Structural and magnetic properties $\text{CuAl}_{1-x}\text{Cr}_x\text{S}_2$ alloys

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Abstract. In this paper computational calculations were performed based on the density functional theory DFT, to investigate the structural, electronic and magnetic properties of $\text{CuAl}_{1-x}\text{Cr}_x\text{S}_2$ ($x=0.0$, 0.50 and 1.00) alloys. Pseudopotential method was used, as is implemented in the Quantum-Espresso code. We found that the alloys crystallize in a tetragonal structure belonging to space group 122 (I-42d) with lattice constants $a=5.290\,\text{Å}$, $c=10.378\,\text{Å}$ for $x=0.5$ and $a=5.283\,\text{Å}$, $c=10.366\,\text{Å}$ for $x=1.00$. These values are in good agreement with experimental results. Additionally, we found that the alloys possess an antiferromagnetic behaviour with magnetic moments $4.20\,\mu_\beta$/cell and $4.05\,\mu_\beta$/cell, respectively. From the analysis of the density of states, it is clear that the alloys have a half-metallic behaviour due to the $\text{Cr}$-$d$ and $\text{Cu}$-$d$ states crossing the Fermi level. This compounds can be used in spintronic.

1. Introduction
The I-III-VI$_2$ chalcopyrite compounds were I=Cu; III=Al, Ga, In; and VI=S, Se, the have been attracting considerable attention due to their potential applications in solar-cells, detectors, light-emitting diodes, optoelectronic and nonlinear laser devices applications. Among the I-III-VI$_2$ chalcopyrite semiconductors, CuAlS$_2$ compounds have a wide direct band gap around 3.49eV that useful for ultraviolet absorption [1-8]. This is a typical example of the chalcopyrite structure, space group I-42d with four formula units per one unit cell, which is a ternary analog of the diamond structure and essentially a superlattice or superstructure of zinc blende. Like the atoms in diamond and zinc blende structure, each constituent in these ternary compounds, is tetrahedrally coordinated to four neighbors atoms: every metal ion is coordinated by four sulphur ions, every sulphur ion has two Al y two Cu nearest neighbors (see Figure 2(a)). In this paper we study the structural and electronics properties of $\text{CuAl}_{1-x}\text{Cr}_x\text{S}_2$ ($x=0.0$, 0.50 and 1.00) alloys, due of possible applications in diluted magnetic semiconductors, spin injectors and other spintronics applications.

2. Computational method
Calculations were performed using periodic density functional theory (DFT), such as is implemented in the plane-wave self-consistent field (PWscf) code in the Quantum ESPRESSO package [9]. The exchange and correlation energies were modelled according to the generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof (PBE) gradient-corrected functional [10]. Electron–ion interactions were treated with the pseudopotential method [11,12]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40Ry. For the charge density, a kinetic energy cutoff of 400Ry was used. A $6\times6\times3$ Monkhorst-Pack mesh [13] was used to generate the k-
points in the supercell. To calculate the lattice constant, the bulk modulus and the total energy of each studied compound, the calculated data are fitted with the Murnaghan equation of state [14], equation (1).

\[
E(V) = E_0 + \frac{B_0 V}{B_0 - 1} \left[ \left( \frac{V_0}{V} \right)^{\frac{1}{n}} - 1 \right] + \frac{B_0 V_0}{B_0 - 1}
\]

(1)

Where \(B_0\) is the bulk modulus and its first derivative is \(B_0',\) \(V_0\) is the equilibrium volume of the cell, and \(E_0\) is the binding energy.

3. Results and discussions

3.1. Structural properties

In order to investigate the structural properties of CuAl\(_{1-x}\)Cr\(_x\)S\(_2\) alloys (x=0.0, 0.50 and 1.00), the total energies of different compounds as functions of volume have been calculated in both ferromagnetic (FM) and antiferromagnetic (AFM) states and fitted by Murnaghan’s equation of state equation (1). For x=0.0, namely, the CuAl\(_2\) not have magnetics properties. In the CuAl\(_{0.50}\)Cr\(_{0.50}\)S\(_2\) and CuCrS\(_2\) alloys, the relative stability of the FM phase with respect to the AFM one has been investigated using various AFM structures to obtain the most stable AFM structure. For these purpose, the supercells of 1x1x2 were used to get even numbers of Cr atom for switching spin state up and down.

The calculated total energy differences between the FM and AFM states (\(E = E_{AFM} - E_{FM}\)) are about -0.075eV and -0.008eV for the CuAl\(_{0.50}\)Cr\(_{0.50}\)S\(_2\) and CuCrS\(_2\) alloys, respectively. For the two cases, the AFM states are more favourable in energy than FM states. The Figure 1 shows the total energy-volume curves for three alloys.

![Figure 1](image-url)

**Figure 1.** Total energy as a function of the volume: (a) CuAlS\(_2\), (b) CuAl\(_{0.50}\)Cr\(_{0.50}\)S\(_2\) and (c) CuCrS\(_2\).

| compound            | \(a_0\) (Å) | \(c\) (Å) | \(B_0\) (GPa) | \(E_0\) (eV) | \(\mu\) (\(\mu_B\)) |
|---------------------|-------------|-----------|---------------|-------------|------------------|
| CuAlS\(_2\)         | 5.338       | 5.334\(^a\) | 10.391        | 10.444\(^a\) | 165.31           | -4765.769       | 0.0   | 0.0\(^a\) |
| CuAl\(_{0.50}\)Cr\(_{0.50}\)S\(_2\) | 5.290       | 5.312\(^a\) | 10.378        | 10.389\(^a\) | 155.23           | -3481.331       | -4.20 | 4.10\(^a\) |
| CuCrS\(_2\)         | 5.283       | -         | 10.366        | -           | 155.60           | -4580.122       | -4.05 | 3.90\(^a\) |

\( ^a\)Experimental reference [15].
The calculated volume parameters including equilibrium lattice constant, bulk modulus $B_0$, total energy $E_0$ in AFM phase and magnetic moments, for all alloys are listed in Table 1, our results are compared with experimental values reported in reference [15]. The calculated lattices constant is good agreement with values reported experimentally, since it differs by less than one percent.

The Figure 1 shows that the alloys are stable or metastable due there are a minimum energy in the corresponding curve. The Figures 2 show the crystal structure of the alloys CuAl$_{1-x}$Cr$_x$S$_2$ ($x=0.0, 0.50$ and $1.00$) obtained after structural relaxation. In all cases, the space group obtained is the same, the tetragonal structure $122$ (I-42d).

3.2. Electronic properties

The Figures 3(a), 3(b) and 3(c) shows the total density of states (TDOS) and partial density of states (PDOS) of the orbitals that more contribute near the Fermi level of the alloys CuAl$_{1-x}$Cr$_x$S$_2$ ($x=0.0, 0.50$ and $1.00$), respectively. The calculations were performed with spin polarization up and down. The Figure 3(a) confirm the semiconductor nature of CuAlS$_2$ with a forbidden energy gap of $\sim 2.0$ eV, The magnitude of this gap is smaller than the experimentally reported for CuAlS$_2$ in chalcopyrite structure ($\sim 3.5$eV), this occurs because the GGA approximation underestimates the forbidden energy gap in semiconductors. The Figures 3(b) and 3(c) shows the total and partial spin-polarized density of states of the CuAl$_{0.50}$Cr$_{0.50}$S$_2$ and CuCrS$_2$ alloys. Due to the introduction of the Cr atoms in the structure of CuAlS$_2$, it loses its semiconductor nature, there are a penetration towards prohibited energy zone of the states Cr-d in greater proportion and the states Cu-d and S-p minor proportion, therefore, the allowed ternary compounds has half-metallic behavior determined by such states. These last two alloys have magnetic behavior with magnetic moments of 4.20 and 4.05µ$_B$ respectively.

Figure 2. Unit cell of the alloys: (a) CuAlS$_2$, (b) CuAl$_{0.50}$Cr$_{0.50}$S$_2$ and (c) CuCrS$_2$ after structural relaxation.

Figure 3. Total and partial density of state of (a) CuAlS$_2$, (b) CuAl$_{0.50}$Cr$_{0.50}$S$_2$ and (c) CuCrS$_2$ in the chalcopyrite structure.
4. Conclusion
We executed a study of the alloys CuAl_{1-x}Cr_xS_2 (x=0.0, 0.50 and 1.00) using the Density Functional Theory (DFT) in the frame pseudopotential. The calculated lattices constant calculated are good agreement with values reported experimentally, since it differs by less than one percent. The density states study reveal that due to the introduction of the Cr atoms in the structure of CuAlS_2, it loses its semiconductor nature, there are a penetration towards prohibited energy zone of the states Cr-d in greater proportion and the states Cu-d and S-p minor proportion, the alloys CuAl_{0.50}Cr_{0.50}S_2 and CuCrS_2 have a magnetic moment of 4.20 and 4.05µ_β respectively, these properties show that the alloys are good candidates for possible applications in diluted magnetic semiconductors, spin injectors, and other spintronics applications.

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