



	Experiment title: Valence band electronic structure of magnetoresistive 5d transition metal oxides	Experiment number: HE- 2789
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Shifts: 18	Local contact(s): Marcin Sikora	<i>Received at ESRF:</i>
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Report:

The experiment started with a systematic measurements of non-resonant $5d_{5/2} \rightarrow 2p_{3/2}$ X-ray emission spectra (XES) of tungsten in the series of sulfide and oxide reference compounds were performed in order to probe the sensitivity of the technique to the elemental and symmetric evolution of the first coordination shell. The revealed that, as expected for heavy Z ions, the valence band structure is hardly affected by the evolution of local neighborhood. Typical spectrum resemble that of WO_3 , while only WO_2 shows a considerable difference. Therefore further measurements of the full RIXS planes were performed only using oxide references.

The full $2p_{3/2}5d_{5/2}$ RIXS planes of WO_3 , ReO_3 , WO_2 , and ReO_2 (Fig. 1) were measured and compared to the results obtained for $A\text{FeReO}_6$ ($A=\text{BaSr}, \text{Sr}_2, \text{Ca}_2$) magnetoresistive double perovskites. With decreasing formal charge of the $5d$ ions (from ReO_2 to WO_3) the RIXS spectral width in the excitation energy (unoccupied states) is increasing with simultaneous decrease in the energy transfer (occupied states) as expected for decreasing occupation of the $5d$ band due to metal to ligand charge transfer effect. Moreover, a gradual shift in the spectral intensity towards lower energy transfer with rising formal charge is observed, which is attributed to the closing of the band gap and increase of the $5d$ DOS at the Fermi level. Possible indications of $d-d$ excitations at low energy transfer are currently investigated by means of 2D fitting of the experimental spectra using Kramers-Heisenberg equation and non-resonant X-ray emission and absorption spectra (XAS).

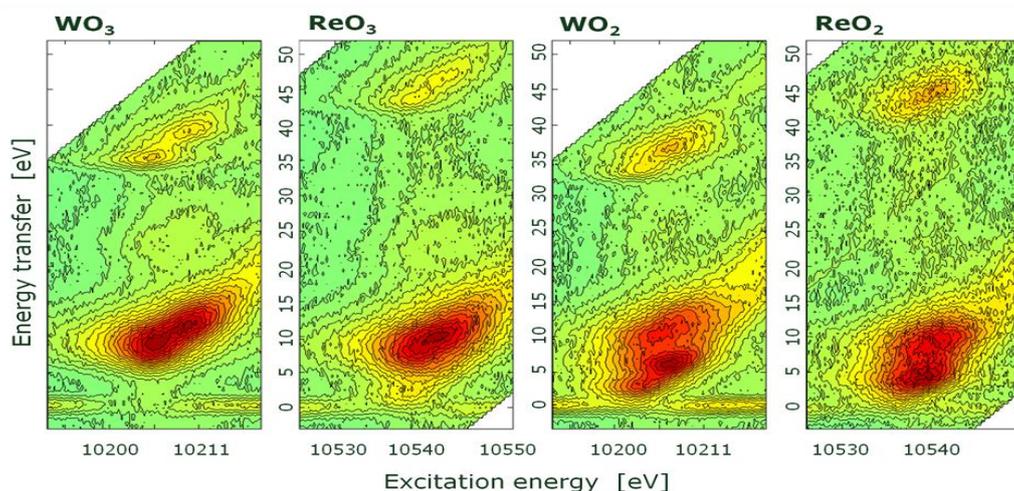


Figure 1.
 $2p_{3/2}-5d_{5/2}$ RIXS spectra of
 WO_3 ($5d^0$), ReO_3 ($5d^1$),
 WO_2 ($5d^2$), and ReO_2 ($5d^3$).

All the spectral features of the non-resonant XES and XAS can be qualitatively reproduced using band structure calculations based on multiple-scattering approach (FEFF 8.4) providing a semi-quantitative way for their detailed analysis (Fig. 2). Both, the excitation and emission energy scales shown in figure were shifted by the same amount for W and Re spectra, respectively. The binding energy scale is taken from calculations (and shifted down by 6.5eV). Further analysis, including DOS broadening and fine shape fitting as well as non-muffin-tin calculations, is in progress.

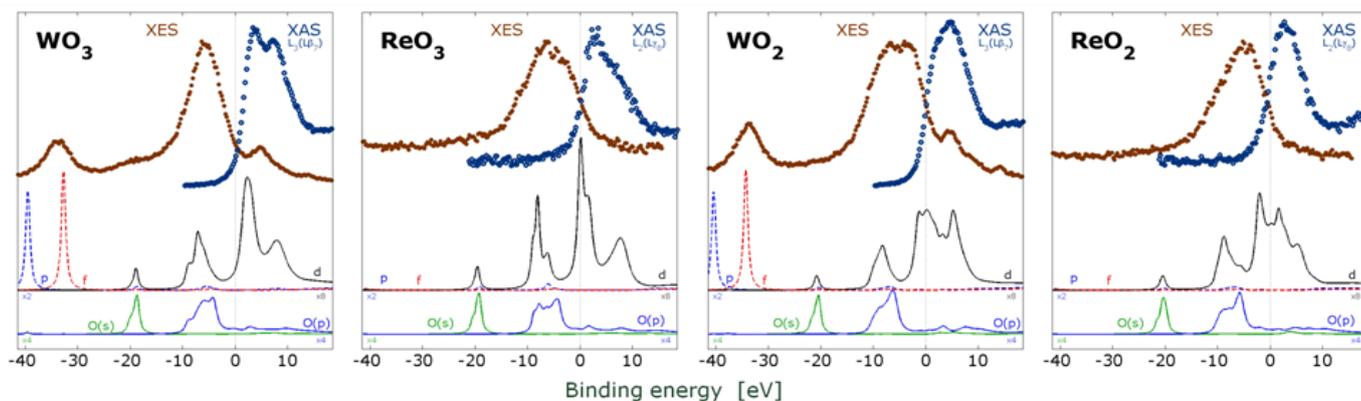


Figure 2. $L\beta_{sat}$ & $L\gamma$ emission and high resolution fluorescence detected $L_{2,3}$ absorption spectra of WO_3 , ReO_3 , WO_2 , and ReO_2 powder samples compared with DOS calculations.

Preliminary results of the experiment were published in: P. Glatzel, M. Sikora, G. Smolentsev, M. Fernandez-Garcia, *Hard X-ray photon-in photon-out spectroscopy*, *Catalysis Today* **145**, 294 (2009), doi:10.1016/j.cattod.2008.10.049.

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