



Electronic structure, optical properties and Compton profiles of RuO₂: Performance of PBEsol exchange–correlation approximation



Khushboo Sharma^a, Jagrati Sahariya^b, B.L. Ahuja^{a,*}

^a Department of Physics, M.L. Sukhadia University, Udaipur 313002, Rajasthan, India

^b Department of Physics, Manipal University, Jaipur 303007, Rajasthan, India

ARTICLE INFO

Article history:

Received 17 February 2015

Received in revised form 12 May 2015

Accepted 14 May 2015

Available online 21 May 2015

Keywords:

Compton scattering

Density functional theory

Electronic and optical properties

ABSTRACT

We present first ever electron momentum density of RuO₂ using 20 Ci ¹³⁷Cs (661.65 keV) Compton spectrometer at a resolution (Gaussian FWHM) of 0.34 a.u. The experimental Compton profile (CP) has been compared with the theoretical profiles computed using linear combination of atomic orbitals (LCAO) within framework Hartree–Fock scheme and of density functional theory. Comparison of theoretical and experimental CPs demonstrates usefulness of revised functional of Perdew–Burke–Ernzerhof (so called PBEsol) in computing the electronic properties of RuO₂. The energy bands and density of states of RuO₂ are also reported using LCAO and full potential linearized augmented plane wave (FP-LAPW) method within PBEsol approximation. The complex dielectric functions computed using FP-LAPW method are explained in terms of transitions within energy bands. Our results for dielectric functions show a good agreement with the available experimental data and confirm the Drude like behavior of RuO₂. The Fermi surface structure and reflectivity spectra computed using FP-LAPW method are found to be in tune with the available measurements.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The transition metal dioxides are interesting materials due to their technological importance. In particular, RuO₂ is a unique material due to its low resistance, high thermal and chemical stabilities under ambient conditions. It has important application in electrochemistry as a corrosion-resistant potential electrode for chlorine or oxygen evolution and a catalytic agent for photodecomposition of water [1,2]. Regarding earlier important studies, Liao et al. [3] have characterized RuO₂ and IrO₂ films deposited on Si substrate. Benyahia et al. [4] have studied the structural and electronic properties of RuO₂ in the rutile and orthorhombic structures using full potential linearized augmented plane wave (FP-LAPW) scheme. The relative stability of RuO₂ and Rh₂O₃ in the corundum and rutile-type structures has been reported by Grillo [5], using the density functional theory (DFT) and classical thermodynamics. Almeida and Ahuja [6] have reported the electronic and optical properties of RuO₂ and IrO₂ using the generalized gradient approximation (GGA) within the FP-LAPW method. Growth and characterization of RuO₂ nanorods have been reported by Chen et al. [7]. Ze-Jin et al. [8] have reported electronic structure and optical

properties of rutile RuO₂ using the plane-wave pseudopotentials within DFT scheme. Su et al. [9] have reported the deposition and characterization of RuO₂ nanocrystals on carbon nanotubes, while Patil et al. [10] have synthesized RuO₂ thin films to check their feasibility in supercapacitor application. Chen et al. [11] have synthesized the RuO₂ nanodots on reduced graphene oxide sheets to demonstrate their supercapacitor application. Separately, these authors have also reported that RuO₂ and the graphene/RuO₂ hybrids dispersed by polyvinylpyrrolidone have superior electrochemical properties [12]. Martinez et al. [13] have investigated the structural, electronic and transport properties of RuO₂ nanotubes using the DFT method. Very recently, Park et al. [14] have deposited the conductive and highly conformal RuO₂ thin films without nucleation delay using atomic layer deposition. They revealed that the formation of RuO₂ phase remains favorable with increasing oxygen partial flow rate and pulsing time, and also with decreasing precursor pulsing time and temperature. Luu et al. [15] have examined the efficiency of RuO₂ and IrO₂ electrodes for chlorine evolution using the thermal decomposition method. Petrovic et al. [16] have synthesized and characterized the nanoparticles of RuO₂.

Compton spectroscopy is a well-known technique to probe the ground state electron momentum distribution in metals, alloys and compounds [17]. Within impulse approximation, Compton profile (CP), $J(p_z)$, is the projection of electron momentum densities

* Corresponding author. Tel.: +91 94 143 17048; fax: +91 294 2411950.

E-mail address: blahuja@yahoo.com (B.L. Ahuja).

(EMDs), $\rho(\mathbf{p})$, along the scattering vector direction. Mathematically, $J(p_z)$ is written as,

$$J(p_z) = \iint \rho(\mathbf{p}) dp_x dp_y, \quad (1)$$

where p_z is the component of the electron momentum along the scattering vector (chosen as the z-axis) which depends upon the incident (E_1) and scattered (E_2) photon energies and also the scattering angle θ . Mathematically,

$$\frac{p_z}{m_0 c} = \frac{\{E_2 - E_1 + E_1 E_2 (1 - \cos \theta)\} / m_0 c}{(E_1^2 + E_2^2 - 2E_1 E_2 \cos \theta)^{1/2}}. \quad (2)$$

Anisotropies in CPs ($\Delta J = J_{hkl} - J_{h'k'l'}$) for crystallographic directions $[hkl]$ and $[h'k'l']$ lead to important information about variation of electron density in different directions.

In this paper, we report the first ever experimental CPs of RuO_2 using 20 Ci ^{137}Cs Compton spectrometer [18]. The experimental CP was compared with the theoretical momentum densities computed using various prescriptions of exchange and correlation energies within DFT approximation and Hartree–Fock (HF) scheme as embodied in linear combination of atomic orbitals (LCAO) method. In addition, we have also computed the energy bands, density of states (DOS), Fermi surface structures and frequency dependent optical properties using FP-LAPW method with revised functional of Perdew–Burke–Ernzerhof (so called PBEsol).

2. Experimental details

To measure the CP, polycrystalline powder sample of thickness 0.51 cm and diameter 2.53 cm was kept in a Mylar ampoule. The sample was placed vertically in the scattering chamber of the Compton spectrometer [18]. Incident γ -radiations of energy 661.65 keV were scattered by the sample for about 254 h at an angle of $160 \pm 0.6^\circ$. The energy of the scattered photons was analyzed using a high purity Ge detector (Canberra, USA, model GL0510P) and associated electronics (Canberra made) namely, spectroscopy amplifier, analog to digital converter, multi-channel analyzer, etc. The raw data were corrected for several systematic corrections, like background, instrumental broadening, sample absorption, Compton cross-section and multiple scattering, etc. [19,20]. The background data were measured separately for a period of 120 h by running the system without sample and after that scaled to measurement timings before its subtraction from the raw Compton data. The overall momentum resolution of the spectrometer was 0.34 a.u. The stability of the system was checked from time-to-time using ^{57}Co and ^{133}Ba γ -emitting calibration sources. Finally, the experimental profile was normalized to CP area of $24.78e^-$ being HF free atom CP area in the momentum range 0–6 a.u. [21].

3. Theory

3.1. LCAO calculations

To compute the theoretical CPs, we have used LCAO method as facilitated in CRYSTAL09 code [22–24]. In LCAO approach, the crystalline orbitals are expanded in terms of the basis sets of the atomic orbitals. Besides HF calculations, this code enables DFT calculations within the local density approximation (LDA), second order corrected GGA (so called SOGGA) and PBEsol. In the LDA and GGA, exchange–correlation density functional energy (E_{xc}) is defined as [22–24];

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}^{\text{LDA}}[\rho(r)] d^3 r, \quad (3)$$

$$E_{xc}^{\text{GGA}}[\rho] = \int \varepsilon_{xc}^{\text{LDA}}[r_s(\vec{r})] F_{xc}[r_s(\vec{r}), s(\vec{r})] d^3 r. \quad (4)$$

Here ε_{xc} is the exchange–correlation energy per particle in uniform electron gas with electron density ρ .

In Eq. (4), $F_{xc}(r_s, s)$ is sum of two terms which is given as

$$F_{xc}(r_s, s) = F_x(s) + F_c(r_s, s). \quad (5)$$

Here r_s is the Wigner–Seitz radius and s is reduced density gradient.

Following the prescription of Becke [25], $F_x(s)$ for exchange potential is given by

$$F_x^{\text{GGA}}(s) = 1 + \xi - \frac{\xi^2}{\xi + \mu s^2}, \quad (6)$$

where μ and ξ are the constants.

In SOGGA, $F_x(s)$ is given by [26],

$$F_x^{\text{SOGGA}}(s) = 1 + \xi + \frac{1}{2} \left(\frac{\xi^2}{\xi + \mu s^2} \right) - \frac{\xi}{2} \left(e^{-(\mu s^2/\xi)} \right). \quad (7)$$

The F_x^{SOGGA} can be understood as an equal (50% each) mixing of PBE [27] and RPBE (revised PBE functional) [28]. In SOGGA, the value of ξ was taken as 0.552 [26] which is smaller than other GGA exchange functional leading to effect in Lieb–Oxford bound. Following the suggestions of Perdew et al. [29] value of parameter μ was set to 0.21951.

We have taken the exchange potential of Dirac–Slater [30] and Zhao and Truhlar [26] for the LDA and SOGGA, respectively, and the correlation function of Perdew et al. [27] in both the prescriptions. In case of PBEsol both the exchange and correction potentials were taken from Perdew et al. [29]. In addition, we have also undertaken HF calculations [22] wherein exact exchange interaction between electrons is taken care of while correlation effects are neglected. The all electron Gaussian basis sets for Ru and O were taken from www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. The basis sets were energy optimized for RuO_2 environment using BILLY software [22]. The optimized basis sets are given in [supplementary materials \(S1\)](#). The lattice constants for the rutile ($P4_2/mnm$) phase with

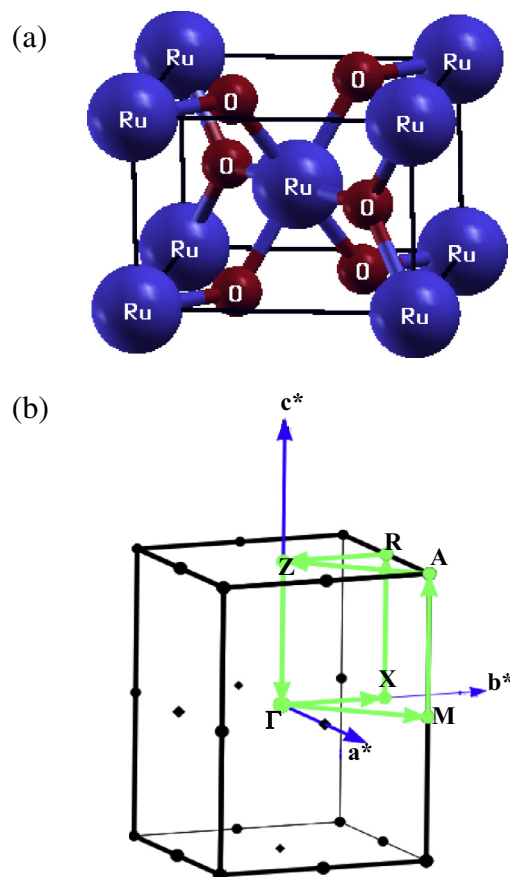


Fig. 1. (a) Crystal structure of rutile phase ($P4_2/mnm$) phased RuO_2 and (b) corresponding standard shape of BZ.

Download English Version:

<https://daneshyari.com/en/article/1608392>

Download Persian Version:

<https://daneshyari.com/article/1608392>

[Daneshyari.com](https://daneshyari.com)