

The Study of Ground State Properties of Chalcopyrites of the type CuXSe_2 (where $X = \text{Al, Ga, In}$) using DFT

¹Nakul Chhetri, ¹Purna Chandra Barman

¹Department of Physics, Raiganj University, Uttar Dinajpur, India

Email address: nakulgorkha@gmail.com

Abstract— We have studied the ground state properties of the ternary chalcopyrites of the type CuXSe_2 (where $X = \text{Al, Ga, In}$) using DFT. In our studies we have used FP-LAPW (full-potential linearized augmented plane wave method) method within DFT using Wien2k code. In our study we found out that they are direct band gap compounds. The physical parameters like structural parameters, electrical properties like DOS, band gap, optical properties like absorption, reflectivity etc. were calculated and they matched to a great extent with the experimental values. When used under specific range, they are found to be potential candidates to be used as photo voltaic materials.

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

I. INTRODUCTION

The ternary chalcopyrites of the type CuXSe_2 (where $X = \text{Al, Ga, In}$) are nonmagnetic semiconductors belonging to space group 122, I-42d. They are structural analogues of ZnS. They are tetragonal materials. And they are widely studied materials owing to various diverse structural, electrical and optical properties [1,2,3]. They therefore serve as suitable materials for use as photovoltaic optical detectors, solar cells, and light emitting diodes [4,5,6]. The compounds in the order CuAlSe , CuGaSe , CuInSe have electrical band gaps are 2.71 eV [7], 1.68 eV [8] and 1.04 eV [9] respectively.

We can see various available literatures regarding the study of these chalcopyrites of the type CuXSe_2 . 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 [10]. They obtained the values of the band gap as 1.65 eV, 0.48 eV, and 0.2 eV respectively for CuAlSe_2 , CuGaSe_2 and CuInSe_2 . The negative sign indicates that their prediction for CuInSe_2 as semimetal materials. Hasan and Reshak [11] studied CuInX_2 ($X = \text{S, Se, Te}$) using FPLAPW as embodied in Wien2k code [12]. They have obtained band gap of CuInSe as 0.416 eV. They also studied the optical properties like birefringence, linear optical response, non-linear optical response, etc. From their studies they found that the birefringence of CuInSe to be negative. They also calculated $\epsilon_2(\omega)$ and found a considerable anisotropy between $\epsilon_2^{\perp}(\omega)$ and $\epsilon_2^{\parallel}(\omega)$. Yadav [13] using the concept of plasma oscillations theory of solids has investigated the electronic properties such as homopolar gap (E_h), heteropolar or ionic gap (E_c), average

energy gap (E_g), bond ionicity (f_i) and electronic susceptibility (χ_e) for the chemical bonds (A-C and B-C) in complex structured AIBIICVI2 ternary chalcopyrite crystals. Their studies showed that the homopolar gap, heteropolar gap, and average energy gap of these bonds were directly related to the plasmon energy and bond ionicity and electronic susceptibility is inversely related to it. Bouguetaia et al [14] using full potential linear muffin-tin-orbital (FP-LMTO) method as employed in the lmtart code to study the structural and elastic properties of $\text{Cu}(\text{In,Ga})\text{Se}_2$ using the FP-LMTO method within the LDA approximation in their chalcopyrite (BCT) and rocksalt phase. In addition, they also studied the elastic property of the both phases.

We will employ FPLAPW method [15] within DFT [16] formalism using code Wien2k. We will study structural properties, electronic properties, and optical properties and relate them previously obtained results. GGA (17), MBJ (18-19) and LSDA [20] will be used exchange correlation potential to see their effectiveness. Our objective will also be to observe and highlight the changes prevailing if any when changing central atom X in CuXSe_2 by Al, Ga and In.

II. STRUCTURE AND METHOD USED

CuXSe_2 belongs to tetragonal space group 122, I-42d. They are structural analogues of ZnS. Each unit cell have within them four formula units. In this structure central atom is Se with four cations at the four corners of regular tetrahedron bonded by sp^3 bonds. Owing to different cations at different corners, the bond lengths cannot be expected to be same. Tetrahedron in this case is therefore distorted with c/a ratio deviating from ideal value of 2.0.

In the present study we will be using Density Functional Theory. We will employ FPLAPW method implemented in Wien2K code to solve the Kohn-Sham equations which ultimately yields electron density. The exchange correlation potential used here are includes GGA, LSDA and MBJ. In this method the unit cell volume is divided into the non-overlapping Muffin-Tin spheres

surrounding every atom and the remaining interstitial region [21]. Out of their electronic configuration, the valence shell orbitals are chosen to be Cu ($3p^6, 4s^2, 3d^9$), Al ($3s^2, 3p^1$), Ga ($3d^{10}, 4s^2, 4p^1$), In ($4d^{10}, 5s^2, 5p^1$), and Se ($3d^{10}, 4s^2, 4p^4$) respectively. For each element, the muffin tin radius have fixed at 2.14 for Cu, 2.19 for Ga, 2.33 for In and 2.13 in

a.u. units for Se respectively so that muffin radius does not coalesce each other. For a plane wave expansion, the product of $K_{max} \times R_{max} = 7$ and $l_{max} = 10$ are kept constant throughout the calculations. The corresponding Wyckoff positions in unit cell of crystals are Cu(0,0,0), Ga(0,0,0.5) and Se(0.235,0.25,0.125) respectively. The volume optimisation was done in the first step from experimentally available values of lattice parameters a and c using $k=7000$ for better results. We have allowed iterations upto 40 times to achieve better self consistency. The convergence criteria for stable system were considered to have achieved when energy convergence criteria of 10-4 Ry and charge convergence criteria of 0.0001 was fulfilled. Now using theoretical values for lattice parameters, we have formed the system and studied DOS, PDOS, bandstructure, and optical properties.

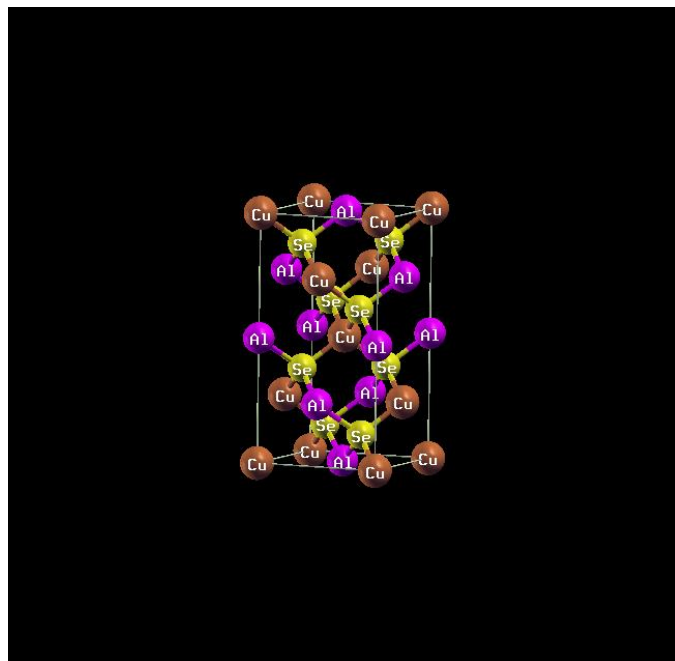


Fig.1: Structure of CuAlSe2

III. RESULTS AND DISCUSSION

Structural properties

To start with we performed Volume optimisation by plotting energy against volume using the experimentally obtained lattice constant as given in the table 1. 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 matched well with the experimental values and previous results using different theoretical techniques. 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, band structures and optical properties the results of which are given in the next sections.

TABLE I. showing the experimental lattice parameters and theoretical lattice parameters of previous works and the present work.

Compound	Exp	Previous works	Present work
a(A°)	5.617	5.596 ²² , 5.606 ¹⁰	5.609 ^a ,
c(A°)	10.92	11.192 ²² , 10.9 ¹⁰	11.0637 ^a ,
a(A°)	5.596	5.63 ²³ , 5.607 ¹⁰	5.70575 ^a , 5.55094 ^b
c(A°)	11.003	11.26 ²³ , 10.99 ¹⁰	11.1233 ^a , 10.869 ^b
a(A°)	5.781	5.77 ¹⁰	5.894 ^a , 5.801355 ^b
c(A°)	11.6422	11.55 ¹⁰	11.8705 ^a , 11.3596 ^b

Ref ^{22, 23, 24, 10} Present calculation using GGA^a and LSDA^b

Density of States

We have also studied about the Density of States. The density of states means distribution of various energy states against energy values. In present work both total density of states (TDOS) and partial density of states (PDOS) have been treated separately with clear pictorial representations using fig. 2. The energy is plotted along the x axis and energy states are plotted along the y axis. The energy is divided into core energy band, valence energy band and conduction band. The dotted line indicates the fermi level (E_F) which separates valence band from the conduction band. We have presented below the TDOS and PDOS using three different exchange correlation potentials namely, GGA, LSDA and MBJ. In study we found that core energy region is mostly occupied by p states of Se and p states of In respectively. Going towards the valence band area, we saw that mostly d states of Cu contributed with small contributions from p states of Se and p states of In. Beyond E_F level in the conduction we see that states are negligible contribution from the all elements. This shows that they are semiconductor materials.

We noticed that these materials have direct band gap. Under treatment of different exchange correlation potential we found out that band gap varied. Using GGA exchange correlation potential bandgap of CuInSe was obtained to be 0.9 eV. The use of LSDA exchange correlation potential yielded same value of bandgap as GGA. Whereas using MBJ as exchange correlation potential, bandgap came out to be 1.3 eV.

While analysing the DOS and PDOS of CuGaSe2, we have found that the curves are similar in nature. The core region is dominated by p states of In and p states of Te. In the valence band region we have total domination of Cu d states. The conduction however very little to be negligible contribution from constituent elements as was expected for semiconductor. This compound too was found out to be direct band gap compound. Under GGA approximation, the band gap was obtained as 0.83 eV. The value turned out to be 0.97 eV under LSDA approximation and finally using mBJ as exchange correlation potential, the value turned out to be 1.4 eV.

DOS of CuAlSe2 yielded pattern that followed previous materials with certain exceptions like occupation energy states have increased in core and valence band area. The core region comprises of s states of Al, the valence band region has mostly d states of Cu. As was expected the conduction band is unoccupied proving their semiconductor nature. The band gaps

were found out to be 1.45eV using LSDA, 1.63 eV under GGA, and finally 2.3eV using MBJ as exchange correlation potential.

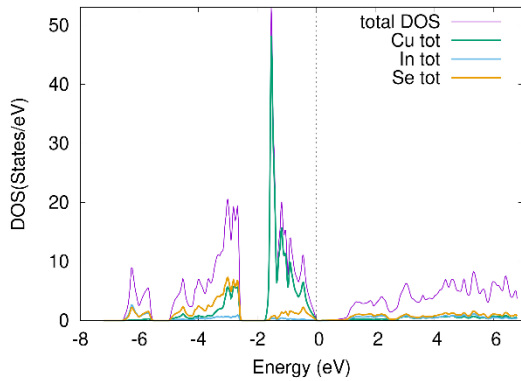


Fig. 2(a)

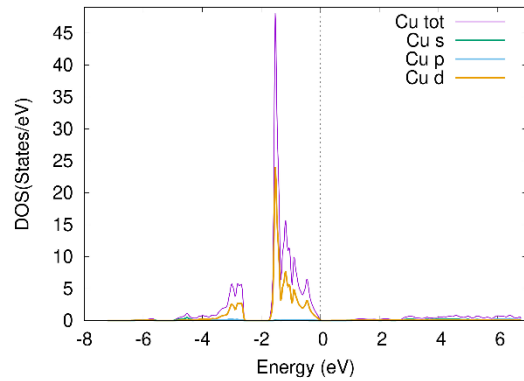


Fig. 2(b)

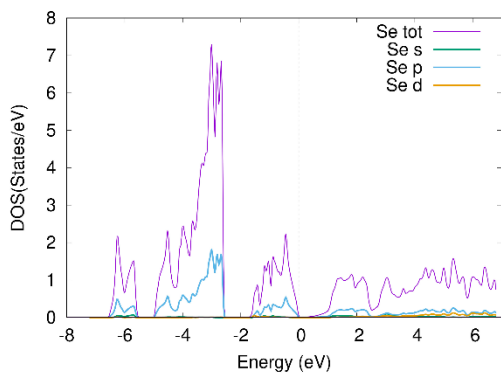


Fig. 2(c)

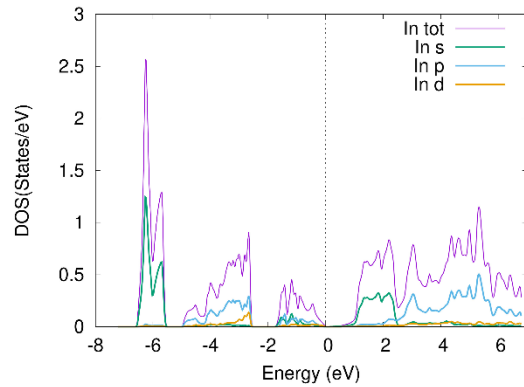


Fig. 2(d)

Fig. 2(a)-Total DOS using GGA; Fig.2(b-d)-Partial DOS

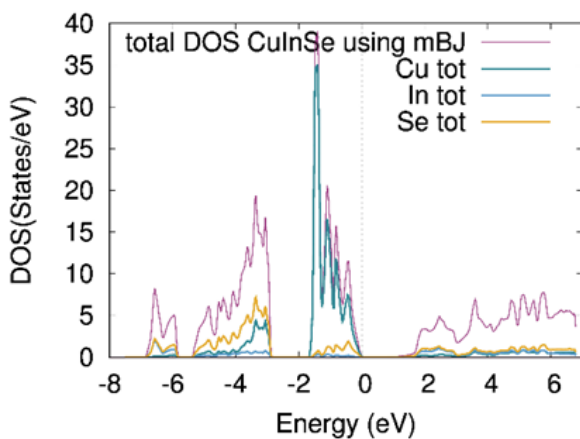


fig. 3(a)

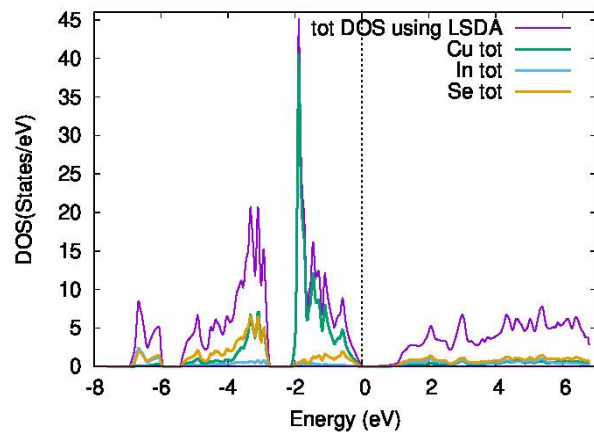


fig. 3(b)

Fig.3(a-b)- Total using MBJ and LSDA.

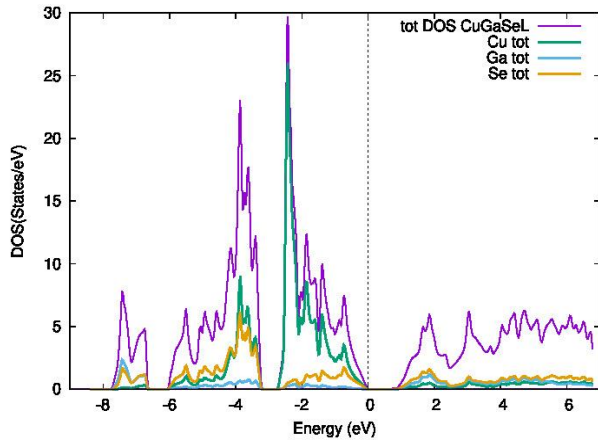


Fig. 4(a)

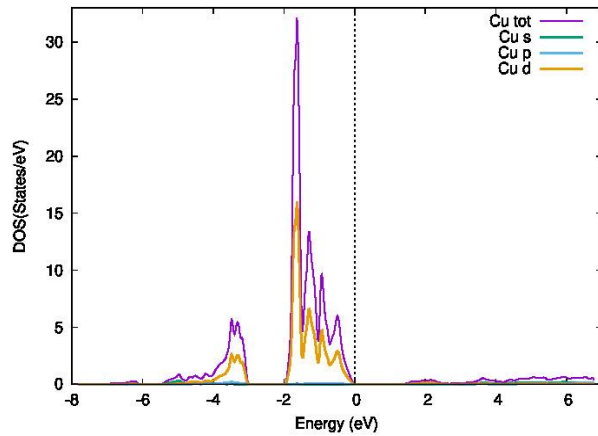


Fig. 4(b)

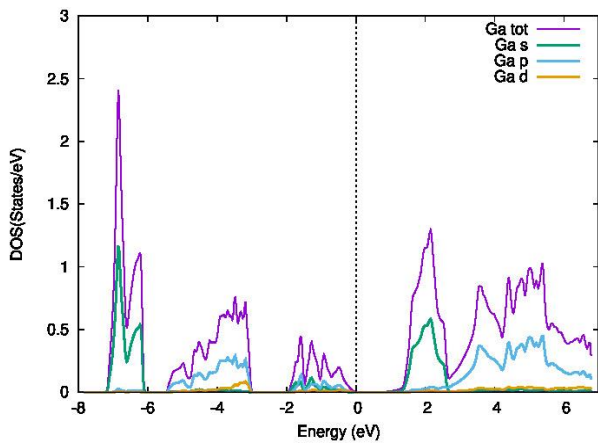


Fig. 4(c)

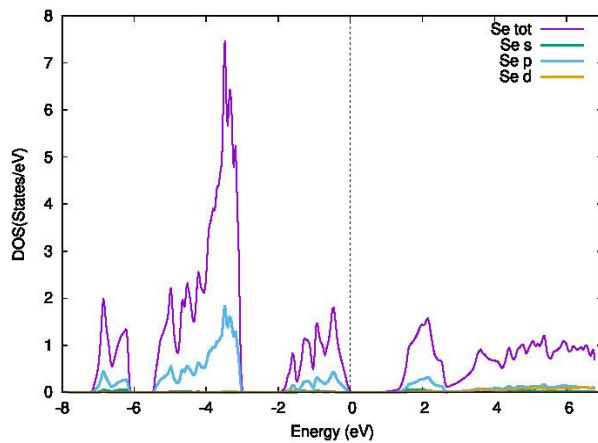


Fig. 4(d)

Fig. 4(a)-Total DOS using LSDA; Fig.4(b-d)-Partial DOS

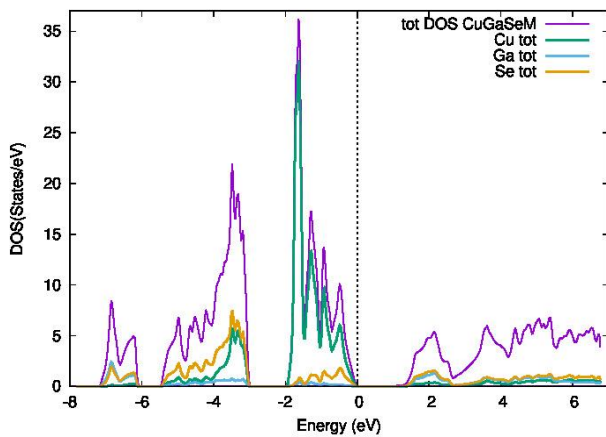


Fig. 5(a)

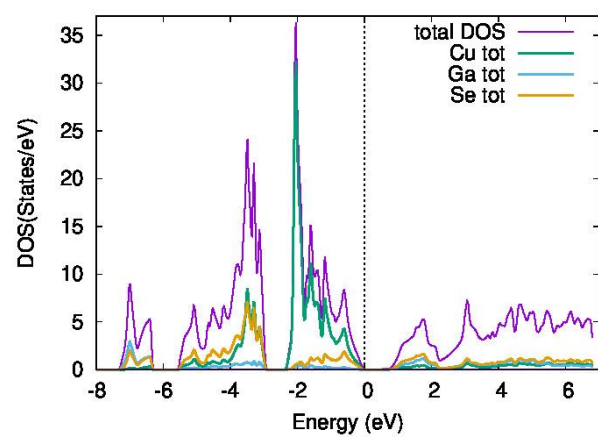


Fig. 5(b)

Fig.5(a-b)- Total using mBJ and GGA.

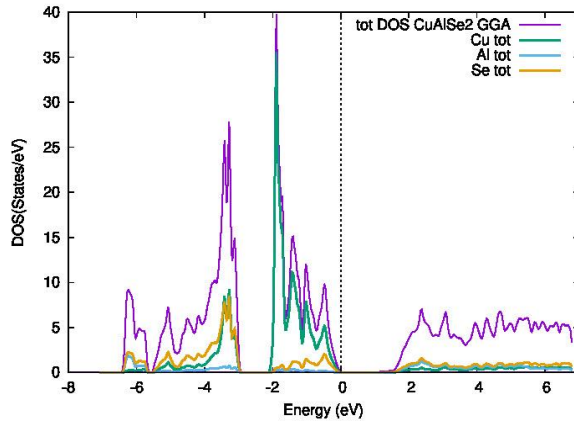


Fig. 6(a)

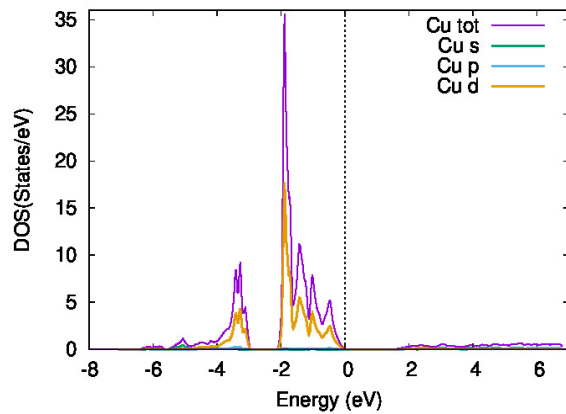


Fig. 6(b)

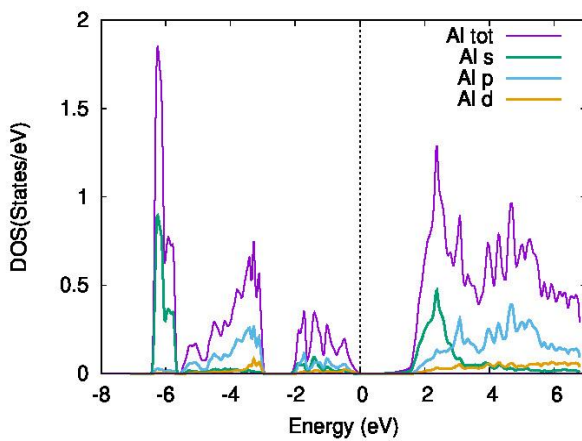


Fig. 6(d)

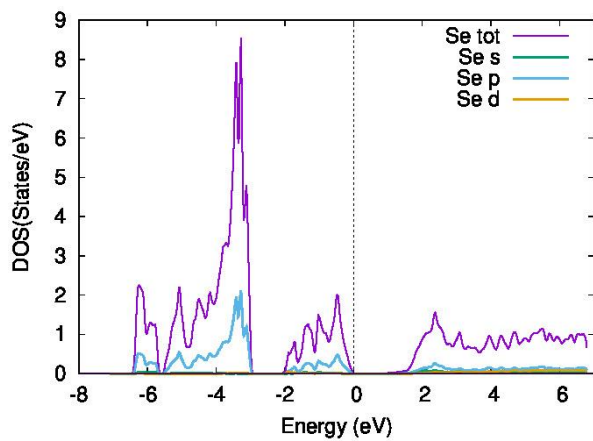


Fig. 6(c)

Fig. 6(a)-Total DOS using GGA; Fig.6(b-d)-Partial DOS

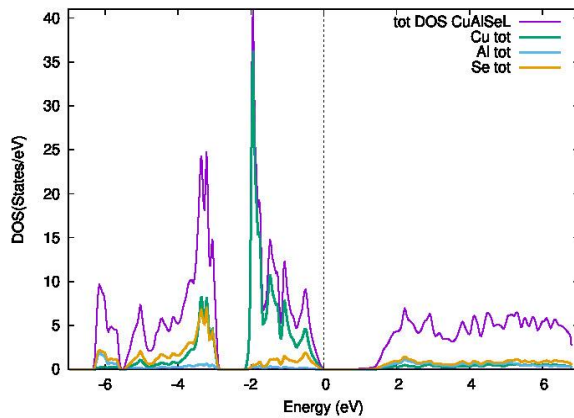


Fig. 7(a)

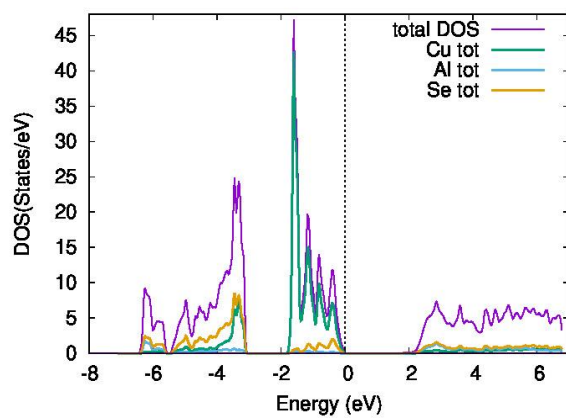


Fig. 7(b)

Fig.7(a-b)- Total using LSDA and mBJ.

TABLE II: Bandgap of CuXSe2 compounds.

Compound		Exp(eV)	Previous calculation (eV)	Present calculation (eV)
CuAlSe2	Band gap(eV)	2.71	1.65 ¹⁰ , 2.1 ¹¹	1.63 ^g , 2.3 ^m
CuGaSe2	Band gap(eV)	1.68	0.029 ²³	0.83 ^g , 1.4 ^m
CuInSe2	Band gap(eV)	1.04	0.416 ¹¹ , 1.01 ²⁴	0.9, 1.3 ^m

Ref^{10,11,23,24} Present calculation using GGA^g and mBJ^m

Band Structure:

We have obtained the band structure for CuGaX2 compounds under LSDA, GGA and MBJ approximations. In all these calculations, the pattern of the curve was similar. The top of the valence band and bottom of the conduction fell at different points on the Γ line. This proved they are direct band gap materials. Measuring the gap between two successive

points on the Γ line also gives band gap. From the graphs we realised that as band gaps increased when in the middle is replaced by Ga and Al respectively. The increase in the band

gap is due to shifting of valence band towards conduction band and due to interplay of s and p orbitals.

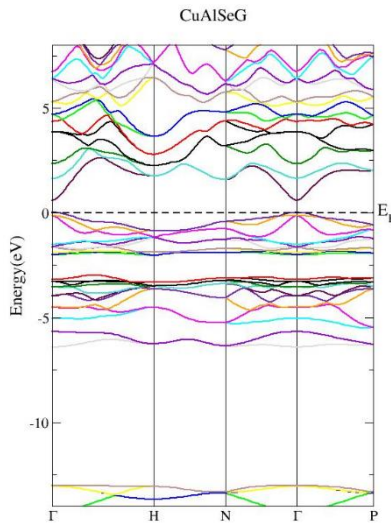


Fig. 8(a)

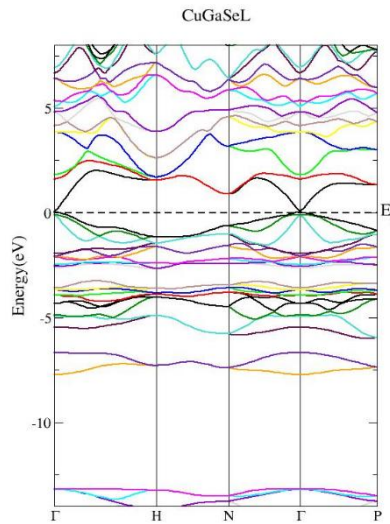


Fig. 8(b)

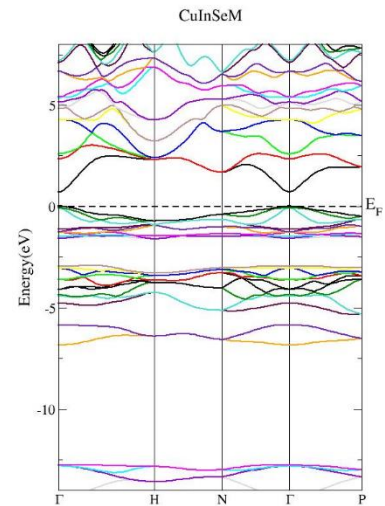


Fig. 8(c)

Fig.8(a-c): Band structure of CuAlSe2, CuGaSe2 and CuInSe2.

Optical Properties

The study of optical properties requires the thorough information of knowledge of frequency-dependent complex dielectric function \mathcal{E} .

We know that the dielectric function consists of real and imaginary parts, i.e $\mathcal{E} = \epsilon_1 + \epsilon_2$. We used the following expressions for the calculations of the real and imaginary parts of dielectric function from the momentum matrix of occupied and unoccupied wave functions and is given by

$$\epsilon_2(w) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_j \langle i|M|j \rangle > f_i(1 - f_j)\delta(E_f - E_i - w)d^3k$$

$$\epsilon_1(w) = 1 + \frac{2}{\pi} p \int_0^\infty \frac{w' \epsilon_2(w')}{w'^2 - w^2} dw'$$

The knowledge of the real and imaginary are necessary to calculate the various optical properties like absorption, reflectivity, refractive indices, etc. Once we have both \mathcal{E}_1 , \mathcal{E}_2 can calculate these properties.

Absorption

We have analysed the optical absorption properties of the materials under the test. Optical absorption is primary criterion for selection of material for use as photovoltaic materials. The absorption coefficient is a significant parameter in absorption studies. The absorption coefficient gives us indication to measure at how far light can go through material before it gets absorbed. In our studies we have found that CuXSe2 compounds have very absorption coefficient making them very apt for their usage for solar cells. 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. The threshold of absorption for CuAlSe2, CuGaSe2 and CuInSe2 commences at 1.313eV, 0.82eV, and 0.82eV respectively. The values of absorption keep on increasing with the increase of energy and reaches maximum between 8.6ev and 10 eV. The peaks values for CuAlSe2 is maximum followed by CuInSe2 and then CuGaSe2. Given the nature of curve obtained we can safely say that the CuXSe2 materials serves as good absorption materials when utilised for energy ranges 8.6eV to 10eV.

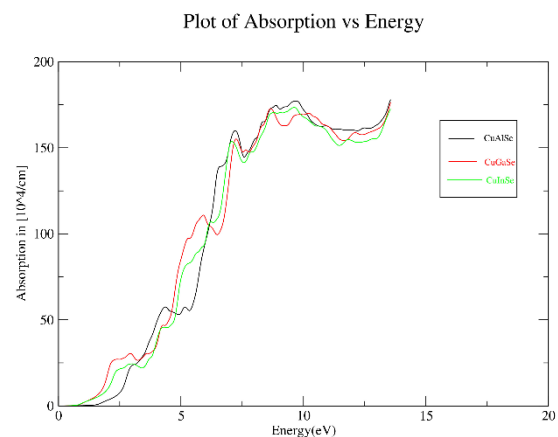


Fig. 9: Absorption curve of CuXSe2

Optical reflectivity: is the measure of the fraction of the radiant energy that is reflected from the surface. We analysed the optical reflectivity of the cuXSe2 materials at various energies and found different percentage of reflectivity. For CuAlSe2 at 2eV, 5eV and 10eV the reflectivity were 23.5%, 25% and 49%

respectively. Similarly, for CuGaSe₂ at the same energy values, the reflectivity's were respectively 33%, 36% and 46%. And finally, for CuInSe₂, the observed values of reflectivity were 26%, 32% and 48% respectively. From our studies, reflectivity is energy dependent parameter. The proportion reflectivity is the highest at around 10eV for all compounds.

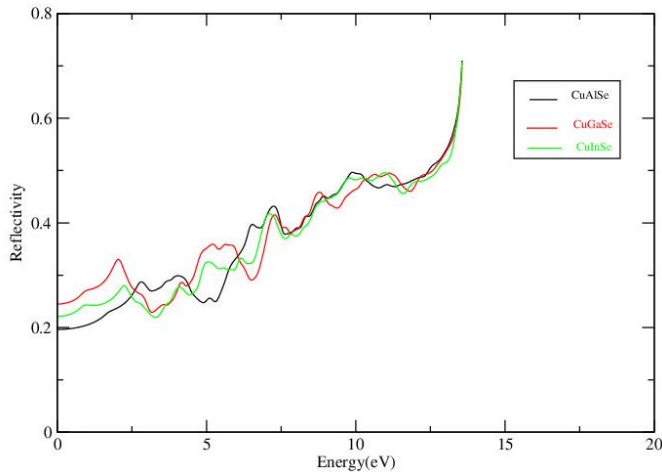


Fig. 10: Reflectivity curve of CuXSe₂

Refractive index: The refractive index is one of the properties that can be calculated from dielectric function. 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 CuAlSe₂, CuGaSe₂ and CuInSe₂ was obtained to be 2.58, 2.96 and 2.77 respectively.

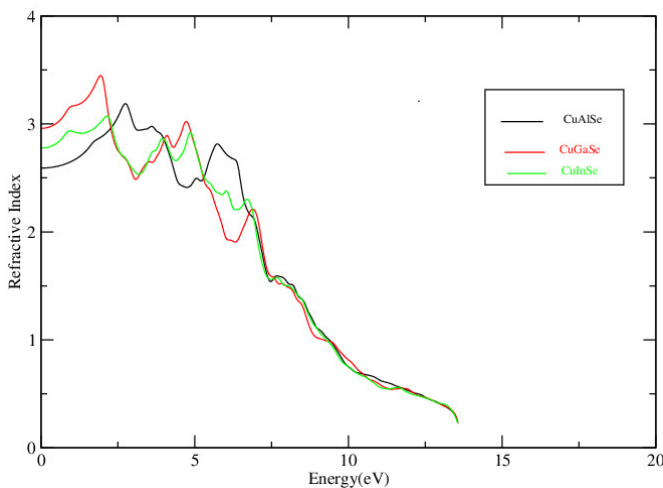


Fig. 11: Refractive indices of CuXSe₂.

IV. CONCLUSION

We studied the structural, electronic and optical properties of CuXSe₂ compounds using FP-LAPW within DFT making use of Wien2k module. In course of our studies we used GGA, LSDA and mBJ as exchange correlation potential to verify the usefulness of exchange correlation potential at different situations. The optimised structural parameters obtained after volume optimisation were in close approximation with the

experimental values as well as the previously obtained values. The materials were found out to be direct band gap compounds. The energy spectrum consists of core region, valence band region and conduction band region. Core region showed the domination of s states of Se and Al, the valence band region contains domination of d states of Cu and negligible contribution in the conduction. Similarly, for CuGaSe₂, the core region has p-states of Se and s-states of Ga and valence band has d- states of Cu. Finally, for CuInSe₂, we obtained core region comprising of p-states of Se and In, whereas the valence band has d- states of Cu. All compounds have negligible contribution in the conduction band region which proves that they are semi-conductor materials. We also observed that if the central atom in the order of Al, In and Ga in interchanged the bandgap kept on decreasing. In addition, we also calculated the optical properties like absorption, reflectivity and refractive index by studying dielectric function. All the optical properties matched with experimental data. When used in the range 8.6 eV to 10 eV these materials serve as good absorbers.

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