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A Study Of The Electronic Band Structure And Vibrational Properties Of The Chalcopyrite Cuals$_2$

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Abstract: *The electronic band structure of the ChalcopyriteCuAlS$_2$and its vibrational properties using the pseudopotential method within density functional theory (DFT) and density functional perturbation theory (DFPT) frameworks respectively. LDA+U technique and the projector augmented wave (PAW) was used in for the electronic band structure calculations, while the norm-conserving pseudopotentials were used for the DFPT computations. The calculated results showed that CuAlS$_2$ is a semiconductor with a wide band gap energy value of 3.13 eV. It was also discovered that the Γ to Z and Γto M transition are critical points in the structure of the material. The vibrational study reveal that CuAlS$_2$might not be dynamically stable as a result of it yielding negative frequencies consistently,*

Keywords: *CuAlS$_2$, Electronic band structure of CuAlS$_2$, Chalcopyrite, Vibrational properties of CuAlS$_2$, Vibrational properties of CuAlS$_2$*

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I. Introduction

CuAlS$_2$ is a member of the Chalcopyrite family of groups I-III-VI compounds. The group VI elements form Chalcogens in addition to other elements [1]. CuAlS$_2$ like other Chalcopyrite have found wide range of applications in photonic devices [2 ,3]. The Chalcoprites have drawn a lot of interest from researchers, both from experimentalists and theorists.

Tariq et al [4] deposited a thin film of CuAlS$_2$on glass substrate using chemical bath deposition technique. The deposited sample structure was analyze by X-ray diffraction and FTTR spectrophotometer, while the optical properties were studied by ultraviolet-visible (UV-VIS spectrophotometer. Their observed that the band gap is direct and ranges from 2.4 ev to 2.81 eV. Vahidshad et al [5] in their investigative study, used the Solvothermal method for the synthesis of CuAlS$_2$, and analysed their sample using x-ray diffraction (XRD) for structure analysis and UV-VIS spectrophotometer for optical properties analysis. They reported that the ratio of the lattice parameters a and c ranges from 1.8019 t0 1.9875, i.e., the value of a ranges from 5.276 5.429 Å and c from 10.04 to 10.4 Å. The energy band gap reported was from 3.33 to 4.26 eV. The chemical vapour transport method has also been used to grow CuAlS$_2$crystal[6]. The crystal was studied by Photoluminescence(PL). The measurements revealed a band gap is 2.9 eV. Chaki et al [7] also used chemical vapour transport (CVT) techniques in closed-spaced geometry to grow single crystal of CuAlS$_2$. The structure of the grown crystal was determined by x-ray diffraction. Recently, [8], deposited thin films of CuAlS$_2$on soda lime glass using metal organic chemical vapour deposition (MOCVD) technique. They studied the effectof of temperature variation on the energy band gap, and found a direct band gap that ranged from 3.28 eV and 2.88 eV at 420 ◦C and 450 ◦C respectively. CuAlS$_2$ and AgAlS$_2$ were studied by [9] by employing the chemical vapour transport technique. The band gap of AgAlS$_2$and CuAlS$_2$ were reported to be 3.2 eV and 3.5 eV respectively. CuAlS$_2$has also attracted theoretical investigators. The earliest of such study was done by [10, 11], in their work, the non self consistent empirical pseudopotential method were used. The results of the investigations were not in agreement with experiment as it predicted the band gap to be indirect. The earliest self consistency calculations were carried out by [12]. While the method used by [12] was numerical, [13] was based on the density functional theory (DFT) framework. The result from [13] predicted a band gap value of 2.05 eV, about 1.45 eV shy of the experiment value of 3.49 eV. The full potential linear augmented plane wave (FP-LAPW) method has been deployed to investigate the electronic band structure of some notable Chalcopyrites, among them is CuAlS$_2$ [14]. They reported that the inclusion of the Cu-d orbital in the computation significantly affects the energy band gap. Their calculated energy band gap was direct, and occurred at the gamma point, and has a value of 2.7 eV. This also fall short of the experimental value.

In this study, we propose to use the LDA+U scheme, to compute the electronic band structure and density of states of CuAlS$_2$. LDA+U is known to give accurate results for correlated systems. And also, the vibrational properties will be investigated. To the best of our knowledge, there is nowhere in the literatures where the vibrational properties were reported.

Computational Detail

The crystal structure of the ternary chalcopyrites belongs to nonsymmorphic space group D_{2d}^{12}(space group number 122) which is a superlattice of zinc-blende structure. Each Sulphur is coordinated by two Cu and two Al cations, whereas each cation is tetrahedrally coordinated by four Sulphur. Cu and Al are at the 4a and 4b Wyckoff's atomic positions respectively. The S atom is at the 8d site. The structure used in this work was adopted from [14]. The lattice parameters and Wyckoff's atomic positions are shown in table I, while figure 1 shows the structure used. The unit cell is made up of four formula unit, which gives a total of 16 atomic coordinates in three (3) types. The paw for Cu contains the 3s and 3p electrons as semi core. The band structure calculations utilized the LDA+U technique within the DFT framework as implemented in the abinit package [15, 16]. For exchange and correlation, the parameterization of [17] was used. A kinetic energy cutoff of 30 Ha was used for the generation of plane waves. A 128 k-point mesh generated by a 4x4x4 regular M-P shifted grid was used in the computation. The consistency calculation was well converged when the difference in energy between subsequent iteration was $1.0*10^{-10}$. For the vibrational properties, the computations were done within the framework of the self-consistent density functional perturbation theory [18, 19, 20] and the local density approximation with norm-conserving pseudopotential were employed in the phonon calculations.

Table 1: Lattice parameters and Wyckoff's atomic positions

a = 10.08 Br, c = 19.7366 Br

Atoms	X	Y	Z	Site
Cu	0.0	0.0	0.0	4a
Al	0.0	0.0	0.5	4b
S	0.275	0.25	0.125	8d

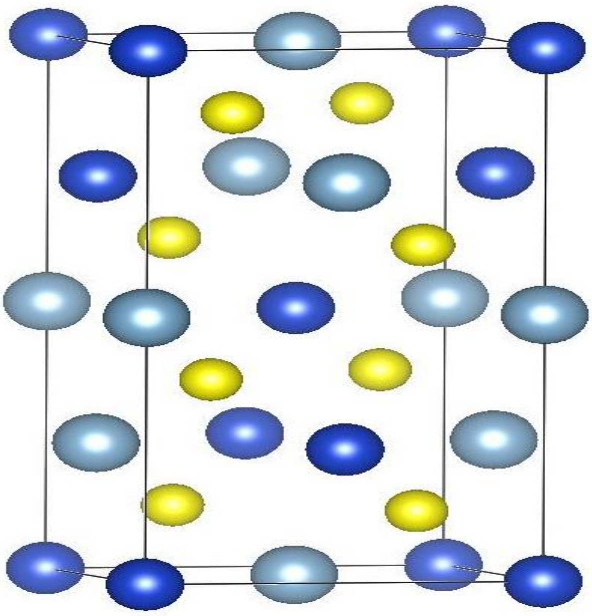

Figure 1: The structure used in the computations. Yellow balls represent S atoms, blue balls for Cu atoms and Grey for Al atoms.

II. Results And Discussion

The electronic band structure of Tetragonal (Chalcopyrite) $CuAlS_2$ is plotted along points of high symmetry in the first brillioun zone as shown in Figure 2. The Fermi level is indicated by the dotted line at the zero energy mark. The band structure showed the valence band maximum (VBM) occurring at the gamma point. Other notable valence band points are the X-point and the M-point. These points are almost at the same energy with the VBM. This may have importance effect during electron transition. This is quite similar to the electronic band structure of $CuSnS_4$ [21]. $CuAlS_2$ is predicted to be a semiconductor having a direct band gap at the gamma point of high symmetry, this indicates that the conduction band minimum (CBM) is also along the gamma point. It was observed that the value of the energy is gap 3.13 eV, which agrees well with the experimental value of 3.49 eV. Beside the CBM and VBM (i.e., $E^{\Gamma}{}_{\Gamma}$) , another important transition points in the conduction band is along the Z high symmetry point ($E^{Z}{}_{\Gamma}$) . The value of the energy gap between the VBM and the conduction band at the Z-point is about 3.44 eV while the band gap between the conduction band at the M-point and the VBM (E^{M}_{Γ}) is 4.01 eV.

The total density of states plot against energy in Hartree is presented in figure 3. The Fermi energy is at -0.08 Ha. The wide gap seen in the band structure is equally well reproduced in the density of states calculation. It is clearly seen that bands are forbidden to cross the energy gap. This is what makes a material a semiconductor.

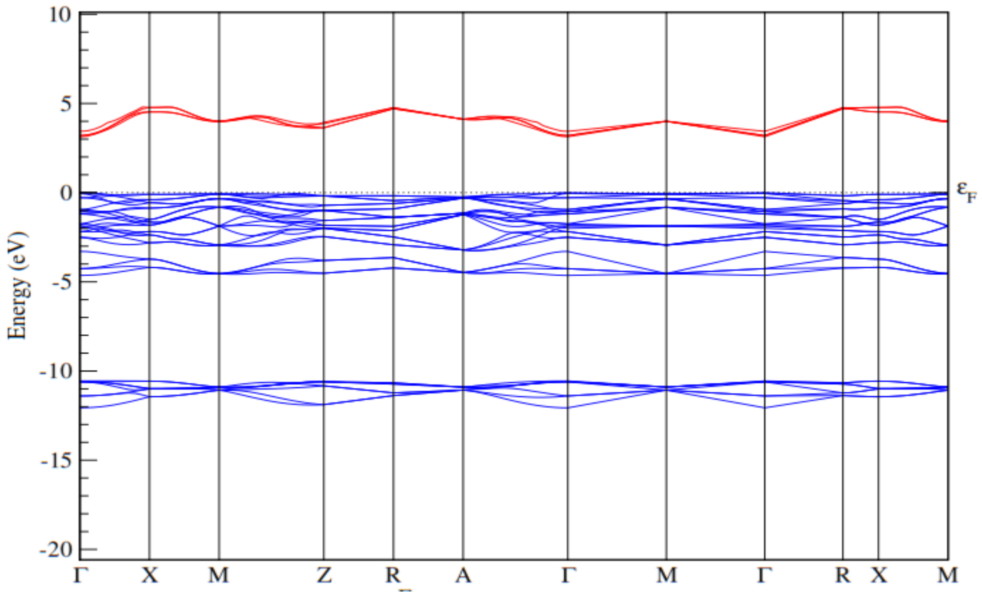

Figure 2: The electronic band structure of CuAlS$_2$. The Fermi energy is at the zero mark and it is indicated by the E_F.

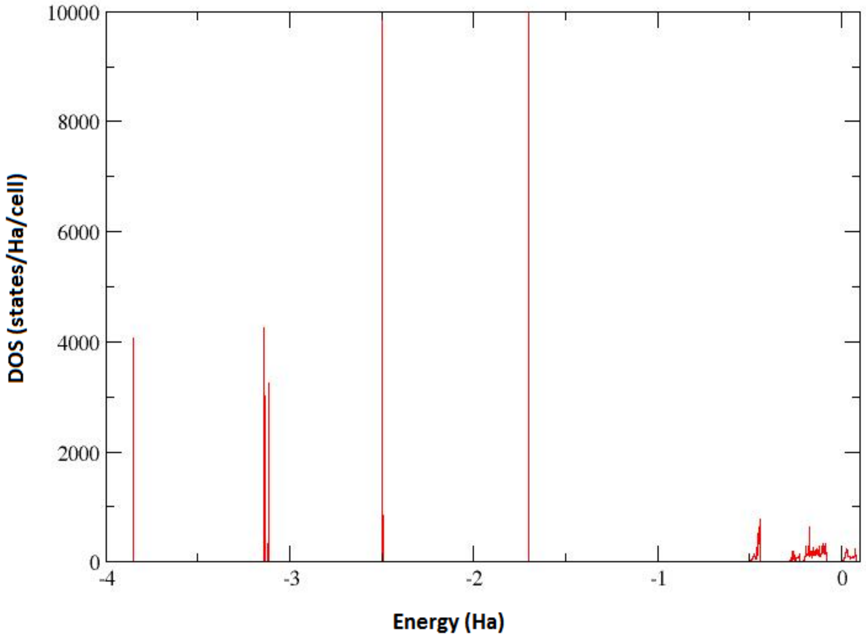

Figure 3: The total density of state. The Fermi level is at -0.08 Ha.

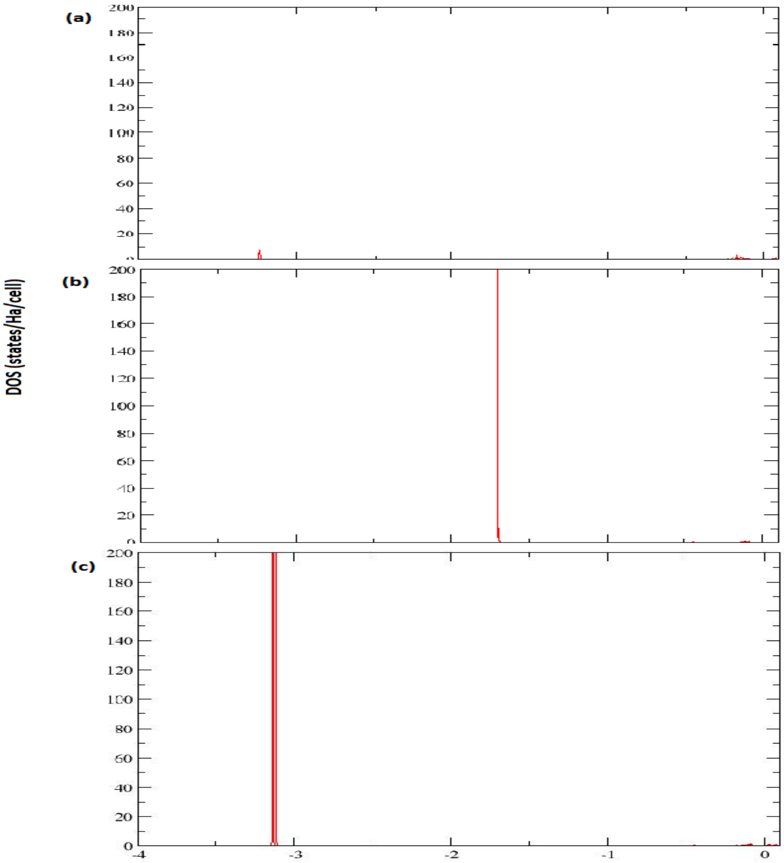

Figure 4: Orbital contribution from Cu to the total density of states. Fermi energy at -0.08 Ha. (a) the orbital contribution from Cu-s (b) the orbital contribution from Cu-p (c) the orbital contribution from Cu-d.

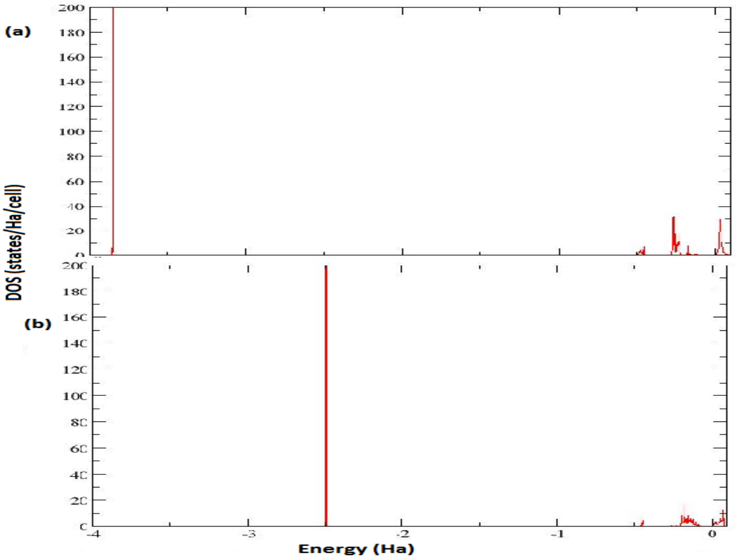

Figure 5: Orbital contribution from Al to the total density of states. Fermi energy at -0.08 Ha. (a) the orbital contribution from Al-s (b) the orbital contribution from Al-p.

The orbital contribution of Cu atom to the total density of states (DOS) is shown in figure 4. The 3s and 3p electrons were included in the calculations as semi core states. And their contributions are visible from the decomposed density of states. Figure 4a shows the contributions from the Cu-3s and Cu-4s states. The 3s state is seen about -0.32 Ha as a small projection. The 4s contribution is around the Fermi level. It is clear that the 4s states are not the dominant states near the Fermi level. The spike seen about -1.6 Ha in figure 4b represents the Cu-3p semi core states. The Cu-d contribution is seen in figure 4c as shape raised spike.

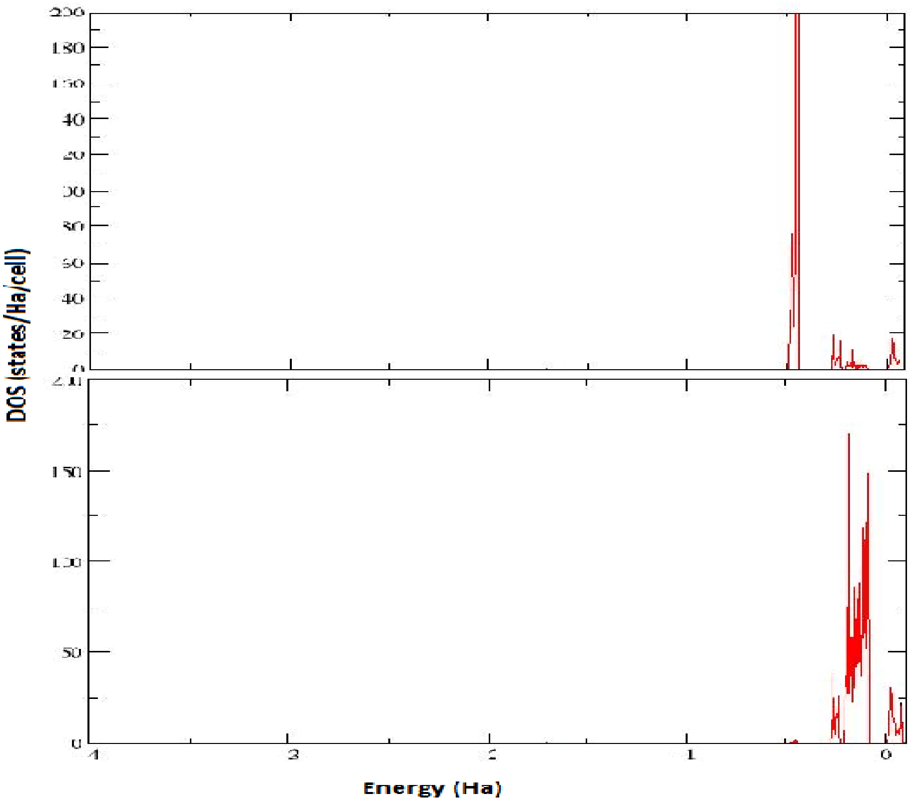

Figure 6: Orbital contribution from S to the total density of states. Fermi energy at -0.08 Ha. (a) the orbital contribution from S-s (b) the orbital contribution from S-p.

Figure 5 shows the orbital contribution to the total density of states from the Al atoms. Like for Cu, the 2s and 2p states were included as semi core states in the calculations. The spike close to the -4 Ha is due to the semi core states of Al-2s. The states at -1.5 Ha are predominantly that of Al-3s orbital as shown in figure 5a. The peak preceeding the Fermi level and that after the energy fundamental gap shows the Al-3s orbital contribution.There are more Al-3s states within the energy range of -0.5 to 0.1 Ha than the Cu contribution and Al-3p contributions. Figure 5b shows the contribution from the 2p and 3p orbitals to total DOS. The sharp raise at -2.5 Ha represents the Al-2p semi core state.

Figure 6 displays the the contribution to the total density from the S atom. There are no semi core state for S. Figure 6a is the contribution from the S-3s while figure 6b is that from the S-3p states. There are more S-3s state around the -0.5 Ha energy mark compared to the contributions from the orbitals of other atoms. It is closely followed by the Al-3s states. The states immeditely below the Fermi level are mostly of the S-3p orbitals are seen from Figure 6b.

For the phonon calculations, it was observed that the $CuAlS_2$ may not be dynamically stable. This is as a result of the consistent negative phonon bands. As pointed out by Jaffe and Zunger, it is quite tasking investigating the structure especially, the phonon bands of $CuAlS_2$. From the analysis of the phonon modesat the zone centre, LO/TO of Γ_{15} obtained was 525/410 cm^{-1}. The exprimental value is 497/444 cm^{-1} [22].

III. Conclusion

We performed the electronic band structure of thin film of the orthorhombic $CuAlS_2$and its vibrational properties using the pseudopotential method within density functional theory (DFT) and density functional perturbation theory (DFPT) frameworks respectively. LDA+U technique and the projector augmented wave (PAW) was used in for the electronic band structure calculations, while the norm-conserving pseudopotentials were used for the DFPT computations. The calculated results showed that $CuAlS_2$is a semiconductor with a wide band gap energy value of 3.13 eV. It was also discovered that the Γ to Zand $\Gamma$to M transition are critical points in the structure of the material. The vibrational study reveal that $CuAlS_2$ might not be dynamically stable.

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