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Compton profiles and Mulliken's populations of cobalt, nickel and copper tungstates: Experiment and theory

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ABSTRACT

We present the first ever studies on Compton profiles of AWO_4 (A=Co, Ni and Cu) using 661.65 keV γ-rays emitted by ^{137}Cs source. The experimental momentum densities have been employed to validate exchange and correlation potentials within linear combination of atomic orbitals (LCAO) method. Density functional theory (DFT) with local density approximation and generalized gradient approximation and also the hybridization of Hartree-Fock and DFT (B3LYP and PBE0) have been considered under LCAO scheme. The LCAO-B3LYP scheme is found to be in better agreement with the experimental data than other approximations considered in this work, suggesting applicability of B3LYP approach in predicting the electronic properties of these tungstates. The Mulliken's population (MP) data show charge transfer from Co/Ni/Cu and W to O atoms. The experimental profiles when normalized to same area show almost similar localization of 3d electrons (in real space) of Ni and Cu which is lower than that of Co in their AWO_4 environment.

1. Introduction

The Compton spectroscopy (CS) is a unique and powerful probe in determining the momentum densities of materials and is very sensitive to behavior of loosely bound electrons [1,2]. The measured quantity in CS is the Compton profile (CP) which is basically a projection of electron momentum density along the scattering vector direction (usually taken along *z*-axis). Validity of CP measurements is subject to the fulfillment of the impulse approximation which dictates that the energy transferred to the target electron is much greater than its binding energy. Theoretically the CP, $J(p_z)$, is defined as,

$$J(p_z) = \int_{p_x}\int_{p_y} n(\boldsymbol{p}_x, \boldsymbol{p}_y, \boldsymbol{p}_z)\, dp_x dp_y, \tag{1}$$

here $n(\boldsymbol{p}_x, \boldsymbol{p}_y, \boldsymbol{p}_z)$is the electron momentum density and p_z is the component of linear momentum of electron along *z*-axis. It is known that the $J(p_z)$ follows the normalization rule given below,

$$\int_{-\infty}^{+\infty} J(p_z)\, dp_z = N \tag{2}$$

where N is the total number of electrons participating in the scattering phenomenon. The experimental CP can be deduced from the measured double differential Compton cross-section $(d^2\sigma/d\Omega\, dE_2)$ as given below,

$$J(p_z) = \frac{d^2\sigma/d\Omega\, dE_2}{C(E_1, E_2, \theta, p_z)}, \tag{3}$$

The factor C in Eq. 3 depends on the experimental condition like incident and scattered photon energies (E_1 and E_2) and scattering angle (θ).

The transition metal tungstates AWO_4 (A=Co, Ni and Cu) have attracted much attention because they are commonly used as scintillation and catalysts materials and also in optical fibers, humidity and gas sensors, photo-anodes, phase-change optical recording devices, etc. [3–17]. Regarding earlier work on these tungstates, electrical conductivity and neutron-diffraction measurements along with full potential linearized augmented plane wave (FP-LAPW) with generalized gradient approximation (GGA) have been reported on $CoWO_4$ [3–6]. Earlier work on $NiWO_4$ includes electrical conductivity, thermoelectric power, dielectric constant, X-ray absorption spectroscopy (XAS), synthesis and characterization along with linear combination of atomic orbitals (LCAO) calculations [7–10]. In case of $CuWO_4$, neutron diffraction measurements, X-ray photoelectron spectroscopy, X-ray emission spectroscopy, X-ray absorption fine structure measurements, XAS, Raman spectra, optical-absorption and reflectance measurements

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along with theoretical computations using FP-LAPW and LCAO methods have been discussed by different workers [11–17].

In this paper, to shed more light on electronic properties, we report first-ever CP measurements on AWO_4 (A=Co, Ni and Cu) using 661.65 keV γ-rays. The experimental Compton data have been used to check the performance of various exchange and correlation potentials within LCAO approximations. The Mulliken's populations (MP) data on charge reorganization and the behavior of 3d electrons of Co, Ni and Cu have also been discussed on the basis of equally normalized CPs of these tungstates.

2. Experiment

We have employed 740 GBq (20 Ci) ^{137}Cs Compton spectrometer [18] to measure the CPs of AWO_4 (A=Co, Ni and Cu) at an intermediate resolution (full width at half maximum) of 0.34 a.u. The ^{137}Cs isotope in the Compton spectrometer is quite suitable because of low photoelectric absorption of radiations, long half-life, large energy transfer to recoil electron, etc. In individual experiments, high purity (99.9+%) polycrystalline samples of AWO_4 (A=Co, Ni and Cu) were exposed by the incident energy of 661.65 keV and energy spectra of scattered photons were measured (at an scattering angle $160 \pm 0.6^{\circ}$) by a high purity Ge detector (Canberra model GL0510P, cross-section of Ge crystal 500 mm^2 and thickness 10 mm) and associated electronics like spectroscopy amplifier and analog-to-digital convertor with 4 K channel analyzer. Other experimental parameters consisting of sample size, sample density, γ-ray exposure time, integrated counts under CP, multiple scattering contribution, free atom (FA) CP area for all the tungstates are listed in Table 1. During the CP measurements, the stability of the electronic system was checked from time-to-time using weak ^{57}Co and ^{133}Ba calibration sources. To obtain true CP, the measured raw data were corrected for several systematic corrections, like background, absorption of γ-rays within sample, detector efficiency, Compton scattering cross-section, etc. using the computer code of Warwick group [19]. Further, the data were corrected up to triple scattering using Monte Carlo simulations as prescribed by Felsteiner et al. [20]. Finally, CPs were normalized to the corresponding FA area [21] as mentioned in Table 1.

3. LCAO method

The directional and isotropic CPs along with MP data have been deduced using LCAO method with density functional theory (DFT) [22]. In the present work, we have considered local density approximation (LDA) and GGA within DFT and also the hybridization of Hartree–Fock (HF) and DFT (under B3LYP and PBE0 approximations). It is worth mentioning that in LCAO method, one calculates the crystal wave functions from one electron Schrodinger's equation,

$$\left(-\frac{1}{2}\sum_{i}^{N}\nabla_i^2 + \hat{V}_{ext} + \sum_{i<j}^{N}\frac{1}{|r_i - r_j|} + \frac{\partial E_{XC}[n(\vec{r})]}{\partial n(\vec{r})}\right)\Psi = E\,\Psi \quad (4)$$

In Eq. 4, first three terms in the left hand side are kinetic energy, external potential (electrostatic potential arising due to interaction of nuclei with electrons) and electron–electron interaction (electrostatic repulsion between electrons). The fourth term is the functional derivative of exchange-correlation density functional energy (E_{XC}) with respect to electron density, $n(\vec{r})$. The E_{XC} in LDA and GGA approximations is defined as,

$$E_{xc}^{LDA/GGA}\left[n(\vec{r})\right] = \int n(\vec{r})\,\varepsilon_{xc}\left[n(\vec{r}),\ |\nabla n(\vec{r})|\right] d\vec{r}, \quad (5)$$

where ε_{xc} is the exchange-correlation energy per particle in homogeneous electron gas. Apart from LDA and GGA, there is possibility of hybrid calculations which basically depend upon an empirical scheme wherein DFT exchange-correlation is hybridized with HF exchange. In the present work, we have used two hybrid schemes namely B3LYP and PBE0 within LCAO approach [22]. In LCAO-B3LYP and LCAO-PBE0 schemes, the E_{XC} is approximated as

$$E_{XC}^{B3LYP} = 0.80*(E_X^{LDA} + 0.90*\Delta E_X^{BECKE}) + 0.20*E_X^{HF} + 0.19*E_C^{VWN} + 0.81*E_C^{LYP} \quad (6)$$

$$E_{XC}^{PBE0} = 0.25*E_X^{HF} + 0.75*E_X^{PBE} + E_C^{PBE} \quad (7)$$

where E_X^{HF}, E_X^{LDA}, ΔE_X^{BECKE} and E_X^{PBE} are the exchange potentials of HF [22], Dirac–Slater [22], Becke gradient correction [22,23] and Perdew et al. [24], respectively. E_C^{PBE}, E_C^{VWN} and E_C^{LYP} are the correlation potentials defined by Perdew et al. [24], Vosko–Wilk–Nusair [25] and Lee–Yang–Parr [26], respectively. In the present computations, we have attempted the following combinations of exchange and correlation energies,

(1) LCAO-DFT-LDA: The exchange and correlation energies of Dirac–Slater [22] and Perdew and Zunger [27], respectively.
(2) LCAO-DFT-GGA: The exchange and correlation energies prescribed by Perdew et al. [28].
(3) LCAO-B3LYP: The exchange of Becke [23] and correlation potentials of Lee-Yang-Perr [26] with 20% hybridization as mentioned by Dovesi et al. [22].
(4) LCAO-PBE0: The exchange and correlation energies of Perdew et al. [24] along with the 25% hybridization as prescribed by Adamo and Barone [29].

The lattice parameters and space group for $CoWO_4$, $NiWO_4$ and $CuWO_4$ have been taken from Rajagopal et al. [5], Kuzmin et al. [10] and Khyzhun et al. [13], respectively. The basis sets of AWO_4 (A=Co, Ni and Cu) have been considered after their energy-optimization using BILLY software [22]. The unit cells of monoclinic $NiWO_4$ and triclinic $CuWO_4$ (Fig. 1) are plotted using visualization code of Kokalj [30]. Since the structure of $CoWO_4$ is monoclinic, it is similar to that of $NiWO_4$. In case of $CoWO_4$ and $NiWO_4$ there are

Table 1
A summary of measurement of experimental Compton profiles of AWO_4 (A=Co, Ni and Cu).

Sample	Sample diameter (thickness) (cm)	Bulk density (g/cm^3)	Exposure time (h)	Integrated counts under CP (x 10^7)	Multiple scattering (−10 to +10 a.u.) (%)	Normalization of profile (0 to 7 a.u.) (e$^-$)
$CoWO_4$	1.35 (0.38)	2.71	253.00	2.46	10.49	54.63
$NiWO_4$	1.26 (0.42)	1.99	184.61	2.41	10.35	55.04
$CuWO_4$	1.23 (0.41)	2.97	229.26	2.32	10.31	55.45