Influence of Te doping in titanium dichalcogenides: LCAO calculations and Compton spectroscopy

D Mali*, K Kumar, P K Jangid, P K Joshi, G Arora and B L Ahuja

Department of Physics, University College of Science, Mohanlal Sukhadia University, Udaipur, 313001 Rajasthan, India.

E-mail: deepikamali31@gmail.com

Abstract. Role of Te doping in titanium disulfide using linear combination of atomic orbitals method and Compton spectroscopy is reported. The theoretical Compton profiles (CPs) of TiSTe derived using various exchange and correlation potentials like Perdew-Burke-Ernzerhof, Perdew-Wang generalized gradient approximation and von Barth-Hedin (VBH) are compared with corresponding experimental CP to check the applicability of considered potentials. From the total and partial density of states, we observe that doping of Te at S site vanishes the narrow band gap of TiS₂ leading to metallic character of TiSTe. A good agreement between experimental and VBH potential based CP of TiSTe shows better performance of VBH approximation in this mixed metal-like dichalcogenide.

Keywords: Electronic structure, Compton scattering, Transition metal dichalcogenides

PACS No.: 71.15.Mb, 77.84. Rw, 32.80.Cy

1. Introduction

Transition metal dichalcogenides (TMDs) like titanium dichalcogenides, TiX₂ (X= S or Te) have got much attention because of their peculiar structural and electronic properties and their possibility as cathode material in Li rechargeable batteries and hydrogen storage, etc. [1-3]. In earlier work, the electronic properties of 1T phase of TiX₂ (X=S, Se, and Te) has been reported by Reshak and Auluck [1] using full potential linearized augmented plane wave (FP-LAPW) method. Using density functional theory (DFT) with the local density approximation (LDA), Yu et al. [2] have discussed pressure dependent structural and vibrational properties of TiS₂. Authors have reported reasonable agreement between experimental and theoretical calculations for the compressional properties and high pressure thermodynamic properties of the trigonal phase. Ding et al. [3] have discussed structural aspects of layered TiX₂ employing vander Waals density functionals (vdW-DFs) and concluded that vDW-DFs calculations lead to better agreement with experimental measurements for lattice constant involving the vDW interactions. Using ab-initio DFT calculations, the electronic and optical properties of TiS₂ have been reported by Kouch et al. [4]. The crystal structure of TiS₂ in a wide pressure range have been studied by Zhou et al. [5] by using the swarm structure technique in combination with DFT. Using first principles DFT theory, Ricci et al. [6] have investigated energetic and electronic properties of TiS₂. Authors obtained an electronic density deformation closer to experimental profile and also a better estimate of the interlayer binding energy. Hu et al. [7] have reported a Fe₂P-type phase in a typical TiTe₂ by using crystal structure and first principles calculations.
To the best of author’s knowledge, the electronic response of Te doped TiS$_2$ using DFT calculations and Compton scattering (CS) technique has not been investigated. It is established that CS is a versatile technique to study the reliability of ground state electronic wave functions in materials [8-11]. The Compton profile (CP), J(p$_z$), is basically projection of the electron momentum density $\rho(p)$ along the scattering vector (usually z-axis).

In the present work, effect of Te doping in TiS$_2$ on its electronic response using linear combination of atomic orbitals (LCAO) method as facilitated in CRYSTAL14 code [12] and CS technique are presented. We have employed exchange and correlation potentials as prescribed by Perdew-Burke-Ernzerhof (PBE) [13], Perdew-Wang generalized gradient approximation (PWGGA) [14] and von Barth-Hedin (VBH) [15] to compute density of states (DOS) and theoretical CPs. Experimental CP of TiSTe is compared with theoretical CPs to check the suitability of exchange and correlation potentials in system like TiSTe.

2. Methodologies

The lattice parameters with space group $\overline{P}$3 m1 were taken from Reshak and Auluck [1]. To get the composition TiSTe, we have substituted one Te atom by one S atom in TiS$_2$. The all electron basis sets (Gaussian-type) for Ti, S and Te (from www.tcm.cam.ac.uk) were optimized for the lowest energy of system using the BILLY software [16] with standard energy tolerance values [12]. The C measurement of TiSTe was performed using 100 mCi (59.54 keV) Am-241 Compton spectrometer [17]. Compton spectra was measured using high purity Germanium detector (GL0210P, USA). The raw data were corrected for background, detector response function, absorption and scattering cross-section, multiple scattering, etc., using data correction programs [9, 18]. All the experimental and theoretical CPs were normalized to area of free-atom profile (37.611 e$^-$) [19] in the momentum range 0-7 a.u.

3. Results and discussion

3.1 Electronic structure

To look the influence of Te doping in TiS$_2$ at S site, we have computed total and partial DOS of TiS$_2$, TiSTe and TiTe$_2$ using LCAO scheme. The total and partial DOS of TiS$_2$, TiSTe and TiTe$_2$ using PBE and PWGGA exchange and correlation potentials are found to have similar overall topology with those computed using VBH approximation, therefore DOS using VBH approximation only is described here (figure. 1 a-c). The DOS derived in present computations are in agreement with those reported by Reshak and Auluck [1]. In figure 1(a), we have observed a narrow band gap about 0.19 eV showing a semiconductor nature of TiS$_2$. Further, it is seen that in valence band (VB) there is strong hybridization between Ti-3d and S-3p states. Also an energy gap of 0.91 eV is found in conduction band (CB) region. Doping of 50% Te at S site (figure 1b) results in disappearance of the narrow band gap due to cross-over of Fermi level (EF) by Ti-3d states. We also spotted widening in the energy gap in CB from 0.91eV in TiS$_2$ to 1.93 eV in TiSTe. It is because the Te doping shifts the energy states in CB region (lying between 4.26 to 5.64 eV) to high energy side.

Complete replacement of S (in TiS$_2$) by Te atom which leads to TiTe$_2$ composition further shifts the Ti-3d energy states towards lower energy side (figure. 1c) leading to reduces energy gap in CB region from 1.93 eV to 0.89 eV. In TiTe$_2$ (figure 1c), we observe that there are more energy states around EF. The energy states of Ti-3d below -2.7 eV energy as found in TiS$_2$ are not visible after complete replacement of S by Te.
3.2 Compton Profile

To compare our experimental Compton line shape, we have derived theoretical CPs using LCAO method. All the theoretical CPs were convoluted to the overall momentum resolution of 0.55 a.u. of spectrometer. In figure 2, we have depicted the differences between convoluted theoretical and experimental CPs. Closeness between theoretical and experimental CPs in the region 4-5 a.u. is due to dominance of well-defined core electrons. Differences observed in low momentum region between theoretical and
experimental CPs may be due to non-relativistic nature of LCAO calculations, and the quality of basis sets used in the LCAO calculations. On the basis of $\chi^2$ fitting, it is concluded that the theoretical CP derived using VBH prescription gives a better agreement with experimental CP, which proves that VBH as a better choice of exchange and correlation potentials to predict the Compton line shape and electronic response of TiSTe.

**Figure 2.** Differences (in the $p_z$ range 0-5 a.u.) between isotropic experimental and convoluted theoretical Compton profile of TiSTe derived using LCAO method within PBE, PWGGA and VBH approximations.

4. **Conclusions**

On the basis of LCAO method and Compton scattering technique, it is concluded that VBH exchange and correlation potentials are a better combination to predict electronic properties of TiSTe. A narrow band gap of 0.192 eV in TiS$_2$ disappears on increasing the concentration of Te at S site.

**Acknowledgements**

We are thankful to Theoretical Chemistry Group, Torino, Italy for providing the CRYSTAL14 code for LCAO calculations. The work is supported by UGC-BSR Research Start-Up Grant (F.30-476/2019(BSR) sanctioned to GA and RUSA 2.0, MHRD, New Delhi.

**References**

[1] Reshak A H and Auluck S 2003 *Phys. Rev. B* **68** 245113-1
[2] Yu Y G and Ross N L 2011 *J. Phys. Condens. Matter* **23** 055401-1
[3] Ding H and Xu B 2012 *J. Chem. Phys.* **137** 224509-1
[4] Kouch H El, Farh L El, Sayah J and Challioui A 2015 *Chin. Phys. Lett.* **32** 096102-1
[5] Zhou D, Xu Y, Bai L, Shen B, Wang X, Zou Y and Tian J 2018 *J. Alloys Compd* **757** 448
[6] Ricci M, Ambrosetti A and Silvestrelli P L 2020 *J. Phys. Chem. C* **124** 27592
[7] Hu K, Lian J, Zhu Li, Chen Q and Xie S Y 2020 *Phys. Rev. B* **101** 134109-1
[8] Cooper M J 1985 *Rep. Prog. Phys.* **48** 415
[9] Cooper M J, Mijnarends P E, Shiotani N, Sakai N and Bansil A 2004 *X-ray Compton Scattering* (New York: Oxford Science Publications)

[10] Schülke W, 2007 *Electron Dynamics by Inelastic X-ray Scattering* (New York: Oxford University Press)

[11] Ahuja B L and Dashora A 2016 *Compton Scattering in Reference Module in Materials Science and Materials Engineering* (UK: Elsevier)

[12] Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson C M, Pascale F, Civalleri B, Doll K, Harrison N M, Bush I J, D’Arco Ph, Llunel M, Causa M and Neol Y 2014 *CRYSTAL14 User’s Manual* (Torino: University of Torino)

[13] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865

[14] Perdew J P and Wang Y 1992 *Phys. Rev. B* 45 13244

[15] Barth U V and Hedin L 1972 *J. Phys. C: Solid State Phys.* 5 1629

[16] Towler M D, Zupan A and Causa M 1996 *Comput. Phys. Commun.* 98 181

[17] Ahuja B L, Sharma V, Rathor A, Jani A R and Sharma B K 2007 *Nucl. Instrum. Meth. B* 262 391

[18] Timms D N 1989 *Compton Scattering Studies of Spin and Momentum Densities* (UK: University of Warwick)

[19] Biggs F, Mendelsohn L B and Mann J B 1975 *At. Data Nucl. Data Tables* 16 201