

Band Gap Engineering of $\text{Cu}_2\text{-II-IV-VI}_4$ Quaternary Semiconductors Using PBE-GGA, TB-mBJ and mBJ+U Potentials

J. Bhavani^{1,2}, Rita John^{1*}

¹Department of Theoretical Physics, University of Madras, Chennai-600 025, (T. N.), India

²Department of Physics, Ethiraj College for Women, Chennai-600 008, (T. N.), India

*Corresponding Author: ritajohn.r@gmail.com, Tel.: +91-9566245138

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Abstract— The structural and electronic properties of $\text{Cu}_2\text{ZnGeX}_4$ ($X = \text{S, Se and Te}$) with a tetrahedral coordinated stannite structure have been investigated using first-principles calculations. The optimized lattice constants, anion displacement u , tetragonal distortion parameter η , band gap, density of states and bulk modulus values are reported. The modified Becke-Johnson exchange potential (TB-mBJ), is used to calculate the electronic properties of Cu based quaternary semiconductors $\text{Cu}_2\text{ZnGeX}_4$ ($X = \text{S, Se and Te}$) and thus the results for the band gap and other electronic properties such as Total Density of States (TDOS) and Partial Density of States (PDOS) are analyzed in detail. Also the results obtained using TB-mBJ potential are compared with the standard local density and generalized gradient approximation (GGA). Even though the comparison of results shows that the results obtained by TB-mBJ are still underestimating the experimental results. This explains the inadequacy of mBJ potential for semiconductors with strongly delocalized d electrons. Thus in this paper an on-site Coulomb U is incorporated within mBJ potential (mBJ + U) which leads to a better description of the pd hybridization and therefore the band gap which is very much comparable with the experimental results.

Keywords— $\text{Cu}_2\text{-II-IV-VI}_4$ ($X = \text{S, Se and Te}$), Band Structure, TB-mBJ potential, mBJ+U, Cu-based semiconductor, importance of d-orbitals.

I. INTRODUCTION

The chalcogenide quaternary semiconductor series, $\text{I}_2\text{-II-IV-VI}_4$ are known to have a potential for applications such as photovoltaic absorbers, optoelectronic and thermoelectric materials [1-4]. Among these compounds Cu-based semiconductors $\text{Cu}_2\text{ZnGeX}_4$ ($X = \text{S, Se and Te}$) have promising band gaps and have emerged as nontoxic, low-cost and high efficiency material for thin film solar cell applications. Although it is widely recognized that these multinary semiconductors provide ample opportunities for material design, it is still very difficult to prepare and design high quality quaternary semiconductors because of the substantial uncertainties in determining their crystal structures, electronic, and optical properties. Theoretically, since last two decades, the first principle calculations have been successfully used to design the crystal structure and study their properties. Several hybrid functionals have been proposed, aiming for a better account of the exchange interaction of localized electrons.

As Cu based quaternary semiconductors are widely used in many optical and optoelectronic devices, it is important to understand their structural and electronic properties. Various

research groups have tried to explore the electronic band structure of binary, ternary and quaternary semiconductors using full potential linearized augmented plane wave method (FP-LAPW) [5,6] within the framework of Density Functional Theory (DFT) [7] using wien2k code [8]. It was found that for most of the compounds, especially for ternary and quaternary semiconductors the band gaps are underestimated by GGA potential [9,10]. In the present study, for copper based quaternary compounds GGA clearly underestimates the band gaps [11-13]. This is because of the fact that GGA does not consider the existence of derivative discontinuity of energy with respect to the number of electrons. For a group of compounds which has similar generic nature, such as ZnX , CuGeX_2 and $\text{Cu}_2\text{ZnGeX}_4$, this derivative discontinuity term is almost the same [12-14]. Therefore, the band gap discrepancy due to the usage of GGA compared to experimental band gap values are expected to be similar for the group of similar compounds [14]. But TB-mBJ is a direct alternate for GW or hybrid functional which yields comparable accuracy with experimental values [17]. The combination of TB-mBJ exchange and GGA correlation has produced better band gaps for various semiconductors and insulators. In this paper the quaternary semiconductors are theoretically investigated

using both PBE and TB-mBJ potentials and the results are analyzed. TB-mBJ, the exchange potential proposed by Becke and Johnson [11] was designed to reproduce the shape of the exact exchange optimized effective potential of atoms [18,19]. The new potential reproduces the band gaps of semiconductors with accuracy several orders of magnitude better than the previous version of the WIEN2k code using either LDA or the GGA [20] but still not able to give a closer agreement with the experimental results. It is a known fact that the electronic structure of strongly correlated materials is characterized by a set of partially filled narrow bands, typically derived from strongly localized atomic d states. The traditional density functional theory (DFT) [7] based electronic structure methods within the local density approximation (LDA) or the generalized gradient approximation (GGA) often fail to describe their properties. Based on Yubo Zhang et al., [21] local or semi-local functionals (or potentials) tend to underestimate the binding energy or d states of Cu and their localization, resulting in an incorrect description of the pd hybridization (bonding) in these systems. The band gap is also often severely underestimated using these functionals. As a result, much research interest has been focused on correlated electronic structure methods which handle the Cu d states and pd hybridization (bonding) reasonably well. Thus in this paper, we show that, applying an on-site coulomb U within mBJ potential. The basic idea behind mBJ+ U is to treat the strong on-site Coulomb interaction of localized electrons, which is not correctly described by LDA or GGA, with an additional Hubbard-like term. The effective method proposed by Anasimov et al., where only a single effective $U_{\text{eff}} = U - J$ parameter accounts for the coulomb interaction. The on-site Coulomb interactions are particularly strong for localized d and f electrons, but can be also important for p localized orbitals. The strength of the on-site interactions are usually described by parameters U (on site Coulomb) and J (on site exchange). These parameters U and J can be extracted from ab-initio calculations. Here the on-site Coulomb interactions to Cu d electrons significantly enhances the localization of d states [22] thus giving a better description of the pd hybridization and therefore the band gap. The total DOS and partial DOS of $\text{Cu}_2\text{ZnGeX}_4$ ($X=\text{S, Se and Te}$) using PBE-GGA, TB-mBJ and mBJ+ U approaches are analyzed, as it is essential for the study of the hybridization of the states within the valence band. The band gap of $\text{Cu}_2\text{ZnGeX}_4$ ($X=\text{S, Se and Te}$) are reported and found that the mBJ + U approach predicts the band gap which is comparable to the experimental results for narrow-gap Cu-based semiconductors. These results suggest that the mBJ+ U approach can serve as a convenient alternative to more sophisticated many-body approaches such as the GW method for fast screening of Cu-based multinary semiconductors for various applications [23]. The paper is organized with the following sections. The introduction of the chosen materials and different potentials used to analyze the properties of the

quaternary material are discussed in section I. Section II deals with the computational details and method of calculations. Section III comprises of results and discussions, in which structural and electronic properties of $\text{Cu}_2\text{ZnGeX}_4$ compounds are analyzed. In the concluding section (IV) the observed and investigated results are summarized.

II. MATERIALS AND METHODS

The calculations are performed using full potential linearized augmented plane wave method (FP-LAPW) within the framework of density functional theory (DFT) using wien2k code [8]. The generalized gradient approximation (GGA) is used in the scheme of Perdew-Barke-Eruzerhof (PBE) [24] and TB-mBJ [11] potential. Basis functions were expanded in combinations of spherical harmonic functions inside non-overlapping spheres surrounding the atomic sites and by plane waves basis set in the remaining space of the unit cell (interstitial region). The maximal value for the wave function expansion I_{max} inside the atomic spheres was confined to $I_{\text{max}}=10$. To achieve the energy eigen value convergence, the wave function in the interstitial region were expanded in plane waves with a cutoff of $k_{\text{max}} = 8/R_{\text{mt}}$, where R_{mt} is the average muffin tin radius and k_{max} gives the magnitude of the largest k vector in the plane wave expansion. The charge density is fourier expanded up to $G_{\text{max}}=12 \text{ a.u.}^{-1}$. Self-consistent calculation converged when the total energy of the system is stable within 10^{-4} Ry . The integrals over the BZ are performed using 175 k-points in the irreducible BZ. The Cu ($3d^{10} 4s^1$), Zn ($3d^{10} 4s^2$), S ($3s^2 3p^4$), Se ($3d^{10} 4s^2 4p^4$), Ge ($3d^{10} 4s^2 4p^2$) and Te ($4d^{10} 5s^2 5p^4$) orbitals are treated as valence states. There are various empirical methods that estimate the parameter of the screened on-site Coulomb energy (U). However, depending on the fitting procedure, the value of U sometimes varies significantly. For example, the screened Coulomb U for the semicore d electrons in ZnO used in the literature varies from 4.7 to 13 eV [25-29]. The Coulomb U for Cu d electrons is calculated using a recently implemented, combined Wannier orbitals and constrained random phase approximation (cRPA) method [30,31]. We first construct the maximally localized Wannier orbitals [32] for all valence states calculated within the PBE + U method using some initial U and J . The screened Coulomb matrices U_{ij} and exchange matrices J_{ij} are then calculated self consistently. The U and J parameters used in the mBJ + U method are the averaged values of the U_{ij} and J_{ij} matrices. The effective Coulomb energy, $U_{\text{eff}} = U - J$, is about 5.2 eV. For simplicity, we will use this screened Coulomb energy for all systems investigated in this work. This is well justified since the variation in the U parameter is rather small ($\sim 0.5 \text{ eV}$) in these Cu-based semiconductors [33]. In addition, the calculated band gap is not sensitive to a small change in the U parameter used. For example, a 0.5 eV variation in the U parameter will only result in less than 0.05 eV change in the calculated band gap.

III. RESULTS AND DISCUSSION

3.1. Structural Properties: The structure of $Cu_2-II-IV-VI_4$ compounds can be derived from its binary equivalent II-VI chalcogenides. When cross-substituting pairs of groups I and III atoms for the group II atoms with the octet rule still obeyed, ternary I-III-VI₂ compounds can be generated [34,35]. These ternary semiconductors exhibit promising electronic properties. For example, the band gap of $AgInS_2$ 1.89 eV, being lower than that of its binary analog CdS 2.45 eV, is more suitable for application in thin-film solar cells [36]. Following this method novel quaternary chalcogenides Cu_2ZeGeX_4 (X=S, Se and Te) can be formed. Goodman [37] and Pamplin [38] pioneered the design of quaternary chalcogenides through cation cross-substitution in ternary I-III-VI₂ systems. While replacing two group III atoms by one II and one IV atom, $I_2-II-IV-VI_4$ compounds can be formed [39]. These quaternary semiconductors have tetrahedrally coordinated crystal structures (derived from zincblende or wurtzite structure) and electronic structure (s-p band gap) similar to the binary II-VI semiconductors (ZnS , $CdTe$), but their properties are much more diverse given the increased number of elements, so they may have wide applications in electronic, optoelectronic, photovoltaics, or photocatalytic applications [40]. Through substituting Cu by other group I (+1 valence) cations, Zn by group II (+2 valence) cations, Sn by group IV (+4 valence) cations, and S or Se by group VI anions (-2 valence), a class of $I_2-II-IV-VI_4$ quaternary semiconductors, such as Cu_2ZnSnS_4 , $Ag_2CdSnSe_4$ and $Cu_2CdGeSe_4$ can be designed.

Using this method a series of quaternary semiconductors had been synthesized, e.g., $I_2-II-IV-VI_4$ with I=Cu,Ag, II=Zn, Cd, IV=Si, Ge, Sn, Pb, and VI=S, Se, as listed in the semiconductor handbooks[41]. The synthesis of some other $I_2-II-IV-VI_4$ compounds had also been reported. For example, $Cu_2ZnSn(S,O)_4$ (alloy of Cu_2ZnSnS_4 and Cu_2ZnSnO_4) was synthesized using chemical vapor deposition method by Washio et al.[42], and Cu_2BaSnS_4 , Ag_2BaSnS_4 and Cu_2SrSnS_4 were synthesized from a mixture of three binary sulfides by Teske et al.[43]. Since there are many elements with +1, +2, +4 and -2 valences, e.g., II = Mg, Ca, Sr, Ba (group IIA), IV = Ti, Zr, Hf (group IVB) and VI = O, Te, their combination can lead to a large number of potential $I_2-II-IV-VI_4$ compounds. As a result of the increased number of elements, quaternary chalcogenides have more structural configurations and more complicated electronic and structural properties than the binary and ternary ones. In this paper a systematic investigation has been carried out to explore the structural and electronic properties of Cu_2ZeGeX_4 (X=S, Se and Te).

3.2. Structural Optimization:

The crystal structures of Cu-based quaternary semiconductors are shown in Figures 1a-c. This structure can be obtained by cation initiation of the group III atoms in

ternary semiconductors to II and IV atoms. The $I_2-II-IV-VI_4$ quaternary semiconductors have two fundamental crystal structures one is kesterite and other is stannite structure [20]. The structure reported here is stannite structure with a space group I42-m. In all structures, Se or S (group IV) atoms are surrounded by two Cu (group I) atoms, one group IV atom (Sn or Ge) and a Zn (group II) atom. Therefore, the octet rule is obeyed, such tetrahedrally coordinated semiconductors, have three different bonds with group VI atom (Se or S) as center in the stannite structure.

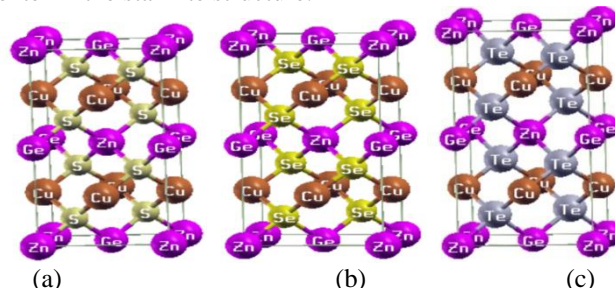


Figure 1. The Crystal Structure of (a) Cu_2ZnGeS_4 (b) $Cu_2ZnGeSe_4$ and (c) $Cu_2ZnGeTe_4$

The ground state properties of these compounds are obtained using the optimized values of the lattice parameters. Figures 2a-c show the E_{tot} versus V curves for Cu_2ZnGeS_4 , $Cu_2ZnSnSe_4$ and $Cu_2ZnGeTe_4$ compounds. These curves were obtained by calculating E_{tot} at reduced and extended volumes and by fitting the calculated values to the Murnaghan equation of states [44]. From the optimization curves (Figure 2), the equilibrium lattice constant (a_0), the bulk modulus (B_0) and the pressure derivative of the bulk modulus (B') are calculated. The calculated values of lattice constant and bulk modulus are presented in Table1. The anion displacement parameter and the c/2a ratio are also optimized for all the compounds.

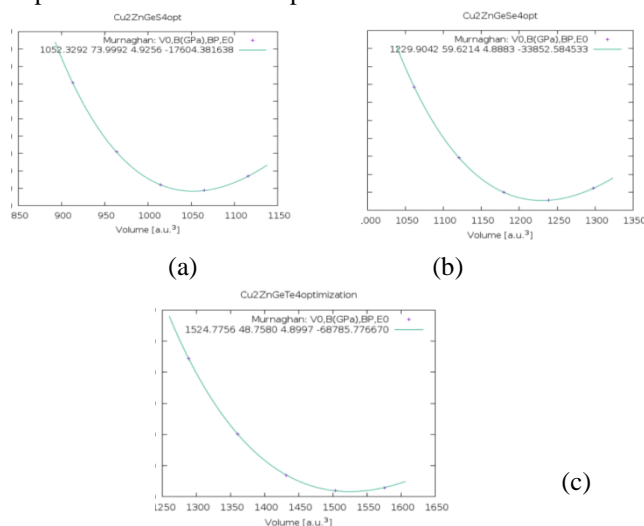


Figure 2. Calculated total energy for reduced and extended volume for (a) Cu_2ZnGeS_4 (b) $Cu_2ZnGeSe_4$ and (c) $Cu_2ZnGeTe_4$

The calculated structural parameter $c/2a$ is more than unity for $\text{Cu}_2\text{ZnGeX}_4$ (S, Se and Te) but the experimental results show that it is less than unity [45]. This discrepancy between theoretical and experimental calculations is due to the fact that the similarity of Cu^+ and Zn^{2+} atoms leads to the cation shift in their experimental structures [6]. Even using X-ray diffraction, it is not easy to detect the cation disorder because only the Zn^{2+} and Cu^+ site ordering is different but both elements have the same X-ray form factor [46,47]. Partial cation disorder has been observed in $\text{Cu}_2\text{ZnSnS}_4$ sample by neutron diffraction measurement [48].

The anion displacement (u) equation for ST structure is given as [48],

$$u_{st} = \frac{0.25 + \left[R_{\text{Cu-VI}}^2 - \frac{(R_{\text{II-IV}}^2 - R_{\text{IV-VI}}^2)}{2} \right]}{a^2}$$

Comparing the u values (Table 1) with band gaps of $\text{Cu}_2\text{ZnGeX}_4$ (S, Se and Te) given in Table 2, it is evident that the band gap decreases with the decrease in anion displacement u . The change in anion displacement sensitively influence the electronic properties of the valence band maximum (composed of Cu d and S p states) and conduction band minimum (composed of Ge s states and S p states) and hence leads to the variation of band gap [32].

Table 1. The equilibrium lattice parameters, a_0 and c_0 , u , tetragonal distortion η , bulk modulus B , its pressure derivative B' and volume V_0 of $\text{Cu}_2\text{ZnGeX}_4$ (S, Se and Te)

3.3. Electronic Properties: Band structure

The band structures of $\text{Cu}_2\text{ZnGeX}_4$ (S, Se and Te) are calculated along high symmetry points of the first Brillouin Zone using PBE-GGA and TB-mBJ potentials and it is shown in the Figure 3. The total and partial DOS were calculated using PBE, TB-mBJ and mBJ+U potentials. It is found that all three compounds have direct band gaps as the valence band maximum and conduction band minimum are located at Γ point. The E_g of $\text{Cu}_2\text{ZnGeS}_4$ using PBE-GGA are 0.53 eV, and for $\text{Cu}_2\text{ZnGeSe}_4$ and $\text{Cu}_2\text{ZnGeTe}_4$ it shows metallic character. Whereas the band gap of $\text{Cu}_2\text{ZnGeX}_4$ ($X = \text{S, Se and Te}$) using Tb-mBJ are found to be 1.492 eV, 1.090 eV and 0.789 eV respectively and the band gap using mBJ+U are 2.34 eV, 1.687 eV and 0.995 eV respectively. Calculated band gap values are compared with other theoretical and the experimental reported values and presented in Table 2. From the comparison it is clear that the calculated energy band gap using mBJ+U are much closer to the experimental results than PBE-GGA and TB-mBJ. It is because of the fact that the local or semi local functionals (or potentials) underestimates the binding energy of Cu d states and their localization, resulting in an incorrect description of the pd hybridization of the system [49]. Hence while

applying an on-site coulomb interaction U , the position of Cu d states are better predicted and hence better description of the pd hybridization.

Structure	a_0 (Å)	c_0 (Å)	u	$\eta = c/2a$	B (GPa)	B'	V_0 (a.u. ³)
$\text{Cu}_2\text{ZnGeS}_4$	5.397 9	10.832 4	0.257 3	1.003	73	4.9 2	1052.3 2
$\text{Cu}_2\text{ZnGeSe}_4$	5.677 9	11.384	0.253 9	1.002	59	4.8 8	1229.9 0
$\text{Cu}_2\text{ZnGeTe}_4$	6.129 9	12.266	0.249 2	1.000	48	4.8 8	1524.7 7

The fermi energy level E_F is set at 0 eV. For all the three the schemes the band structure has the same generic nature. But it is observed that mBJ+U potential causes a rigid displacement of the conduction bands towards higher energies with respect to the top of the valence band with small differences in the dispersion at same regions of the Brillouin zone. Thus reproducing, in general is the characteristic behavior of the bands for semiconductors according to experiment [14-16] as the WIEN2k code used to. For all the three schemes the valence band (VB) has two main sub-bands. Comparing the schemes for the compound $\text{Cu}_2\text{ZnGeS}_4$, the first valence band at Γ occupies the region between (0 to -2.0 eV), (0 to -0.8 eV) and (0 to -1.2 eV) for PBE-GGA, TB-mBJ and mBJ+U respectively. It shows that the width of first valence band using PBE-GGA is larger than other two schemes. It is to be noticed that the width of first VB for TB-mBJ is very small ranging from 0 to -0.8 eV. It indicates the overestimation of interaction between pd states of Cu and anion atoms in $\text{Cu}_2\text{ZnGeS}_4$ compound. Another interesting observation is that the width of the second VB using all the three schemes are more or less the same and it ranges between -3.0 eV to -3.4 eV.

Table 2. Calculated band gap (E_g) using PBE-GGA, TB-mBJ and mBJ+U potentials and other theoretical (E_g) compared with experimental values.

COMPOUND	E_g^{GGA} (eV)	E_g (eV) Theoretical	E_g (eV) Experimental
$\text{Cu}_2\text{ZnGeS}_4$	0.47 ^a 0.53	2.14 ^a 1.5 ^b 1.492 (TB-mBJ) 2.34 (mBJ+U)	2.15 2.04
$\text{Cu}_2\text{ZnGeSe}_4$	-0.22 ^a -0.18	1.32 ^a 1.0 ^b 1.090 (TB-mBJ) 1.687 (mBJ+U)	1.29 1.16 1.23
$\text{Cu}_2\text{ZnGeTe}_4$	-0.55 ^a -0.13	0.55 ^a 0.789 (TB-mBJ) 0.995 (mBJ+U)	--

[50]^a, [51]^b, Experimental data references [52-55]

But the gap between first and second VB for all the three schemes shows significant variations. For TB-mBJ potential the gap between first and second VB is maximum (-3.9 eV) and for others it is -1.0 eV and -1.8 eV using PBE-GGA and mBJ+U potentials respectively which indicates the need of high energy for the lower VB electrons to reach the upper conduction band, thus underestimating the band gap when compared to mBJ+U scheme. The second valence band at Γ falls at (-3.0 eV to -6.0 eV), (-4.6 eV to -8.00 eV) and (-3.0 to -6.0 eV) for PBE-GGA, TB-mBJ and mBJ+U respectively. The energy range of first VB is minimum for TB-mBJ and here for second VB it gives maximum energy range.

3.4. Density of States

The partial DOS of $\text{Cu}_2\text{ZnGeX}_4$ (X=S, Se & Te) compounds are analyzed. Total DOS together with partial DOS using GGA, TB-mBJ and mBJ+U potentials for $\text{Cu}_2\text{ZnGeS}_4$ are presented in Figure 4 and 5. The results obtained using GGA, TB-mBJ and mBJ+U potentials reveals the generic nature of the band structures and density of states of all three compounds and it is confirmed from other experimental results for Cu based quaternary semiconductors [9]. The results show a linear decrease of the band gap when replacing S with Se and Te. The reduction in the energy gap is not expected as Se/Te is slightly more electronegative, which should result in the larger band gap. However the influence of electronegativity is considerably smaller than the influence of p-d hybridization, as explained by Jaffe et al, [56,57]. The degree of pd hybridization between the Cu-d states and anion-p states determines the valence band energies and band offsets [14-16] in which a good mixing of pd orbitals ensures more Cu d states being located at the valence band edge [56]. This mixing is mainly controlled by the energy levels of the atomic orbitals of the constituents, and changing bond length directly affect this degree of hybridization. Therefore by replacing the anion atoms from S to Se and Te, the anion displacement parameter shows considerable variations. This change in the structure plays a predominant role in determining the valence band energies (Table 2). This is evident from the band structures of $\text{Cu}_2\text{ZnGeX}_4$ compounds, as more Cu d states are located in the valence band edge when the anion atom changes from S to Se to Te. In the present study the displacement of anion leading to larger bond lengths for telluride when compared

with selenides and sulfide. As a direct consequence the increasing bond length lead to decreasing bonding interactions and a subsequent reduction in the band gaps in these quaternary chalcopyrites [57]. Similar observation has been reported by us in II-IV-V2 pnictides [26,27].

As discussed in the electronic properties of $\text{Cu}_2\text{ZnGeX}_4$, the valence band of all the three compounds consist of two main subbands. Here mainly the contribution of individual orbitals using PBE-GGA, TB-mBJ and mBJ+U potential for $\text{Cu}_2\text{ZnGeS}_4$ compound are analyzed since other two compounds follow same pattern of orbital contribution. For $\text{Cu}_2\text{ZnGeS}_4$, first, the upper valence band (UVB) which extends from (0 to -2.0 eV), (0 to -0.7 eV) and (0 to -1.2 eV) for PBE-GGA, TB-mBJ and mBJ+U potentials respectively is predominantly from Cu 3d states mixed with p states of anion atoms. Following Yamasaki et al [49], the degree of hybridization can be defined by the ratio of Cu d states and anion p states within the muffin tin sphere.

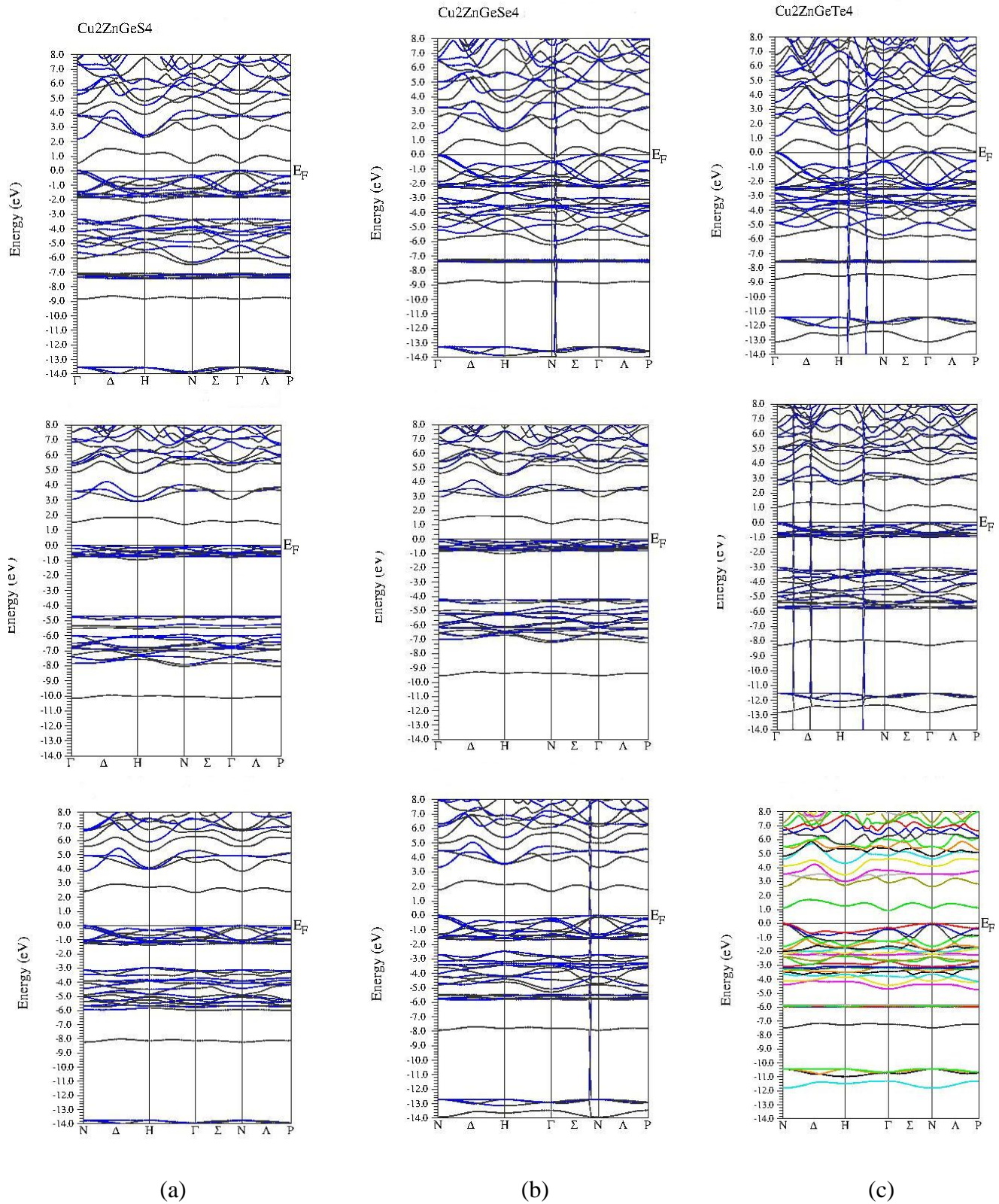


Figure 3. Calculated band structures along the high symmetry lines in the first Brillouin zone for (a) $\text{Cu}_2\text{ZnGeS}_4$ (b) $\text{Cu}_2\text{ZnGeSe}_4$ (c) $\text{Cu}_2\text{ZnGeTe}_4$ using PBE_GGA, TB-mBJ and mBJ+U potential respective

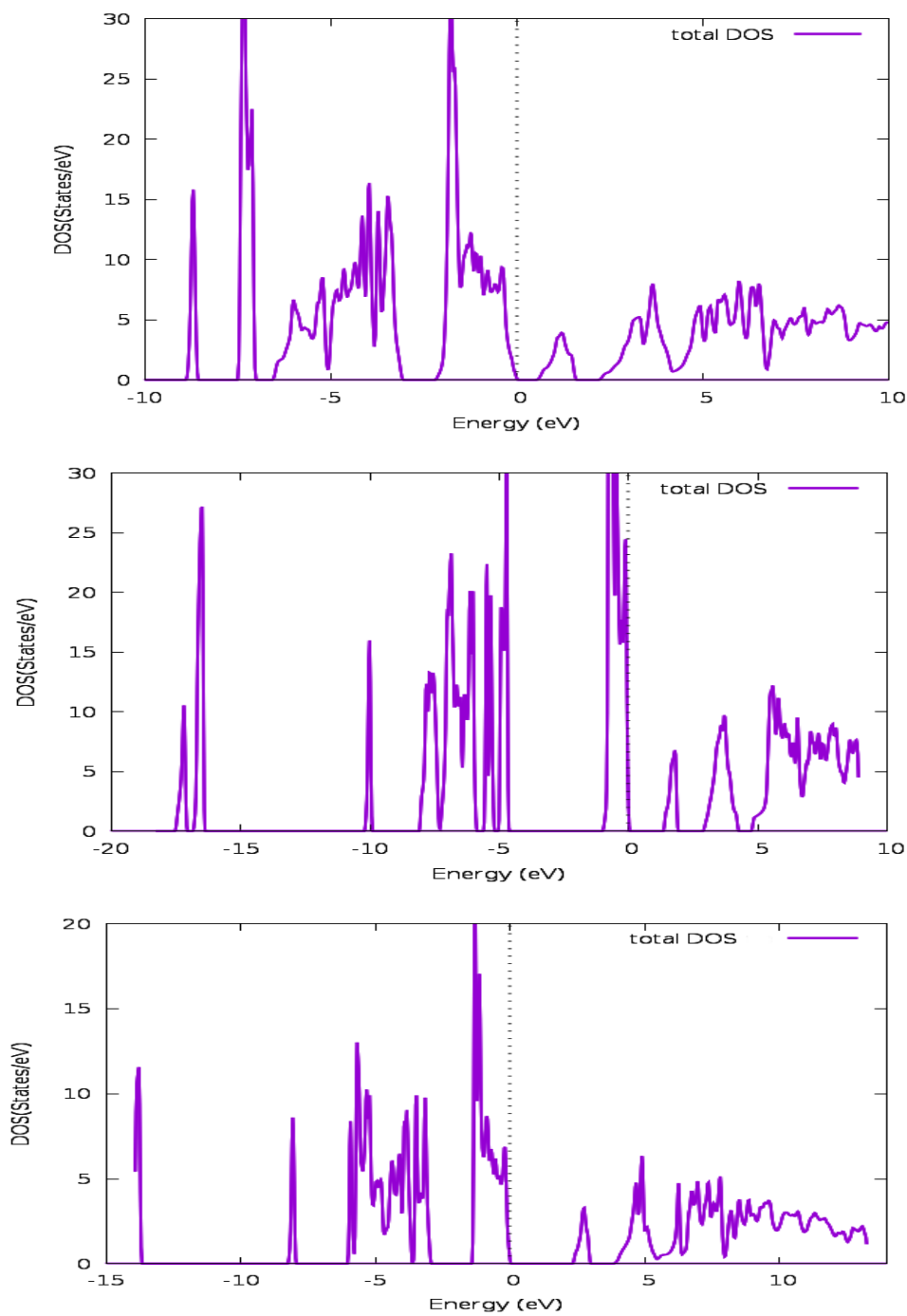


Figure 4: TDOS using PBE-GGA, TB-mBJ and mBJ+U potential for $\text{Cu}_2\text{ZnGeS}_4$ compound

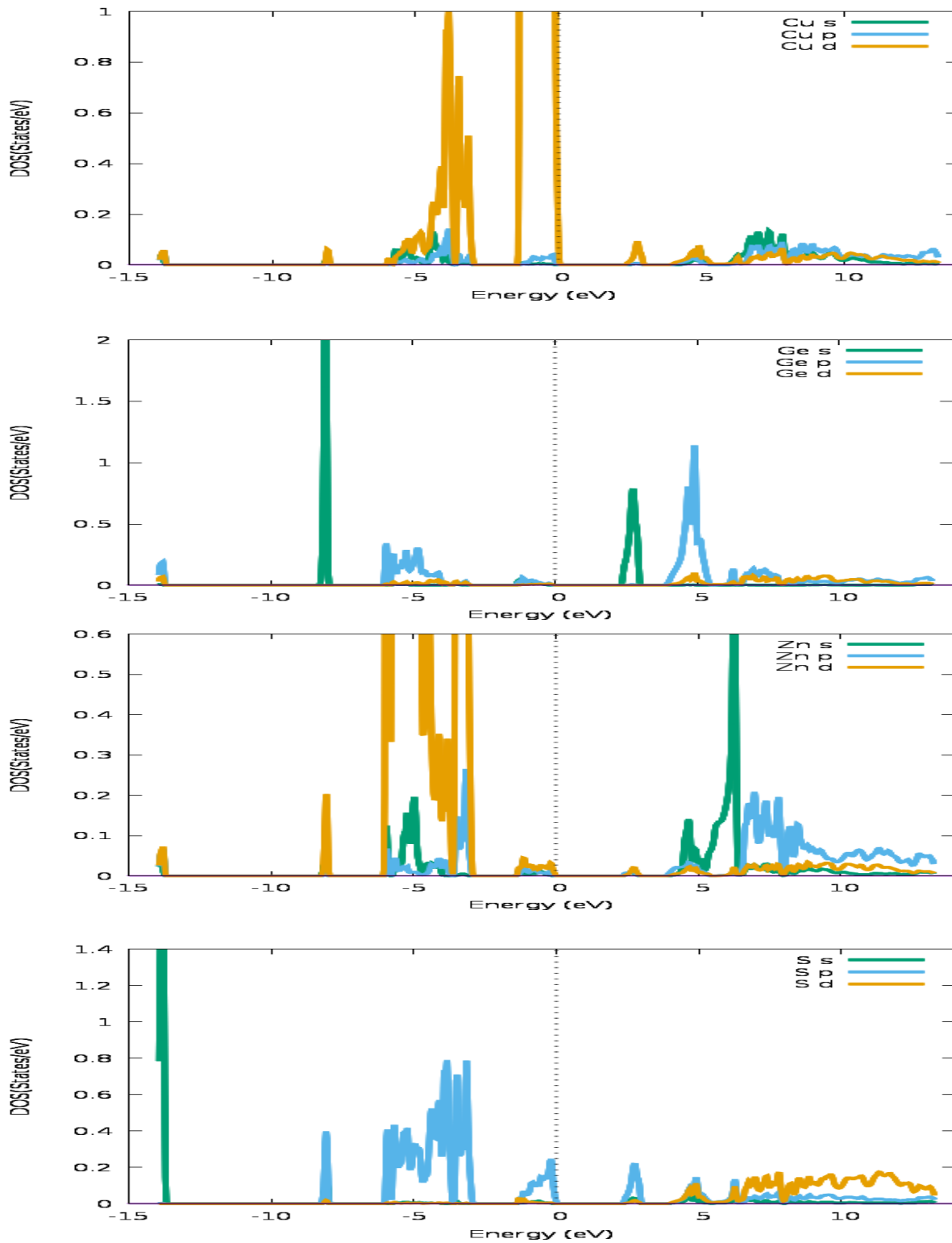


Figure 5: PDOS using PBE-GGA, TB-mBJ and mBJ+U potential for Cu₂ZnGeS₄ compound

Based on this, it can be concluded that the hybridization between Cu d and anion p states becomes weak leading to the broadening of peaks (figure 4). The lesser interaction between Cu d and S p states, results in lower band gaps when the group VI atom changes from S to Te. The second valence band region are mainly comprised of S 3p states hybridized with Cu 3d state. Some traces of Ge p orbitals are also seen in this region. The band structure shows a solo conduction band (CB) and it is derived from the Ge 4s and anion p states. It is observed that this band shifts to lower energy when the anion atomic number increases from S to Te. This reveals the influence of anion displacement parameter u over the energy gap of any compound as already discussed in the structural properties.

On applying the on-site potential U , it is observed that in the conduction band the Zn s states are seen completely detached from Zn p states whereas for TB-mBJ potential the overlapping of Zn s and p states are observed. This indicates the strong interaction of orbitals in the upper most valence band that pushes the Zn p orbitals to the higher energy region. The higher conduction bands do not contribute to the band gap values. It is observed that, the broadening of peaks between the energy range of valence and conduction band in TDOS and PDOS for all the three compounds reveals the lesser interaction of orbitals in PBE-GGA potential.

4. CONCLUSION:

In summary, we have investigated systematically the structural and electronic properties of $\text{Cu}_2\text{ZnGeX}_4$ ($X=\text{S, Se}$ and Te) quaternary compounds using PBE-GGA, TB-mBJ and mBJ+ U potentials implemented in wien2k. The calculated results are compared with the experimental and other theoretical results. For moderate-gap Cu-based semiconductors, the mBJ method underestimates the band gaps by about 0.25 to 0.85 eV. Thus by applying an on-site Coulomb U within mBJ potential, improved the description of Cu d states, leading to more reasonable results. The importance of the role of Cu d states in determining the electronic properties of $\text{Cu}_2\text{ZnGeX}_4$ are analyzed. It is observed that the lesser interaction between Cu d and S p states, results in reduction of band gaps, when the group VI atom changes from S to Te. The influence of anion displacement parameter u over the energy gap of any compound is discussed. The calculated anion displacement parameter agrees well with experimental results. It is observed that the conduction band shifts downward (lesser band gap) when the group VI anion atomic number increases from S to Se to Te. i.e., compound with Te shows lesser band gap when compared with Se and S. The calculated results show that the energy gaps are substantially enhanced by mBJ+ U over TB-mBJ and GGA.

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AUTHORS PROFILE

Rita John is Professor and Head, Department of Theoretical Physics, University of Madras, Chennai, India. She is Fulbright Visiting Professor at the Department of Physics and Astronomy, Texas Christian University, Fort Worth, Texas, USA (2014). She has been teaching solid state physics for graduate students over 20 years. The book, ‘Solid State Physics’ authored by her and published by Tata McGraw Hill publisher (2014) is used globally by graduate students. Her area of research is Condensed Matter Physics. She guides Ph.D., M.Phil., M.Sc., and M.Tech. projects. She has over 100 international publications. She is the recipient of various awards and prizes for her academic and research contributions.



MS. J. Bhavani, doing Ph. D under the guidance of Dr. Rita John, Professor and Head, Department of Theoretical Physics, University of Madras, Guindy Campus, Chennai - 600 025, T.N., India. She is currently working as assistant professor in Ethiraj College for Women, Chennai, Tamilnadu, India. Her research work focuses on DFT studies for electronic structure and various properties of quaternary semiconductors.

