Study of the Electronic Structure of Rhenium and Tungsten Oxides on the O K-Edge


aInstitute of Solid State Physics, Kengaraga street 8, LV-1063 Riga, Latvia
bLURE, Université Paris-Sud, Bât. 209D, 91405 Orsay Cedex, France

Abstract. Oxygen K-edge x-ray absorption spectra were studied on the electrochromic amorphous thin film a-WO3 in the comparison with crystalline oxides having variable electronic (d°, d, d2) and atomic structure: monoclinic m-WO3 (insulator - d°), cubic Na0.6WO3 (metal - d1), cubic ReO3 (metal - d1), layered-type hexagonal h-WO3, WO3H2O and with intercalated H2ReO3 (metal - d2), H2WO3 oxides having a metal-isulating transition. The changes in the XANES range 10-15 eV above the absorption edge are interpreted based on the known band-structure calculations. The high-energy features are related to the multiple-scattering processes (EXAFS) on the nearest atoms. The intensity of the feature at 550-560 eV is attributed for the first time to the value of the metal-oxygen-metal bond angle.

1. Introduction
X-ray absorption spectroscopy (XAS) studies on the O K-edge have been intensively conducted during the last years on 3d transition metal (TM) oxides and perovskites [1, 2]. However, there are only few contributions related to the O K-edge in 5d TM oxide compounds (Na0.6WO3 [3] and WO3 [4, 5], which were performed using electron energy loss spectroscopy (EELS). Here we present the XAS results on the O K-edge in 5d perovskite-type compounds (ReO3, H2ReO3, m-WO3, H2WO3 and Na0.6WO3), layered-type compounds (hex-WO3 and WO3H2O), and evaporated electrochromic amorphous thin film a-WO3. The results are obtained with high-resolution using synchrotron radiation. The first group of studied compounds (ReO3, H2ReO3, m-WO3, H2WO3 and Na0.6WO3) belong to the perovskite-type structure with a general formula ABO3. Cubic rhenium trioxide is composed of regular ReO6 octahedra \( R(\text{Re-O}) = 1.875 \text{ Å} \) joined by vertices with the A places being vacant. In monoclinic m-WO3 tungsten trioxide, the WO6 octahedra are distorted \( R(\text{W-O}) = 1.73-2.19 \text{ Å} \) with tungsten ions being displaced off-centre. Upon formation of hydrogen bronze, it is believed that the hydrogen ions form the O-H bonds and modify the host structure. These modifications lead to the local symmetry lowering in \( H2\text{ReO3} \) due to a tilting of the ReO6 octahedra (the value of the Re-O-Re angle decreases from 180 to 170 degree). On the opposite, an increase of the crystal symmetry occurs in \( H2\text{WO3} \) due to the WO6 octahedra symmetrization and an increase of the W-O-W angle. At \( x > 0.5 \), the \( H2\text{WO3} \) structure becomes cubic. The sodium tungsten bronze Na0.6WO3 has cubic structure with \( R(\text{W-O}) = 1.919 \text{ Å} \) and W-O-W angle equal to 180 degree as in ReO3.

The second group of studied compounds (hex-WO3 and WO3H2O) has a layered-type structure. Two-dimensional (2D) perovskite-like layers of distorted WO6 octahedra joined by vertices exist in hydrate, whereas the 2D-layers in hex-WO3 are built up of WO6 octahedra sharing their corners arranged in six-member rings in layers normal to the hexagonal c-axis [6]. In c-axis direction of hex-WO3, the WO6 octahedra sharing their corners arranged in the chain parallel to c-axis, therefore hex-WO3 has two type of oxygens. It is supposed that tungsten ions are in the center of the WO6 octahedra with four equivalent bonds W-O1 in the hexagonal layer \( R = 1.89 \text{ Å} \) (intralayer bonds) and two W-O2 bounds \( R = 1.95 \text{ Å} \) between the layers with the linear W-O-W1 chain and possible disorder within the set of (001) planes. The WO3H2O compound has three types of oxygen: intra- (O1) and interlayer (O2)
oxygen (O\textsubscript{3}) of interlayer water molecule. They have four different distances W-O in the first coordination shell. The tungstyl oxygen O\textsubscript{3} has very short distance 1.68 Å, the intralayer oxygen has two medium distances (1.82 Å and 1.93 Å), and the interlayer water oxygen has long site (2.33 Å). On the other hand, only one value (about 160 degree) of the tilting angle exists between four neighbouring octahedra within the layer.

From previous structural data (EXAFS) obtained by us for the a-WO\textsubscript{3} thin films [7, 8], one can separate three groups of distances which are well observed on RDFs as three peaks of different height and width. In crystalline m-WO\textsubscript{3} and hex-WO\textsubscript{3}, the peaks are well defined even at long distances (~ 2.15 Å) and are split into three main groups: sharp peak from 1.7 to 1.8 Å, broad peak 1.8 to 2.0 Å, and broad peak from 2.0 to 2.4 Å. In amorphous thin films, the shape of the distribution differs essentially from the crystalline case: the longest bonds have greater Debye-Waller factor values; therefore the last peak is very broadened and the center of the distribution is shifted to the region of smaller distances. The average tungsten-oxygen distances, calculated by the relationship \( \langle R \rangle = \frac{\sum_i R_i N_i}{\sum_i N_i} \), are equal to 1.929 Å (m-WO\textsubscript{3}) and 1.881 Å (a-WO\textsubscript{3}). Moreover, from XRD data it is suggested the nanocrystalline hexagonal model of a-WO\textsubscript{3} with the WO octahedra sharing their corners arranged in six-member rings in layers.

2. Experimental Details

Pure ReO\textsubscript{3} and Na\textsubscript{0.6}WO\textsubscript{3} oxides were commercially available polycrystalline powders for which single-phase structure was confirmed by XRD. Green m-WO\textsubscript{3} monocystal and yellow WO\textsubscript{3}H\textsubscript{2}O powder were prepared (ISSP), and its single phase structure was confirmed by XRD and Raman spectroscopy. The hex-WO\textsubscript{3} is obtained by de-hydration of hydrate precursors [6]. The H\textsubscript{4}ReO\textsubscript{3} and H\textsubscript{4}WO\textsubscript{3} bronzes were prepared in-situ in vacuum chamber by hydrogen intercalation into platinized oxide ReO\textsubscript{3} and m-WO\textsubscript{3} powders during 4 hours. The amorphous tungsten trioxide (a-WO\textsubscript{3}) thin films were prepared by thermal evaporation of WO\textsubscript{3} powder in medium vacuum on a glass substrate at 200 °C.

X-ray absorption experiments at the O K-edge were carried out at room temperature in the total electron yield (TEY) mode on the SA22 beam line at the LURE Super-ACO storage ring (Orsay, France), which operated at the energy 800 MeV with the current from 215 to 407 mA.

The samples were measured at the magic angle to average polarization effects. The energy scale was calibrated by setting the position of the first peak for polycrystalline NiO to 531.7 eV [1]. The energy resolution was 0.2 eV.
3. Results and Discussion

The normalised XAS spectra are shown in Figs 1 and 2, and the energy positions of the main features are given in

Table 1. No shift in the position of the absorption edge was observed upon intercalation with hydrogen, but a small difference (about 0.7 eV) is present between rhenium and tungsten oxides. According to the dipole selection rule, the O K-edge spectra show transitions from O 1s to unoccupied states with p-character which are relaxed due to the 1s core-hole positive charge.

The first intense peak (A,B) at 530 eV has complex shape consisting of the main contribution A and shoulder B. The peak is related to oxygen 2p(O) states in the 5d(t_2g) conduction band due to 5d(t_2g)(TM)-2p(O) interaction. The shoulder B is related to the two type of oxiges and the anisotropy of the t_2g-band, presented in the non-cubic perovskites [9]. The peak intensity depends on the number of the 2p(O) empty states, which are defined by the occupancy of the conduction band and very strongly by the degree of the TM-O bond covalency (or the value of the oxygen-to-metal charge transfer) [1]. In particularly, this peak is absent for purely ionic bonds even for the empty d-band [1].
Table 1. XANES O K-edge structure energies for rhenium and tungsten oxides. I(A) is the intensity of the peak A (or A+B if B is present). The edge position was set at the half-height of the first peak A. The energy scale was determined using the known position of the peak A in NiO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Edge</th>
<th>I(A)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO₃</td>
<td>529.1</td>
<td>4.8</td>
<td>529.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HₓReO₃</td>
<td>529.3</td>
<td>4.0</td>
<td>530.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-WO₃</td>
<td>529.8</td>
<td>6.5</td>
<td>530.7</td>
<td>531.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HₓWO₃</td>
<td>529.7</td>
<td>6.5</td>
<td>530.5</td>
<td>531.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₀.₆WO₃</td>
<td>529.7</td>
<td>7.2</td>
<td>530.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-WO₃</td>
<td>529.7</td>
<td>6.9</td>
<td>530.5</td>
<td>531.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hex-WO₃</td>
<td>529.8</td>
<td>5.8</td>
<td>530.3</td>
<td>531.6</td>
<td>536.1</td>
<td>537.4</td>
<td>541.9</td>
<td>544.0</td>
<td>551.6</td>
<td>567.2</td>
</tr>
<tr>
<td>WO₃H₂O</td>
<td>529.7</td>
<td>5.3</td>
<td>530.5</td>
<td>531.9</td>
<td>536.1</td>
<td>538.2</td>
<td></td>
<td>543.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNbO₃</td>
<td>529.9</td>
<td>6.5</td>
<td>531.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>543.3</td>
<td>550.3</td>
</tr>
<tr>
<td>NiO</td>
<td>530.8</td>
<td>3.2</td>
<td>531.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The intensity of the first peak (A) significantly increases in the series from m-WO₃, HₓWO₃ to Na₀.₆WO₃, while the area under the peak increases only slightly (see table and Fig. 1). Well visible broadening of the peak is observed for monoclinic m-WO₃. In the series from m-WO₃, WO₃H₂O to a-WO₃ the intensity of the peak (A) increases and the area under the peak increases also. The form of the asymmetric peak practically not change and consists from well visible two asymmetric subpeaks separated about 1.2 eV. Finally, the intensity of the peak (A) decreases and the area under the peak decreases also from ReO₃ to HₓReO₃. These compounds correspond, respectively, to the d⁰, d⁴, d⁶, d⁸ and d¹⁰ TM ion formal configurations with an increasing number of d-electrons. Thus, no simple correlation is observed between the first peak intensity and the number of d-electrons. On the contrary, the TM-O bond covalency is the main factor influencing the area of the first peak, and, therefore, cubic Na₀.₆WO₃ are considered to have the most covalent TM-O bonds. The full width (about 3.5 eV) of the first peak in the cubic perovskites is determined by the experimental resolution (0.2 eV), the natural 1s(O) core-hole level width (~ 0.22 eV), the 5d spin-orbit coupling (~ 1.5 eV) and the t₂g-band width (~ 3 eV). It is comparable to the

![Graph](https://example.com/graph.png)

Fig. 4. Multiple-scattering calculations of the O K-edge EXAFS as a function of the tilting Me-O-Me angle (160, 170, 180 degree) and the metal ion off-center displacement (0.1, 0.2 Å) in comparison with experimental data for hydrogen intercalated HₓReO₃ (tilted), ReO₃ (ideal cubic) and monoclinic m-WO₃ (off-center displaced). The spectra are vertically shifted for clarity.
one (3 - 4 eV) estimated from theoretical calculations in [10]. On the other hand, in the distorted perovskites (m-
WO₃) and in the layered compounds (hex-WO₃ and
WO₃-H₂O) as well as in amorphous a-WO₃ the broadening
or splitting of the first peak (A) is due to inequivalent
oxygen sites in these structures. Particularly, layered
compounds have two type (two intralayer and one
interlayer) oxyges giving two subpeaks (A and B) with
the ratio of about 2:1.

The peaks C and D are due to 5d(e₆)(TM)-2p(O) hybri-
dization, influenced strongly by competitive 2p(O)-1s(H)
or 3s(Na) interaction. An increase of the C and D peaks
intensity suggests partially covalent interaction between
oxygen and hydrogen/sodium ions. One can estimate the
splitting between the t₂g and e₆ subbands from the diffe-
rence between A and C peaks: it is about 4 eV compared
to the theoretical estimate 5.5 eV [10]. The peaks E and F
are attributed to 6sp(TM)-2p(O) interaction: their variation
has a behaviour similar to the C and D features. The next
features G and H are identified as scattering resonances at
the nearest atoms. Our multiple-scattering calculations
show that the peak H is due to single-scattering process
on 8 oxygen atoms at ~ 2.7 Å. The intensity of the
feature G is attributed to the value of the TM-O-TM
angle: it is higher for the linear atomic chain.

4. Conclusion
Our results show that the O K-edge absorption spectra in
5d metal oxides can serve as a sensitive probe of highly
detailed information on the chemical bonding and pecu-
liarities of the local atomic structure.

5. Acknowledgements
JP is grateful to the LURE laboratory for providing the
beam time (project CS041-96, 036-97) and financial
support (PECO). JP is also indebted to Dr. C. Guéry
(Université de Picardie Jules Verne) for platinization of
samples.

6. References
(1989).
Soc. 138, 2403 (1991); J. Appl. Phys. 69, 933
5, 2333 (1993).

Paper presented at the 5th Euroconference on Solid State