Electronic Band Structure of Solar Cell Material by Range Separated Hybrid Theory

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Abstract : In this paper we report the electronic structure calculations of cubic chalcopyrite $CuGaSe_2$ using density functional theory, within various exchange and correlation operators of linear combination of atomic orbitals method. The chalcopyrite results in a direct-gap semiconductor with valence band maximum and the conduction band minimum at the Γ point of irreducible Brillouin zone.

Index Terms **- Solar Cell Materials; Band Structural Calculations; Density Functional Theory**

I. INTRODUCTION

Ternary chalcopyrite semiconductors have been extensively studied due to wide variety of technological applications. The compounds with I-III-VI_2 type structure are isoelectronic with the Zinc-blend semiconductor compounds. They are abundantly used in visible light emitting diode, infrared LED, infrared detectors and far infrared generation [1]. Due to wide band-gaps of the chalcopyrites containing copper, $CuGaSe_2$ has potential application as absorber materials in thin film solar cells [2]. Their efficiency mainly depends on the composition and crystal structure and purity of the compounds involved [3]. Sajid et al. [4] have studied the electronic and optical properties of $CuYZ_2$ compounds using the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method of density functional theory (DFT). Kumar et al. [5] have applied Tran-Blaha modified Becke-Johnson (TB-mBJ) potential to study the optical properties of Cu-based chalcopyrite semiconductors $CuXS_2$ (X=Al, Ga, In) [5]. Soni et al. [6] have employed linear combination o f atomic orbitals (LCAO) and FP-LAPW methods studied various properties of solar cell compounds. Alnaso et al. [7] have performed few ellipsometry spectroscopic measurements to study the optical constants of these chalcogenides.

II. COMPUTATIONAL METHOD

The present study has been undertaken by applying local density approximation (LDA), generalized gradient approximation (GGA) and range separated hybrid (RSH) middle range functional, HISS, within the DFT using CRYSTAL14 code [8]. For LDA scheme we have applied the LDA-PZ theory [9, 10] and for GGA we have used exchange and correlation functional of PBE [11]. In RSH-HISS theory, the HF exchange energy depends on the distance between different electrons. The Middle-range corrected functional is based on the PBE exchange hole [12, 13] together with PBE correlation. The electronic band structure calculations of $CuGaSe_2$ have been performed using the all-electron Gaussian basis sets for Cu, Ga and Se, which have been taken from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. The lattice parameters for $CuGaSe_2$, were taken as a = 5.61Å and c = 11.0Å [4]. The BRODYEN scheme [15] has been incorporated for faster convergence of self consistent-field cycles for all the calculations.

III. RESULTS AND DISCUSSION

The electronic properties of $CuGaSe_2$ have been derived by employing DFT-LDA, DFT-GGA and RSH-HISS approaches of CRYSTAL14 method. All the theories give similar topology of bands. The band gaps for the solar cell compound as calculated using various approximations of LCAO methods along with the available data are summarized in Table 1.

Table 1 Energy band gap of $CuGaSe_2$ (in eV) using theoretical and experimental methods

Present work			**Previous studies**					**Available Experiment**
DFT-LDA (PZ)	DFT-GGA (PBE)	RSH (HISS)	LMTO (LDA)	FP-LAPW (GGA-WC)	FP-LAPW (GGA-PBE)	FP-LAPW (LDA-PW)	FP-LMTO (GGA-PBE)	
0.0638	0.1806	1.76	0.20 [3]	0.093 [6]	0.199 [6]	0.83 [15]	0.28 [16]	1.68 [1]

In Figs. 1 and 2, we have plotted the energy bands (E–k relations) and density of states (DOS) of $CuGaSe_2$ chalcopyrites using DFT-GGA approach. The energy scale is chosen as Hartree. The valence band maximum (VBM) and the conduction band minimum (CBM) occurs at the Γ point resulting in a direct band gap semiconductor. Except for some fine structures and band gaps, the overall shape of our energy bands is in agreement with the earlier reported data [4-7]. All previous theoretical works and our LDA and GGA theory give underestimated band gap, whereas, the RSH approach gives band gap comparable to the reported experimental work. Hence, proves the validity of range separated hybrid theory. From DOS figure, we can observe that the lowest valence bands (around -0.85 Hartree) are due to Se atomic states region and bands around -0.7 Hartree are produces by 4s and 4p

states of Ga and Se atoms. The valence band states upto Fermi energy are dominated by Cu electronic states and hybridization of Ga and Se states. The conduction states are due to mixing of Ga and Se-4sp electronic states.

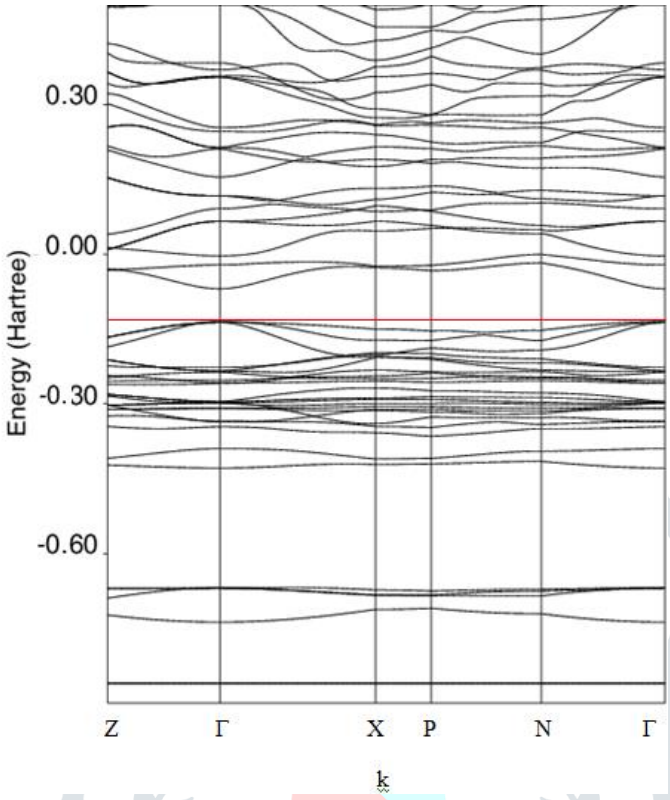

Fig.1 Energy bands curve for $CuGaSe_2$ computed using RSH-HISS theory of LCAO method. The high symmetry directions coordinates are X(0 0 0.5), N(0 0.5 0), Z(0.5 0.5 –0.5), Γ(0 0 0) and P(0.25 0.25 0.25).

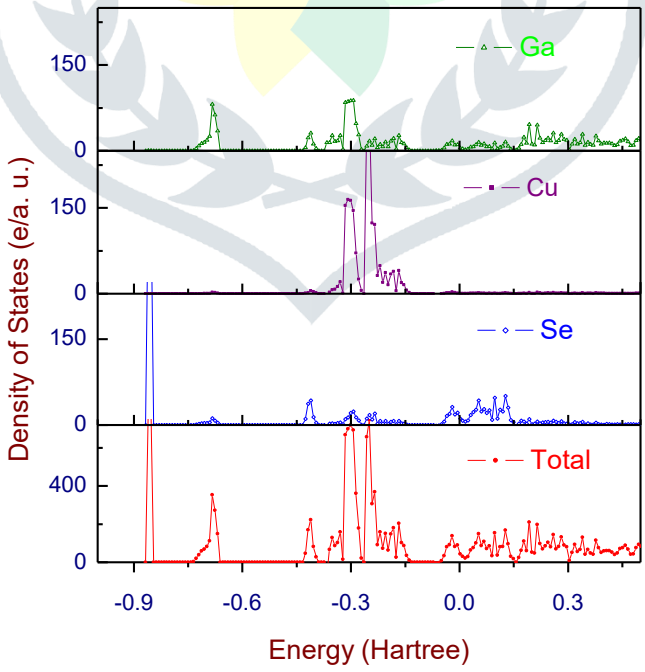

Fig.2 Total and partial density of states (DOS) curves for $CuGaSe_2$ computed using RSH-HISS theory of LCAO method.

IV. CONCLUSIONS

In present work, we have studied the performance of range separated hybrid (RSH) middle range functional HISS over local density approximation (LDA) and generalized gradient approximation (GGA) methods. We can clearly observe that LDA and GGA theories underestimate the band gap whereas RSH agrees well with the experimental data. The band structure calculations reveal that the semiconductor studied has direct band gap at Γ point.

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