ELECTRONIC STRUCTURE OF HYDROGEN BRONZES H_xWO_3 AND H_xMoO_3 AS STUDIED BY X-RAY PHOTOELECTRON AND EMISSION SPECTROSCOPY METHODS

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Tungsten and molybdenum trioxides, WO_3 and MoO_3, are of great interest both in technology and in theory in particular due to their ability to incorporate alkali metals, ammonium ions and hydrogen to form bronzes A_xMO_3, where A is an incorporating atom and M is either W or Mo atoms. Physical and chemical properties of the bronzes can vary dramatically with concentration x of an incorporating element, A.

The hexagonal tungsten bronzes, H_xWO_3, are substoichiometric compounds and have been characterized in the range $0 < x \leq 0.46$ [1,2]. With respect to molybdenum bronzes, it is well-known that hydrogen is fairly easy implanted into the orthorhombic matrix of MoO_3 forming H_xMoO_3 bronzes with the x content of hydrogen in the range $0 < x < 1.72$ [3]. The bronzes are obtained due to reaction of MoO_3 with atomic hydrogen in a gas or aqueous phase, or due to the so-called "hydrogen spillover" effect [3]. However, in Ref. [4] the activation of arbitrary oriented very thin plate-like MoO_3 crystal layers was performed by an impregnation of the layers with palladium salt and following heating in air at 300 °C. On the second stage, the activated MoO_3 layers were exposed to hydrogen at 200°C for synthesis of cubic molybdenum hydrogen bronze, H_xMoO_3, with lattice parameter a=0.380 nm [4]. Content of hydrogen in the studied H_xMoO_3 bronze was found to be x=1.63 [4,5]. The obtained $H_{1.63}MoO_3$ bronze differs from classic $H_{1.55\text{-}1.72}MoO_3$ Glemser's phases, which are orthorhombic and their crystal structure is based on a non-distorted MoO_3 lattice.

The H_xWO_3 and H_xMoO_3 bronzes possess metallic conductivity and represent a new and important electrode material. Additionally, the compounds are prospective sensor materials which possess good electrochromic properties [3,4]. Some properties of the hydrogen bronzes H_xWO_3 and H_xMoO_3 can be understood by considering their electronic structure. The electronic structure of cubic H_xMoO_3 and hexagonal H_xWO_3 phases was investigated in the present work in a comparative study with that of molybdenum and tungsten trioxides.

For this purpose, X-ray photoelectron (XPS) and emission (XES) spectroscopy methods were used. The experimental technique was similar to that described in details in Refs. [5,6].

Results of studies of the O $K\alpha$ XES bands of orthorhombic MoO_3 and cubic $H_{1.63}MoO_3$ compounds are presented in Fig. 1, but those of monoclinic WO_3 and hexagonal $H_{0.24}WO_3$ samples in Fig. 2.

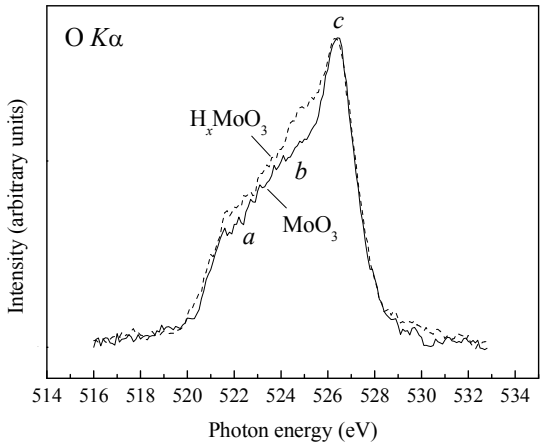

Fig. 1. X-Ray emission O $K\alpha$ bands of MoO_3 (solid curve) and H_xMoO_3 (dashed curve).

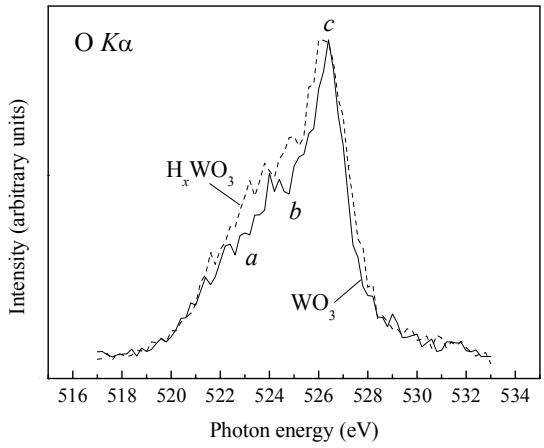

Fig. 2. X-Ray emission O $K\alpha$ bands of WO_3 (solid curve) and H_xWO_3 (dashed curve).

As can be seen from Figs. 1 and 2, implantation of hydrogen into the orthorhombic MoO_3 and monoclinic WO_3 matrices leading to formation of cubic $H_{1.63}MoO_3$ and hexagonal $H_{0.24}WO_3$ bronzes, respectively, results in increasing the relative intensities of the low-energy fine-structure features "*a*" and "*b*" of the O *K*α emission bands. As a results, half-widths of the bands increase in the sequence $MO_3 \rightarrow H_xMO_3$ (M = W, Mo). The above peculiarities of the spectra are the results of two factors: the formation of new O–H bonds in the studied H_xMO_3 bronzes and the transformation of the crystal structure in the sequence $MO_3 \rightarrow H_xMO_3$ [5,6].

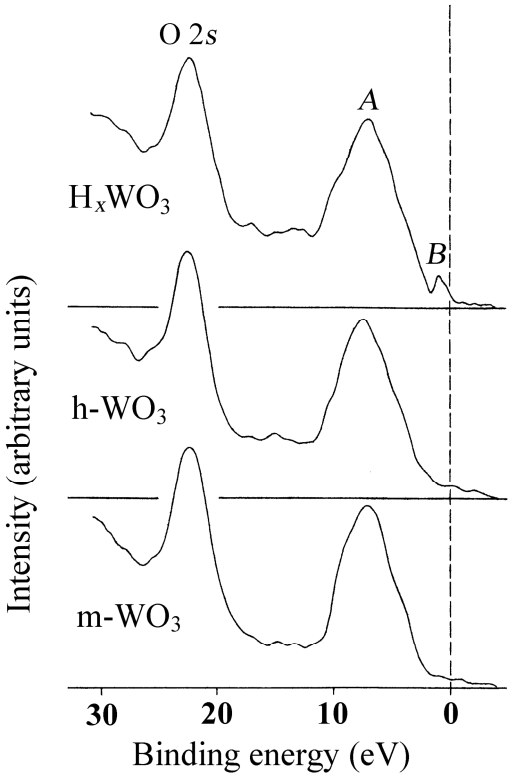

Fig. 3. XPS valence-band spectra of hexagonal hydrogen tungsten bronze (H_xWO_3), hexagonal and monoclinic tungsten trioxides (h-WO_3 and m-WO_3, respectively).

The XPS valence-band spectra in hexagonal tungsten hydrogen bronze $H_{0.24}WO_3$ and in monoclinic and hexagonal tungsten trioxides are presented in Fig. 3. Similar studies of molybdenum hydrogen bronze $H_{1.63}MoO_3$ and molybdenum trioxide MoO_3 were carried out in Ref. [5]. As can be seen from Fig. 3, the XPS valence-band spectrum of tungsten hydrogen bronze $H_{0.24}WO_3$ reveals a creation of an additional near-Fermi sub-band "*B*". The sub-band, as Fig. 3 shows, is absent on the XPS valence-band spectra of monoclinic and hexagonal forms of tungsten trioxide (m-WO_3 and h-WO_3, respectively). The similar near-Fermi sub-band was detected also on the XPS valence-band spectrum of $H_{1.63}MoO_3$ hydrogen bronze [5]. According to the results of Refs. [5,6], the above near-Fermi sub-band on the XPS valence-band spectra of the H_xMO_3 hydrogen bronzes under investigation can be explained by filling the W (Mo) dt_{2g}-like bands, which are empty in WO_3 and MoO_3 trioxides, due to extra hydrogen electrons. It should be mentioned that the formation of the near-Fermi sub-band was also observed in Ref. [7] when studying XPS valence-band spectra of orthorhombic molybdenum trioxide and monoclinic tungsten trioxide partly reduced by ultraviolet irradiation in the presence of molecular hydrogen. Similar to the effect observed for the O*K*α emission bands, half-widths of the XPS valence-band spectra increase somewhat when going from MO_3 to H_xMO_3 (M = W, Mo).

Results of the present XPS studies reveal that the O 1*s* core-level binding energies do not change in the sequence $MO_3 \rightarrow H_xMO_3$. These results indicate that the charge states of oxygen atoms in the studying tungsten and molybdenum hydrogen bronzes are similar to those in the corresponding trioxides.

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