANES (HERFD-XANES)

$E_e = 8398.5 \pm 0.2$ eV



Below the resonance

$E_i = 10190$ eV

Above the resonance

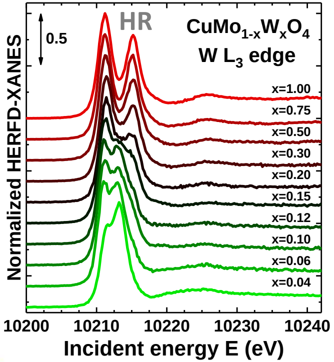
$E_i = 10242$ eV

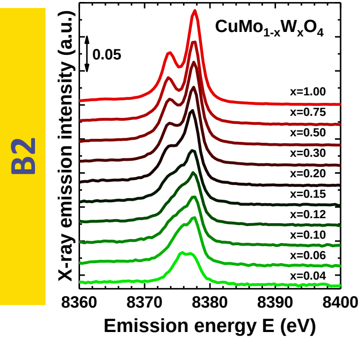
High-energy resolution off-resonant X-ray emission spectra

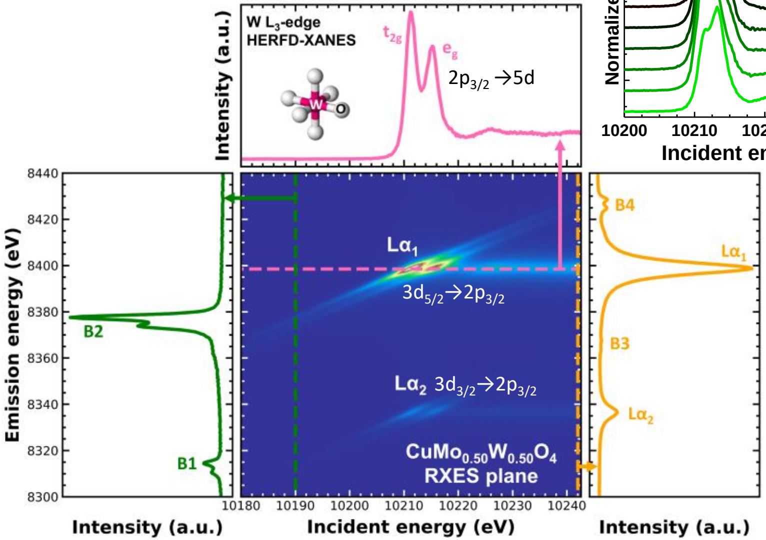
RXES PLANE

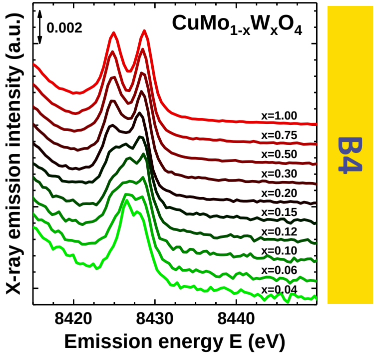
High-energy resolution fluorescence detected XANES (HERFD-XANES)

$E_e = 8398.5 \pm 0.2$ eV









Below the resonance

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Above the resonance

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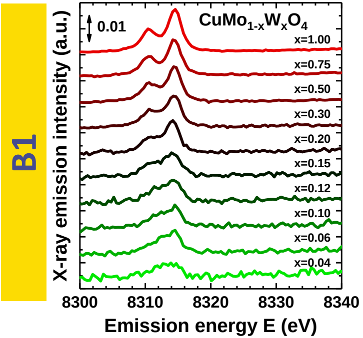
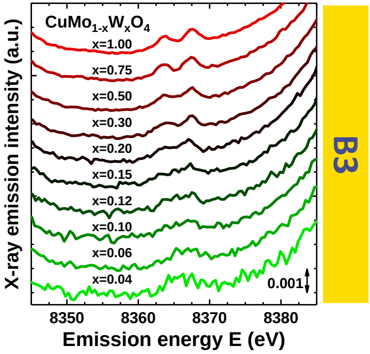
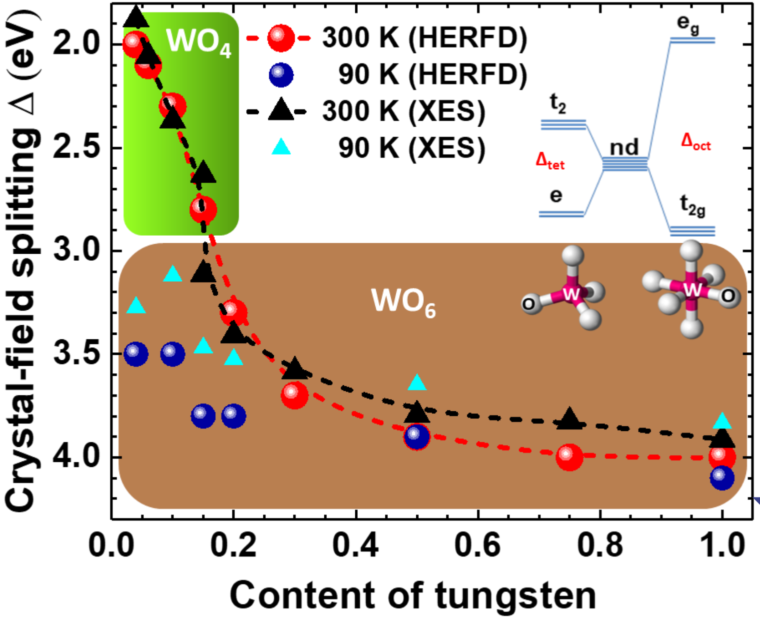


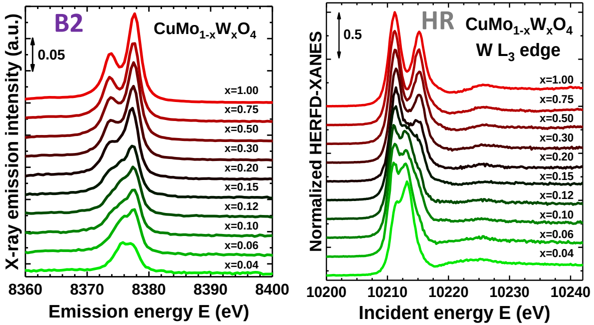


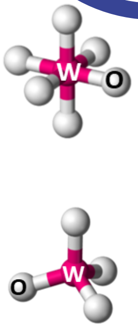
High-energy resolution off-resonant X-ray emission spectra

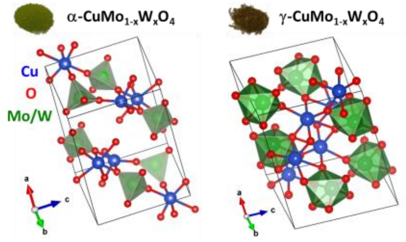
RESULTS – COMPOSITION EFFECT



$E_i = 10190\ eV$

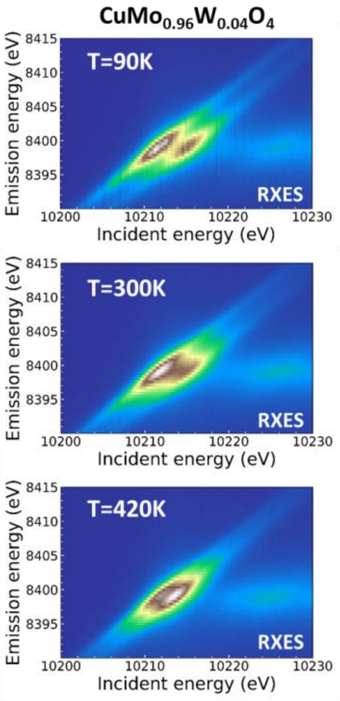


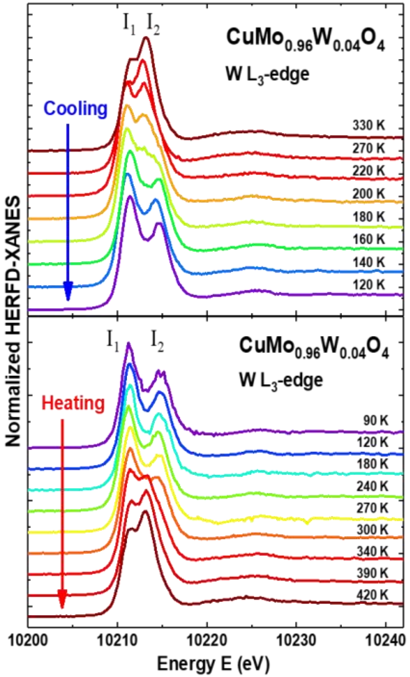


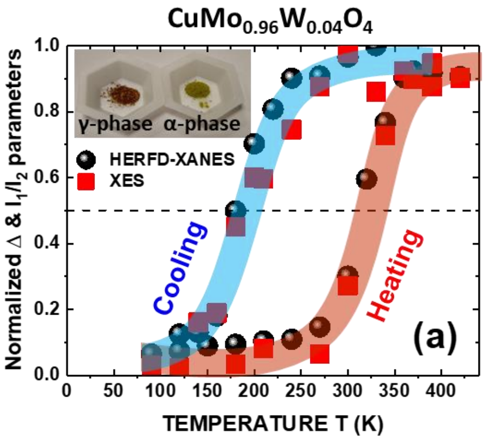


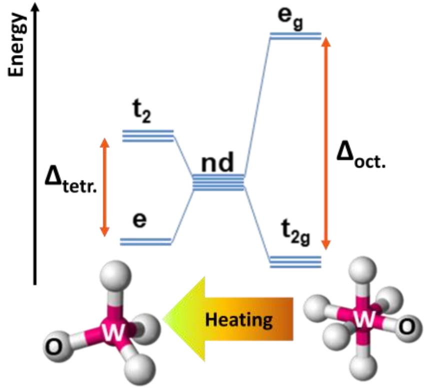
W ions in $CuMo_{1-x}W_xO_4$ solid solutions have octahedral coordination for x>0.15 at all temperatures, whereas their coordination changes from tetrahedral to octahedral upon cooling for smaller tungsten content. Nevertheless, some amount of tungsten ions co-exists in the octahedral environment at room temperature for x<0.15.

RESULTS – TEMPERATURE EFFECT





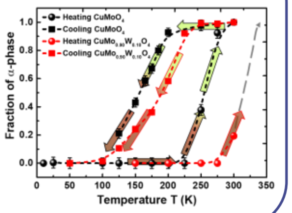




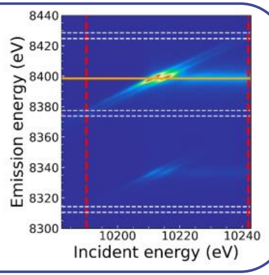
RXES measurements were successfully employed to determine the hysteretic behaviour of the structural phase transition between the α and γ phases in $CuMo_{1-x}W_xO_4$ solid solutions on cooling and heating.

SUMMARY

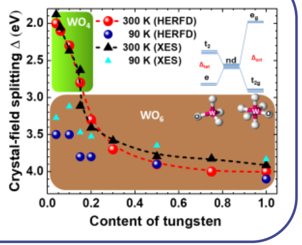
Analysis of the **Mo K-edge** XANES and EXAFS data allows one to reconstruct the **hysteresis** that describes the phase transition.



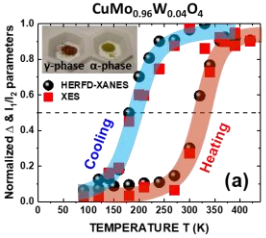
The analysis of the RXES planes shows a clear advantage over conventional XANES due to revealing spectral features with much **higher resolution**.



The analysis of the RXES plane provides useful bulk sensitive information on the coordination of tungsten atoms and allows one to determine the **crystal-field splitting parameter** Δ for the 5d(W)-states.



RXES method is well suited for **in-situ measurements** and was used here to determine the hysteretic behaviour of the first-order structural phase transition between α and γ phases in $CuMo_{1-x}W_xO_4$ solid solutions on cooling and heating, even at low (x < 0.10) tungsten content.



For more details:

I. Pudza, A.Kalinko, A. Cintins, A.Kuzmin, Acta Mater. 205 (2021) 116581.

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FLPP
FUNDAMENTĀLO UN LIETIŠĶO PĒTĪJUMU PROJEKTI

THANK YOU

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