Direct observation of crystal field splitting in tungstates by resonant X-ray emission spectroscopy

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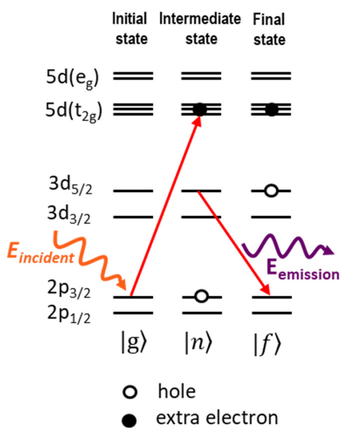
Abstract

A splitting in the energy levels of the *d*-orbitals of transition metal due to the presence of ligands depends on the local symmetry and is known as crystal field splitting. Here, we demonstrate the use of the resonant X-ray emission spectroscopy (RXES) to probe the crystal field splitting in a series of AWO_4 (A=Mg, Ca, Mn, Zn, Cd, Sn, Pb) tungstates with the tetrahedral and octahedral coordination of tungsten atoms.

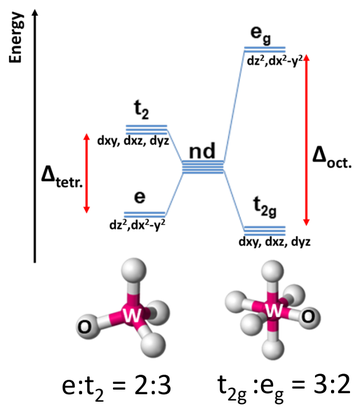
Introduction

Resonant X-ray emission spectroscopy (RXES) is a photon-in/photon-out X-ray technique which provides information on the electronic states [1] and elemental excitations (phonons, magnons, etc) [2] in a material exploiting both the energy and momentum dependence of the photon scattering cross section. The technique requires a tunable high-flux X-ray source as synchrotron and is element and orbital specific, bulk sensitive, and needs only small sample volumes.

Recently, we have employed the hard RXES with synchrotron radiation from PETRA-III storage ring to study phase transitions in $CuMo_{1-x}W_xO_4$ solid solutions [3]. The method allows one to measure the high-energy resolution fluorescence detected W L_3-edge X-ray absorption near-edge structure (HERFD-XANES) with a resolution of $\Gamma_{\text{core-hole}}(3d_{5/2}) \approx 2.01$ eV significantly better compared to the $\Gamma_{\text{core-hole}}(2p_{3/2}) \approx 4.57$ eV in the conventional XANES.

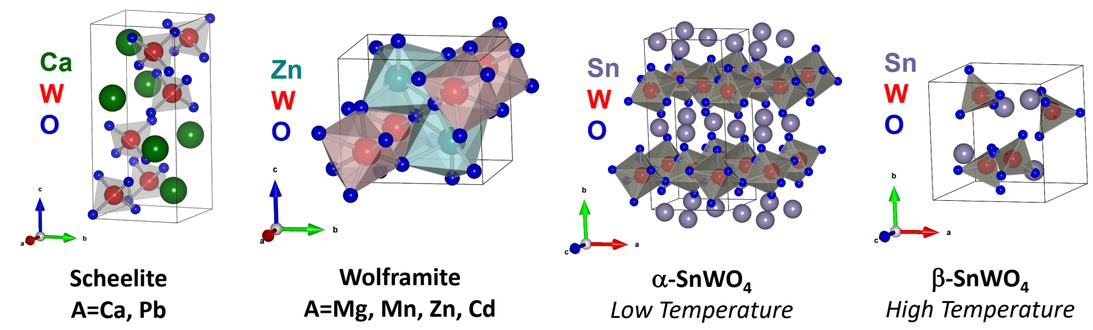


2p3d RXES experiment



Crystal field splitting

In this study, we demonstrate the ability of the RXES method to measure the crystal field splitting Δ_{cf} in a series of **AWO_4** (A=Mg, Ca, Mn, Zn, Cd, Sn, Pb) tungstates with the tetrahedral and octahedral coordination of tungsten atoms.



Scheelite
A=Ca, Pb

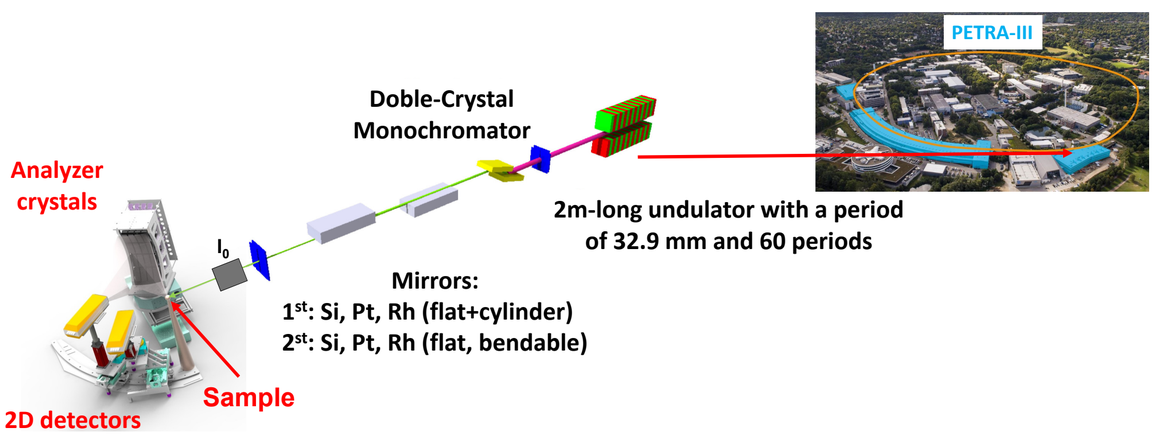
Wolframite
A=Mg, Mn, Zn, Cd

α-$SnWO_4$
Low Temperature

β-$SnWO_4$
High Temperature

Experimental

High-Energy Resolution von-Hamos X-ray Emission Spectrometer at the P64 beamline [4]



Spectrometer specifications

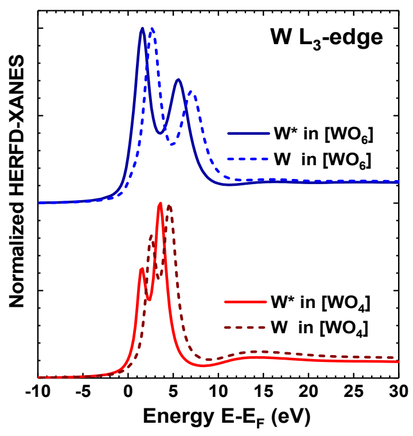
- Incident energy: **4.5 – 40 keV**
- Emission energy: **4.5 – 20 keV**
- Dispersion: **20 – 300 eV**
- Resolution: **0.15 – 1 eV**
- Bragg angles: **50° – 82°**

Analyzer crystals

- 300μm **Si(311)**
- 6 crystals simultaneously

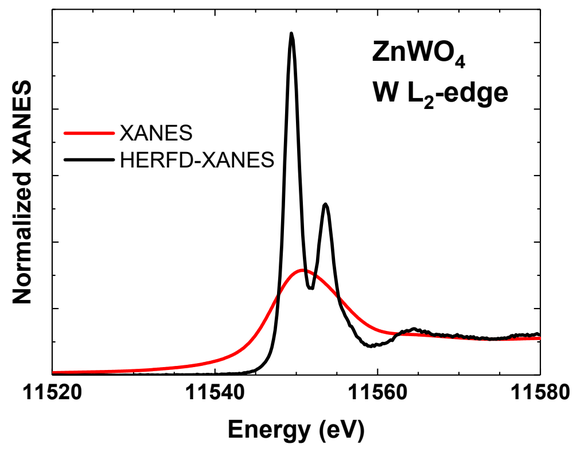
230×100 μm focused beam

Results



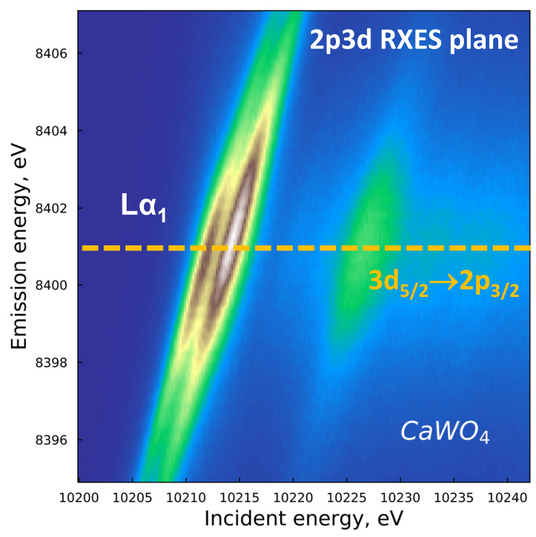
Calculated by the FDMNES code [5] W L_3-edge XANES spectra for octahedral [WO_6] and tetrahedral [WO_4] coordination.

The results for the excited state with the core hole (W∗ , solid curves) and non-excited state without the core hole (W, dashed curves) are shown.

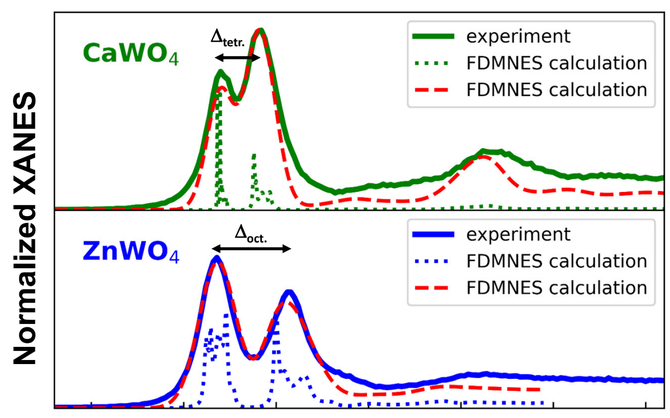


Comparison of the conventional W L_2-edge XANES and HERFD-XANES for octahedral [WO_6] coordination in $ZnWO_4$.

The high energy resolution of the HERFD-XANES spectra is due to the small value of the core hole lifetime broadening $\Gamma_{\text{core-hole}}(3d_{3/2})$ in the final state.

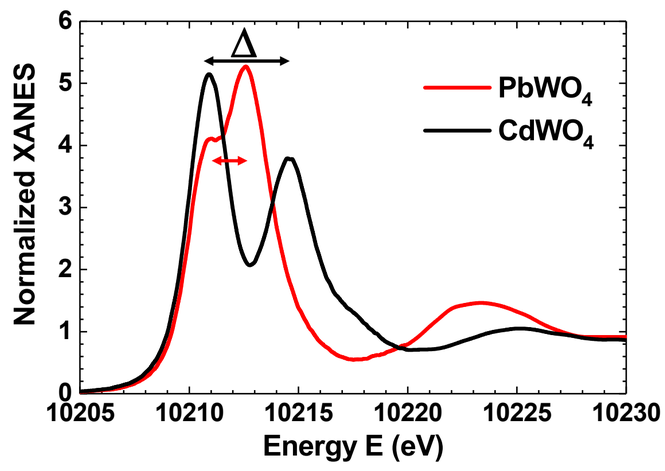


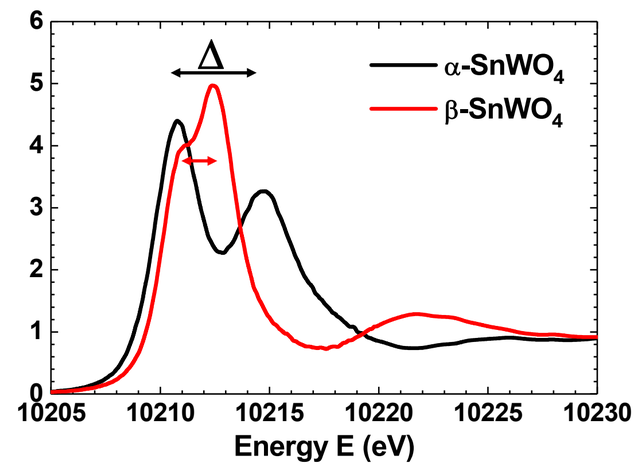
Resonant X-ray emission spectroscopy (RXES) map for $CaWO_4$ measured by detecting W $L\alpha_1$ emission while scanning across W L_3-edge. RXES map is plotted as a function of the incident and emitted photon energy.

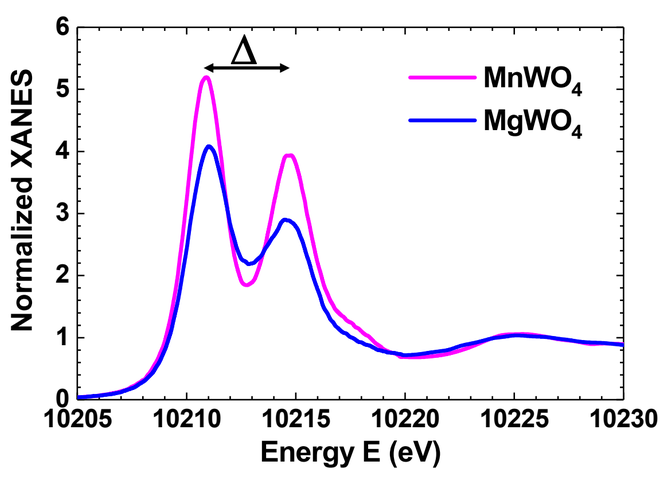


High-energy resolution fluorescence detected XANES (HERFD-XANES).

The results of the calculations by the FDMNES code [5] with (dashed curves) and without (dotted curves) broadening are shown.







Crystal field splitting

	Δ (eV)	
$CaWO_4$	2.1	[WO_4]
$PbWO_4$	1.8	
β-$SnWO_4$	1.3	
$MgWO_4$	3.6	[WO_6]
$MnWO_4$	3.9	
$ZnWO_4$	4.0	
$CdWO_4$	3.7	
α-$SnWO_4$	3.9	

Conclusions

- **High-energy resolution fluorescence detected W L_3-edge X-ray absorption near-edge structure (HERFD-XANES) spectra provide information on the crystal field splitting parameter Δ in tungstate compounds with the formula AWO_4.**
- **The values of $\Delta_{tetr.}$=1.3-2.1 eV, while $\Delta_{oct.}$=3.6-4.0 eV.**
- **The ratio $\Delta_{tetr.}/\Delta_{oct.} \approx 0.45$ is in agreement with the prediction by the crystal field theory for similar ligands $\Delta_{tetr.}/\Delta_{oct.} = 0.44$.**

References

[1] P. Glatzel, M. Sikora, G. Smolentsev, M. Fernández-García, Catal. Today 145 (2009) 294-299.
[2] L.J.P. Ament, M. van Veenendaal, T. P. Devereaux, J. P. Hill, Rev. Mod. Phys. 83 (2011) 705.
[3] I. Pudza, A. Kalinko, A. Cintins, A. Kuzmin, Acta Mater. 205 (2021) 116581.
[4] A. Kalinko, W. A. Caliebe, R. Schoch, M. Bauer, J. Synchrotron Rad. 27 (2020) 31-36.
[5] Y. Joly, Phys. Rev. B 63 (2001) 125120.

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