CuAl_xCr_{1-x}S₂ (X= 0.25, 0.75) DISULFIDES A COMPUTATIONAL CALCULATION OF PHYSICAL PROPERTIES

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ABSTRACT

In this work the results of study of structural, electronic, and magnetic properties of alloys system CuAl_xCr_{1-x}S₂ (x = 0.25 and 0.75) in the chalcopyrite are reported. The calculations were performed using spin-polarized density functional theory along with pseudopotential method. After of relaxation structural calculations we found that lattices constant of the CuAl_{0.25}Cr_{0.75}S₂ and CuAl_{0.75}Cr_{0.25}S₂ were $a = 5.309(1) \text{ \AA}$ and $a = 5.320(3) \text{ \AA}$, respectively. The studies of the electronic properties show that these alloys have a metallic and antiferromagnetic behavior and present magnetic moments of $4.39 \mu_B/\text{cell}$ and $4.19 \mu_B/\text{cell}$, respectively. The density of states analyzes reveal that the half-metallic and antiferromagnetic character comes from hybridization between Cr-d, Cu-d y S-p states that cross the Fermi Level.

KEYWORDS: DFT, CuAl_{1-x}Cr_{1-x}S₂ alloys, structural and electronic properties

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INTRODUCTION

The CuAlS₂ chalcopyrite disulfides has been studied theoretical and experimental due to application in light emitting diodes, nonlinear laser devices, solar-cells, detectors and optoelectronic [1-6]. Recently, there has been a lot of interest in the study of semiconductors that have some magnetic ordering. This for the purpose of using them in spintronic devices. Very semiconductors have been doped with metal transition atoms in order to study the properties of diluted magnetic semiconductor materials. For these reason in this paper we have studied the structural, electronic and magnetic properties of alloys system CuAl_xCr_{1-x}S₂ (x = 0.25 and 0.75) in the chalcopyrite structure. With the goal of determining the possibility of applying the compounds in the field of spintronic.

COMPUTATIONAL METHODOLOGY

The calculation we carry out using the pseudopotential method [7] in the frame of density functional theory [8] using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [9] as it is implemented in the Quantum Espresso computational code. We are using a kinetic energy cutoff of 40 Ry for the plane wave and 400 Ry for the density charge. A mesh of k points of 6x6x3 was using, generated with the Monkhorst-Pack method [10]. All the calculation was performed with spin polarized. In order to determine the most favorable structure magnetic, we calculated the ferromagnetic (FM) and antiferromagnetic (AFM) structures. For AFM phase we calculated several configurations until obtained the most stable. All position of CuAlS₂ and alloys system CuAl_xCr_{1-x}S₂ (x = 0.25 and 0.75) in the chalcopyrite structure were optimized until all force reached a value most small that $10^{-4} \text{ eV/\AA}$.

RESULTS AND DISCUSSIONS

In this section we present the results of the structural, electronics and magnetic proprieties of CuAlS₂ and alloys system

$\text{CuAl}_x\text{Cr}_{1-x}\text{S}_2$ ($x = 0.25$ and 0.75).

STRUCTURAL PROPERTIES

The structural parameters of CuAlS_2 , $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ compounds in the chalcopyrite structure figure 1, were determined calculating the total energy as a function of the volume of the cell and the calculated values were fitted to the Murnaghan equation of state. Additionally, to calculate the most stable magnetic phase, the total energy was calculated in the FM and AFM structures.

Figure 1: Conventional cell of chalcopyrite structure. (a) CuAlS_2 compound, (b) $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and (c) $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ alloys

The total energy variation versus of the volume of the CuAlS_2 compound and alloys system $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ are shown in the figure 2, (a), (b) and (c), respectively. The structural parameters are listed in the table 1 along with values reported theoretical and experimentally. As we can see in the table 1, the lattice constant of the CuAlS_2 calculated in this paper $5.341(2) \text{ \AA}$ is good agreement with the theoretical values reported $5.341 \text{ \AA}$ [11] and is in excellent agreement with the experimental report $5.334(1) \text{ \AA}$ [12]. For the alloys $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ we note that the lattices constant decrease with increase of the Cr concentrations, being this decrease of $\sim 0.4\%$ and $\sim 0.43\%$, respectively. This happen because the atomic radius of Cr ($1.27 \text{ \AA}$) it is smaller than atomic radius of Al ($1.43 \text{ \AA}$). On the other hand, as we can see in the table 1 and the figure 2 the total energy in the AFM state is greater than total energy of FM states, being the energies differences between AFM y FM states ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) of -72 meV for $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and 76 meV for $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$. Therefore, the magnetic ordering of $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ is AFM.

Figure 2: Variation of total energy of cell as a function of the volume. (a) CuAlS_2 compound, (b) $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and (c) $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ alloys

(c) CuAl_{0.75}Cr_{0.25}S₂ alloys.Table 1: Structural parameters. Lattice constant a_0 , total energy in the FM and AMF states

Compound	a_0 (Å)	E_0 (eV) FM	E_0 (eV) AFM
CuAlS ₂	5.340(2) 5.3410 ^a 5.334 (1) ^b	-4765.769	-4756.763
CuAl _{0.25} Cr _{0.75} S ₂	5.320(3)	-2931.961	-2932.033
CuAl _{0.75} Cr _{0.25} S ₂	5.318(2)	-4.030.512	-4030.587

^aTheoretical reference [11], ^bExperimental reference [12]

ELECTRONIC PROPERTIES

To calculate the electronic properties the equilibrium parameters listed in the table 1 were used to compute the total and partial density of state with spin up and spin down. In all calculation we choose the Fermi Level as zero of the energy. The DOS is shown in the figure 3.

Figure 3: Total and partial density of states. (a) CuAlS₂ compound, (b) CuAl_{0.25}Cr_{0.75}S₂ and (c) CuAl_{0.75}Cr_{0.25}S₂ alloys

The figure 3(a) show the DOS of CuAlS₂. The ternary compound has a semiconductor behavior and is a no magnetic material because the channel the spin up it is symmetrical with channel spin down. These results are in good agreement with the theoretical [11] and experimental results [12].

The figures 3(b)-(c) show the DOS of CuAl_{0.25}Cr_{0.75}S₂ and CuAl_{0.75}Cr_{0.25}S₂, we can see that due to the introduction of Cr atoms into the matrix of the CuAlS₂. The CuAlS₂ loses its semiconductor character. Therefore, CuAl_{0.25}Cr_{0.75}S₂ and CuAl_{0.75}Cr_{0.25}S₂ alloys have a metallic behavior determinated by Cr-d, Cu-d and S-p states that crosses the Fermi Level. Finally, the CuAl_{0.25}Cr_{0.75}S₂ and CuAl_{0.75}Cr_{0.25}S₂ alloys have an antiferromagnetic character with magnetic moments of 4.39 μ_B /cell and 4.19 μ_B /cell, respectively. The magnetic properties come from hybridization between Cr-d, Cu-d and S-p states. This property opens the doors to these alloys for potential applications in the spintronics field

CONCLUSIONS

- The structural, electronic, and magnetic properties of the alloys system CuAl_xCr_{1-x}S₂ (x = 0.25 and 0.75) were studied using the density functional theory.

- We found that $\text{CuAl}_{0.25}\text{Cr}_{0.75}\text{S}_2$ and $\text{CuAl}_{0.75}\text{Cr}_{0.25}\text{S}_2$ alloys have a metallic and antiferromagnetic behavior.
- With magnetic moment of $4.39 \mu_B/\text{cell}$ and $4.19 \mu_B/\text{cell}$, respectively. The magnetic moments are the result of hybridization between Cr-d, Cu-d and S-p states.

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