Electronic Properties of Monoclinic and Tetragonal Phases of Copper Germanium Sulphude (Cu2ges3)

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Abstract

Cu_2GeS_3 is a chalcopyrite-like structured material that can crystalize in different structural phases. Each phase exhibits distinct electronic properties due to variations in atomic arrangement and bonding characteristics. In this study, we investigated the electronic properties of the monoclinic and tetragonal phases of Cu_2GeS_3 using first-principles calculations based on density functional theory (DFT+U). Precisely, the ALBINIT software was used to generate and analyse data. The outcome of this theoretical study showed that the monoclinic phase exhibit an indirect band gap and a calculated bandgap value of 1.2ev. Critical analyses of the electronic band structures showed that the monoclinic phase of Cu_2GeS_3 is a semiconductor while that of the tetragonal phase presented with metallic features as there was no bandgap due to the overlapping of the valence and conduction bands. Diligent examination of the total and partial density of states revealed that the valence band of the monoclinic phase is primarily composed of Cu-3d states, Ge-4p states with a significant contribution from S-3p states while the conduction band is dominated by Ge-4p and Ge-4s states. For the tetragonal phase, the TDOS and PDOS showed that the valence band is dominated by Cu-3d and contributions from the three Ge orbitals and the two S orbitals. The conduction band minimum in the tetragonal phase is also dominated by Ge-4s states with significant contribution from the Ge-4d, 3p states, as well as the S-3s and 3p states. Our findings suggest that the electronic properties of Cu2GeS3 can be tuned by controlling the crystalline phase, making it a promising candidate for future optoelectronic devices.

Keywords*- Copper germanium sulphide, Albinit, electronic band structure, density of states, partial density of states, monoclinic, tetragonal.*

I. INTRODUCTION

Cu_2GeS_3 is a ternary chalcogenide semiconductor that has garnered significant attention due to its potential applications in various optoelectronic devices. The material exhibits polymorphism, crystallizing in different structures such as orthorhombic, cubic, monoclinic, and tetragonal phases. Understanding the electronic properties of these different phases is crucial for optimizing their performance in applications like solar cells, photodetectors, and thermos electrics [1]. The crystal structure of Cu_2GeS_3 can be influenced by factors such as synthesis conditions, temperature, and pressure. The monoclinic and tetragonal phases are particularly interesting due to their distinct structural features and potential electronic properties. The monoclinic phase is characterized by a distorted octahedral coordination of Cu atoms, while the tetragonal phase exhibits a more symmetric arrangement [2].

In a more recent study by Kada et al.[3], they performed first-principles calculations on the structural and optoelectronic properties of Cu_2GeS_3 compound in the Cc and Imm2 structures.

They applied the linear augmented plane wave method for all electrons (FPLAPW), which is based on density functional theory (DFT) by using the local density approximation (LDA) and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). In addition, the modified Becke Johnson Tran and Blaha potential (TB-mBJ) combined with the Hubbard potential (U), which successfully corrects the band gap problem. They found that the structural properties such as lattice parameter, compressibility modulus and its derivative for Cu_2GeS_3 -Cc were in good agreement with the available data, but for Cu_2GeS_3 -Imm 2 there were no research work in the literature. The band structure results show that the Cu_2GeS_3 -Cc compound has a direct gap (Γ-Γ) and that Cu_2GeS_3 -Imm 2 is a metal. The optical properties were calculated by determining the real and imaginary parts of the dielectric function ε(ω), the absorption coefficient, the reflectivity and the refractive index. These results indicate that these alloys are very useful for UV photo catalysis applications

An experiment was done in 2023 [4], Cu_2GeS_3 (CGS) as a member of the DL chalcogenides was synthesized by a high-temperature solid-state method, and the optical properties were carefully studied experimentally and theoretically. The results revealed that CGS has a large second harmonic generation (0.8 x AgGaSe2) and a moderate birefringence of 0.06 at 1064nm. In addition, the linear and NLO properties of the A2MS3 (A = Cu, Li; M = Ge, Si) Series of compounds were evaluated and compared with the help of first-principles calculations.

In another study, Wujisiguleng Bao and team [5] used the first principle calculation method to study the band structure for Cu_2GeS_3/CdS and Cu_2SnS_3/CdS heterointerface The tetragonal structure of Cu_2GeS_3 and Cu_2SnS_3 was adopted in this study and the results gotten showed that the valence band maximum(VBM) of CdS is lower than CGS by 1.4eV and the conduction band minimum(CBM) of CdS is lower than CGS by 0.5eV. It was also gotten that the valence band maximum(VBM) of CdS is lower than CGS by 1.4eV and the conduction band minimum(CBM) of CdS is higher than CTS by 0.1eV which meant that the CGS/CdS is a type II interface while the CTS/CdS is a type I interface.

In the study of the optoelectronic properties of $Cu_2Ge(Se_xS_{1-x})3$ monocrystalline powders [6], the monlcrystalline powders were synthesized in lil flux by molten salt synthesis growth method. X-ray diffraction was uesd to determine the crystal structure and lattice parameters of the $Cu_2Ge(Se_xS_{1-x})3$ (CGSSE) and it was shown that Cu_2GeS_3 crystallize in the monoclinic structure while Cu_2GeSe_3 crystallize in the orthorhombic structure. There were transfers of the crystal structure of $Cu_2Ge(Se_xS_{1-x})3$ from monoclinic to orthorhombic and these occurred between x=0.2 and x=0.4. In all, these results showed that $Cu_2Ge(Se_xS_{1-x})3$ (X=0.4 - 0.6) materials have potential as absorber materials in solar cells.

There was a study that synthesized Cu_2GeS_3, a I2 IV VI3 semiconductor, by the combination of its elemental components in vacuum-sealed quartz ampoules. The samples were analyzed using single crystal X-ray diffraction techniques. It crystallizes in the monoclinic space group Cc, with β = 108.37(2) ◦, and Z = 4. Finally, the disagreement factors of the structure refinement carried out with SHELXL-93 were R(F) = 0.0454, wR(F2) = 0.1087 and S = 1.103 for all 557 independent reflections merged from the 1086 reflections measured [7]

Thin films of Cu_2GeS_3 were grown by annealing copper layers in GeS and S gaseous atmosphere above 460°C. Below 500°C the cubic polymorph was formed, having inferior optoelectronic properties compared to the monoclinic phase, formed at higher temperature. The bandgap of the

cubic phase lies below that of the monoclinic phase: they were determined from absorption measurements to be 1.23 and 1.55 eV respectively. Photoluminescence measurements were performed and only the monoclinic Cu_2GeS_3 shows a photoluminescence signal with a peak maximum at 1.57 eV. This difference between cubic and monoclinic was attributed to the higher quasi fermi level splitting of the monoclinic phase. Wavelength dependent photoelectrochemical measurements demonstrate the Cu_2GeS_3 to be p-type with an apparent quantum efficiency of less than 3 % above the band gap [8]

In the present work, the DFT+U method would be applied, using Albinit to study the electronic properties of monoclinic and tetragonal phases of Cu_2GeS_3.

II. COMPUTATIONAL DETAILS

Cu_2GeS_3, a I2 IV VI3 semiconductor, is a ternary chalcopyrite material with the I-42d space group. The monoclinic phase of Cu_2GeS_3 belongs to the space group C2/m with lattice parameters typically given as a = 6.269 Å, b = 3.480 Å, c = 10.377 Å, β = 110.4° (Yan, 2020). In the tetragonal phase, Cu_2GeS_3 typically crystallizes in the space group I4/mcm with lattice parameters a = b = 4.110 Å, c = 11.255 Å [9]. The atoms in Cu_2GeS_3 are in the 8D, 4A, 8D wycoff positions respectively. There are 4 formula units of Cu_2GeS_3 per unit cell. The unit cell contains four times the number of atoms as a single formula unit: eight copper, four germanium and twelve sulphur atoms which is consistent with the chemical composition Cu_2GeS_3. The electronic band structure, the total and partial density of states and the dielectric response function were computed in this study.

The electronic structure calculations were performed using Albinit , a widely used DFT software for solid-state systems; The LDA+U scheme, which includes the coulombs interaction term U, for d- electrons was used in the study to calculate the electronic band structure and density of state. This scheme uses the projector augmented wave (PAW) as the pseudopotential. The dielectric functions were calculated using the norm-conserving psuedopotential. The self consistency calculations have energy tolerance of 10-6, a kinetic energy cutoff of 12 Hatree (Ha), and a 256 K-point mesh for brillouin zone integration. The following orbitals were included in the valence state of the respective atoms; Cu- 3s, 3d, 3p, 4s, Ge- 3d, 4s, 4p, S- 3s, 3p.

III. RESULTS AND DISCUSSION

The electronic properties analyzed include the band structure, band gap, density of states (DOS) and total density of states (TDOS). These provide insights into the material's potentials.

The electronic band structure was calculated along high-symmetry paths in the Brillouin zone for both phases. The band structures provide critical insight into the nature of the material's band gap, whether it is direct or indirect, and the energy range over which the valence and conduction bands extend.

1. Band Gap of Monoclinic Phase: The band structure of the monoclinic phase was plotted with energy (eV) against high-symmetry points, in this direction; Γ-Y-A-M in the Brillouin zone. As shown in fig1, the fermi energy Ef is indicated by the dotted line.
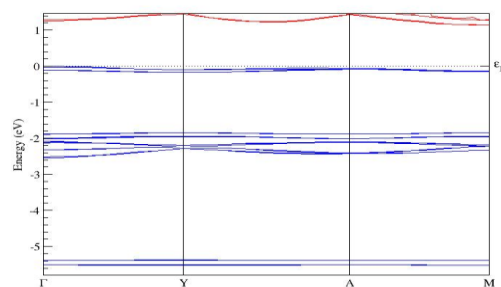
Fig.1: Electronic band structure of monoclinic phase of Cu_2GeS_3

The valence band maximum (VBM) is located at the Γ position of high symmetry while the conduction band minimum (CBM) is located between the Y and A position of high symmetry. This results shows that the monoclinic phase has an indirect band gap, where the maximum of the valence band does not align with the minimum of the conduction band. This electronic band structure showed that Cu_2GeS_3 is a semiconductor. The calculated band gap for the monoclinic phase was approximately 1.2eV. There are several research studies on the monoclinic phase of Cu_2GeS_3 that either support or contradict a band gap of 1.2 eV. One study by K. Kayakan et al. [10] reported a band gap of approximately 1.7 eV for the monoclinic phase of Cu_2GeS_3, which is higher than the proposed value of 1.2 eV. This discrepancy could be due to differences in experimental techniques or sample preparation methods. On the other hand, a study by S. A. Mulay et al. [11] found that the band gap of the monoclinic phase of Cu_2GeS_3 was approximately 1.2 eV, in agreement with the proposed value. This research utilized spectroscopic ellipsometry to determine the band gap of the material. There are some disagreement among research studies regarding the band gap of the monoclinic phase of Cu_2GeS_3, with some reporting values higher or lower than 1.2 eV. Further research is needed to reconcile these differences and determine the accurate band gap of this material

2. Band Gap of Tetragonal Phase: For the tetragonal phase, the band structure was calculated along the high-symmetry path Γ-X-P-X-Γ-N-M-X, plotted against energy (eV) as shown in fig.2. In contrast to the monoclinic phase, the tetragonal phase shows zero band gap at the M point of high symmetry. The VBM and CBM overlap at the M point. This is suggestive that the tetragonal phase of Cu_2GeS_3 is metallic in nature. The overlap allows for a large number of free electrons that can move throughout the material which enables it to conduct electricity efficiently.
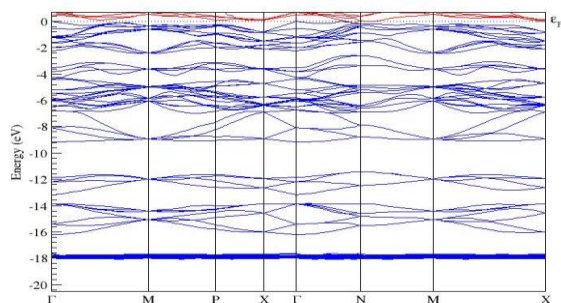
Fig. 2: Electronic band structure of the tetragonal phase of Cu_2GeS_3

Several research studies on the tetragonal phase of Cu_2GeS_3 have reported conflicting results regarding its band gap and metallicity. One study conducted in 1992 [12], suggested that Cu_2GeS_3 exhibits a direct band gap of 0.88 eV at the M point, indicating a semiconductor behavior with a nonzero band gap and distinct valence band maximum (VBM) and conduction band maximum (CBM) energies at that point. However, a more recent study [13] reported that the VBM and CBM of Cu_2GeS_3 overlap at the M point, indicating a metallic behavior with a zero band gap. This finding contradicts the earlier study but is in agreement with the data of this work and suggests that Cu_2GeS_3 may exhibit different electronic properties depending on the specific crystal structure and experimental conditions. Overall, the conflicting results highlight the importance of further research on the electronic properties of Cu_2GeS_3 to better understand its potential applications in electronic and optoelectronic devices.

3. TDOS of Monoclinic Phase Cu_2GeS_3: The total density of state for the monoclinic phase is shown in figure 3. DOS is plotted against energy (Ha). The features or peaks in the plot represent the decomposed orbital contributions to the Total density of state. All the subbands in the electronic band structure of the monoclinic phase of Cu_2GeS_3 are shown in fig.3 with higher concentration within the valence band periphery. The fermi level is at about -0.08Ha.
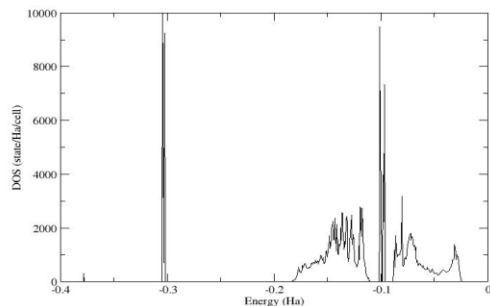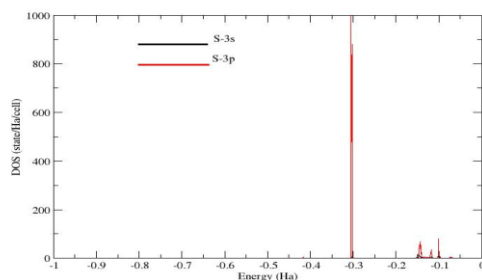

Fig.3: TDOS of monoclinic phase of Cu_2GeS_3

4. PDOS Of Monoclinic Phase Of Cu_2GeS_3: The partial density of states for the monoclinic phase of Cu_2GeS_3 are displayed in figures 4a-4c. These plots represent the orbital decomposition for copper, germanium and sulphur respectively.

Fig.4a shows the various copper's orbitals contribution to the density of state of Cu_2GeS_3. The Cu-3p states are shown in red while Cu-3d and Cu-4s states are shown in green and black respectively. The Cu-3p states are are at lower energy and concentrated at -3.2Ha. The Cu-3d states is seen to have an expanded energy width, dispersed at -0.3Ha, around -0.2Ha to -0.05Ha and the lower part of the conduction band, given that the fermi level is at -0.08Ha. There's an overlap of the Cu-3d state with the Cu-4s states, seen around -0.15Ha to -0.1Ha.

Fig.4b shows the various germanium's orbitals contribution to the TDOS. The Ge-3d state is depicted with green while Ge-4p and Ge-4s states are indicated with red and black respectively. The feature at -1.3Ha is the contribution from Ge-3d states. The Ge-4p state is seen with a larger width and dispersed around -0.15Ha to -0.05Ha. The contribution of the Ge-4s state is very minimal and is fairly seen dispersed around -0.14Ha and -0.05Ha, overlapping with the Ge-4p state around the fermi level.

The contributions of the sulphur atom to TDOS comes from S-3s and S-3p orbitals depicted in black and red respectively as shown in Fig.4c. The valence band is largely dominated by the S-3p state, which is concentrated at -0.3Ha. Both states have bands near the fermi level.
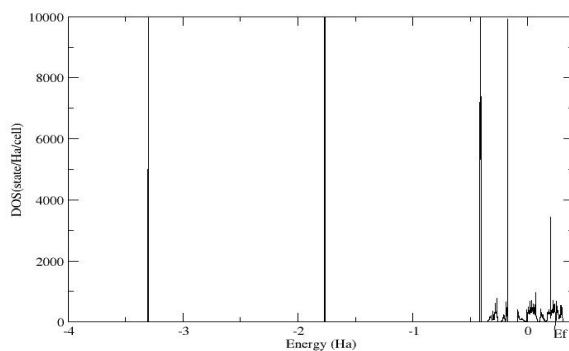
The TDOS plot for the monoclinic phase shows that the valence band is primarily composed of Cu-3d states, Ge-4p states with a significant contribution from S-3p states. The Cu 3d states are centered around -0.2Ha below the Fermi level, with S-3p states extending from -3Ha to the Fermi

level. The conduction band is dominated by Ge-4p and Ge-4s states. The conduction band minimum occurs at approximately -0.05Ha above the Fermi level, confirming the indirect band gap nature of the monoclinic phase.
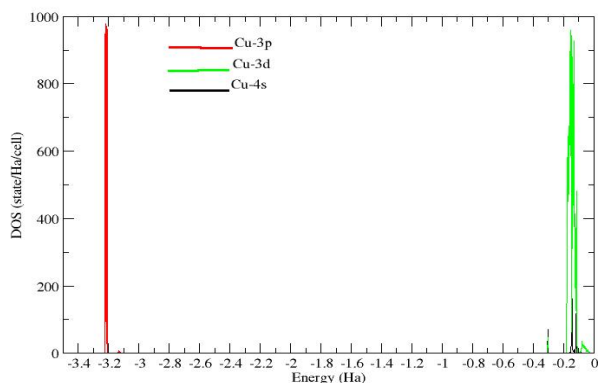

Fig.4a: PDOS of Cu in monoclinic Cu₂GeS₃
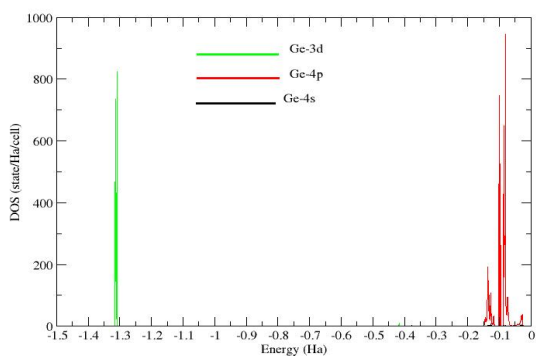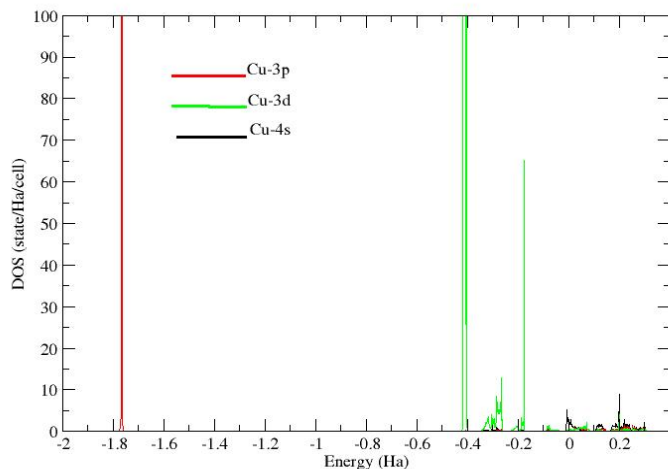

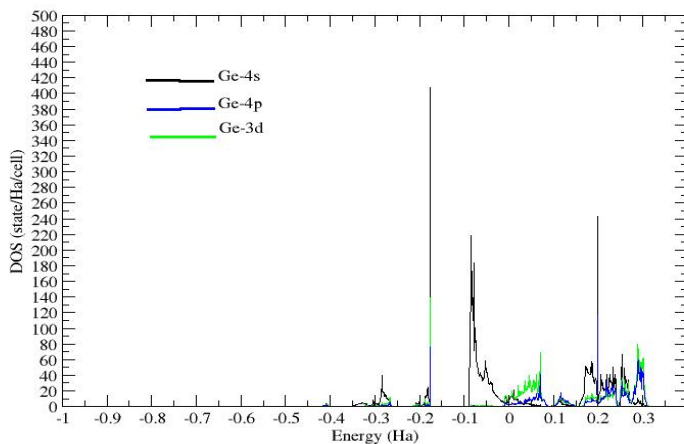Fig.4b: PDOS of Ge in monoclinic Cu₂GeS₃

Fig.4.4c: PDOS of S in monoclinic Cu_2GeS_3

5. TDOS of Tetragonal Phase Of Cu_2GeS_3: The total density of states of the tetragonal phase of Cu_2GeS_3 is presented in figure 5. TDOS is plotted against energy (Ha), showing the features of each atom to the electronic structure of Cu_2GeS_3. The fermi level is at 0.2Ha.
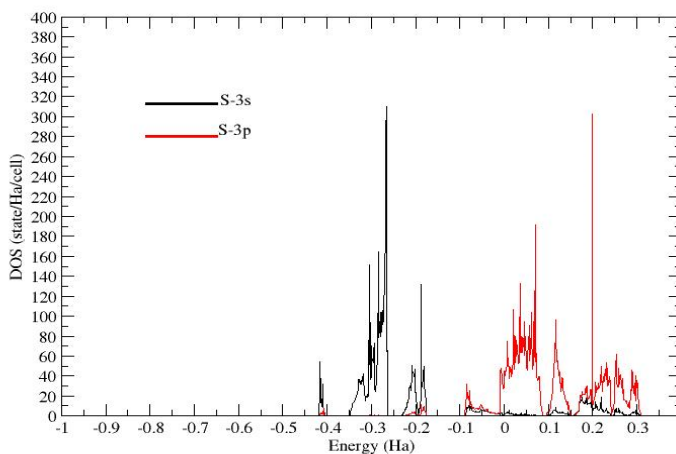
Fig.5: TDOS of tetragonal phase of Cu$_2$GeS$_3$

Fig.5: TDOS of tetragonal phase of Cu$_2$GeS$_3$

6. PDOS Of Tetragonal Phase Of Cu$_2$GeS$_3$: The contributions of the various atoms in the tetragonal phase of Cu$_2$GeS$_3$ to TDOS are shown in figs. 6a-6c. The orbital contributions from copper atom are shown in fig.6a. Similar to the monoclinic phase, three copper orbitals are displayed, Cu-3p, Cu-3d and Cu-4s in red, green and black lines respectively. The Cu-3p state is concentrated at -1.8Ha. Cu-3d has a large energy width, indicating a well dispersed state (-0.4Ha to 0.15Ha). The Cu-4s state is localized more around the fermi level and the conduction band.

Figure 6b shows the contributions from the various germanium orbitals included in the computation. These are Ge-4s, Ge-4p, Ge-3d, shown in black, blue and green respectively. The conduction band is filled with overlapping of the three orbitals. The highest peak in the valence band was formed from the concentration of all three orbitals at -0.2Ha with a more predominant Ge-4s state.

The contributions from sulphur's orbitals are shown in fig.6c. S-3s and S-3p orbitals are displayed with black and red lines respectively. Both orbital posses wide energy ranges and a dispersed among the valance and conduction bands.

The TDOS for the tetragonal phase is similar to that of the monoclinic phase, with the valence band dominated by Cu-3d and contributions from the three Ge orbitals and the two S orbitals. However, the band widths and peak intensities are slightly different due to the higher symmetry of the tetragonal phase, which leads to more delocalized bonding. The conduction band minimum in the tetragonal phase is also dominated by Ge-4s states with significant contribution from the Ge-4d, 3p states, as well as the S-3s and 3p states. The fermi level is at 0.2Ha as seen in the TDOS (fig.5). Overlapping of some orbitals of the Copper, Germanium and Sulphur atoms is visible around the fermi level as shown in figures 6a-6c. This implies that there is zero band gap in the tetragonal phase.

IV. CONCLUSION

The band structures for both phases were computed along high-symmetry paths in the Brillouin zone, revealing that the monoclinic phase has an indirect band gap, where the maximum of the valence band does not align with the minimum of the conduction band. This electronic band structure showed that Cu_2GeS_3 is a semiconductor at the monoclinic phase. The calculated band gap for the monoclinic phase was approximately 1.2eV. There are some disagreement among research studies regarding the band gap of the monoclinic phase of Cu_2GeS_3, with some reporting values higher or lower than 1.2 eV. Further research is needed to reconcile these differences and determine the accurate band gap of this material. In contrast to the monoclinic phase, the tetragonal phase showed zero band gap at the M point of high symmetry. The valence band maximum and conduction band minimum overlap at the M point. This is suggestive that the tetragonal phase of Cu_2GeS_3 is metallic in nature. The overlap allows for a large number of free electrons that can move throughout the material which enables it to conduct electricity efficiently. This result is in agreement with a study by Gilbert et al. [13] which reported that the VBM and CBM of Cu_2GeS_3 overlap at the M point, indicating a metallic behavior with a zero band gap

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