

## X-Ray Photoelectron Spectroscopy Study of Nonstoichiometric Tungsten Oxides

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Powdered samples of  $\text{WO}_{2.96}$ ,  $\text{WO}_{2.90}$ ,  $\text{WO}_{2.72}$ ,  $\text{WO}_2$ , and  $\text{WO}_3$  were studied by X-ray photoelectron spectroscopy. The spectra of the  $4f$  doublet of tungsten could be decomposed into contributions from several different oxidation states.  $\text{WO}_{2.96}$  and  $\text{WO}_{2.90}$  were found to contain  $\sim 13\%$  of  $\text{W}^{5+}$  and  $\sim 23\%$  of  $\text{W}^{5+}$ , respectively, in fair agreement with that expected from their stoichiometry.  $\text{WO}_{2.72}$  contained  $\sim 56\%$  of  $\text{W}^{6+}$ ,  $\sim 32\%$  of  $\text{W}^{5+}$ , and  $\sim 12\%$  of  $\text{W}^{4+}$ . Problems such as X-ray induced reduction of the samples, the high binding energy asymmetry of the spectra, and surface oxidation of the  $\text{WO}_2$  are also briefly discussed. The spectra of the valence band region showed an increase of the intensity of the peak due to the conduction band as the defect concentration increased. The data were discussed by assuming the presence of  $\text{W}^{5+}$  at the  $CS$  planes and the existence of a partially filled antibonding  $\pi^*$  band. For  $\text{WO}_2$  and, partly, for  $\text{WO}_{2.72}$ , the formation of a cation sublattice band, in addition to  $\pi^*$ , is possible, due to the short  $\text{W}-\text{W}$  distance occurring in these compounds.

### Introduction

Tungsten trioxide loses oxygen readily under reducing conditions and a series of oxides having well-characterized structural features are formed (1-7). Among these oxides, those with formula  $\text{W}_n\text{O}_{3n-1}$  contain crystallographic shear ( $CS$ ) planes on  $\{102\}$  planes, those with formula  $\text{W}_n\text{O}_{3n-2}$  contain  $CS$  on  $\{103\}$  planes. The other intermediate oxide  $\text{W}_{18}\text{O}_{49}$  (or  $\text{WO}_{2.72}$ ) contains units formed by five octahedra around a pentagonal bipyramid and linked into pairs by the edge sharing of octahedra (5) and does not contain  $CS$  planes.  $\text{WO}_2$  has a distorted rutile structure, with chains of cations along the  $c$ -

axis having alternating short and long separations (8).

In the present work the results of X-ray photoelectron spectroscopy (XPS or ESCA) studies are reported for the oxides  $\text{WO}_2$ ,  $\text{WO}_{2.96}$  (which is of the type  $\text{W}_n\text{O}_{3n-1}$ ),  $\text{WO}_{2.90}$  ( $\text{W}_n\text{O}_{3n-2}$ ), and  $\text{WO}_{2.72}$ .

Recently, the XPS spectrum of  $\text{Na}_{0.547}\text{WO}_3$  has shown the presence of  $\text{W}^{6+}$ ,  $\text{W}^{5+}$ , and  $\text{W}^{4+}$  in this bronze. A similar finding is to be expected for the  $\text{WO}_{3-x}$  oxides. (9) They have been considered mixed valence compounds (10) although the presence of  $\text{W}^{5+}$  and  $\text{W}^{4+}$  does not seem well established experimentally. XPS is a technique well suited to such an investigation; moreover, it

can give information on the band structure of these oxides.

### Experimental

$\text{WO}_3$  and  $\text{WO}_2$  were commercial products (Alfa-Ventron). The preparation and characterization by X-ray diffraction and electron microscopy of  $\text{WO}_{2.96}$ ,  $\text{WO}_{2.90}$ , and  $\text{WO}_{2.72}$  has been described elsewhere (11).

XPS measurements were carried out with a AEI ES 100 spectrometer, at a pressure of  $10^{-6}$  Torr.  $\text{AlK}\alpha$  excitation (1486.6 eV), operated at 300 W, was used. The samples, in powdered form, were pressed with a spatula into a trough, 2 mm deep and  $6 \times 15 \text{ mm}^2$  area, on a gold-plated metallic sample backing. The pressed powder completely covered the metallic backing so that no Au 4f spectrum was detectable. The impurity carbon 1s line (285.0 eV) was taken as reference. The carbon peak increased slightly over the period of several hours. No cleaning procedure was attempted since it was found that heating caused some reduction of the samples, besides lowering somewhat the intensity of the carbon peak. The signal-to-noise ratio was in the range 50 to 100 for the 4f level and 10 to 20 for the valence band region, depending on the time constant.

Curve decomposition was carried out with a Du Pont 310 curve resolver.

### Experimental Results

The spectrum of the  $4f^{3/2,5/2}$  doublet of tungsten in commercial  $\text{WO}_2$  (Fig. 1) shows that this compound is largely oxidized on the surface. The decomposition of the spectrum is similar to that previously reported (12) and it is useful to establish the relative positions of the three oxidation states of tungsten. The binding energies of  $\text{W}^{6+}$  and  $\text{W}^{4+}$  are easily determined from the peaks at  $\sim 33.5$  and  $\sim 38.2$  eV. By difference the  $\text{W}^{5+}$  doublet is obtained (curve b). Once the relative positions of the three oxidation states are known, the decomposition of the spectra of the other samples is greatly simplified.

Figures 2 and 3 show the 4f doublet in  $\text{WO}_{2.96}$  and  $\text{WO}_{2.90}$ , respectively. The spectra

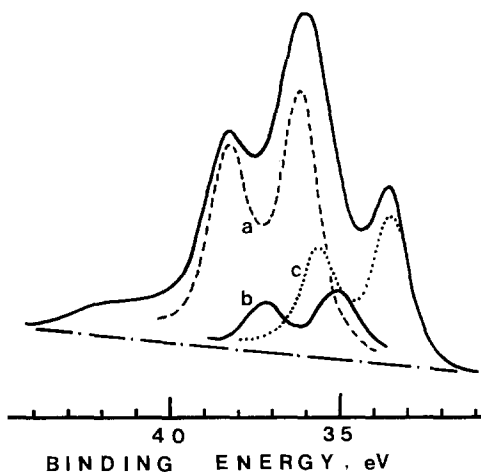


FIG. 1. XPS spectrum of the 4f levels of tungsten in  $\text{WO}_2$ . Curve (a)  $\text{W}^{6+}$ ; (b)  $\text{W}^{5+}$ ; (c)  $\text{W}^{4+}$ .

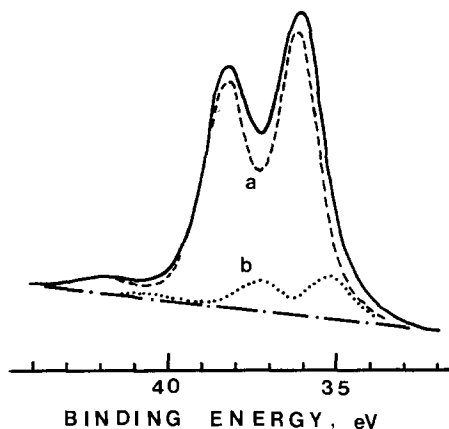


FIG. 2. XPS spectrum of the 4f levels of tungsten in  $\text{WO}_{2.96}$ . Curve (a)  $\text{W}^{6+}$ ; (b)  $\text{W}^{5+}$ .

can be decomposed into contributions from  $\text{W}^{6+}$  and  $\text{W}^{5+}$ , yielding the percentages reported in Table I. These values are somewhat larger than those expected on the basis of the oxygen deficiency; however, the discrepancy can be disregarded because of the error involved in the curve decomposition and because of slight uncertainty in the determination of the stoichiometry. Some  $\text{W}^{4+}$  might be present in  $\text{WO}_{2.90}$ , but in too small an amount to be revealed. The percentages of  $\text{W}^{6+}$ ,  $\text{W}^{5+}$ , and  $\text{W}^{4+}$  for  $\text{WO}_{2.72}$ , (Table I) are obtained from Fig. 5. The presence of  $\text{W}^{4+}$  can be explained by assuming a dismutation

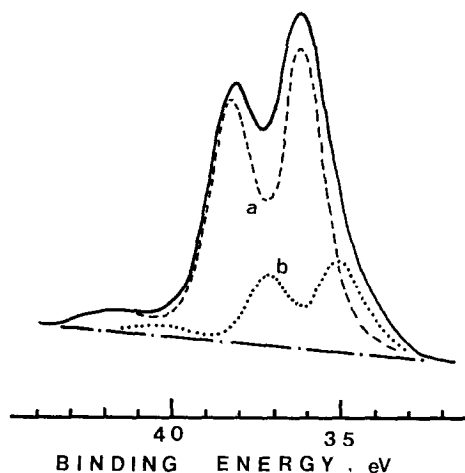


FIG. 3. XPS spectrum of the 4f levels of tungsten in  $\text{WO}_{2.90}$ . Curve (a)  $\text{W}^{6+}$ ; (b)  $\text{W}^{5+}$ .

TABLE 1

PERCENTAGES OF THE THREE OXIDATION STATES OF W OBTAINED FROM FIGS 2, 3, AND 5<sup>a</sup>

	$\text{WO}_{2.96}$	$\text{WO}_{2.90}$	$\text{WO}_{2.72}$
$\text{W}^{6+}$	87 (92)	77 (80)	56 (44)
$\text{W}^{5+}$	13 (8)	23 (20)	32 (56)
$\text{W}^{4+}$	0 (0)	0 (0)	12 (0)

<sup>a</sup> The figures within parentheses are those expected on the basis of stoichiometry; the estimated errors in the above figures are of a few percent.

of a part of  $\text{W}^{5+}$  such that ~24 out of 56% gives ~12%  $\text{W}^{6+}$  and ~12%  $\text{W}^{4+}$ .

Figure 4 shows the effect of the X-ray beam on  $\text{WO}_{2.90}$  after 5 hr of irradiation inside the spectrometer: an increased reduction is observed. Similar effects were observed on all the samples investigated here. Our spectra were recorded within half an hour or so after the introduction of the samples into the spectrometer. This procedure allowed the recording of all the spectra in the same conditions and minimized the X-ray induced reduction.

A feature of the spectra is the weak peak on the high-binding energy side of the main

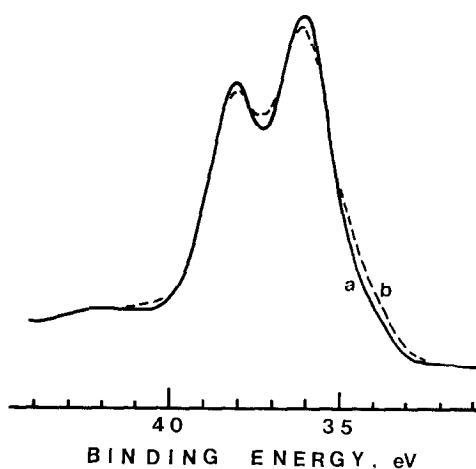


FIG. 4. XPS spectrum of the 4f levels of tungsten in  $\text{WO}_{2.90}$ . Curve (a) immediately after the introduction of the sample into the spectrometer; (b) after 5 hr irradiation by the X-ray beam at room temperature.

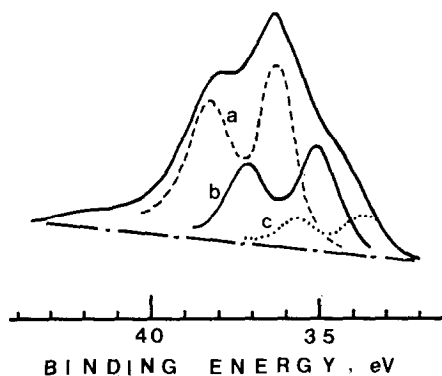


FIG. 5. XPS spectrum of the 4f levels of tungsten in  $\text{WO}_{2.72}$ . Curve (a)  $\text{W}^{6+}$ ; (b)  $\text{W}^{5+}$ ; (c)  $\text{W}^{4+}$ .

doublet. This peak seems to be present in the spectra of all compounds of tungsten but its origin is not well established. Madey *et al.* (13) have assigned it to the  $5p^{3/2}$  level of W. For our purposes it is not necessary to have a definite assignment of this "satellite" peak. It is sufficient to remark that the sum of the satellites of the three oxidation states (+6, +5, +4) explains rather well the high-binding energy side asymmetry in the spectrum of  $\text{WO}_2$  (Fig. 4),  $\text{WO}_{2.72}$  (Fig. 5) and  $\text{Na}_{0.547}\text{WO}_3$  (9). Campagna *et al.* (14) explained this asymmetry in the  $\text{Na}_x\text{WO}_3$  bronzes as due to the interaction of the core hole with the conduc-

tion electrons. The explanation based on the satellite peaks of the three oxidation states (9) seems more reasonable.

The spectrum in the valence band region (Fig. 6) of  $\text{WO}_{2.96}$ ,  $\text{WO}_{2.90}$ ,  $\text{WO}_{2.72}$ ,  $\text{WO}_2$ , and  $\text{WO}_3$  shows two main features: a conduction band (0–3 eV) and a strong valence band (4–11 eV). The intensities are not normalized, but they still allow one to see the increase of the population of the conduction band in going from  $\text{WO}_{2.96}$  to  $\text{WO}_{2.72}$ . The conduction band is due to the  $5d$  electrons. XPS gives a visualization of the filling of the conduction band when the concentration of the  $5d$  electrons increases, as has been already observed for the  $\text{Na}_x\text{WO}_3$  bronzes (14). The picture, thus obtained, of the density of occupied states is only qualitative, owing to the different, and unknown, ionization cross sections of the  $p$  and  $d$  orbitals. The valence band is largely due to the  $2p$  orbitals of oxygen

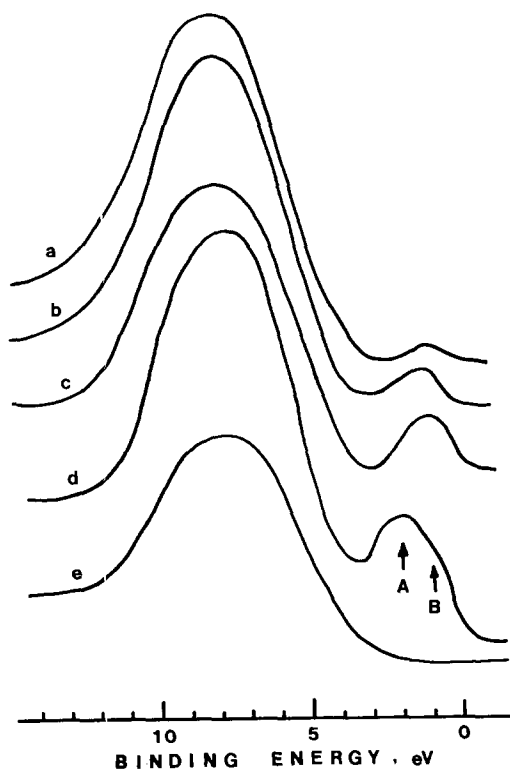


FIG. 6. XPS spectrum of the valence band region of  $\text{WO}_{2.96}$ . Curve (a)  $\text{WO}_{2.90}$ ; (b)  $\text{WO}_{2.72}$ , (c)  $\text{WO}_2$ , (d) and (e)  $\text{WO}_3$ .

with, possibly, some small contribution from the  $5d$  orbitals via covalent mixing. Covalent admixture of  $d$  states into the  $2p$  band occurs to a remarkable degree in the closely related oxide  $\text{ReO}_3$  (15).

Since  $\text{WO}_2$  is oxidized on the surface, the intensity in the 4–11 eV region is due also to the part of the surface oxidized to  $\text{W}^{6+}$  and  $\text{W}^{5+}$ . The conduction band is largely due to  $\text{W}^{4+}$ , with a contribution from the  $\text{W}^{5+}$  containing part of the surface. By reducing the  $\text{WO}_2$  sample (for example, in  $\text{H}_2$  at  $500^\circ\text{C}$ ) the amount of  $\text{W}^{4+}$ , relative to  $\text{W}^{6+}$  and  $\text{W}^{5+}$ , can be considerably increased and the intensity of the peak due to the conduction band consequently increases.

### Discussion

The spectra reported in this work have been recorded on powdered samples previously exposed to the atmosphere. The problem arises of how representative of the bulk are our results. The ideal conditions (vacuum cleaved single crystals, ultra high vacuum) could give a higher degree of confidence in the data and allow the observation of finer details, particularly in the valence band region. However, the important features of the spectra, such as those discussed in this work, can be obtained under the conditions used here.

The amount of surface oxidation that may have occurred by exposition to the atmosphere is not known, but is not likely to have changed drastically the relative amounts of the three oxidation states of tungsten. Anyway, the considerations that we make would remain valid even because of their basically qualitative nature.

### CS structures ( $\text{WO}_{2.96}$ and $\text{WO}_{2.90}$ ) and $\text{WO}_2$

The results we have reported show the presence of  $\text{W}^{5+}$  in  $\text{WO}_{2.96}$  and  $\text{WO}_{2.90}$ . The structure of these two oxides consists of slabs of  $\text{WO}_3$ , with corner sharing by octahedra and of defect regions (CS planes) where edge sharing by octahedra and a higher metal-to-oxygen ratio is present. The conduction processes in the two regions are expected to be different (7). The removal of oxygen has occurred at the shear planes and these are the

places where  $W^{5+}$  is likely to be formed. The W–W distance at the CS is  $\sim 0.38$  nm, considerably shorter than in  $WO_3$  ( $\sim 0.53$  nm). It has been observed that this distance is too large to have a large overlap of the  $5d_{t_{2g}}$  orbitals and W–W bonds, as in  $WO_2$  where the distance is 0.25 nm but the “incipient W–W bonds” could act as shallow traps for the electrons (16).

The XPS data, indicating that a part of the tungsten ions have an electron density corresponding to  $W^{5+}$ , is an argument in favor of some sort of localization of the  $5d$  electrons. The known low stability of  $W^{5+}$  (17) undoubtedly favors electron exchange and therefore hopping may occur via an intermediary anion, in a way similar to that postulated for vanadium bronzes (18), which could account for a low activation energy.  $WO_{2.90}$  has been reported as having metallic conduction (7), a conclusion that can also be drawn from the data of Fig. 6 showing the presence of a partially filled conduction band.

The data of Fig. 6 can be compared with and discussed on the basis of the band structure schemes of Goodenough (19, 20). In  $WO_2$ , which has a distorted rutile structure, the availability of two electrons for each  $W^{4+}$  cation allows the formation of both a cation sublattice band (because of the small W–W distance that results in collective  $t_{||}$  electrons) and a partially filled  $\pi^*$  antibonding band. The intensity of the peak due to the conduction band (Fig. 6) is the result of the contribution from the cation sublattice band and from the  $\pi^*$  band: they are superposed or the separation between the two is too small to be resolved, under our experimental conditions. However, in Fig. 6 a shoulder (B) is seen on the side of the main peak (A), so that two components can be distinguished. Our  $WO_2$  spectrum should be compared with that reported by Colton and Rabalais (21), where two well-resolved peaks are present. We could assign A to the cation sublattice band and B to the  $\pi^*$  band, in agreement with the band schemes of Goodenough (20).

For the CS phases, since the W–W distance is too large for the formation of W–W bonds, the XPS data can be explained by the presence of a partially filled  $\pi^*$  band. The resulting

band scheme is similar to that of  $ReO_3$  (19, 20). The presence of this  $\pi^*$  band in the CS phases and, therefore, the enhanced electrical conductivity, is a direct consequence of the CS planes. The mobility of the  $5d$  electrons should be greater inside the CS planes and lower in a direction perpendicular to them. Measurements on single crystals with known orientation of the CS planes would be of great interest and could demonstrate the existence of anisotropy.

#### $WO_{2.72}$

This oxide has been less studied than those containing CS planes. Its structure (5) shows some rather short W–W distances of 0.26 nm, comparable with those present in  $WO_2$ . It is likely that the  $W^{4+}$  ions are linked with the short W–W distances. The conduction band of  $WO_{2.72}$ , in Fig. 6, is stronger than that of  $WO_{2.90} \cdot WO_{2.72}$  is, therefore, certainly metallic in character. The intensity of the conduction band is due to a partially filled  $\pi^*$  band as in the shear phases and also to a cation sublattice band. While  $W^{5+}$  ions contribute only to  $\pi^*$ , the  $W^{4+}$  ions contribute both to  $\pi^*$  and to the cation sublattice band. The two are not resolved in our spectrum. The electronic structure of  $WO_{2.72}$  seems to have, therefore, similarities both with the shear phases and with  $WO_2$ .

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