JOURNAL OF SOLID STATE CHEMISTRY 49, 318–324 (1983)

XPS Studies on $WO_{2.90}$ and $WO_{2.72}$ and the Influence of Metallic Impurities

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Received March 11, 1983; and in revised form May 5, 1983

The excess electrons in reduced tungsten oxides appear in the X-ray induced photoelectron spectrum of $WO_{2.90}$ as W^{5+} signals. The ratio of the integrated intensities of the W^{5+}_{4f} and W^{6+}_{4f} peaks vary with chemical composition. A further increase in the W^{5+}_{4f} density of states appears for the doped crystals in proportion to the density of dopants. In $WO_{2.72}$ the charge carriers produce fivevalent tungsten only fractionally, the remaining electrons filling up the conduction band. A structural interpretation is proposed. The introduction of metallic impurities of V, Ni, and Nb increases the density of the fivevalent states.

1. Introduction

Charge carriers in WO_3 interact strongly with the surrounding lattice, forming polaronic states of variable size depending on the temperature and structural deformation (*1–4*). Their relaxation times in the W positions are much longer than the interaction time in XPS experiments giving rise to the appearance of the W^{5+} states (*5*). Salje *et al.* (*6*) showed that the W^{5+} state remains stable in all phases of WO_{3-x} ($x \leq 0.1$), independent of the bipolaron formation at low temperatures and that additional reduced states such as W^{4+} appear in highly distorted material, like fine grained powders. The degree of reduction was found by De Angelis and Schiavello (*7*) to be equivalent to the intensity ratio W^{5+}/W^{6+}, which indicates that each carrier is attached to a different W position (*4*).

The hypothesis that all electrons are mobile corresponds well with a plasmon relaxation time of $\tau = 0.129 \times 10^{-14}$ sec and a carrier density close to the theoretical value of 1.1×10^{22} cm^{-3} (*8*). Extrapolating the τ values, determined by Owen *et al.* (*9*) on Na_xWO_3, as a function of chemical composition, a sodium content of ca. 20% should correspond with $WO_{2.72}$, as far as the effective carrier density is concerned. Nevertheless, a different transport mechanism must be considered for $WO_{2.72}$ as compared to WO_{3-x} ($x \leq 0.1$) and to the sodium bronzes, because its optical absorption bands at 1.1 and 2.0 eV, are different from the polaronic absorption peak W^{5+}–W^{6+} in WO_3 at 0.7 eV, as well as the Drude-like reflectance in the sodium bronzes (*4, 9, 10*). Furthermore, the specific conductivity (364 Ω cm^{-1}) at room temperature is much lower than the value expected for a carrier con-

0022-4596/83 $3.00

centration of 1.1×10^{22} cm^{-3} and for a mobility close to that of WO_3. We have therefore reexamined the XPS of $WO_{2.72}$ to gain further insight into the nature of the carrier transport.

The carrier transport mechanism is heavily influenced by possible impurities. In practically all WO_3, a certain amount of Mo was found, as deduced from the observation of the Debye relaxation near 1.5 kHz (*5*) which serves as trapping center on the formation of Mo^{5+} (*4, 6*). Recently, in some cases (*11*) even Mo^{4+} was detected. On the other hand, doping with H, for example, from adsorbed water in thin films and powders, increases the carrier concentration, and is predominantly responsible for the electrochromic behavior of WO_3 (*12, 13*). Here we report on the influence of V, Ni, and Nb on the XPS of tungsten oxide.

2. Experimental

Crystals of $WO_{2.72}$ and $WO_{2.90}$ have been prepared by heating an appropriate mixture of WO_3 and W, and the metallic dopant in evacuated sealed silica tubes at 950–1050°C. Care was taken in that during incorporation of the metal substitute for W, the metal-to-oxygen ratio was not changed. The product consisted of small black-bluish or metallic red to purple needles ($WO_{2.72}$) and plates ($WO_{2.90}$). Powder X-ray examination revealed no mixture with other phases. In some cases, the fine-ground starting material was pressed into pellets before heating. The reaction product always was a very dense ceramic which could easily be cut by a diamond saw.

The XPS experiments were performed by using a Vacuum Generators spectrometer (Sussex, England) with an Al X-ray source (Al$K\alpha_{1,2}$ radiation, $h\nu = 1486.6$ eV) operating under pressure in the spectrometer of $<2 \times 10^{-7}$ Pa. For the XPS experiments, the ceramic material was ground in an agate mortar. The Ni- and Nb-doped samples were fixed on the sample holder (area ca. 2 cm^2) by adhesive tape. The V-doped samples were pressed on an indium foil and the foil mounted on the sample holder using a silver glue (Leitsilber, Degussa-Demetron No. 245). This preparation method proved to give the best XPS intensities.

3. Results

a. Tungsten Oxides

XPS data of the valence states of WO_3, $WO_{2.90}$, and $WO_{2.72}$ are shown in Fig. 1. The WO_3 spectrum is similar to that published by Fleisch and Mains (*11*), although the fine structure is better resolved here. Four peaks can be identified at 5.0, 6.5, 7.8, 10 eV. The first three also appear in the spectra of Hollinger *et al.* (*12*) for crystallized WO_3 films. In the reduced compounds only the second and third peak appear, with energies shifted slightly to higher binding energies. The free carrier states increase with increasing degree of reduction.

The photoelectron spectra of the W_{4f} levels are shown for the same samples on Fig. 2. They are similar to the results of De Angelis and Schiavello (*7*), but show a better spectral resolution. A complete curve fit was obtained using two $4f$ doublets of W^{6+} and W^{5+}. The fitted chemical shifts are 1.47 eV ($WO_{2.90}$) and 1.7 eV ($WO_{2.72}$). Small deviations between the calculated and the observed spectra, appear only in the case of $WO_{2.72}$, at the high energy tail. In contrast to De Angelis and Schiavello, no W^{4+} was found; it is believed that the appearance of W^{4+} in their experiments, was due to powder effects or to a mixture of WO_{3-x} phases with different degrees of reduction.

The ratio of the integrated intensities of the W^{5+}_{4f} and the W^{6+}_{4f} peaks, is a direct measure for the degree of reduction under the condition that all carriers are bound to W^{5+}. In fact, we obtain, in good accord with De Angelis and Schiavello, an agreement be-

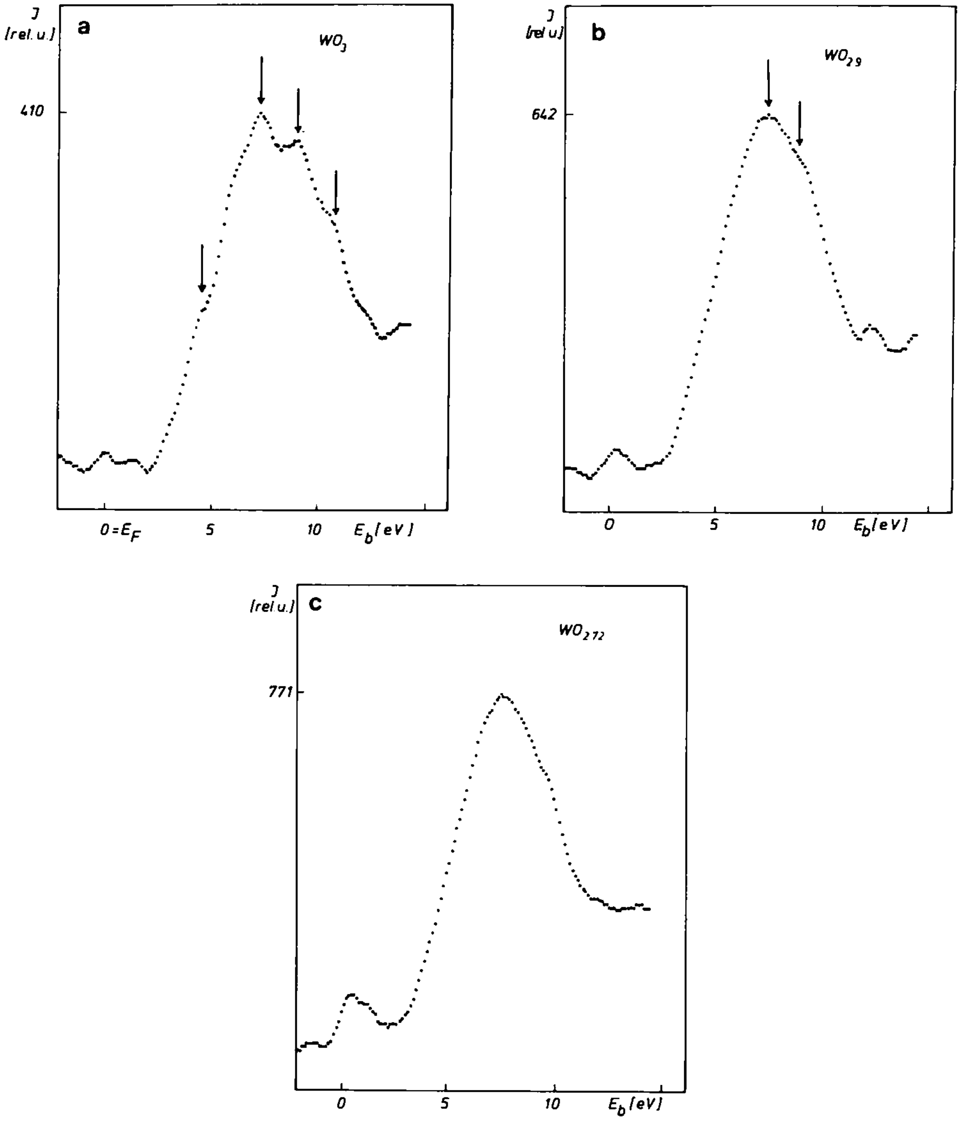

FIG. 1. XPS spectra of the valence bands of WO_3 (a), $WO_{2.9}$ (b), and $WO_{2.72}$ (c).

tween the theoretical value W^{5+}/W^{6+} (0.25) and the ratio of corresponding XPS signals in $WO_{2.90}$ (0.20). On the contrary, the observed W^{5+}/W^{6+} ratio in $WO_{2.72}$ of ca. 0.4 is much smaller than the theoretical value of 1.27. Similar behavior was reported for the sodium tungsten bronzes by Wertheim *et al.* (*14*), where no W^{5+} appear in $Na_{0.65}WO_3$. According to their interpretation, the possible appearance of the excitonic states at the bottom of the conduction band must be taken into consideration (*15*). Theoretically, such exciton level produces a splitting, due to the core ionization, with both levels filled according to the fractional filling of the original band. A filled final state then corresponds to the usual W^{6+} transition, whereas the unscreened final

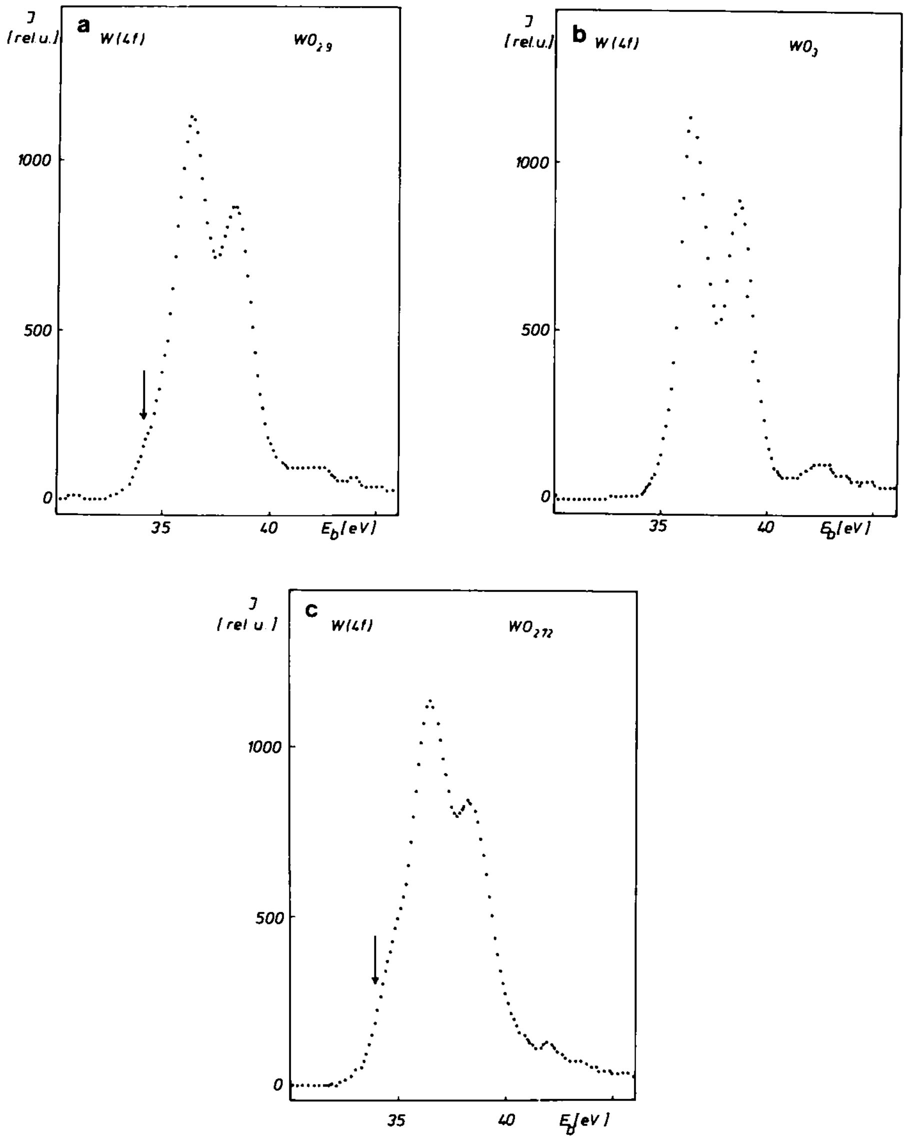

FIG. 2. The W_{4f} levels in WO_3 (a), $WO_{2.9}$ (b), and $WO_{2.72}$ (c). Curve fits were performed using two doublets W^{6+} and W^{5+} with variable energy splits. The resulting intensity ratios are $W^{5+}/W^{6+} = 0.20$ (b) and 0.40 (c).

state, which lies at higher binding energies, corresponds to the observed diffuse higher energy tail of the W_{4f} spectrum.

Thus, two types of carriers seem to exist in $WO_{2.72}$. First, those which are bound to W^{5+} positions and appear as W^{5+} in the photoelectron spectrum. Their density is roughly one-third of the entire carrier density. Second, the majority of the carriers are delocalized conduction electrons similar in behavior to the metallic sodium bronzes. As discussed earlier (*8*), the crystal structure of $WO_{2.72}$ contains two types of tungsten positions, one linked together as continuous chains of WO_6 octahedra and the other, i.e., 3 of the 9 independent tungsten positions, lying between these chains. The identification of the tungsten positions between the chains with the W^{5+} states and the assumption that the remaining electrons in the conduction band are limited to the tungsten positions in the chains, well explains the XPS data. However, a unequivocal structural identification of the W^{5+} positions through X-ray structure analysis is probably impossible, because of the nearly

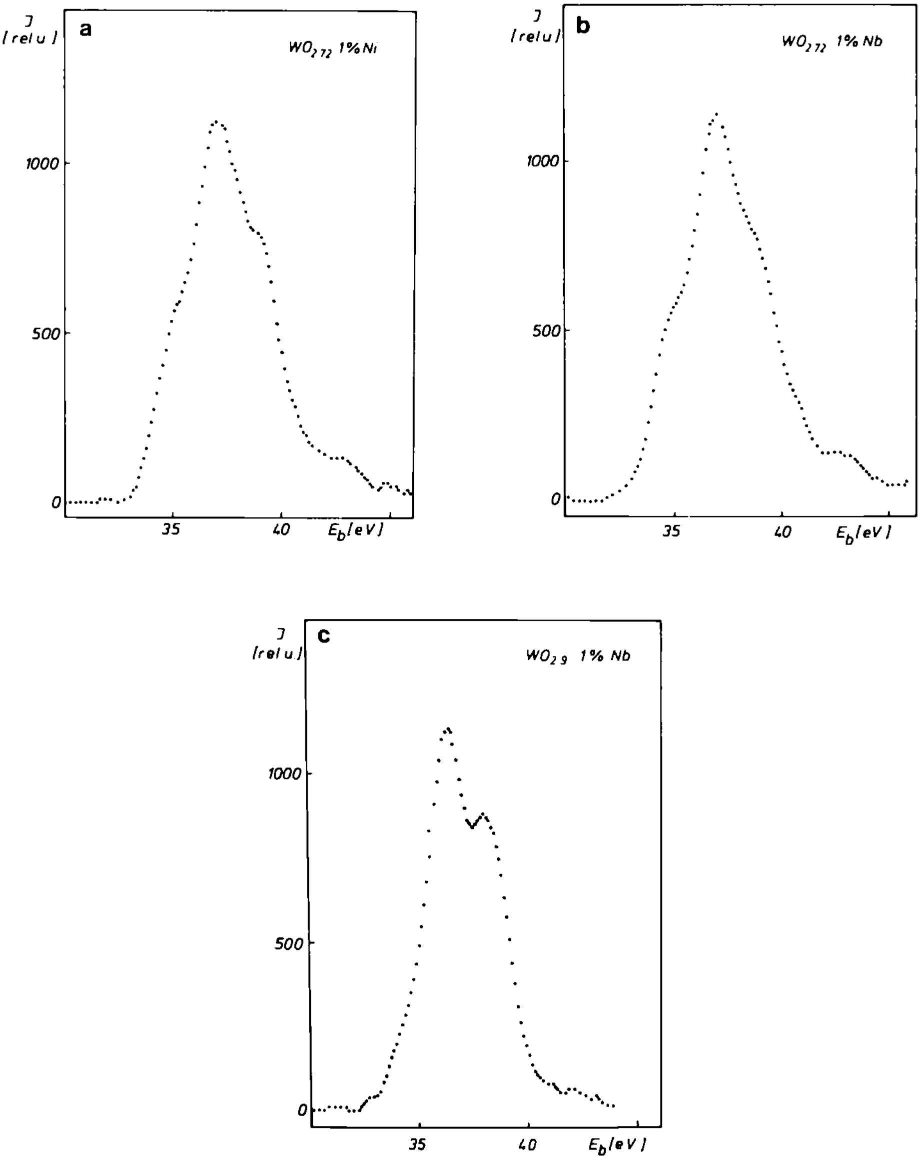

FIG. 3. XPS data of the W_{4f} level showing the increase of W^{5+}_{4f} by doping with Ni and Nb: (a) $WO_{2.72}$: 1% Ni with $W^{5+}/W^{6+} = 0.52$. (b) $WO_{2.72}$: 1% Nb with $W^{5+}/W^{6+} = 0.56$. (c) $WO_{2.9}$: 1% Nb with $W^{5+}/W^{6+} = 0.21$.

identical atomic scattering functions of W^{5+} and W^{6+} and the large unit cell of $WO_{2.72}$ (*8*).

b. Metallic Dopants

Although no complete miscibility between tungsten oxide and other metal oxides, with exception of MoO_3 (*1*), seems to exist, a small amount of metallic dopant could be incorporated in the WO_3 structure (*16*). We examined the XPS of $WO_{2.90}$ and $WO_{2.72}$ with 1, 4, and 8% V, Ni, Nb. Experimentally, the excess metal peaks could not be detected. We conclude that all dopants are in the bulk material and no surface segregation takes place. The main effect appears in the W_{4f} levels (Fig. 3), as an additional increase of the W_{4f}^{5+} state with no observable change of the chemical shift. In Fig. 4 is shown the dependence of the W_{4f}^{5+}/W_{4f}^{6+} ratio on the vanadium content. A rough estimate of the slope of low vanadium content is in agreement with the two-valent state of vanadium.

With increasing V content, a saturation of the reduction of W^{5+} appears to set in which may be indicate that no more V is being incorporated in the crystal structure.

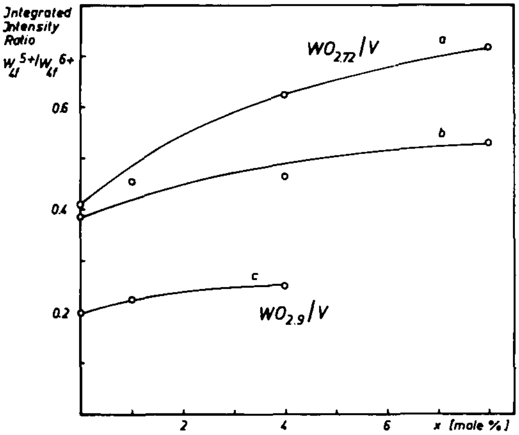

FIG. 4. Dependence of the W_{4f}^{5+}/W_{4f}^{6+} ratio on the V content in $WO_{2.72}$: V (multiple scanning 50× (a) and single scanning (b)) and $WO_{2.9}$: V (multiple scanning 50× (c)).

The situation encountered in $WO_{2.72}$: V is comparable to that of $WO_{2.90}$: V. Unfortunately, radiation effects, (as seen in the difference between spectra curves (a) and (b) in Fig. 4) prevent us from repeating the measurements, and hence the experimental error is slightly higher here. The increase of the W^{5+}/W^{6+} ratio in Fig. 4 parallels the increase in the $WO_{2.90}$: V ratio, so that the metal positions are again the donor centers. The same effect was found for the other dopants. Surprisingly, the excess electrons are practically all found on the W_{4f}^{5+} level (without considerable change to the valence band spectra), although we should expect that most of them should contribute to the filling of the conduction band. A possible explanation follows from the consideration of the lattice strains around the dopant positions, which may lower the tungsten levels in their vicinity. The W^{5+} state can thereby be favored over the conduction band states close to the Fermi level.

Acknowledgments

R. G. is greatful to the British Council for a travel grant. We also acknowledge the help of Mr. S. R. Grubb and Mr. D. A. Geeson, Dept. of Physical Chemistry Cardiff, during experimental work. We thank the German Science Foundation (DFG) for financial support (Sa 245/7).

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