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Study of the electronic structure of rhenium and tungsten oxides on the O K-edge

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Abstract

Hydrogen intercalated ReO_3 and WO_3 oxides have been studied by X-ray absorption spectroscopy at the O K-edge. 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. © 1999 Elsevier Science B.V. All rights reserved.

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The X-ray absorption studies of the O K-edge have been intensively conducted in the past few years on 3d transition metal (TM) oxides and perovskites [1,2]. However, there are only few works related to the O K-edge in 5d TM oxide compounds (Na_xWO_3 [3] and WO_3 [4,5,8]), which were performed using electron energy loss spectroscopy (EELS). Here we present the results on the O K-edge in 5d perovskite-type compounds (ReO_3 , H_xReO_3 , WO_3 , H_xWO_3 and $\text{Na}_{0.6}\text{WO}_3$) obtained with high resolution using synchrotron radiation.

The studied compounds belong to the perovskite-type structure with a general formula ABO_3 . Cubic rhenium trioxide is composed of regular ReO_6 octahedra ($R(\text{Re–O}) = 1.875 \text{ \AA}$) joined by vertices with the A places being vacant. In monoclinic tungsten trioxide, the WO_6 octahedra are distorted ($R(\text{W–O}) = 1.73\text{--}2.19 \text{ \AA}$) 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 H_xReO_3 due to a tilting of the ReO_6 octahedra (the value of the Re–O–Re angle decreases from 180° to

$\sim 170^\circ$). Conversely, an increase of the crystal symmetry occurs in H_xWO_3 due to the WO_6 octahedra symmetrization and an increase of the W–O–W angle. At $x > 0.5$, the H_xWO_3 structure becomes cubic. The sodium tungsten bronze $\text{Na}_{0.6}\text{WO}_3$ has cubic structure with $R(\text{W–O}) = 1.919 \text{ \AA}$ and W–O–W angle equal to 180° as in ReO_3 .

Pure ReO_3 and WO_3 oxides were commercial polycrystalline powders whose single-phase structure was confirmed by XRD. The H_xReO_3 and H_xWO_3 bronzes were prepared by hydrogen intercalation into platinized oxide powders within a duration of 4 h. Sodium tungsten bronze $\text{Na}_{0.6}\text{WO}_3$ was used for comparison.

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 an energy of 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.

The normalized spectra are shown in Fig. 1, and the energy positions of the main features are given in Table 1. No shift in the position of the absorption edge was

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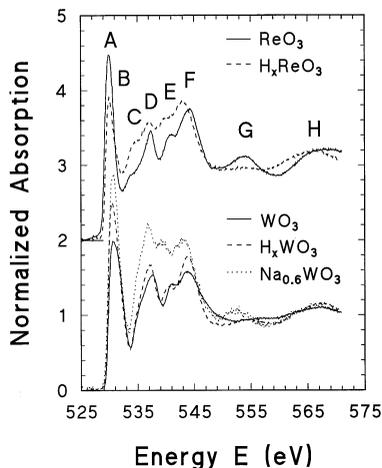


Fig. 1. Oxygen K-edge X-ray absorption spectra in pure oxides ReO_3 and WO_3 , sodium tungsten bronze $\text{Na}_{0.6}\text{WO}_3$ and hydrogen intercalated H_xReO_3 and H_xWO_3 . All spectra are normalized to the absorption edge jump. The spectra for ReO_3 and H_xReO_3 are vertically shifted for clarity.

observed upon intercalation with hydrogen, but a small difference (about 0.5 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 $5d(t_{2g})(\text{TM})-2p(\text{O})$ interaction. The shoulder B is related to the anisotropy of the t_{2g} -band, presented in the non-cubic perovskites [6]. 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 particular, this peak is absent for purely ionic bonds even for the empty d-band [1]. The intensity of the peak increases in the series from WO_3 , H_xWO_3 to $\text{Na}_{0.6}\text{WO}_3$ and decreases from ReO_3 to H_xReO_3 . These five compounds correspond, respectively, to the d^0 , d^x , $d^{0.6}$, d^1 and d^{1+x} 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 intensity of the first peak, and, therefore, cubic perovskites ReO_3 and $\text{Na}_{0.6}\text{WO}_3$ are considered to have the most covalent TM–O bonds. The full-width (about 3.5 eV) of the first peak 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 t_{2g} -bandwidth (~ 3 eV). It is comparable to the one (3–4 eV) estimated from theoretical calculations in Ref. [7].

Table 1

XANES O K-edge structure energies (eV) for rhenium and tungsten oxides. The edge position was set at the half-height of the first peak A

	ReO_3	H_xReO_3	WO_3	H_xWO_3	$\text{Na}_{0.6}\text{WO}_3$
Edge	529.1	529.3	529.8	529.7	529.7
A	529.9	530.0	530.7	530.5	530.7
B			522.7	522.7	
C	533.9	534.5	535.4	535.0	535.4
D	537.4	537.0	537.6	537.1	537.6
E	541.0	540.0	541.1	540.6	541.1
F	544.2	543.0	543.8	543.8	543.8
G	553.9	554.0	556.1	553.9	556.1
H	568.1	565.9	567.2	567.3	567.2

The peaks C and D are due to $5d(e_g)(\text{TM})-2p(\text{O})$ hybridization, influenced strongly by competitive $2p(\text{O})-1s(\text{H})$ or $3s(\text{Na})$ 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 t_{2g} and e_g subbands from the difference between A and C peaks: it is about 4 eV compared to the theoretical estimate of 5.5 eV [7]. The peaks E and F are attributed to $6sp(\text{TM})-2p(\text{O})$ 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 a 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.

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 peculiarities of the local atomic structure.

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