



# Study of electronic structure and Compton profiles of transition metal diborides



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## ABSTRACT

We report Compton profiles (CPs) of transition metal diborides (MB<sub>2</sub>; M= Ti and Zr) using a 740 GBq <sup>137</sup>Cs Compton spectrometer measured at an intermediate resolution of 0.34 a.u. To validate the experimental momentum densities, we have employed the linear combination of atomic orbitals (LCAO) method to compute the theoretical CPs along with the energy bands, density of states (DOS) and Mulliken's population response. The LCAO computations have been performed in the frame work of density functional theory (DFT) and hybridization of Hartree-Fock and DFT (namely B3LYP and PBE0). For both the diborides, the CPs based on revised Perdew-Burke-Ernzerhof exchange and correlation functions (DFT-PBESol) lead to a better agreement with the experimental momentum densities than other reported approximations. Energy bands, DOS and real space analysis of CPs confirm a metallic-like character of both the borides. Further, a comparison of DFT-PBESol and experimental data on equal-valence-electron-density scale shows more ionicity in ZrB<sub>2</sub> than that in TiB<sub>2</sub>, which is also supported by the Mulliken's population based charge transfer data.

## 1. Introduction

Transition metal diborides (like MB<sub>2</sub>, where M = transition metal) have several applications due to their peculiar properties such as high melting point, hardness, chemical stability, high thermal conductivity and low electrical resistivity [1–3]. Out of several MB<sub>2</sub> compounds, ZrB<sub>2</sub> is useful in ultra-high-temperature ceramic and is used in high temperature aerospace components and nose caps for hypersonic re-entry vehicles [4,5]. TiB<sub>2</sub> is a potential despersoid for light-weight high-temperature structured materials which are employed in cutting tools, electrodes and wear-resistant components [1,6]. Due to technological importance of both the diborides, several theoretical attempts have been made to investigate their structural, mechanical and electronic response using density functional theory (DFT) [7–13]. The electronic structure of ZrB<sub>2</sub> has also been experimentally studied by Tsuda et al. [14] using X-ray absorption and valence band photoemission spectroscopy. Compton profiles (CPs) of TiB<sub>2</sub> and VB<sub>2</sub> have been measured by Mahapatra and Padhi [15] using 200 mCi <sup>241</sup>Am point source with a momentum resolution of 0.6 a.u. (Gaussian, full width at half maximum). The experimental data was compared with simple free atom based superposition profiles. Kumar et al. [9] have reported the CP measurement on ZrB<sub>2</sub> using 59.54 keV  $\gamma$ -rays (with poor momentum resolution, 0.6 a.u.) and compared their results with the linear

combinations of atomic orbitals (LCAO) method within density functional theory (DFT) and also a crude ionic model. Recently, our group has reported the electronic properties of transition metal diborides namely NbB<sub>2</sub> and TaB<sub>2</sub> using Compton spectroscopy [16,17].

It is worthwhile to mention that Compton scattering (CS) is a unique and powerful tool for scrutinizing the electronic properties of materials [18,19]. The broadening in Compton scattered  $\gamma$ -radiations is sensitive to behavior of electronic state of the materials. The spectrum of inelastically scattered photons, so called the CP,  $J(p_z)$ , is related to electron momentum density  $n(\mathbf{p})$  of the electronic system. Mathematically,

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

where  $p_z$  is the linear momentum of electron along the scattering vector direction ( $z$ -axis). The  $p_z$  is related to the incident and scattered photon energies ( $E_1$  and  $E_2$ , respectively) and also the scattering angle  $\theta$  [18,19],

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

In this paper, we present experimental CPs of TiB<sub>2</sub> and ZrB<sub>2</sub> using 661.65 keV photon energy at high resolution (0.34 a.u.) using our 740 GBq <sup>137</sup>Cs Compton spectrometer [20,21]. In Compton profile measurements, the critical limiting parameters are the instrumental

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resolution and fulfillment of criteria of impulse approximation (IA) [18–21]. There is failure of IA for core electrons of 3d and 4d transition elements (like Ti and Zr) when a low incident photon energy *viz.* 60 keV from  $^{241}\text{Am}$  source is used [9,15]. Therefore, the present Compton spectroscopy measurements are expected to be more accurate and reliable. On the theoretical side, we have used LCAO-DFT to calculate the CPs, energy bands, density of states (DOS) and Mulliken's population (MP) data. We have employed more accurate exchange and correlation potentials to check their performance in reproducing the electronic properties and momentum densities. Moreover, the relative nature of bonding in both the isoelectronic diborides has also been discussed on the basis of equal-valence-electron-density (EVED) scale and MP data. Bonding characteristics in both the diborides are also explored using real space analysis of CP data, energy bands and DOS.

## 2. Methodology

### 2.1. Experiment

740 GBq  $^{137}\text{Cs}$  Compton spectrometer with an overall resolution of 0.34 a.u. [20,21] has been used to measure the CPs of polycrystalline  $\text{TiB}_2$  and  $\text{ZrB}_2$ . Both the compounds were procured from M/s Alfa Aesar, USA (purity 99.5%). The measurements were made on polycrystalline powder samples because of difficulties in getting the large size single crystals and a reliable comparison of nature of bonding in  $\text{TiB}_2$  and  $\text{ZrB}_2$  on EVED scale. In individual experiments, a collimated beam of 661.65 keV  $\gamma$ -ray was allowed to fall normally on the ampoule consisting of polycrystalline  $\text{TiB}_2$  and  $\text{ZrB}_2$  samples. The scattering angle in the present measurements was  $160 \pm 0.6^\circ$ . The diameter and thickness of pellet of  $\text{TiB}_2$  ( $\text{ZrB}_2$ ) were 2.41 and 0.24 cm (2.53 and 0.35 cm), respectively. It is worth mentioning that use of 661.65 keV photon energy ensures the validity of impulse approximation, because in the high energy based scattering process the energy transferred to electrons is much larger than the binding energy of all the atomic electrons. Therefore, the area under the present CPs corresponds to the number of electrons which also includes all the core electrons, in contrast to  $^{241}\text{Am}$  based measurements [9,15]. The scattered photons were energy-analyzed using a high purity Ge detector (Canberra, USA) which was cooled to 77 K (liquid nitrogen temperature). In the present measurements, the  $\text{TiB}_2$  and  $\text{ZrB}_2$  samples were exposed to  $\gamma$ -rays for about 209 and 154 h, respectively. The electronic drift in spectra during the measurements was checked from time-to-time and was found to be negligible. The background contribution was estimated from an independent measurement after removing the sample from the sample holder in the scattering chamber. Further, the raw data were processed for systematic corrections, namely, background, stripping-off the low energy tail, sample absorption, Compton cross-section and multiple scattering using methodology of Warwick group [22,23]. In the present measurements, effects of multiple scattering were found to be 5.04% and 8.12% for  $\text{TiB}_2$  and  $\text{ZrB}_2$ , respectively. Finally, the experimental profiles were normalized to respective free-atom CP areas, which are 14.86 and 21.54  $e^-$  (in the  $p_z$  range 0–7 a.u.) for  $\text{TiB}_2$  and  $\text{ZrB}_2$ , respectively [24].

### 2.2. LCAO approximation

The directional and isotropic CPs, energy bands, total and partial DOS and MP data of both the diborides have been calculated using LCAO-DFT approach as embodied in CRYSTAL09 program [25–27]. We have used the second order generalized gradient approximation (SOGGA) and the revised Perdew-Burke-Ernzerhof functional for solids (PBEsol) within DFT along with two schemes of hybridization of HF and DFT (namely B3LYP and PBE0) methods. Different approximations differ in terms of the exchange-correlation density functional energy ( $E_{xc}$ ). For DFT-SOGGA and DFT-PBEsol schemes, the  $E_{xc}$  is defined as,

$$E_{xc}^{\text{SOGGA/PBEsol}}[\rho(\vec{r})] = \int \rho(\vec{r}) \epsilon_{xc}^{\text{GGA}}[\rho(\vec{r})] F_x^{\text{SOGGA/PBEsol}}(s) d\vec{r} \quad (3)$$

Here  $\epsilon_{xc}^{\text{GGA}}$  is the exchange-correlation energy density per particle,  $s$  corresponds to reduced density gradient and  $F_x^{\text{SOGGA/PBEsol}}$  is enhancement factor of exchange component for SOGGA/PBEsol scheme.

Further, the  $E_{xc}$  for B3LYP and PBE0 are approximated as,

$$E_{xc}^{\text{B3LYP}} = 0.80 \times E_x^{\text{LDA}} + 0.72 \times \Delta E_x^{\text{BECKE}} + 0.20 \times E_x^{\text{HF}} + 0.19 \times E_c^{\text{VWN}} + 0.81 \times E_c^{\text{LYP}}, \quad (4)$$

and

$$E_{xc}^{\text{PBE0}} = 0.25 \times E_x^{\text{HF}} + 0.75 \times E_x^{\text{PBE}} + E_c^{\text{PBE}} \quad (5)$$

The nomenclatures of the various exchange and correlation components used in the present work are:

- DFT-SOGGA: Exchange energy of SOGGA [28] and correlation energy of PBE [29].
- DFT-PBEsol: Exchange and correlation energies with PBEsol approximation [30].
- B3LYP: Exchange of Dirac-Slater [25], Hartree-Fock [25] and Becke [31], and correlation energies of Vosko-Wilk-Nusair [32] and Lee-Yang-Parr [33] with 20% of HF exchange energy [25].
- PBE0: Exchange of HF [25] and PBE [29] and the correlation functional of PBE [29] with 25% of HF exchange energy [25].

The all electron Gaussian basis-sets for Ti, Zr and B were taken from [www.tcm.phy.cam.ac.uk/~mdt26/basis\\_sets](http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets). The basis-sets were energy optimized for  $\text{TiB}_2$  and  $\text{ZrB}_2$  environment [25]. The experimental lattice parameters  $a$  and  $c$  for  $\text{TiB}_2$  ( $\text{ZrB}_2$ ) with space group  $P6/mmm$  were taken as 3.027 (3.170) Å and 3.240 (3.530) Å, respectively [4,6]. The self-consistent field calculations have been performed at 270  $\mathbf{k}$  points in the irreducible Brillouin zone for both  $\text{TiB}_2$  and  $\text{ZrB}_2$ . To derive absolute total profiles, the CPs for core electrons were taken from the conventional tables of Biggs et al. [24]. It may be noted that one can also take core electrons CP contribution from the LCAO calculations which produce similar type of core contribution as reported by Biggs et al. [24]. The core contributions were added to the valence isotropic theoretical profiles. In the present LCAO computations, the spherical average value of momentum density  $n(\mathbf{p})$  are expected to be quite precise because these are evaluated as the average of the function values at 60 points  $\mathbf{p}_n$  ( $n = 1, 2, 3, \dots, 60$ ) lying on the surface which form an orbit under the icosahedral group [25].

## 3. Results and discussion

### 3.1. Energy bands and DOS

In Figs. 1 and 2, we have shown the energy bands and DOS of  $\text{TiB}_2$  and  $\text{ZrB}_2$ , respectively, computed using DFT-PBEsol scheme. Since overall shapes of the energy bands and DOS computed using DFT-PBEsol scheme are found to be almost similar (except few fine structures and energy values) to those computed using DFT-SOGGA, B3LYP and PBE0 schemes, only PBEsol based electronic response is shown. In general, present energy bands and DOS for both the diborides are in reasonable agreement with those available in literature [1,8–12]. From Figs. 1, 2, it can be seen that the energy bands and DOS cross the Fermi level ( $E_F$ ) which show a metallic character of both the diborides. From the energy bands reported in Figs. 1 and 2, the lowest energy band within the energy range  $-13.70$  to  $-8.49$  eV ( $-12.49$  to  $-7.64$  eV) for  $\text{TiB}_2$  ( $\text{ZrB}_2$ ) is mainly due to B-2s states. Since this band is away from the  $E_F$ , it suggests a localized behavior of 2s states of both the diborides and hence plays a little role in formation of bonds in both the diborides. The energy bands in the energy range  $-2.53$  to  $2.25$  eV ( $-2.70$  to  $3.39$  eV) for  $\text{TiB}_2$  ( $\text{ZrB}_2$ ) which cross the  $E_F$  at different branches of Brillouin zone are the strongly hybridized bands arising

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