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ELECTRONIC STRUCTURE OF Na_xWO_3 NEAR THE METAL-SEMICONDUCTOR TRANSITION

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New photoemission experiments on Na_xWO_3 cast some doubt on the rigid band model which has been used to explain earlier data. A peak remains in the conduction band in the XPS data for the semiconducting samples. Our experiments on WO_3 show that this behaviour is probably due to oxygen defect states produced by high energy electrons.

I. Introduction

The sodium tungsten bronzes (Na_xWO_3, $o<x<1$) have long been of interest because of their wide range of properties including a metal-semiconductor transition and superconductivity. The bronzes are in many respects similar to the transition metal oxides, particularly ReO_3, and their electronic structure has for many years been the source of controversy. Recently Kopp et al.[1] calculated the band structures of cubic $NaWO_3$ and cubic WO_3 and were able to interpret the available data from transport measurements in terms of the rigid band model.

Previous photoemission measurements (XPS [2] and UPS [3]) have only been made on samples with high values of x. The availability of single crystals over the entire range of x-values in this system has allowed us to obtain both XPS and angular resolved UPS data for both semiconducting and metallic samples.

II. Results

Crystals of Na_xWO_3 were prepared by the electrolysis of a melt of Na_2WO_4 and WO_3 using the method described by Shanks [4]. The XPS spectra were obtained with an HP 5950A ESCA spectrometer, for a series of semiconducting Na_xWO_3 crystals, $x<0.28$ and four metallic crystals, $x>0.28$. The spectra show a sharp peak near the Fermi energy with FWHM = 1.2eV which arises from states associated with the sodium electrons in the conduction band and a broader structure representing the valence band. The latter has its maximum at a binding energy of about 7eV. The dependence on Na concentration of the ratio of conduction band intensity I(CB) to valence band intensity I(VB) is shown in Fig.(1a).

Within the experimental uncertainty of about 0.2eV there is no x dependence in the width and the position of the maximum of the conduction band peak. The maximum of the valence band moves by ∿1.3 eV to higher binding energies when x increases from 0 to 1, nevertheless the top of the valence band shows no x dependence and is located about 3.1eV below E_F.

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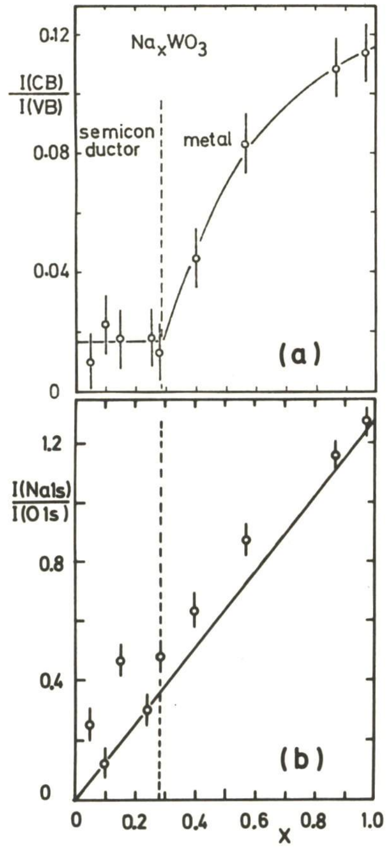

Fig. 1

Intensity ratios for a) conduction band to valence band and b) Na-1s to O-1s peaks as a function of sodium concentration

The intensity ratios of the Na-1s to O-1s peaks as a function of x-value are shown in Figure (1b). The solid line represents the expected x-dependence assuming oxygen stoichiometry, known values for the cross-sections [5], energy dependence of the escape depth [6] and instrumental corrections. All of the measured ratios fall on or above the line.

The angular resolved UPS spectra were obtained with a V.G. ADES 400 spectrometer. Results for WO_3 and $Na_{0.86}WO_3$ are shown in Figure (2) for normal emission from a [100] surface for different photon energies. The XPS result for WO_3 (bottom curve in Fig.(2a)) was taken from the work of Hollinger [7].

The broad valence band peaks in the XPS spectra are similar for all x-values but the UPS spectra contain considerably more structure and show a variation with x. A prominent peak occurs in the UPS spectra near 4eV which is independent of hν indicating that it is a density of states effect.

In order to make a more direct comparison with the calculated band structure, data were obtained for a number of angles of electron emission. Selected spectra for $Na_{0.85}WO_3$ are shown in Figure (3) along with the appropriate part of the calculated band structure from [1].

III. Discussion

The electronic behaviour of the sodium tungsten bronzes has been explained by a rigid band model in the metallic region. Within this model, the Fermi level moves through the conduction band as the Na concentration is increased. Consequently we would expect to see the valence band and the core levels moving with respect to the Fermi energy, and a broadening of the conduction band as the concentration is varied. None of these effects were observed in the XPS results. The UPS results of Fig.(2) show that the valence band shape is significantly different for WO_3 and $Na_{0.86}WO_3$ with a strong peak at a binding energy of about 7eV and a shoulder near 3.2eV being present only for the sodium bronze. From these observations we conclude that the rigid band model is, not surprisingly, inapplicable over the entire concentration range.

The peak positions in the UPS spectra of Fig.(2) are independent of photon energy suggesting that they correspond to indirect transitions. The XPS results are not expected to be similar as the experiment integrates over all k-vectors and cross-sections are quite

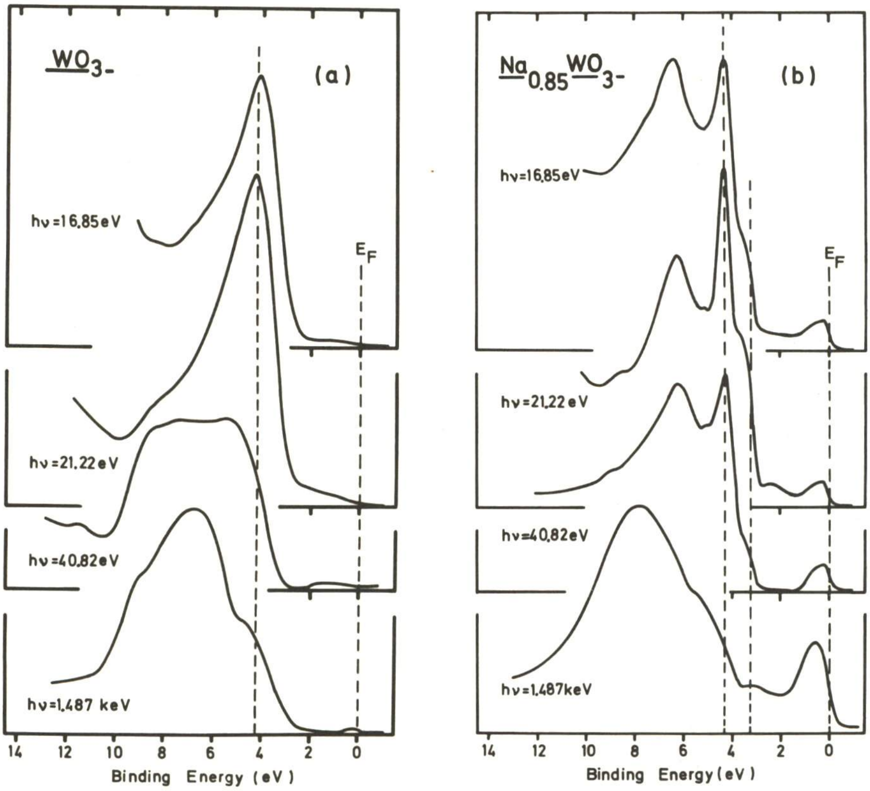

Fig. 2

Photoemission spectra of various photon energies for a) WO_3 and b) $Na_{0.85}WO_3$ single crystals

different at such a high photon energy. Figure (3) compares angle resolved UPS results at three different angles with the appropriate one-dimensional band structures from [1]. Comparison between the spectra and the one-dimensional density of states is poor and in particular the conduction band feature does not show the drastic changes with angle expected from the indirect transition model. This feature should be strongest in Fig.(3b) considerably weaker in Fig.(3c) and completely absent in Fig.(3d).

The presence of a peak near E_F in the XPS but not in the UPS spectra for WO_3 is probably due to defects induced by the X-radiation or the excited electrons. It was found that exposure to a beam of electrons with energies between 200eV and 1.5kV caused changes in the UPS spectra in the region above the valence band. The states induced by the electrons could be removed again by exposure to atomic oxygen. Oxygen defects may also explain the flat behaviour in the semiconducting region in Fig.(1a) and could in fact conceal much of the intrinsic x-dependent behaviour.

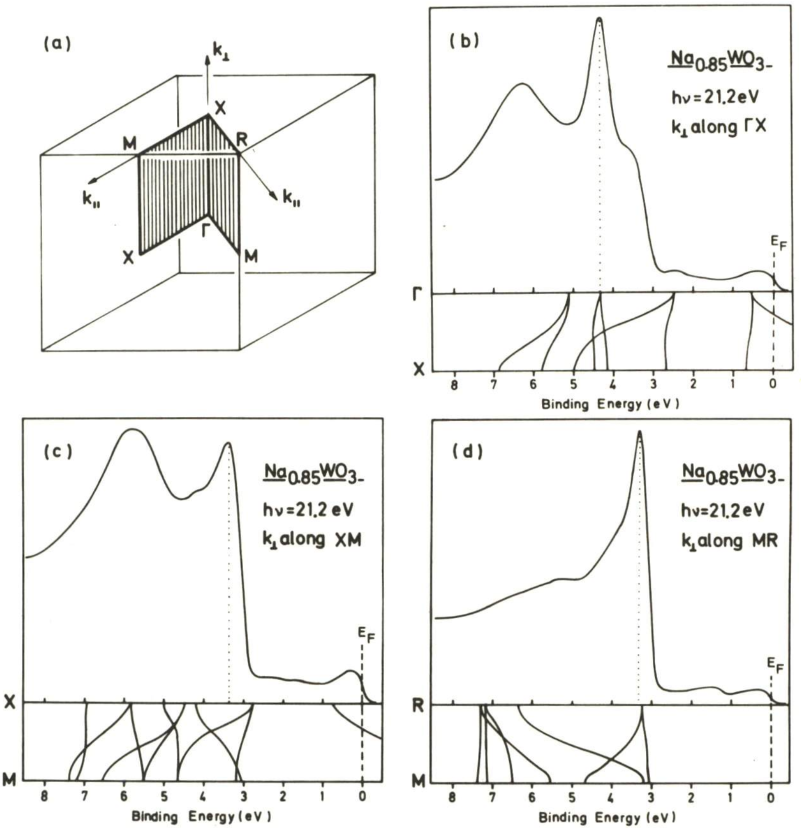

Fig. 3

Angular resolved photoemission spectra of $Na_{0.85}WO_3$ along specified regions in the Brillouin zone

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