PAPER • OPEN ACCESS

Structural and magnetic properties $CuAI_{1-x}Cr_xS_2$ alloys

To cite this article: C Ortega López et al 2016 J. Phys.: Conf. Ser. 687 012051

View the article online for updates and enhancements.

You may also like

- <u>The bioengineering of perfusable</u> endocrine tissue with anastomosable blood vessels Hiroki Yago, Jun Homma, Hidekazu Sekine et al.
- A 3D bioprinted hybrid encapsulation system for delivery of human pluripotent stem cell-derived pancreatic islet-like aggregates Dong Gyu Hwang, Yeonggwon Jo, Myungji Kim et al.
- Economic 3D-printing approach for transplantation of human stem cell-derived <u>-like cells</u> Jiwon Song and Jeffrey R Millman





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 18.117.72.224 on 04/05/2024 at 15:41

Structural and magnetic properties CuAl_{1,x}Cr_xS₂ alloys

C Ortega López, G Casiano Jiménez¹ and M J Espitia²

¹ Universidad de Córdoba, Montería, Colombia.

² Universidad Distrital Francisco José de Caldas, Bogotá, Colombia.

E-mail: cortegal@unicor.edu.co

Abstract. In this paper computational calculations were performed based on the density functional theory DFT, to investigate the structural, electronic and magnetic properties of $CuAl_{1x}Cr_xS_2$ (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=5.290Å, c=10.378Å for x=0.5 and a=5.283Å, c=10.366Å 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 $4.20\mu_{\rm B}$ /cell and $4.05\mu_{\rm B}$ /cell, respectively. From the analysis of the density of states, it is clear that the alloys have a half-metallic behaviour due to the Cr-d and Cu-d states crossing the Fermi level. This compounds can be used in spintronic.

1. Introduction

The I-III-VI2 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, lightemitting diodes, optoelectronic and nonlinear laser devices applications. Among the I-III-VI2 chalcopyrite semiconductors, CuAlS₂ 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 o 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 $CuAl_{1-x}Cr_xS_2$ (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 6×6×3 Monkhorst-Pack mesh [13] was used to generate the k-

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution $(\mathbf{\hat{t}})$ (cc` of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

Journal of Physics: Conference Series 687 (2016) 012051

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).

$$E(V) = E_0 + \frac{B_0 V}{B_0} \left[\frac{\left(\frac{V_0}{V}\right)^{B'}}{B_0 - 1} + 1 \right] - \frac{B_0 V_0}{B_0 - 1}$$
(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 $CuAl_{1-x}Cr_xS_2$ 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 CuAlS₂ not have magnetics properties. In the CuAl_{0.50}Cr_{0.50}S₂ and CuCrS₂ 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}S₂ and CuCrS₂ 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. Total energy as a function of the volume: (a) $CuAlS_2$, (b) $CuAl_{0.50}Cr_{0.50}S_2$ and (c) $CuCrS_2$.

Table 1. Structural parameters: lattice constants (a_0) and (c), bulk modulus (B_0) , total energy (E_0) and magnetic moment.

compound	a ₀ (Å)		c (Å)		B ₀ (GPa)	$E_0 (eV)$	$\mu~(\mu_{\beta}~)$	
CuAlS ₂	5.338	5.334ª	10.391	10.444 ^a	165.31	-4765.769	0.0	0.0^{a}
$CuAl_{0.50}Cr_{0.50}S_2$	5.290	5.312ª	10.378	10.389ª	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 $CuAl_{1-x}Cr_xS_2$ (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).



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.

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 $CuAl_{1-x}Cr_xS_2$ (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 ~2.0 eV, The magnitude of this gap is smaller than the experimentally reported for $CuAlS_2$ in chalcopyrite structure (~3.5eV), 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 $4.05\mu_{\beta}$ respectively.



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 $\text{CuAl}_{1-x}\text{Cr}_x\text{S}_2$ (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 CuAlS₂, 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}S₂ and CuCrS₂ have a magnetic moment of 4.20 and $4.05\mu_{\beta}$ respectively, these properties show that the alloys are good candidates for possible applications in diluted magnetic semiconductors, spin injectors, and other spintronics applications.

References

- [1] Kodigala S 2010 *Cu*(*In1-xGax*)*Se2 Based thin film solar cells* (San Diego: Academic Press Elsevier)
- [2] Harichandran G and Lalla N P 2008 *Materials Letters* **62** 1267
- [3] Caglar M, LLincan S and Caglar Y 2008 Optics Communications 281 1615
- [4] Yue G H, Wang X, Wang L S, Wang W and Peng D L 2008 Physics Letters A 372 5995
- [5] Hsiang Y, Wang A, Bao N and Gupta A 2010 Solid State Sciences 12-3 387
- [6] Chen S, Gong Z G, Walsh A and Wei S H 2009 Appl Phys Lett 94 041903
- [7] Bid S and Pradhan S K 2002 J Appl Crystallogr 35 517
- [8] Bose P, Pradhan S K and Sen S 2003 Mater Chem Phys 80 73
- [9] Giannozzi P, Baroni S and Bonin N 2009 J Phys Condens Matter 21 395502
- [10] Perdew J P, Burke K and Ernzerhof M 1996 Phys Rev Lett 77 3865
- [11] Vanderbilt D 1990 *Phys Rev B* **41** 7892
- [12] Laasonen K, Pasquarello A, Car R, Lee C and Vanderbilt D 1993 Phys Rev B 47 10142
- [13] Monkhorst H and Pack J 1976 Phys Rev B 13 5188
- [14] Murnaghan F D 1944 Proc Natl Acad Sci USA 30 244
- [15] Villarreal M A, Grima P, Quintero M, Moreno E, Fernández J, Silva P and Villegas J 2013 Revista Mexicana de Física 59 521