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Compton profiles and electronic structure of monoclinic zinc and cadmium tungstates

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HIGHLIGHTS

- Presented first-ever Compton profile (CP) measurements on $ZnWO_4$ and $CdWO_4$.
- Analyzed CP data in terms of first-ever LCAO–DFT calculations.
- Computed energy bands and DOS using LCAO and FP-LAPW schemes.
- Discussed DOS in terms of Mulliken's population.
- Interpreted bonding employing equal-valence-electron-density scale of CPs.

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ABSTRACT

We report the first ever Compton scattering study of $ZnWO_4$ and $CdWO_4$ using 20 Ci ^{137}Cs Compton spectrometer at momentum resolution of 0.34 a.u. To compare the experimental Compton profiles, we have also deduced the momentum densities using density functional theory (DFT) within linear combination of atomic orbitals (LCAO) methods. It is seen that the experimental Compton profiles of both the tungstates give a better agreement with LCAO–DFT calculations within generalized gradient approximation (GGA) employing Perdew–Becke–Ernzerhof (PBE) exchange and correlation energies than other approximations included in the present work. Further, energy bands, density of states (DOS) and band gaps have also been calculated using LCAO–DFT–GGA–PBE scheme and full potential linearized augmented plane wave method. Both the computational schemes show a semiconducting nature of both the tungstates, with a direct band gap at Y point of Brillouin zone. Further, a relative nature of bonding on equal-valence-electron-density scale shows more covalent character in $ZnWO_4$ than $CdWO_4$ which reconciles with the conclusions drawn using integrated DOS and Mulliken's population data.

1. Introduction

The tungstate materials like $ZnWO_4$ and $CdWO_4$ are very useful in scintillators, optical fibers, sensors, optical recording, masers, photocatalyst devices and security systems, etc. Regarding earlier studies, Nagirnyi et al. (2002) have reported energy transfer in $ZnWO_4$ and $CdWO_4$ while the scintillation pulse shape discrimination is discussed by Danevich et al. (2005). Itoh et al. (2006, 2007) have reported X-ray photoelectron spectroscopy (XPS) to investigate the electronic structures, reflection, luminescence-excitation, luminescence decay kinetics, photo-stimulated luminescence and photo-induced infrared absorption in both the tungstates. Huang and Zhu (2007) have reported high photocatalytic activity of $ZnWO_4$. Fujita et al. (2008) have performed polarized reflection and XPS measurements and also the electronic structure of $CdWO_4$. Kalinko et al. (2009) have undertaken *ab-initio* calculations with density functional theory (DFT) and pseudopotential schemes along with the linear combination of atomic orbitals (LCAO) within DFT for $ZnWO_4$. Also in case of $CdWO_4$, DFT calculations for electronic and optical properties were performed by Abraham et al. (2000). Lacomba-Perales et al. (2008) have reported room temperature experimental band gap between 3.9 and 4.4 eV for $ZnWO_4$ and 4.15 eV of $CdWO_4$ using optical–absorption and reflectance measurements. Evarestov et al. (2009) have applied LCAO method to probe the electronic and phonon properties of $ZnWO_4$ and compared their results with available crystallographic data. Raman and photoluminescence spectroscopic measurements of $ZnWO_4$ have been undertaken by Kalinko and

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Kuzmin (2009), whereas electronic and optical properties with oxygen vacancy in $CdWO_4$ are reported by Zhou et al. (2010). Kim et al. (2011) have combined the electronic band structure calculations and electro-chemical measurements to investigate the electronic and photovoltaic properties of such materials. Brik et al. (2012) have employed DFT within CASTEP code for optical and electronic properties of $ZnWO_4$ and $CdWO_4$ and compared their results with the available XPS and reflectivity spectra. Recently, Khyzhun et al. (2013) have applied full potential linearized augmented plane wave (FP-LAPW) method to calculate the electronic properties of $ZnWO_4$. In second attempt, Brik et al. (2013) have applied the DFT within CASTEP module to calculate the structural, electronic and elastic properties of both the tungstates at the ambient pressure and elevated pressure ranging between 5 and 10 GPa.

Compton scattering is a well established technique to probe electronic properties of the materials (Cooper et al., 2004; Heda and Ahuja, 2010). In this technique, the measured quantity is known as Compton profile (CP) $J(p_z)$, which is projection of electron momentum density (EMD), $\rho(\mathbf{p})$, along the direction of scattering vector (conventionally z-axis). Mathematically,

$$J(p_z) = \int\int \rho(\mathbf{p}) dp_x dp_y \propto \frac{d^2\sigma}{d\Omega dE_2}. \quad (1)$$

In Eq. (1), p_z is the component of linear momentum of electron along the z-axis and E_2 is the energy of the scattered radiations. The $\rho(\mathbf{p})$ can be evaluated using the momentum space wave function, $\chi_i(\vec{p})$, which is derived from the Fourier transformation of real space wave function $\psi_i(\vec{r})$.

In this paper, we report the first ever CP measurements of $ZnWO_4$ and $CdWO_4$ using 661.65 keV γ-rays emitted by 20 Ci ^{137}Cs source (Ahuja et al., 2006). On the theoretical side, we have employed the LCAO and FP-LAPW schemes (Dovesi et al., 2009; Blaha et al., 2011) to compute the theoretical CPs, energy bands, partial and total density of states (DOS), band gap and Mulliken's population (MP) data. Further, bonding aspects in these isoelectronic compounds have been analyzed using their equal-valence-electron-density (EVED) profiles.

2. Experiment

The CPs of monoclinic $ZnWO_4$ and $CdWO_4$ have been measured using 20 Ci ^{137}Cs Compton spectrometer at resolution of 0.34 a.u. (Gaussian full width at half maximum) (Ahuja et al. 2004, 2006). In such experiments, the overall resolution factor depends upon the resolution of detector and geometrical broadening of the incident and scattered photons. In individual experiments, the incident photons of energy 661.65 keV were scattered by the polycrystalline samples at scattering angle of $160 \pm 0.6°$ and the data were accumulated using a high purity Ge detector (Canberra, Ge crystal size 500 mm^2 and 10 mm thickness) and associated electronics. Here, the intrinsic character of the Ge crystal was maintained by cooling it at liquid nitrogen temperature (77 K). The high purity (more than 99.5%) sample was kept in an ampoule constructed using Mylar foil on both the sides. Due to difficulties in getting the large size single crystals (say 15 mm diameter and 2 mm thickness) and to compare the relative nature of bonding in terms of EVED profiles, we have measured the isotropic profiles. The density and thickness of $ZnWO_4$($CdWO_4$) were 1.33(2.60) g/cm^3 and 0.55(0.42) cm, respectively. During the total exposure time of 238.15(321.84) h for $ZnWO_4$($CdWO_4$), an integrated Compton intensity of 2.10×10^7(5.05×10^7) photons in the momentum range -10 to $+10$ a.u. (Compton region) was obtained. To extract true Compton profile, the raw data were corrected for background, detector response function (limited to stripping-off the low energy tail), detector efficiency, sample absorption, Compton scattering cross-section, etc. (Timms, 1989). Further, the data were corrected for multiple scattering events (Felsteiner et al., 1974) upto triple scattering. It was found that the effect of multiple to single scattering phenomena was 10.23(10.57) % in the momentum range -10 to $+10$ a.u. for $ZnWO_4$ ($CdWO_4$). We have not corrected our data for Bremsstrahlung background contribution because its contribution in the Compton profile region is very small (Mathur and Ahuja, 2005). Finally, the isotropic CP was normalized to the corresponding free atom (FA) CP area 55.81 e$^-$ (61.97 e$^-$) for $ZnWO_4$ ($CdWO_4$) (Biggs et al., 1975). A good agreement between the FA CPs and the experimental data in the high momentum regions validates the accuracy of data acquisition and process to extract true CPs.

3. Theory

3.1. LCAO method

The directional and isotropic CPs, energy bands, partial and total DOS, MP charge transfer data and band gap have been computed using the LCAO–DFT method (Dovesi et al., 2009) with local density and generalized gradient approximations (LDA and GGA, respectively). Using DFT theory, the Schrodinger equation can be written as,

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r})}{|r - r'|} dr' + \frac{\partial E_{xc}\left[\rho(\vec{r})\right]}{\partial \rho(\vec{r})}\right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}). \quad (2)$$

In Eq. (2) the first three terms in the Hamiltonian energy (left hand part) are kinetic, external potential and Coulomb exchange operators and the fourth term is the first order density derivative of E_{xc}. The exchange-correlation density functional energy E_{xc} for LDA/GGA is expressed as,

$$E_{xc}^{LDA/GGA}\left[\rho(\vec{r})\right] = \int_{d\vec{r}} \rho(\vec{r})\, \varepsilon_{xc}\left[\rho(\vec{r}) / \rho(\vec{r}),\ \left|\nabla \rho(\vec{r})\right|\right] \quad (3)$$

here $\varepsilon_{xc}$is the exchange-correlation energy per particle in uniform electron gas and is defined differently in LDA and GGA (Dovesi et al., 2009). Further, the different kinds of exchange and correlation energies (Dovesi et al., 2009; Vosko et al., 1980; Perdew et al., 1996, 2008) have been used within LDA and GGA as listed in Table 1. For the present computations, we have considered the all electron Gaussian basis sets of Zn, Cd and O taken from http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html, while due to non availability of all electron basis sets for W we have used its pseudopotential basis sets as reported by Wadt and Hay (1985). The basis sets were energy optimized using BILLY software (Dovesi et al., 2009). The self-consistent field (SCF) calculations have been performed with 170 ***k***-points in the irreducible Brillouin zone (BZ) for both $ZnWO_4$ and $CdWO_4$. All theoretical CPs have been normalized to corresponding FA CPs area, as mentioned in Section 2.

3.2. FP–LAPW method

In addition to LCAO calculations, the energy bands, partial and total DOS and band gap of both the samples have been deduced using FP–LAPW–DFT with more accurate exchange and correlation potentials of Perdew–Becke–Ernzerhof (PBE) (Blaha et al., 2011). It is worth mentioning that in FP–LAPW method, the crystal potential outside the muffin–tin (MT) atomic spheres is