

Investigation of the Structural and electronic properties of Ternary AB_2X_4 based material via Density Functional Theory (DFT) for Optoelectronic Applications

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Abstract: *Developing inexpensive, non-toxic, high-efficiency, earth-abundant optoelectronics material is critical for implementing electronic devices. $CdAl_2S_4$ is a promising earth-abundant absorber AB_2X_4 material that has attracted attention recently for optoelectronic applications including solar cells and light-emitting diodes. However, very little is known about the relationship between structural and electronic properties such as the band gap, density of state, and partial density of state. This information is, however, very essential for the design and fabrication of $CdAl_2S_4$ optoelectronics devices to achieve higher power conversion efficiencies. In this article, first-principles calculation based on the state-of-the-art methodology of density functional theory (DFT) has been employed to comprehensively characterize the structural and electronic properties of $CdAl_2S_4$ material. From band structure analysis, $CdAl_2S_4$ is demonstrated to have a direct band gap with a predicted band gap of 2.322 eV. It is evident from the calculated Total Density of State (TDOS) and Partial Density of State (PDOS) that $CdAl_2S_4$ exhibited the characteristics of a semiconductor and it is a potential material for optoelectronic applications. This study provides a comprehensive understanding of AB_2X_4 materials' structural and electronic behaviors, paving the way for their development in next-generation optoelectronic technologies.*

Keywords: Density functional theory, Band gap, Total density of state, Partial density of state.

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1.0 Introduction

The challenge to ameliorate climate change coupled with the need for energy growth by our society as it enlarges and the depletion of conventional non-renewable energy sources necessitated the demands for the development and improvement of safe, renewable and low-cost clean energy technologies. It cannot be overemphasized that the most abundant renewable energy source is gotten from the sun: it has been shown that the total amount of solar radiation incident on the Earth's surface is about 1.4×10^{17} W. Covering just 1% of the Earth's surface incident solar radiations with photovoltaic (PV) modules operating with efficiency of 10% would produce around 25 TW Peter (2011). So, there is a need to develop cheap materials, earth-abundant and environment friendly. Currently, commercial photovoltaic cells are made from silicon, though earth abundant but expensive due to the purification process. Thus, the development of

low-cost and efficient photovoltaic (PV) materials is critical for providing energy to the growing.

World population and combating man-made climate change. Photovoltaic technology makes use of the naturally abundant and available energy from the Sun to generate electricity has shown enormous benefits in the environment, economy, and society at large (Wadia *et al.*, 2009, Alharbi *et al.*, (2011). However, for this technology to deliver a substantial fraction of the energy the world demands, the materials these devices are made of must be cheap and readily available. Science and engineering are responsible in addressing the challenge of discovering a method to design and develop earth-abundant, cheap, and non-toxic new materials that possess the perfect electronic properties for applications of photovoltaic cells.

The prospect of scientists developing highly efficient and affordable photovoltaic solar panels made from readily available materials remains an intriguing possibility. The development and improvement of materials with optoelectronic properties that are perfect for applications in photovoltaic solar panels demands exploiting many degrees of freedom including different chemical compositions and structures. Overall reliance on laboratory experiments for the rational design and discovery process of new materials may be slow, and time-consuming and may lead to wastage of valuable materials if results are not achieved. The use of first-principles Density Functional Theory (DFT) calculations performed on high-efficiency computers can significantly reduce the amount of time spent on laboratory experiments processes in testing new materials. Predictive modelling and simulations offer the most intelligent and efficient path forward to significantly expand the parameter space whilst lowering both costs and development times.

AB_2X_4 based materials are promising earth-abundant absorber materials that have attracted

attention recently for optoelectronic applications including photovoltaic solar cells. Among them, $CdAl_2S_4$ is a particularly attractive absorber candidate. Despite these promising properties of $CdAl_2S_4$, very little is known about the relationship between structural and optical properties such as the dielectric function. This information is very essential for the design and fabrication of $CdAl_2S_4$ photovoltaic devices to achieve higher power conversion efficiencies.

Understanding the electronic band structure of semiconductor materials is fundamental for their applications in optoelectronics, photovoltaics, and electronics. Cadmium Aluminum Sulphide ($CdAl_2S_4$) is a ternary semiconductor compound known for its potential in various applications due to its favourable optical and electronic properties. This review focuses on the electronic band structure of $CdAl_2S_4$ to highlight its unique characteristics and applications.

Isyaku, (2019) used first-principles calculations using advanced screened hybrid density functional theory (DFT) have been utilized to thoroughly characterize the structural, electronic, and optical properties of Cu_2SnS_3 material. From the band structure analysis, he concluded that Cu_2SnS_3 is demonstrated to be a direct band gap material with a predicted band gap of 0.9 eV, which is in good agreement with available experimental values of 0.9 - 1.3 eV. It was also concluded that it is evident from the calculated partial density of states (PDOS) that the anti-bonding Cu-d, Sn-p and S-p states are involved in the transition from valence to conduction band. Nnamdi and Emeruwa, (2024), used the density functional theory framework to investigate defect materials such as $ZnLn_2Se_4$ and $ZnLn_2Te_4$. They used the pseudopotential method in conjunction with the LDA+U technique and the projector augmented wave to calculate the electronic band structure, total density of state, and partial density of state. Also, they applied the norm-conserving

pseudopotential to calculate the dielectric response function with scissor shift. They predicted from their result that both ZnLn_2Se_4 and ZnLn_2Te_4 are semiconductors with a bandgap of 1.66 and 1.33 eV respectively.

This research aims to exploit first-principles DFT calculations to thoroughly analyze the structural and electronic properties of CdAl_2S_4 and explore their significance for photovoltaic applications.

2.0 Density Functional Theory

Density Functional Theory (DFT) is one of the most popular and effective Quantum Mechanics (QM) approaches for studying large systems Isyaku, (2019). It is widely employed for "ab initio" calculations of the structures of atoms, molecules, crystals, surfaces, and their interactions. DFT is now routinely used to calculate properties such as the binding energy of molecules in chemistry and the band structure of solids in physics. Its application is increasingly extending to fields that were traditionally considered more distant from quantum mechanics, such as biology and mineralogy are beginning to appear. Superconductivity, atoms in the focus of strong laser pulses, relativistic effects in heavy elements and atomic nuclei, classical liquids, and magnetic properties of alloys have been studied with DFT (Klaus, 2002).

The Hamiltonian for a real material consisting of N electrons and M nuclei is given by Isyaku, (2019).

$$H = -\sum_i \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_l \frac{\hbar^2}{2m_e} \nabla_l^2 - \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,l} \frac{Z_\alpha e^2}{|r_i - R_\alpha|} + \frac{1}{2} \sum_{i,\alpha} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |R_\alpha - R_\beta|} \quad (1)$$

where R_α , Z_α , and M_α represent the position, nuclear charge, and mass of the α -th nucleus and r_i is the position of electron i . The variables m and e are the mass and charge (magnitude) of the electron. If we invoke the Born-Oppenheimer approximation in which nuclei

masses are set to infinity, we arrive at the 'electronic' Hamiltonian for a system with nuclei fixed at positions $R_\alpha, \alpha, \dots, M$

$$H_{e1} = -\sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{4\pi\epsilon_0 |r_i - R_\alpha|} \quad (2)$$

This Hamiltonian is then used in the Schrödinger equation:

$$H_e \Psi(\mathbf{x}1; \dots; \mathbf{x}N) = E \Psi(\mathbf{x}1; \dots; \mathbf{x}N) \quad (3)$$

and solved for the wave-function $\Psi(\mathbf{x}1; \dots; \mathbf{x}N)$ and energy E . Here $\mathbf{x}_i = (r_i; \sigma_i)$ represents the position r_i and spin σ_i of the i th electron. Solving Eq. (2) is for systems with more than two particles ($N > 2$), finding an analytical solution is a formidable challenge, and in fact, none exists. Computational methods can be applied but become increasingly complex as N increases. Density Functional Theory (DFT) offers an approach to determine the ground state energy of a system without relying on the wave function, which depends on $4N$ variables. Instead, DFT uses the ground state density, which depends on only four variables, regardless of the number of electrons in the system.

DFT's versatility stems from the generality of its fundamental concepts and the flexibility in their implementation. Despite this flexibility, DFT is grounded in a rigorous conceptual framework. The theoretical foundation of DFT was established by the Thomas-Fermi (TF) model and solidified by the two theorems of Hohenberg and Kohn. The success of DFT can largely be attributed to the resemblance between the electron density in a molecule and that in a hypothetical substance known as the uniform electron gas (UEG), or jellium.

The local density approximation (LDA) is a particularly simple yet effective idea: by understanding the properties of jellium, one can model the electron cloud in a molecule by dividing it into small density chunks, each treated as a piece of jellium. This model allows for a focus on quantum effects and electron-electron repulsive interactions in solids, without the need to explicitly consider the

atomic lattice and structure of a real material. At zero temperature, the properties of jellium are determined solely by its constant electronic density, making it well-suited for treatment within DFT, and the formalism of DFT provides the foundation for the LDA to the exchange-correlation energy density functional.

2.1 First-Principle Calculations

The properties of materials are fundamentally determined by the interactions between electrons and nuclei, which require a quantum mechanical description. In 1929, shortly after the Schrödinger equation (SE) was developed, Dirac famously noted that the general theory of quantum mechanics was nearly complete. He stated, "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. Although the Schrödinger equation is challenging to solve analytically, numerical methods for approximating solutions to electronic structure problems have become crucial in chemistry and materials science.

A significant breakthrough occurred in 1964 when Hohenberg and Kohn, and later Kohn and Sham, reformulated the Schrödinger equation, which involves all the $3N$ spatial coordinates of N interacting electrons, into density functional theory (DFT). DFT focuses on electron density, a function of only three spatial coordinates, simplifying the problem. The Kohn–Sham (KS) equations transformed the complex many-body interactions into a more computationally feasible form through the use of an effective single-particle potential, known as the exchange-correlation functional.

While the exact wave function that would make this reformulation exact is still being sought, approximate functionals have been highly successful in predicting many material

properties. As a result, DFT has become a cornerstone of materials science, with DFT calculations playing a critical role in many research efforts. The development of efficient algorithms to solve the KS equations has led to the creation of increasingly sophisticated general-purpose codes. These powerful tools, combined with the continuous expansion of computational resources, have significantly extended the range of problems that can be studied using DFT. Among the commonly used DFT-based electronic structure codes that utilize plane waves and related methods are the Vienna Ab initio Simulation Package (VASP), the Cambridge Serial Total Energy Package (CASTEP), and Quantum-Espresso (an open-source package for research in electronic structure, simulation, and optimization) Giannozzi et al., (2009).

2.2 Schrödinger Equation

The properties of matter at the nanoscale are governed by the laws of quantum mechanics. The behaviour of atoms and electrons in a system as it evolves over time is described by the time-dependent Schrödinger equation, which has the general form:

$$i\hbar \frac{\partial \Psi}{\partial t} = \Psi H \quad (4)$$

where i is the imaginary unit, \hbar represents Planck's constant divided by 2π , Ψ denotes the wave function of the quantum system, and \hat{H} is the Hamiltonian operator, which defines the total energy of the wave function and varies depending on the context. The notation $\partial/\partial t$ is partial derivative with respect to time, t . In scenarios where the system is in a stationary state, the Hamiltonian is time-independent, and the time-independent Schrödinger equation takes the following form:

$$E\Psi = H\Psi \quad (5)$$

In simple terms, the equation means that if the Hamiltonian operator acts on a wave function Ψ and yields a result that is proportional to Ψ itself, then Ψ represents a stationary state. The proportionality constant E is the energy

associated with that state Ψ . The Hamiltonian H for interacting electrons and nuclei in a condensed matter system can be expressed by the following equation:

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2m_e} \nabla_I^2 - \sum_{iI} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{i,\alpha} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |r_i - R_\alpha|} \quad (6)$$

Electrons are indicated by lower-case subscripts, while nuclei are represented by upper-case subscripts. M_I and Z_I denote the masses and charges of the nuclei, and m_e is the mass of an electron. R_I and r_i represent the positions of the i th nucleus and i th electron, respectively. The first two terms in the equation account for the kinetic energy of the electrons and nuclei. The remaining three terms describe the electrostatic interactions: the attractive forces between electrons and nuclei, and the repulsive forces due to electron-electron and nucleus-nucleus interactions. Solving this many-body problem exactly within the quantum mechanical framework is practically infeasible, so physically meaningful approximations are required to make the problem manageable.

3.0 Materials and Method

In this section, the method applied in the computation and the parameters used in computing the results shall be discussed.

3.1 Lattice Parameter

Lattice parameters are fundamental to understanding the crystallographic properties of a material. For CdAl_2S_4 , it is essential to investigate how variations in these parameters impact the electronic structure since it is a ternary semiconductor compound that crystallizes in a Cubic (spinel) structure. Understanding its crystal structure and lattice parameters is crucial for predicting and interpreting its physical, chemical, and electronic properties.

The lattice parameter, often denoted as “a”, represents the edge length of the tetragonal unit cell in which the CdAl_2S_4 crystal is packed. For

tetragonal structures, the lattice parameter “a” is uniform for the three axes $a=b=c = 10.4 \text{ \AA}$ and the angles are all 90° since the structure is cubic.

3.2 Computational details

The defect stannite structure to which CdAl_2S_4 is a member shows that it belongs to the I-42m space group. It has a vacancy at the 2b Wyckoff site (0.0,0.0,0.5). The group II atom occupies the 2a Wyckoff site, group III atom occupies the 8i site. The atomic positions for the 8i site used in the calculations and lattice parameters were adopted (Madelung, 2004). There are two formula units per unit cell, this makes it a total of fourteen atoms in one unit cell.

The pseudopotential plane wave method implemented in the Abinit Quantum suite (Gonze et al., 2002) and (Gonze et al., 2020) was used in all computations. The lattice parameters and atomic positions used in this work were adopted from (Olekseyak et al., 2020). The band structure, total density of states (DOS), and partial density of states (PDOS) were calculated for CdAl_2S_4 compound. The DFT + U scheme was employed in conjunction with the projector augmented wave (PAW). The tolerance on energy was fitted at 10^{-10} Ha/Bohr, the cutoff kinetic energy was fitted at 15Ha and a shifted grid of 4x4x4 was used. The pseudopotential method was employed in the investigations. The ability to software code (Gonze et al., 2002) was used in the study. The calculations carried out are the electronic band structure, density of states (total and partial). The LDA+U technique was used in the electronic band structure and density of states study. The projector augmented wave (PAW) was used as the pseudopotential for the electronic band structure and density of state (DOS) calculations while the norm-conserving pseudopotential was used for the dielectric response calculations. For the ground state calculations, the tolerance on energy was 10^{-6} , a kinetic energy cutoff of 12 Ha and a k-point

mesh of 256 were used. The following states were included in the PAW used in the computations. Cd: 4d 5s, Al: 3s 3p, S: 3s 3p

4.0 Results and Discussion

The electron band structures of Cadmium Aluminum Sulfide (CdAl_2S_4) is presented in Figs 1. The band structure is a plot of energy (eV) against high symmetry points in the Brillouin zone. The direction of the plot in the Brillouin zone is along $\Gamma - \text{M} - \text{P} - \text{X} - \Gamma - \text{N} - \text{M}$ high symmetry k-points. The Fermi

energy is marked at the zero point. The conduction band minimum (CBM) and the valence band maximum (VBM) occur at the centre of the zone, that is, at the gamma (Γ) point. The band gap is direct and the calculated direct band gap is 2.322 eV. The band structure calculated for CdAl_2S_4 is not spin-polarized and does not exhibit magnetic behaviours. It is a semiconductor as predicted from the calculation results, which are in excellent agreement with experimental values and other DFT results in the literature.

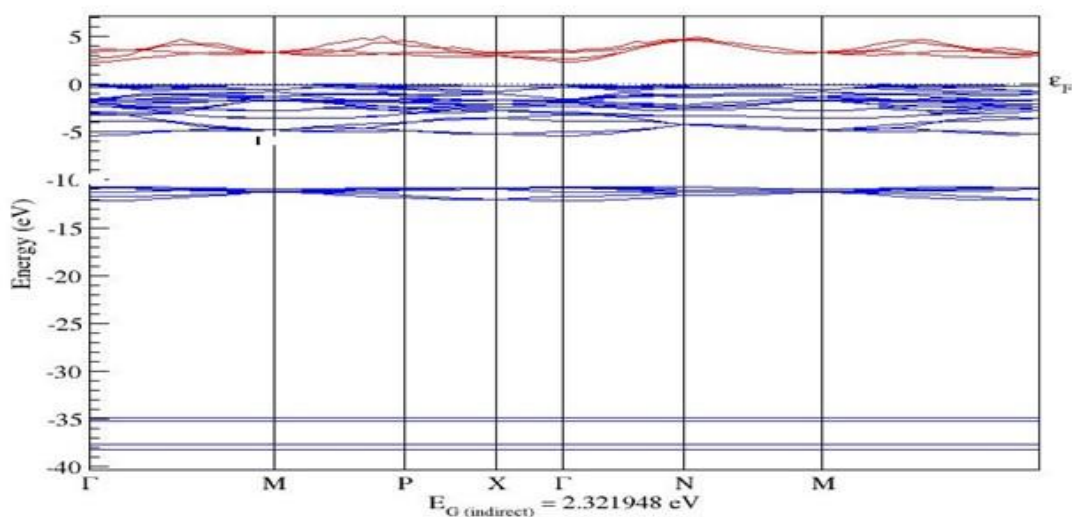


Fig 1. The electronic band structures of Cadmium Aluminum Sulphide (CdAl_2S_4)

The total density of states (TDOS) for CdAl_2S_4 is presented in Figs 2. The plot is DOS in states/Ha/cell against energy in Hartree. The energy axis has a range of -1.95 to 0.3 Ha. The X-axis represents the energy levels (in Hartree, Ha) relative to the Fermi level (E_F), which is shown as the dotted vertical line at 0.11 Ha. Energy values to the left of the Fermi level are occupied states, while those to the right are unoccupied states. Y-axis (DOS in states/Ha/cell) indicates the number of electronic states available at each energy level. A higher DOS value means more electronic states are available at that specific energy. The Fermi level is marked by the dotted line at 0.11

Ha. In semiconductors or insulators, this is the energy level separating the valence band

(occupied states) and the conduction band (unoccupied states). There appears to be a gap around the Fermi level, which suggests that CdAl_2S_4 has a band gap. This is a characteristic of semiconductors.

The occupied States (Left of E_F) shows a significant peak just below -1.2 Ha, this suggests that there is a large number of states available at this energy level, which is part of the valence band. The sharp nature of this peak indicates strongly localized states. The smaller peaks between -0.2 Ha and -0.1 Ha likely represent states in the upper portion of the valence band. There are very few states

immediately above the Fermi level, which indicates the presence of a band gap. The small peaks that appear right after 0.11 Ha suggest that the conduction band starts just after the Fermi level, meaning the material has a small band gap. The gap between the highest peak in the valence band and the region with zero states

at the Fermi level (E_f) suggests that CdAl_2S_4 is a semiconductor.

The total DOS is a reflection of all the state's contributions included in the computations. An important feature of the total DOS is that it corroborates the results from the band structure calculations.

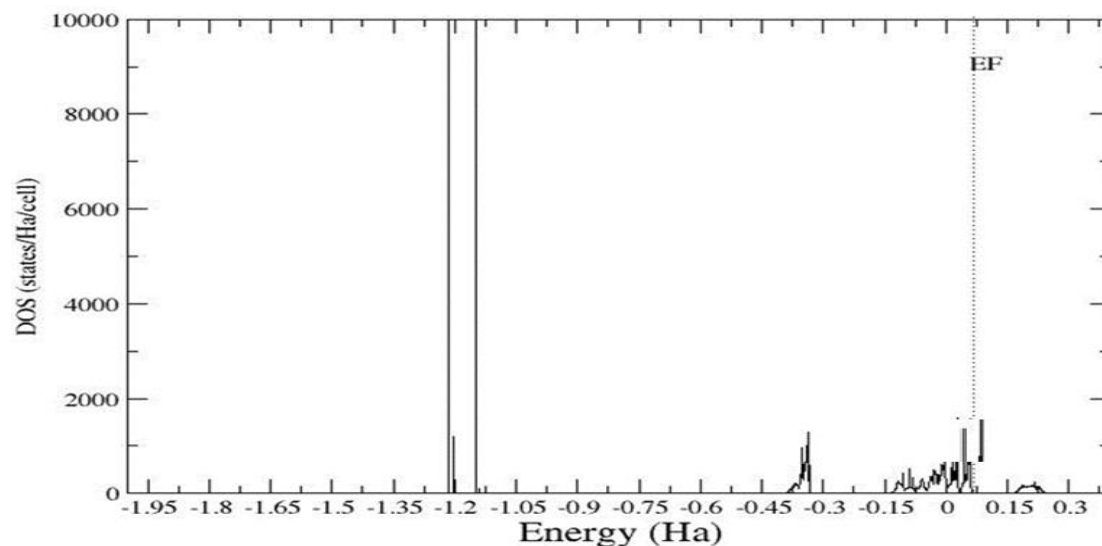


Fig 2. Total density of state, E_f represents Fermi energy level for Cadmium Aluminum Sulphide (CdAl_2S_4)

The PDOS for Cd is shown in Fig 3, the x-axis shows the energy in Hartrees (Ha). The range spans from approximately -1.5 Ha to 0.3 Ha. The energy axis is likely referenced to the Fermi level. The y-axis represents the density of states in terms of states/Ha/cell. The plot displays two PDOS components for Cd (Cd-5s and Cd-4d Contributions). Cd-5s (red line) represents the projected density of states of the 5s orbital of Cd. Cd-4d (black line) represents the projected density of states of the 4d orbital of Cd.

There is a large peak around -1.2 Ha, which corresponds to the 4d orbitals. This indicates that the Cd 4d electrons are deep core states, with a sharp, high-intensity peak far below the Fermi level. This suggests that the 4d states are highly localized and do not contribute significantly to the bonding or electronic conduction near the Fermi level. Closer to the Fermi level (around -0.15 Ha to 0 Ha), there are

smaller peaks for both the Cd-5s and Cd-4d states. This suggests that both orbitals contribute, though weakly, to the valence band and conduction band near the Fermi level. The Cd-5s states (red line) appear mostly between -0.3 Ha and -0.15 Ha. These states may be involved in bonding but contribute less to the density of states compared to the Cd-4d orbitals.

The PDOS for Al is shown in Fig 4, the x-axis shows the energy in Hartrees (Ha). The range spans from approximately -0.9 Ha to 0.3 Ha. The energy axis is likely referenced to the Fermi level. The y-axis represents the density of states in terms of states/Ha/cell. The plot displays two PDOS components for Al (Al-3s and Al-3p Contributions). Al-3s (black line) represents the projected density of states of the 3s orbital of Al. Al-3p (red line) represents the projected density of states of the 3p orbital of Al.

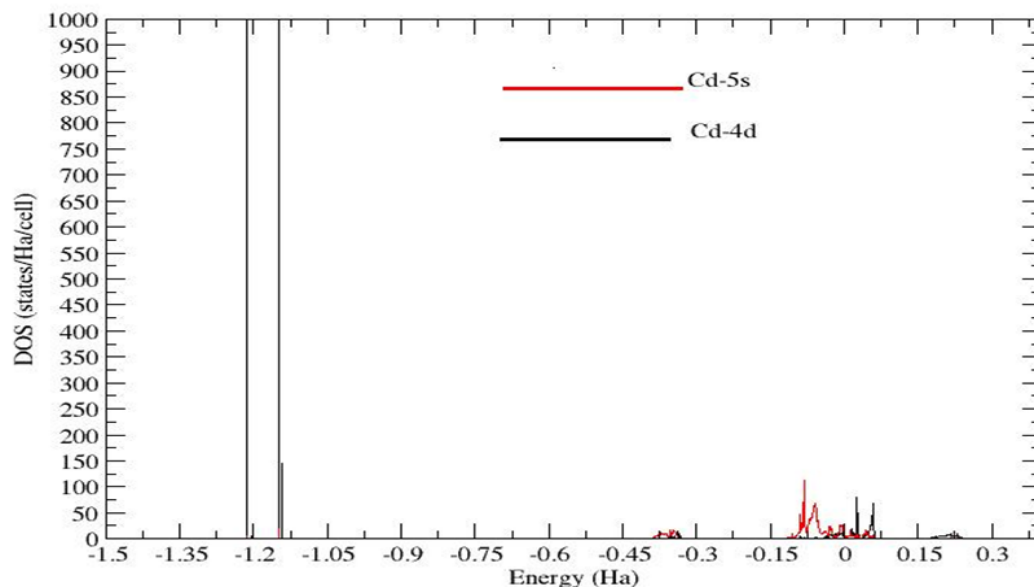


Fig 3. Partial DOS for Cd atom in TDOS of CdAl₂S₄

The Fermi energy (E_F) is depicted by the dotted line. The Al-3p states are spread out more and have contributed more across a wider range of energy. There are several peaks in the DOS for Al-3p states around -0.12 Ha and towards the Fermi energy. The most notable sharp peak is around -0.2 Ha to -0.3 Ha and -0.45 Ha. Al-3p

states contribute significantly right up to the Fermi level, indicating these states are more involved in the bonding and potential conductivity properties of the material. The top of the valence band is a mix of Al-3s and Al-3p and the bottom of the conduction band is also a mix of the two states as shown between 0.15 to about 0.2 Ha.

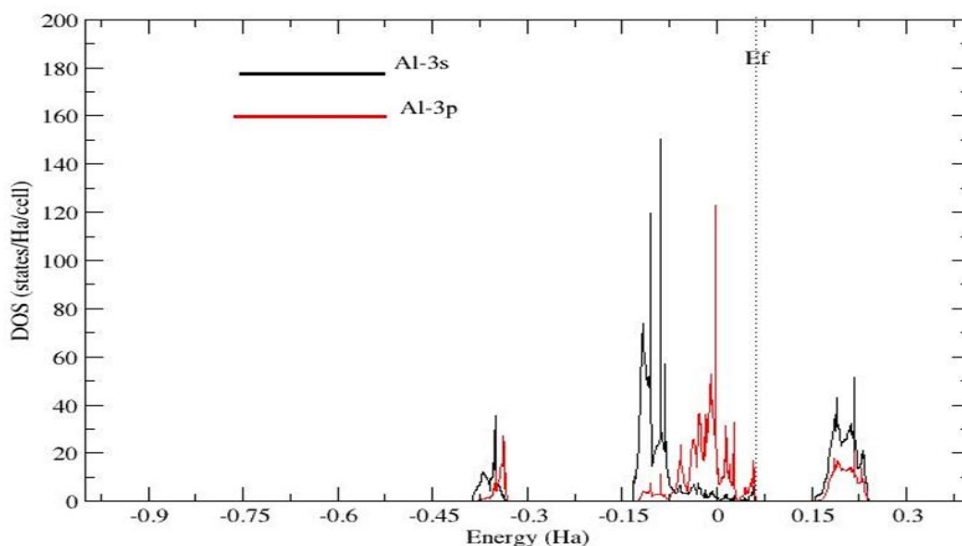


Fig 4. Partial DOS for Al atom in TDOS of CdAl₂S₄

The PDOS for S is shown in Fig 5, the x-axis shows the energy in Hartrees (Ha). The range s

pan from approximately -0.9 Ha to 0.3 Ha. The energy axis is likely referenced to the

Fermi level. The y-axis represents the density of states in terms of states/Ha/cell. The plot displays two PDOS components for S (S-3s and S-3p Contributions). S-3s (black line) represents the projected density of states of the 3s orbital of S. S-3p (red line) represents the projected density of states of the 3p orbital of S.

The S-3s states appear primarily sharp between -0.374 Hartree and -0.337 Hartree. The S-3p states are spread out between -0.15 Ha toward the Fermi energy level. This shows that the top of the valence band is dominated by S-3p in

CdAl₂S₄. The PDOS analysis shows that the sulfur 3p orbitals have more states closer to the Fermi level compared to the 3s orbitals, which suggests that the 3p orbitals are more involved in bonding interactions within the CdAl₂S₄ structure. The presence of states near the Fermi level, especially from the 3p orbitals, could suggest potential electrical conductivity or optical properties that could be explored for semiconductor applications. The sharp peaks in the PDOS near the Fermi level are indicative of localized states which could affect the electronic properties of the material.

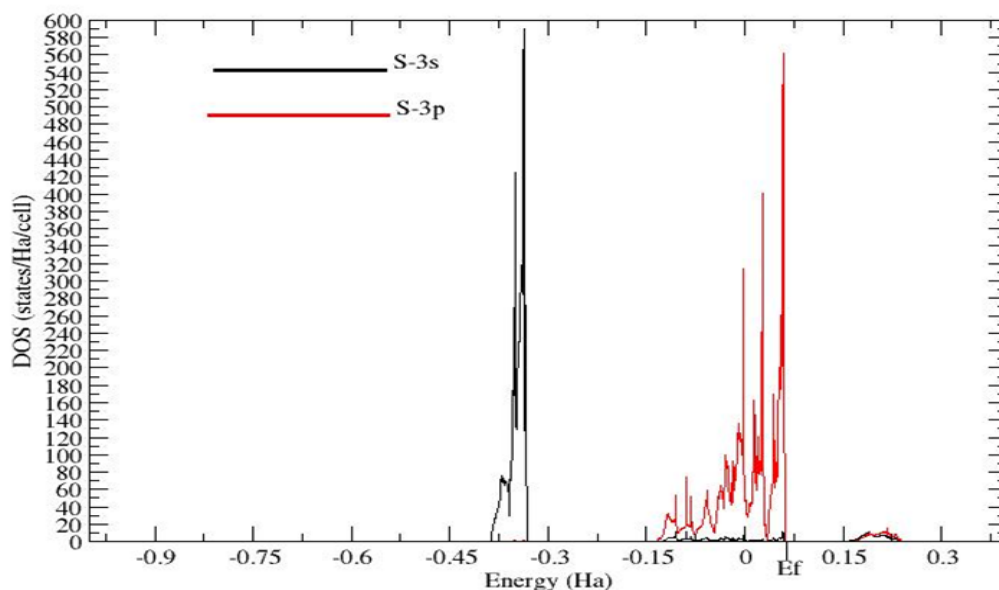


Fig 5. Partial DOS for S atom in TDOS of CdAl₂S₄

5.0 Conclusion

Density Functional Theory (DFT) has proven to be an invaluable tool in understanding the properties of complex systems by using electron density instead of the wave function, making it computationally manageable for large systems. DFT's capability to compute the structure of atoms, molecules, and solids has led to significant advances in fields like materials science and physics. Through first-principle calculations and the application of DFT, this study effectively modeled the electronic band structure and density of states (DOS) for CdAl₂S₄, a semiconductor with a

direct band gap of 2.322 eV, which aligns with experimental and other theoretical results.

The results highlight the non-spin-polarized, non-magnetic nature of CdAl₂S₄, confirming its semiconducting properties as seen through the direct band gap. The analysis of the total density of states further supports this, with a clear band gap observed around the Fermi level, distinguishing the valence band from the conduction band. The computational approach, employing the LDA + U technique and PAW pseudopotentials, provided reliable insights into the material's electronic properties.

To advance the understanding and practical application of DFT-based methods, future research should focus on exploring the temperature dependence of CdAl₂S₄'s electronic properties and its behavior under external fields or doping conditions. Additionally, the development of more accurate exchange-correlation functionals could further improve the predictive power of DFT for complex systems like CdAl₂S₄, broadening its application in semiconductor design and materials optimization.

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Compliance with Ethical Standards Declaration

Ethical Approval

Not Applicable

Competing interests

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Availability of data and materials

Data would be made available on request.

Author's Contribution

Simulations, analysis and interpretations of simulation results were performed by Isaac Chukwutem Abiodun while the write up of the various sections were carried out by Monday Edward Edem and Obasesam Ebri Agbor.