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Electronic properties and Compton scattering studies of monoclinic tungsten dioxide

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HIGHLIGHTS

- Presented first-ever Compton profile (CP) measurements on WO_2.
- Analyzed CP data in terms of LCAO–DFT calculations.
- Discussed energy band, DOS and Mulliken's population.
- Discussed equally scaled CPs and bonding of isoelectronic WO_2, WS_2 and WSe_2.
- Reported metallic character and Fermi surface topology of WO_2.

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ABSTRACT

We present the first ever Compton profile measurement of WO_2 using a 20 Ci ^{137}Cs γ-ray source. The experimental data have been used to test different approximations of density functional theory in linear combination of atomic orbitals (LCAO) scheme. It is found that theoretical Compton profile deduced using generalized gradient approximation (GGA) gives a better agreement than local density approximation and second order GGA. The computed energy bands, density of states and Mulliken's populations (MP) data confirm a metal-like behavior of WO_2. The electronic properties calculated using LCAO approach are also compared with those obtained using full potential linearized augmented plane wave method. The nature of bonding in WO_2 is also compared with isoelectronic WX_2 (X=S, Se) compounds in terms of equal-valence-electron-density profiles and MP data, which suggest an increase in ionic character in the order $WSe_2 \rightarrow WS_2 \rightarrow WO_2$.

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1. Introduction

Tungsten dioxide (WO_2) is an interesting material due to its high melting point which makes it suitable for high temperature applications. It exhibits great potential for industrial interests, relevance for solar energy technology, catalytic applications, etc. Among earlier studies, Ben-Dor and Shimony (1974) have presented the x-ray diffraction (XRD) analysis of pure and doped WO_2 while the x-ray photoelectron spectroscopy (XPS) study of several oxidation states of tungsten oxide was reported by De Angelis and Schiavello (1977). The monoclinic structural parameters of WO_2 were refined using powder neutron diffraction data at room temperature by Palmer and Dickens (1979) and in framework of the Rietveld method by Bolzan et al. (1995). Gulino et al. (1996) have checked the influence of metal–metal bonds in WO_2 by measuring the photoemission and electron energy loss spectra. The photoemission spectra of WO_2 was reported by Jones et al. (1997) for the surface structure and spectroscopy, while Bigey et al. (1998) have correlated the catalytic activity in the surfaces and bulk tungsten oxides using XRD, XPS and x-ray absorption spectroscopy. Further, an experimental study of low-lying electronic states of WO_2 was undertaken by Davico et al. (1999). Regarding earlier theoretical data on WO_2, plane-wave pseudopotential (PP) calculations using local density approximation (LDA) have been reported by Dewhurst and Lowther (2001). Jiang and Spence (2004) have discussed WO_2 in terms of experimental high-energy transmission electron energy-loss absorption spectra and density of states (DOS) of both the oxygen atoms. The *ab-initio* structural, energy bands and DOS of monoclinic (room temperature stable state) and orthorhombic (high temperature metastable state) phases of WO_2 have been presented by Shaposhnikov et al. (2011).

Since the last three decades, the Compton scattering technique has been recognized as a versatile and unique tool to estimate the ground state electronic properties of materials (Cooper et al., 2004;

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Heda and Ahuja, 2010). In this technique, the measured quantity so called Compton profile (CP) $J(p_z)$ is the projection of the electron momentum density $n(\mathbf{p})$ along the scattering vector direction (usually taken along the z-axis). In fact, the $J(p_z)$ is experimentally deduced from the measured double differential scattering cross-section ($d^2\sigma/d\Omega d\omega_2$). Mathematically,

$$J(p_z) = \frac{1}{C(\omega_1, \omega_2, \theta, p_z)}\left(\frac{d^2\sigma}{d\Omega d\omega_2}\right). \quad (1)$$

The conversion function $C(\omega_1, \omega_2, \theta, p_z)$ depends upon ω_1 and ω_2 (incident and scattered energies of the γ-ray) and the scattering angle θ.

It may be noted that $n(\mathbf{p})$ is a square modulus of the momentum space wave function, $\chi_i(\mathbf{p})$, which is basically the Fourier transformation of the real space wave function, $\psi_i(r)$, as given below,

$$n(\mathbf{p}) = \sum_i^{occ} |\chi_i(\mathbf{p}) = M \int \psi_i(\mathbf{r}) e^{i\mathbf{p}.\mathbf{r}} d^3r|^2. \quad (2)$$

In Eq. (2), M is the normalization factor (Cooper et al., 2004).

To the best of our knowledge, CP measurements on monoclinic WO_2 have not been reported yet. To shed some more light on the electronic properties using momentum densities, we present the first ever experimental CP of WO_2 using 20 Ci ^{137}Cs Compton spectrometer (Ahuja et al., 2006). It may be noted that in case of Compton profile measurement of materials involving high-Z elements (like 5d transition metals), a high energy γ-emitting source like ^{137}Cs is preferred (due to impulse approximation criteria) than low-energy ^{241}Am source as used by Raykar et al. (2013) for the measurement of CPs of CdTe. The theoretical CPs, energy bands, DOS and Mulliken's population (MP) analysis have also been reported for the first time using linear combination of atomic orbitals (LCAO) scheme as embodied in the CRYSTAL09 code (Dovesi et al., 2009). In addition, the energy bands, partial and total DOS and Fermi surfaces have also been computed using the full potential linearized augmented plane wave (FP-LAPW) method (Blaha et al., 2011). Further, relative nature of bonding among isoelectronic W-compounds namely WO_2, WS_2 and WSe_2 has been studied on the basis of equal-valence-electron-density (EVED) profiles and MP analysis.

2. Methodologies

2.1. Experiment

The isotropic CP of monoclinic WO_2 was measured by employing 20 Ci ^{137}Cs Compton spectrometer (Ahuja et al., 2006) with a resolution of 0.34 a.u. (Gaussian full width at half maximum). A pellet of 17 mm diameter and 3.3 mm thickness was prepared under argon environment using high purity polycrystalline WO_2 sample. The pellet was sealed in a perspex ampoule using thin Mylar sheets on both sides. The incident photons of energy 661.65 keV were scattered by the sample, which was held vertically in the scattering chamber. The scattered photons were detected by a high purity Ge detector (Canberra, USA) in which the cross-sectional area and thickness of the Ge crystal were 500 mm^2 and 10 mm, respectively. An integrated Compton intensity of 2.02×10^7 photons was accumulated during the exposure of about 150 h. Throughout the measurement, the electronic drift was checked from time to time using weak ^{57}Co and ^{133}Ba calibration sources and was found to be negligible. To extract the true CP, raw Compton data were corrected for background, detector response (limited to stripping-off the low energy tail), sample absorption, Compton cross-section and multiple (up to triple) scattering (Timms, 1989; Felsteiner et al., 1974). Finally, the CP was normalized to free atom (FA) Compton profile area of 34.97e$^-$ in the momentum (p_z) range from 0 to +7 a.u. (Biggs et al., 1975). Due to the non-availability of the large sized single crystals (15 mm diameter and 2 mm thickness) of WO_2 and to explore the relative nature of bonding in isoelectronic WO_2, WS_2 and WSe_2 compounds on EVED scale, we have only measured the isotropic CP of WO_2.

2.2. Theory

2.2.1. LCAO method

To compute the directional and isotropic $J(p_z)$, energy bands, DOS and MP data, we have employed LCAO-PP scheme (Dovesi et al., 2009) in the framework of density functional theory (DFT) within LDA and generalized gradient approximation (GGA) along with the hybridization of Hartree–Fock (HF) and DFT (the so called B3LYP) scheme. For the second order GGA (SOGGA) (Zhao and Truhlar, 2008) exchange enhancement factor is taken as equal (50% each) mixing of Perdew–Becke–Ernzerhof (PBE) (Perdew et al., 1996) and revised PBE (Hammer et al., 1999) exchange functionals. It is worth mentioning that the SOGGA is claimed to be an advanced GGA functional as it mends the gradient expansion for both exchange and correlation through second order. In case of B3LYP, the standard exchange of Becke (1988) and Lee–Yang–Parr (LYP) (Lee et al., 1988) correlation energies along with 20% mixing of the HF exchange has been used. The exchange and correlation potentials used in the present computations are compiled in Table 1. In the present effective core pseudopotential (ECP) calculations, we have taken a large core PP for W and all-electron Gaussian basis sets for oxygen (O) ions. The basis sets were energy optimized for WO_2 environment using BILLY software (Dovesi et al., 2009). Further, self consistent field (SCF) calculations have been performed using 205**k** points in the irreducible Brillouin zone (IBZ) and the absolute isotropic CPs were calculated by adding the FA core CP contribution (Biggs et al., 1975) to the normalized valence CPs.

2.2.2. FP-LAPW method

In addition to the LCAO scheme, we have also computed energy bands, partial and total DOS and Fermi surfaces of monoclinic WO_2 using the FP-LAPW method in the framework of DFT–GGA (Blaha et al., 2011) using the formulation of Wu and Cohen (2006). It is

Table 1
Exchange and correlation energies within the LCAO-PP approach (Dovesi et al., 2009), as used in the present work.

Scheme	Exchange energies	Correlations energies	Nomenclature used in the text
DFT with LDA	Dirac-Slater (Dovesi et al., 2009)	Perdew and Zunger (1981)	DFT–LDA-PZ
DFT with GGA	Wu and Cohen (2006)	Perdew and Wang (1992)	DFT–WCGGA
DFT with GGA	Second order GGA (Zhao and Truhlar, 2008)	Perdew–Becke–Ernzerhof (Perdew et al., 1996)	DFT–SOGGA
Hybridization of Hartree-Fock and DFT (B3LYP)	Becke (1988)	Lee–Yang–Parr Lee et al. (1988)	B3LYP

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