

The Electronic Structure of Tungsten Carbide

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INTRODUCTION

Transition metal carbides have long been used in industry because of their resilient physical properties. Strength at high temperatures, high melting points, and corrosion and wear resistant properties make them obvious candidates for many commercial applications.[1] WC has been shown to be an effective catalyst in some chemical reactions usually catalyzed by noble metals such as Pt.[2,3] Carbides, particularly WC alloyed with other monocarbides, are the basis for “cemented carbide” cutting tools and wear resistant coatings.

The electronic structures of transition metal carbides have been studied experimentally using photoelectron spectroscopy [2,4-6] and photoemission spectroscopy.[7] The purpose of this study was to obtain detailed soft x-ray emission (XES) and absorption (XAS) data to directly observe hybridization of the occupied states and probe the structure of the unoccupied states of these compounds. Since soft x-ray valence emission represents the partial density of states (PDOS) of a specific angular momentum of the valence band, C 1s emission spectra were compared to p-projected PDOS (p-PDOS) from LMTO-ASA and full-potential KKR electronic structure calculations.

EXPERIMENTAL

All fluorescence and TFY data were measured at undulator beamline 8.0 at the Advanced Light Source (ALS) at Lawrence-Berkeley National Laboratory (LBNL), Berkeley, CA. The samples were illuminated with monochromatic synchrotron radiation via a spherical grating monochromator. Fluorescent soft x-ray radiation was analyzed with a Rowland geometry, spherical grating spectrometer under ultrahigh vacuum (UHV) conditions. The spectrometer has a fixed entrance slit, four spherical diffraction gratings, and a position sensitive area detector. All measurements were made with a 50 μm entrance slit. C 1s spectra were obtained with a 1000 lines/mm, 10 meter radius grating. The band pass of the spectrometer was estimated to be less than 0.4 eV at the carbon edge. Pressure in the sample chamber was below 5×10^{-9} torr. Details of this beamline and endstation are described elsewhere.[8]

WC

C 1s XES spectra are shown as a function of incident energy in Fig. 1. The spectra were normalized to the incident intensity and calibrated using published carbon spectra.[10] Spectra excited far above threshold exhibited four peaked features centered at about 278 eV. Photoelectron measurements yield an estimate of the binding energy of the C 1s electron in WC to be 282.6 eV.[2]

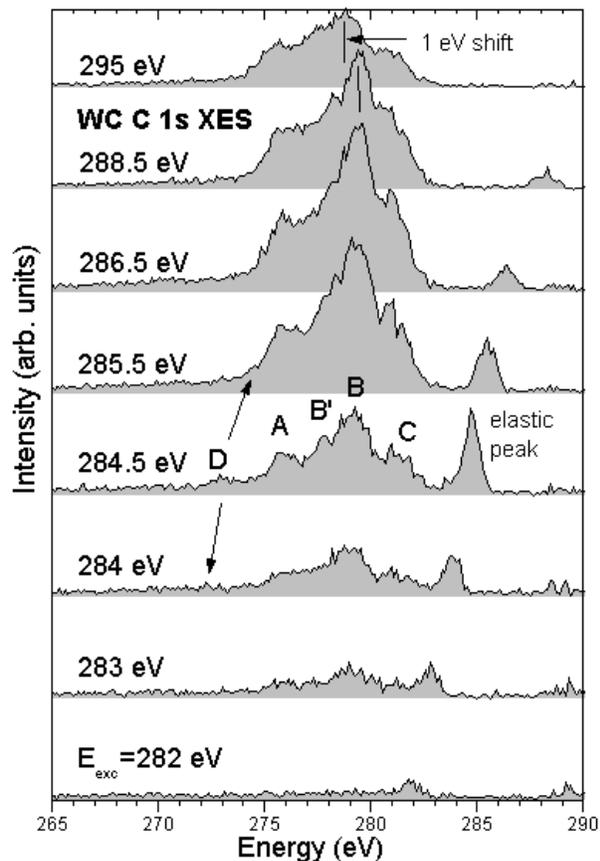


Fig. 1. The C 1s XES of hexagonal WC. Four main features were observed in the spectra: A, B, B', and C. The feature D appearing in the spectrum excited at 284.5 eV was identified as either a Raman effect or a feature of the C p-PDOS. The arrows indicate evidence of tracking of the peak D with excitation energy. The spectrum excited at 295 eV, and all other spectra excited at higher energies, were shifted by about 1 eV relative to the spectra excited at energies lower than 295 eV. The shift is explained as an effect of core hole screening by the C 1s electron excited to a localized level of p-symmetry above the Fermi level.

LMTO Calculations for WC

Tungsten carbide (WC) is hexagonal with a unimolecular cell of dimensions $a=2.9065 \text{ \AA}$ and $c=2.8366 \text{ \AA}$, and has the symmetry of the $D_{3h}^1(P\bar{6}3m)$ space group.[15] The atomic positions in hexagonal coordinates are $(0,0,0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ for W and C, respectively. The Wigner-Seitz radii were chosen in ratio of their published ionic radii and to have a total unit cell volume $\Omega=140.041 \text{ a.u.}^3$. [16] The radii computed for W and C were 2.9687 and 1.9370 a.u., respectively. 288 k -points were sampled in the irreducible wedge.

The LMTO energy bands are shown in Fig. 2 and agree well with previously published calculations.[17-20] Other electronic structure calculations have been performed on the high-temperature NaCl phase of WC.[20-22] The local C p-PDOS of WC was compared to C 1s emission excited at $E_{\text{exc}}=320 \text{ eV}$ (Fig. 3). C p-PDOS was broadened to account for experimental broadening with $\Delta E=1.0 \text{ eV}$. The experimental data agree well with these calculations, as well as with previously published ones, verifying conclusions drawn from them regarding bonding

The elastic peak resonates at about 284.5 eV, which is indicative of a localized unoccupied state of p-symmetry above the Fermi level. The largest feature, B, shifts by about 1 eV to higher energy between $E_{\text{exc}}=290.5$ and 288.5 eV as the excitation energy is lowered through threshold. This shift of emission spectra to higher energy when the excitation is near threshold (in the elastic resonance) implies that the C 1s electron is excited to a 2p level that is localized at the carbon atom, thereby screening the valence electrons from the core hole. By the same reasoning, the excited electron is no longer localized at the C atom when the excitation energy exceeds 290.5 eV.

CALCULATIONS

Linear muffin-tin orbital (LMTO) calculations were performed within the atomic sphere approximation (ASA).[12] The exchange and correlation effects are treated within the local density approximation (LDA) of density functional theory.[13] Self-consistent solutions to the Kohn-Sham equations were obtained for all electrons in the system by using the exchange-correlation potential as formulated by Hedin and Lundqvist.[14] The core electron states were obtained as solutions of the Dirac equation, and scalar relativistic terms were retained in the LMTO Hamiltonian for band states.

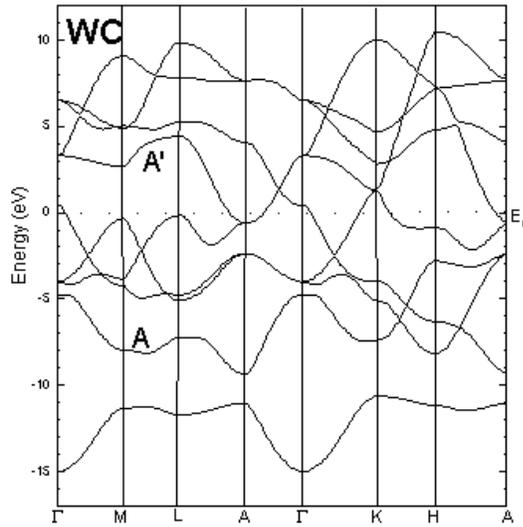


Fig 2. The LMTO energy bands of WC (left) and the corresponding symmetry points of the Brillouin zone. The points A and A' label flat bands that represent an energy loss mechanism, in the form of an interband transition, which may account for the peak D in Fig.1.

It was concluded that the d-band is split into bonding-antibonding states implying d-d hybridization acts as a metal-metal, second-nearest-neighbor bonding mechanism in WC. It was also noted that the W p states hybridize with those of C p and W d .

The p-d hybridization and the filling of only the bonding d-d hybrids was deduced as the reason for the high strength of WC.[23] This experiment confirms the p-d hybridization, but valence s and d emission from W was too weak to make any conclusions about the d-d hybridization.

The peak A in Fig. 3 is a subband of the p-PDOS that is the result of hybridization between C 2s and W 5d electrons. Evidence of this s-d hybridization was apparent in the C s-and W d-PDOS. The s-d hybridization may be an alternative explanation (the other one was Raman scattering) of why peak D appears in the XES spectrum of Fig. 1 excited at 284.5 eV.

A localized unoccupied state above the Fermi level is indicated by peak B in the C p-PDOS in Fig. 3. It was concluded that localized p-PDOS is responsible for resonant elastic scattering in WC.

CONCLUSIONS

XES spectra excited near the C 1s threshold of WC were presented and exhibited little or no dispersion. Calculated LMTO DOS were in good agreement with experimental data. A localized state above the Fermi level was revealed by resonant elastic scattering. The effect of this localized electron was realized by a shift of the emission spectra to higher energies. At the elastic resonance a peak appeared in the emission spectrum at about 273 eV. The peak was identified as either an energy loss facilitated by an interband transition or emission from the C s-d hybrid subband.

Agreement of LMTO calculations with experimental data and full potential (LAPW) calculations indicates that the LMTO method is sufficient regarding the calculation of electronic properties of

mechanisms and electronic structure.[17-20,23] The fact that the LMTO calculations agree well with full potential calculations[24] and the experimental data is important in evaluating the performance of the LMTO method in modeling these systems. One inference drawn from these calculations includes the interpretation of hybridization between C p and W d electrons as a covalent bonding mechanism. Since C p- and W p-PDOS have the same shape and relative intensities in the region between -2.5 and -8.0 eV, it was concluded that hybridization occurs between the C 1s and W 5d states, which is indicative of covalent bonding in WC. In addition to this p-d hybridization, it was noted that the d-band is much larger than the p-band, indicating that some of the W d-states are not involved in the p-d hybridization. The d-states that are not involved in p-d hybridization form a peak at about -2.0 eV. This peak matches another peak in the W d DOS at about +2.5 eV.

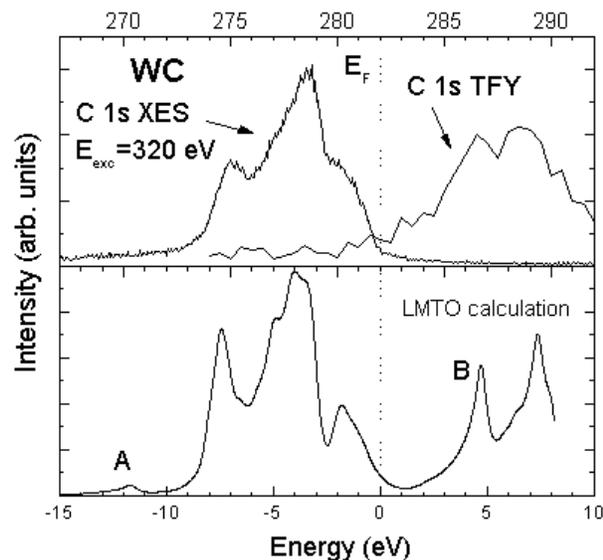


Fig. 3. The C 1s XES excited above threshold and TFY spectra are compared to the LMTO C p-PDOS. The C p-PDOS were broadened by 1.0 eV. The feature A, a C s -W d hybrid subband, may account for the feature D of the WC C 1s spectrum (Fig. 1.) excited at 284.5 eV. The peak B is a localized unoccupied band of p-symmetry that may be responsible for the observed resonance in elastic scattering.

these systems. Interpretations of previous calculations regarding bonding mechanisms and electronic structure, particularly hybridization, were verified.

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