Study of Structural, Electronic and Optical Properties of CuXY$_2$ (where X= Al, Ga, Ge and Y= S, Se, In) Using DFT

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Abstract— The ternary compounds of the general formula CuXY2 (where X= Al,Ga,Ge and Y= S, Se, In) are one of the most studied materials as an alternative green sources of energy as an alternate to conventional sources of energy. They are widely used materials in various opto-electrical instruments. In the present study, we have studied the structural, electronic and optical properties of these chalcopyrites using FP-LAPW (full-potential linearized augmented-plane-wave method) method within DFT as implemented within Wien2k code. In the study, it was found that the theoretical values of various physical parameters matched to a great extent with the experimental values. Therefore, it allows us to formulate and design new materials by doping the ternary compounds of the general formula CuXY2 with dopants and predict and design new materials of desired characteristics.

Keywords— Chalcopyrites, DFT, FP-LAPW, Wien2k, Structural, Electronic, Optical properties.

I. INTRODUCTION

Cu-based ternary chalcopyrite of the general formula CuXS2 (where X=Al,Ga,In) with I-42d space group are one of the most sought materials for study by researchers all around the globe owing to their wide uses. They are non-magnetic semiconductors and are the structural analogues of ZnS. They possesses diverse structural, electrical and optical properties [1,2,3]. On account of their diverse properties, they are extensively used in photovoltaic optical detectors, solar cells, and light emitting diodes [4,5,6]. The experimental values of the band gaps of CuAlS2, CuGaS2 and CuInS2 are 3.5eV, 2.43eV and 1.55eV respectively [7]. Among these compounds, CuInS2 has good absorption coefficient and has the optimum band gap of 1.55 eV for use in solar cells. CuAlS2 ternary compound with chalcopyrite crystal structure has a large direct energy gap of 3.5 eV and has the potential applications for optoelectronic devices in the short wavelength region i.e. from blue to ultraviolet region of the spectrum.

There are reports of the both experimental as well as the theoretical works on CuXS2 chalcopyrites by previous workers. Jaffe and Zunger have carried out the studies of the chemical trends in the band structures, electronic charge densities, density of states and chemical bonding of six Cu-based ternary chalcopyrite semiconductors using the potential-variation mixed-basis (PVMB) approach [8]. They have also calculated the band gaps of CuAlS2 and CuGaS2 as 2.05 eV and 1.25 eV respectively. However, their band energy calculation of CuInS2

of -1.4eV tells us about semi metal character of the same compound. Oguchi et al. have applied the self-consistent linear combination of atomic orbitals (LCAO) to study the band structure of CuAlS2 and CuGaS2[9]. "Nayebi et al. have studied the structural, electronic structure and optical properties of CuXY2 (X =In, Ga and Y=S, Se) chalcopyrite semiconductors within density functional theory using numerical atomic orbital pseudopotential method with both local-density and generalized gradient approximations. They have found the values of the band gaps of CuGaS2 and CuInS2 as o.7 eV and 0.07 eV respectively" [10]. "Brik et al. with the GGA approximation and plane-wave (PW) pseudo potential method studied electronic and optical properties of CuXS2. They obtained the band gaps of the CuAlS2, CuGaS2 and CuInS2 as 1.94 eV, 0.9 eV and zero, respectively" [11]. Reshak and S. Auluck using the full potential linear augmented plane wave (FP-LAPW) method within the framework of DFT have found the values of the band gap of CuAlS2 as 2.7 eV [12]. Ahuja et al. with the full-potential linear muffin-tin orbital (FP-LMTO) method, studied the electronic structure of CuGaS2 and have found the band gap of the same compound to be 1.2 eV [13]. *Xiao* et al. calculated the band gap of CuAlS2, CuGaS2 and CuInS2 materials as 3.47 eV, 2.47 eV and 1.6eV respectively by using B3PW91 hybrid functional, with standard molecular Gaussian-type basis sets [14]. Thus we see that there is huge mismatch between the theoretical and experimental bandgaps of the chalcopyrites mentioned above except the use of the hybrid potential.

Our objective in the present paper is to study the structural, electronic and optical properties of the chalcopyrites using Full Potential- Linear Augmented Plane Wave (FP-LAPW) method [15] within the formalism of Density Functional Theory (DFT) [16] using Wien2k package [17] using Generalised Gradient Approximation (GGA) [18], Local Density Approximation (LDA)[19] and Tran–Blaha modified Becke–Johnson (TB-mBJ) [20-21] as exchange correlation potential. We will also see how the properties change when the central atom X in CuXS2 is replaced by Al,Ga and In respectively.

II. STRUCTURE AND METHOD USED

The ternary CuXS2 compounds crystallize in the chalcopyrite structure with a tetragonal space group having four formula units in each unit cell. They are ternary analog of the

diamond structure and can be regarded as a superlattice (or superstructure) of the zincblende structure. In these structures each atom has four neighbours arranged at the corners of a regular tetrahedron bonded by sp3 bonds. Each S atom in the lattice is at the center of a tetrahedron with four cations at each corner. Since in a chalcopyrite structure, in contrast to the zincblende, the Sulphur atom is bonded to two types of cations, the respective bond lengths are not necessarily identical. As a result the tetrahedron is no longer regular but is distorted along the crystal such that the c/a ratio deviates from the ideal value of 2.0.
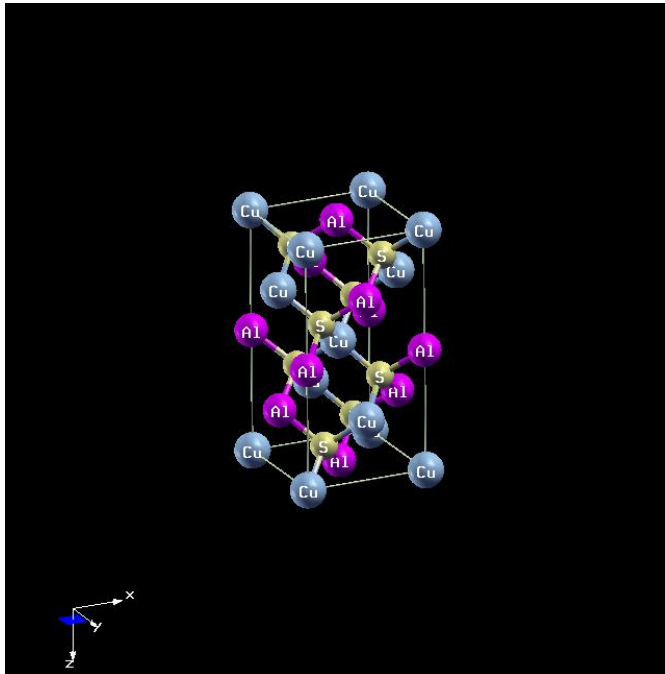

Fig. 1: Structure of CuXS2 compounds.(Here CuAlS2 is shown as reference)

We have performed first-principles study within a density functional theory using the FP-LAPW method as implemented in Wien2K code [22], to solve the Kohn–Sham equations. The generalized- gradient approximation (GGA) within the Perdew–Burk– Ezrenhof (PBE) parameterization, Local-density approximations (LDA) and Tran–Blaha- modified Beck and Johnson (TB-mBJ) potential have been used as the exchange correlation potential. In this method the unit cell volume is divided into the non-overlapping Muffin-Tin spheres surrounding every atom and the remaining interstitial region. The Muffin T in sphere radii (RMT) for each atom are Cu=2.28 a.u.; Al=2.00 and S=1.87 a.u; Ga=2.35 a.u, and In=2.5 a.u. respectively. We have taken the product of minimum of the Muffin Tin radius of atoms (R_{mt}) and maximum value of the wave vector (K_{max}), i.e., R_{mt}. K_{max} = 7.0 and make the expansion of the valence wave functions inside the Muffin Tin sphere into spherical harmonics up to l max = 10 while in the inter- stitial region plane waves are used. We have ensured while choosing Muffin Tin radii do not overlap each other, and core charge do not leak out of the spheres. The electronic configurations in the ground state for the valence electrons are Cu:4s1 3d10, S: 3s2 3p4, In: 3d10 5s2 5p1, Ga: 4s2 4p1 and

Al:3s2 4p1 respectively. The corresponding Wyckoff positions of atoms in the unit cell, Cu (0,0,0), (In, Ga,Al) (0,0,1/2) and S (u,1/4,1/8) (where u=0.235 for CuAlS2, u=0.2538 for CuGaS2 and u=0.22946 got CuInS2)are used. In the first step the volume optimisation was done using wave vector k= 1000 with experimentally obtained values of a and c of CuXS2 as supplied in table 1. The theoretical values of the lattice parameters thus obtained using each of GGA and LDA exchange correlation potentials were then applied to study the DOS and energy bands of CuXS2 compounds. Within first Brillouin zone total 1000 k-points have been taken that reduces into 99 k-points in irreducible Brillouin zone. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4}Ry. In order to study the optical properties using TB-mBJ exchange correlation potential, we have used scissor operators of desirable magnitudes to fit our theoretical values of band gap with the experimental values.

III. RESULTS AND DISCUSSION

Structural properties

In the first step, the Volume optimisation was performed by plotting energy against volume using the experimentally obtained lattice constant as given in the table1. The curve is obtained by fitting the calculated values of energies to the Murnaghan equation of state

The configuration with the minimum energy is the ground state of the system and the corresponding volume was used for determination of theoretical lattice constant and bulk modulus of the compounds. From table 1 it is clear that the calculated lattice parameters are in between the experimental and previous theoretical values. We can therefore conclude that they are in qualitative agreement with the previous results. The optimized lattice parameters thus obtained were used to calculate the electronic properties, the results of which are given in the next sections.

TABLE 1. showing the experimental lattice parameters and theoritical lattice parameters of previous works and the present work

Compound		Exp	Previous works	Present work
CuAlS2	a(A°)	5.3336	5.334[8], 5.2816[11], 5.388[14]	5.372[a], 5.242[b]
	c(A°)	10.444	10.4439[8], 10.4429[11], 10.545[14]	10.52[a], 10.264[b]
CuGaS2	a(A°)	5.351	5.356[8], 5.3137[10], 5.4070[10a]; 5.356[11], 5.412[14]	5.44[a], 5.289[b]
	c(A°)	1.480	10.433[8], 10.5944[10]10.7682[10a]; 10.629[11], 10.602[14]	10.653[a], 10.36[b]
CuInS2	a(A°)	5.523	5.523[8], 5.499[10],5.5734[10a]; 5.5775[11], 5.6[14]	5.631[a], 5.524[b]
	c(A°)	11.120	2.9416[8], 11.0330[9],11.2280[9a]; 11.2379[11],11.304[14]	11.337[a], 10.82[b]

[a] This work using GGA , [b] This work using LDA; and Ref[8, 9, 9a, 10, 10a, 11, 14]

Density of States

We present here the total density of states (DOS) and partial density of states (PDOS) of CuXY2 compounds using both GGA and LDA approximation. The DOS represents the

distribution of various energy states against energy. The total density of states (TDOS) along with the partial DOS(PDOS) for $CuXS_2$ compounds is shown in Fig. 2(a-i). The energy axis can be considered to be comprising of core energy band, valence energy band and conduction band. A dotted vertical line in the energy bands (DOS) shows the position of Fermi energy (E_F). The total DOS plot of $CuAlS_2$ using LDA exchange potential shows a sharp peak at the upper valence with smaller peaks at lower valence band and core region. The conduction band shows a small occupation as can be expected for semi conductors. Core region between -15 eV and -12.75 eV is dominated by the s- states of S with feeble contribution of Cu p-states. Lower VB, the region between -7 eV and -3 eV, is an admixture of Cu and S. The upper VB, the region between -3

eV and 0 eV has the highest density of state. This is mostly contributed by Cu d-state with smaller contributions from S and Al. In the conduction region above E_F from 0 eV to 3 eV we have very small contribution from all elements as expected for semiconductors materials. Similarly, the DOS plot of $CuGaS_2$ is shown in fig.3. The core region is dominated by d state of Ga with a very sharp peak at around -15 eV. The lower V.B. region is an admixture of Cu d-state, S p-state and Ga s-state respectively. In the upper valence band region we have Cu as the dominant contributor with sharp peak at around -2 eV. As in case of $CuAlS_2$, the contribution of various elements in the conduction band in almost nil. Finally, the DOS plot of $CuInS_2$ is depicted in the fig. 4.
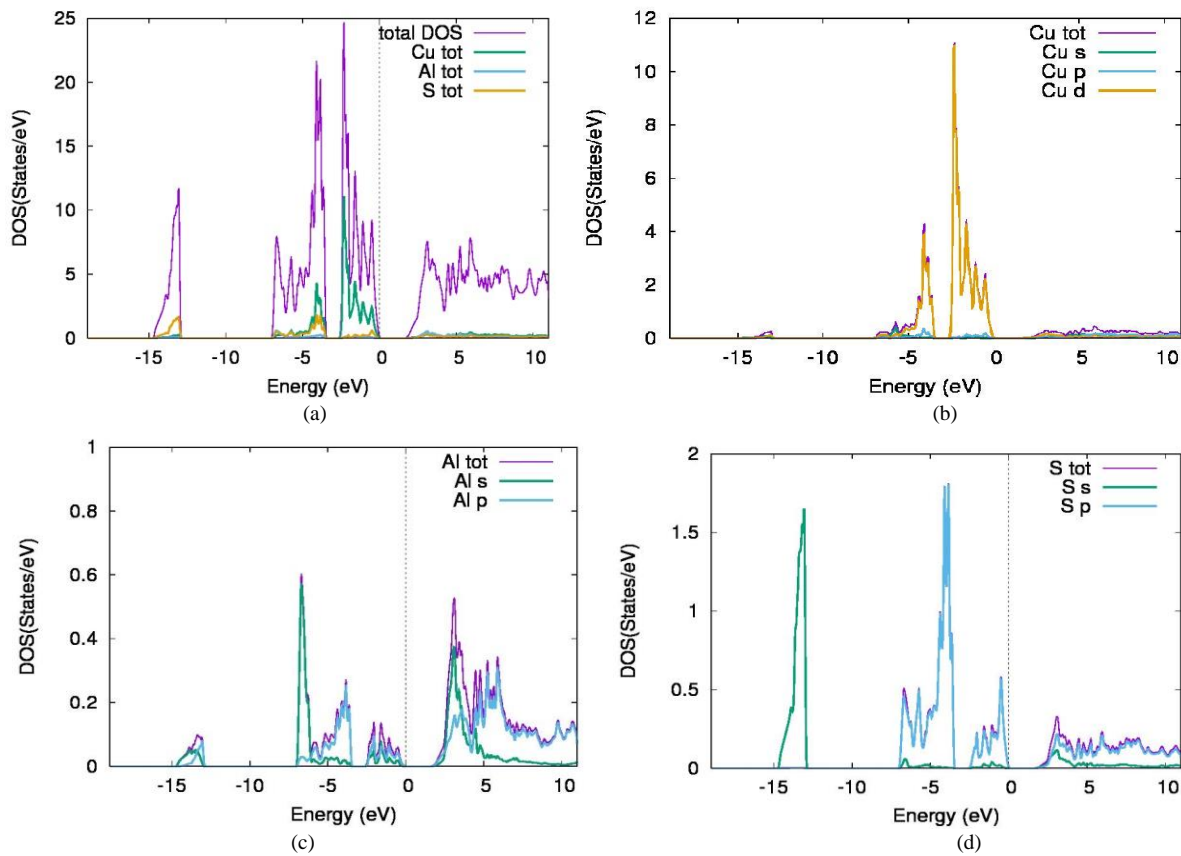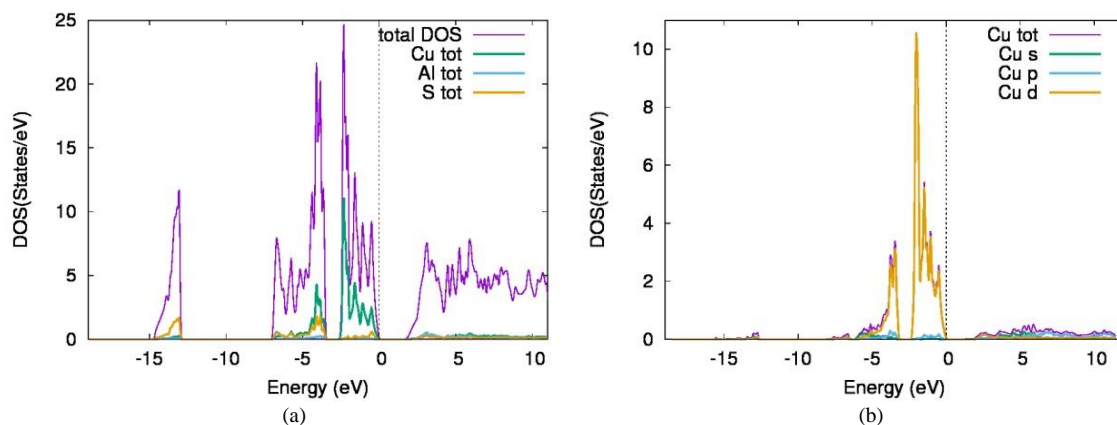

(a)

(b)

(c)

(d)

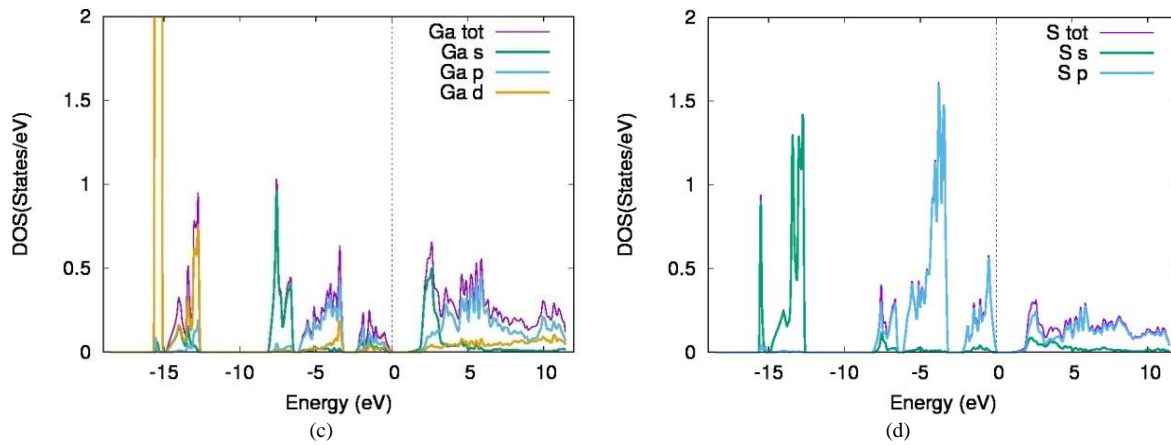Fig. 2: a) Total DOS, b-d) partial DOS of $CuAlS_2$

(a)

(b)

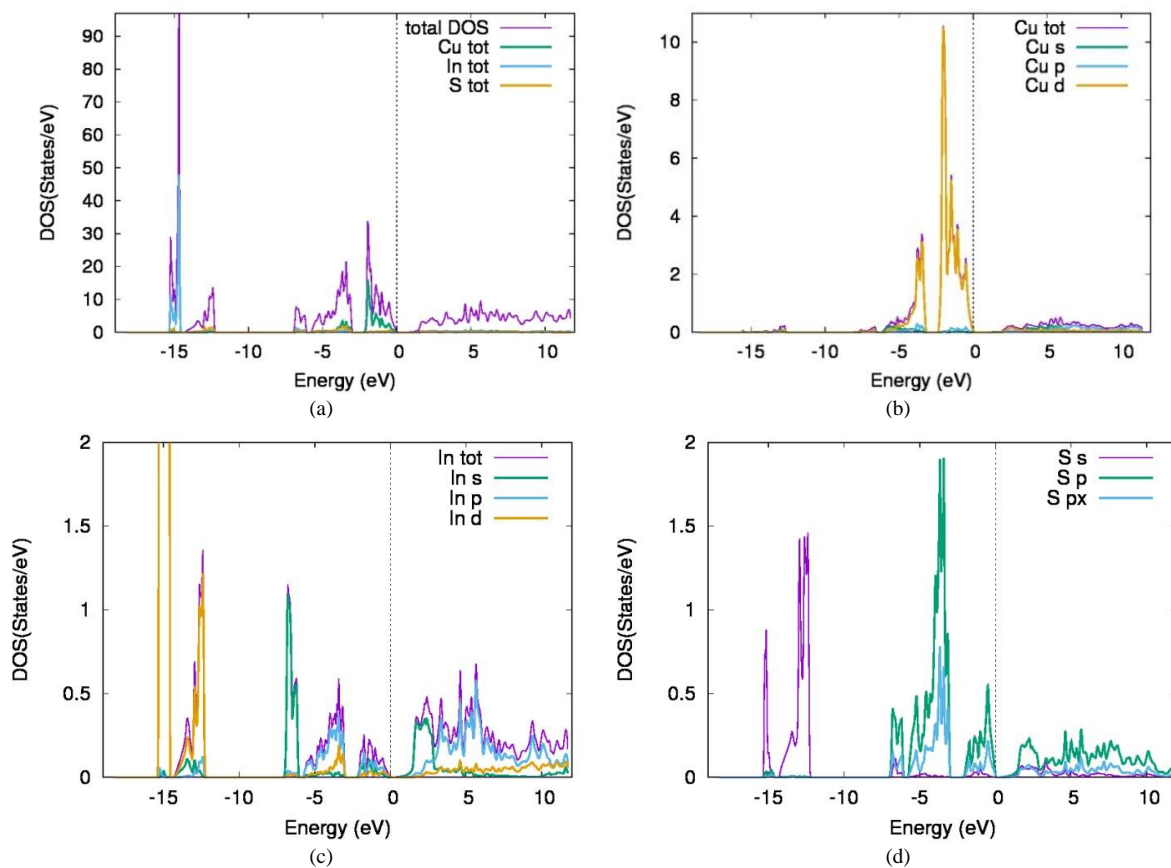Fig. 3: a) Total DOS, b-d) partial DOS of CuGaS2

Fig. 4: a) Total DOS, b-d) partial DOS of CuInS2.

The plot is almost the replica of CuGaS2 DOS plot with core region dominated by In. The lower V.B. comprises of smaller peaks of Cu and S whereas the upper valence band region is dominated by Cu d-state. As expected for semi-conducting materials, the conduction region has negligible contribution from all elements. The DOS of the above compounds shows same pattern when GGA exchange potential was used.

Band Structure

Fig. 5(a-c) shows the electronic band structure curves of CuXS2 calculated at equilibrium volume using GGA–PBE and LDA approximations. In both the figures zero of the energy is chosen to coincide with the top of the upper valance band (UVB) which occurs at the gamma point. The bottom of the conduction band is also located at the gamma point. Thus at the equilibrium volume all CuXS2 compound studied are direct band gap materials. The experimental and theoretical band gaps are listed in table 2. From the table it is seen that as we move from Al to Ga to In of the central atom position, the band gap decreases. This decrease in the band gap is due to the shifting of the conduction band towards Fermi Energy level. From the

band structure graphs we came to know that CuXS2 are direct band gap materials.
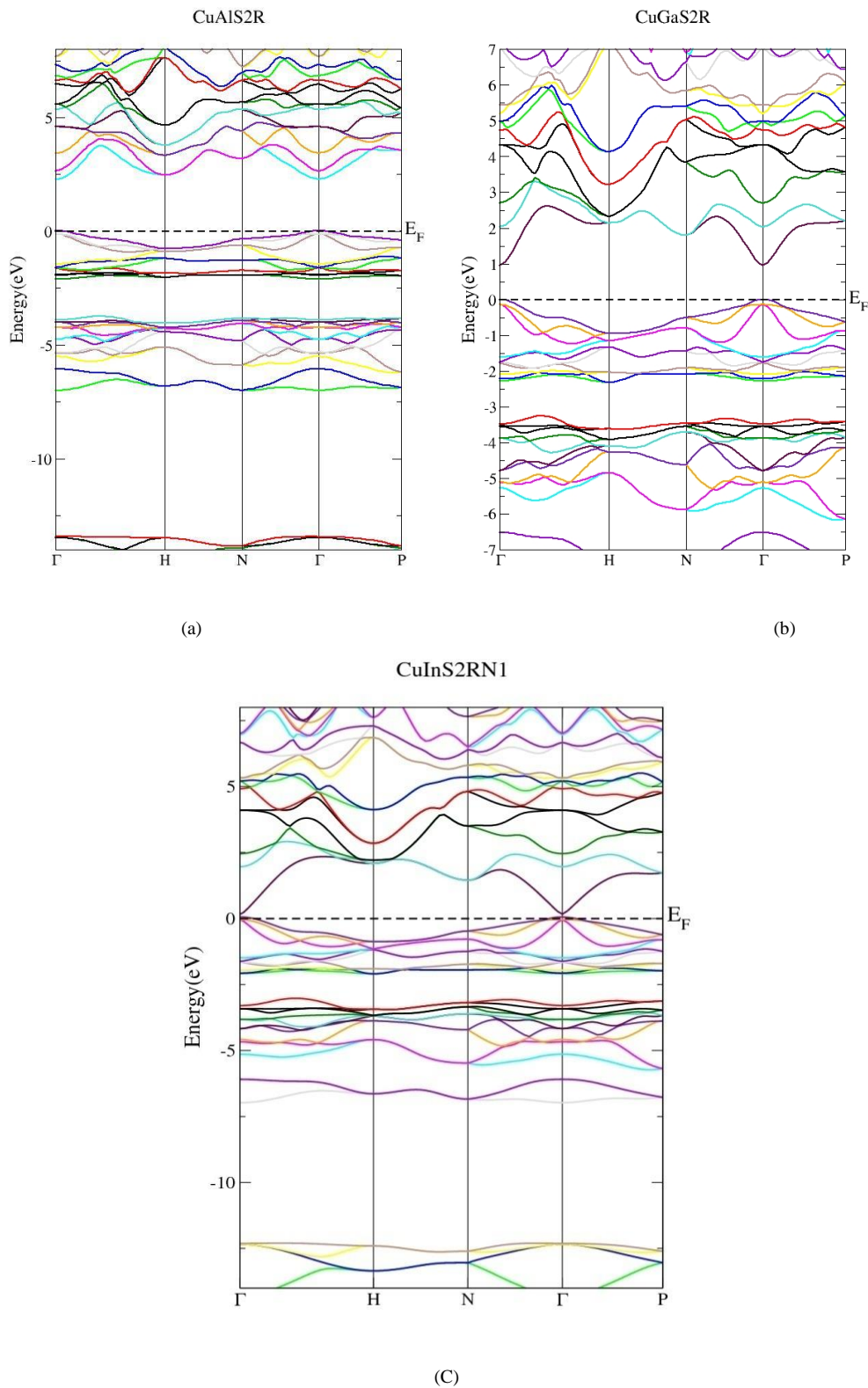

(a)

(b)

(C)

Fig. 5: a)-c) Band Structure of CuAlS2, CuGaS2 and CuInS2 using LDA.

TABLE 2. showing the band gap experimental, previous calculations and the present calculation

Compound		Exp	Previous calculation	Present calculation
CuAlS2	Band gap(eV)	3.5	2.05[8], 1.94[11], 2.7[12], 3.47[14]	1.3[a], 1.62[b],
CuGaS2	Band gap(eV)	2.43	1.25[8], 0.7[10], 0.9[11], 1.2[13], 2.47[14]	0.67[a], 0.95[b],
CuInS2	Band gap(eV)	1.55	-1.4[8], 0.07[10], 0[11], 1.6[14]	0[a], 0.16[b],

|[a] This work using GGA , [b] This work using LDA; and Ref[8, 10, , 11, 12, 13, and 14]

Optical Properties:

In order to study the optical properties of the tetragonal structures the knowledge of frequency-dependent complex dielectric function $\mathcal{E}$ becomes necessary. The dielectric function comprises of two parts - real and imaginary parts expressed as $\varepsilon_1 + i\varepsilon_2$. The dielectric function describes optical response of the medium at all photon energies E=ℏω meaning the interaction of photons to electrons. The imaginary part of the dielectric function is calculated from the momentum matrix elements between the occupied and unoccupied wave functions and is given by

$$\varepsilon_2(w) = \left(\frac{4\pi^2 e^2}{m^2\omega^2}\right)\Sigma\int < i|M|j$$
$$> f_i(1 - f_i)\delta(E_f - E_i - w)d^3k$$
$$\varepsilon_1(w) = 1 + \frac{2}{\pi}p\int_0^\infty \frac{w'\varepsilon_2(w')}{w'^2 - w^2}dw'$$

Once the real and imaginary parts of the dielectric function are known, we get all the necessary optical properties such as reflectivity, refractive indices and absorption coefficient can be calculated.

The imaginary part depends strongly on the band gap, while dealing with the calculations of the optical properties using TB-mBJ approach we have used a scissor operator to fit our theoretical gap with the reported experimental results by using the convenience of energy shift for CuXS2 compounds wherever it was necessary. The magnitude of the scissor operators for CuAlS2, CuGaS2 and CuInS2 are 1.3eV, 0.43eV and 0.5eV respectively. The main peaks at the real part of dielectric function arises due to the transitions from the upper valence band to the conduction band. Peaks are observed at 5.13eV, 3.5eV and 3eV for CuAlS2, CuGaS2 and CuInS2 respectively.

TABLE 3. Band gap calculation using mBJ exchange correlation potential along with scissor correction

Compounds	Band gap using mBJ potential(eV)	Magnitude of Scissor correction(eV)	Corrected band gap (eV)
CuAlS2	2.2	1.3	3.5
CuGaS2	2	0.43	2.43
CuInS2	1	0.5	1.5

One of the properties that can be calculated from dielectric function is the refractive index. At the zero frequency or the infinite wavelength the real part of the dielectric function is equal to the refractive index of the material. The zero frequency

refractive indices for CuAlS2, CuGaS2 and CuInS2 have found to be 2.2, 2.4, and 2.42 respectively which is comparable to the existing works and the experimentally obtained values.
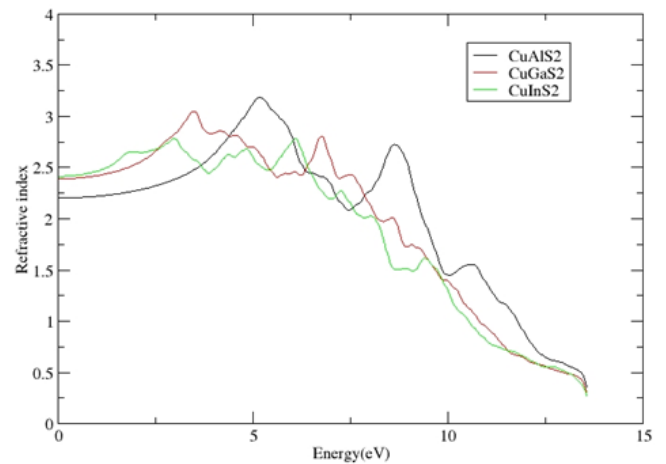

Fig.6: Refractive indices of CuXS2 compounds.

TABLE 4. Refractive indices of CUXS2 compounds

Compounds	ε(0)	Previous calculation of refractive indices	Experimental values of refractive indices	Present calculation of refractive indices
CuAlS2	4.85	2.26[11], 2.4[15],	2.0–2.5[24]	2.2
CuGaS2	5.7	2.46[11], 2.62[10],	2.2–2.9[23]	2.4
CuInS2	5.8	2.57[11], 2.76[10],	1.6–3[23]	2.42

Ref [10, 11, 13,15]

The absorption coefficient is an important criterion for determining the optical properties of the material. The absorption coefficient is a parameter, which indicates the fraction of light lost by the electromagnetic wave when it passes through a unit thickness of the material. In our calculation we have found CuXS2 to be good absorption material in the range 0 to 10eV. From the absorption spectra it can be seen that absorption threshold i.e. the energy from where absorption take place is actually the energy of the fundamental gap. From our absorption spectra the absorption threshold for the CuAlS2, CuGaS2 and CuInS2 in the order starts at 3.6eV, 2.3eV and 1.6eV respectively which matches very closely to the experimental band gaps of these compounds. Levcenko et al. have observed the absorption threshold at around 1.5 eV for CuInS2 [24]. This originates from the direct Γ-Γ transition of anion-p valance state electrons located at the top of the valence band in the unoccupied X-s state which dominates the bottom of the conduction band. The value of absorption coefficient increases as the energy increases to its higher value and after 9.5eV the drops abruptly. From the absorption spectra, the peaks of CuAlS2 are observed at 6.05ev, 7eV and 9eV. Similarly for CuGaS2 the peaks are observed at 3.6eV, 5.3eV, 6.2eV, 7eV, 7.8eV, 8.7ev respectively. Finally the peaks for CuInS2 are observed at 3.7eV, 4.9eV, 6.3eV, 7.4eV, and 8.2eV respectively. If the energy of photon lies between 6-10 eV then high absorption coefficient is shown by the compounds. The beyond this range the absorption coefficient drops. In the

following figure it is seen that above 10 eV, there is a severe increase and the value of coefficient is very little. About the region 0.2-0.4 eV absorption is high merely. So the materials are very useful to custom for photovoltaic and solar applications.
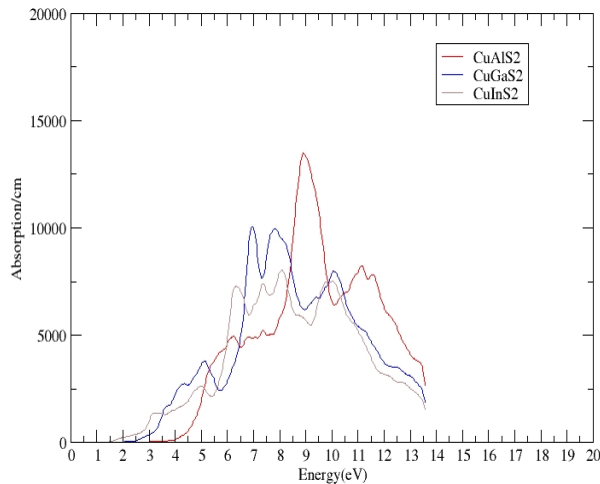

Fig. 7: Absorption spectra of CuXS2 compounds.

Optical reflectivity measures the fraction of the radiant energy that is reflected from the surface. The optical reflectivity of CuXS2 compounds are shown in the fig. The optical reflectivity are found to be 31% at 6eV, 28% at 7eV, 44% at 9.8eV for CuAlS2,while that for CuGaS2 the optical reflectivity are 27% at 3.5eV, 32% at 7eV, 35% at 8eV and 38% at 8.8eV respectively and finally for CuInS2 it is 23% at 3eV, 25% at 5eV, 30% at 6.2eV, 32% at 7.4eV and 369% at 8.3eV respectively. Of the three materials, CuAlS2 has the highest reflectivity.
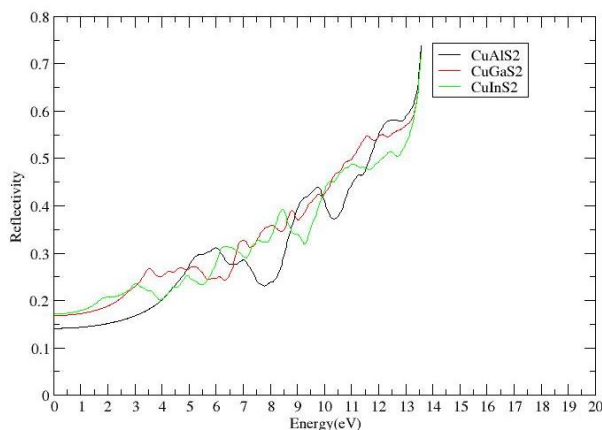

Fig. 8: Reflectivity of CuXS2 compounds

IV. CONCLUSIONS

We have performed the total energy calculation to study the structural, electronic and optical properties of the CuXS2 ternary compounds using FP-LAPW method as implemented in Wien2K code [20] within DFT. We have used GGA, LDA and mBJ as exchange correlation potential. The calculated lattice parameters as well as band gaps are in close approximation with the experimental values and with the previously calculated values. Since the top of the upper valance band (UVB) and the bottom of the conduction band of all compounds studied are both located at the Gamma point, therefore they are direct band gap compounds. It has also been observed that when the central atom in CuXS2 is replaced in the order of increasing atomic number from Al to Ga to In, the band gap decreases. However, the lattice parameters follow the reverse order, i.e. with the increase in atomic number of the central atom the lattice parameters also increases. The general features of the band structure of the CuXS2 shows the following features:

The core region is mostly contributed by s-states of S, Ga and In of the compound in the order CuAlS2, CuGaS2 and CuInS2 respectively. The valence band is almost dominated by Cu d-state for all compounds with smaller contribution coming from S S-state, and Ga p-state, whereas there is negligible contribution in the conduction band from all elements suggesting their semiconductor property.

We have also observed the optical properties of CuXS2 compounds by calculating dielectric function. Thus various properties like refractive index, reflectivity, absorption coefficient have been calculated and calculated values have been found to be in close approximation to the experimental values. High absorption of all CuXS2 compounds in the region 0-10eV make them suitable for use as solar absorption material.

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