

Investigations of Structural, Electronic, and Magnetic Properties of CuMnAlSe₃-Chalcogenide: FP-LAPW Method

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A theoretical study of the structural, electronic and magnetic properties of the quaternary chalcogenide CuMnAlSe₃ crystal is done by means of spin-polarized density functional theory calculations. The framework of FP-LAPW method is used within the generalized gradient approximation, based on Perdew 2008 functional GGA-PBEsol. The calculated equilibrium structural parameters are in good agreement with the available experimental data. Based on the analysis of the spin-polarized band structures and density of states, we predict the half-metallic character of the studied compound, with a half-metallic gap of 0.962 eV, and a total magnetic moment of $6\mu_B$ per unit-cell. We find that the inclusion of the electronic exchange-correlation through the newly developed TB-mBJ improves the description of the electronic structure. The TB-mBJ yields an indirect band gap ($X - \Gamma$) of 1.825 eV.

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1. Introduction

The quaternary $A^I_2B^{II}C^{II}D_3^{VI}$ materials can be derived from $A^I_2B^{IV}C_3^{VI}$ compounds [1, 2]. In 1983, de Groot et al. [3] discovered half-metallic ferromagnetism in semi-Heusler compound NiMnSb by using *ab initio* calculation based on density functional theory (DFT). After that half-metallicity attracted much attention [4] because of its prospective application in spintronics [5, 6]. Among this family of materials, the quaternary CuMnAlSe₃ was studied by Delgado and collaborators [7], who reported the synthesis, structural characterizations, and magnetic susceptibilities. Using X-ray powder diffraction data it was found that the CuMnAlSe₃ compound is a semiconductor that crystallizes in the tetragonal structure CuAlSe₂. The crystal structure characterization indicated a degradation of symmetry from the chalcopyrite structure $I42d$ to a related structure $P42c$ [8] with a sphalerite derivative structure and it is isomorphic with CuFeInSe₃. To the best of our knowledge, this is the only study available in the literature on this material. Therefore, investigation of the electronic and magnetic properties of this compound can give insight into its performance in the field of spintronic applications.

In this work, we report a detailed *ab initio* analysis of CuMnAlSe₃-chalcogenide compound [9]. The calculations are performed using the full potential linearized augmented plane wave (FP-LAPW) method [10]

within the generalized gradient approximation based on the Perdew 2008 functional GGA-PBEsol [11]. Furthermore, the density of states and band structure have been obtained using the newly developed Tran–Blaha modified Becke–Johnson potential denoted TB-mBJ [12, 13] which is very appropriate for the prediction of the band gap energy.

Our paper is organized as follows. Section 2 provides a description of the calculation scheme. Results and a discussion are presented in Sect. 3. Finally, the conclusion of this work is given in Sect. 4.

2. Computational details

The present *ab initio* study is done with the FP-LAPW method which is based on the DFT [14–16] as implemented in the Vienna package Wien2k [17, 18]. The exchange-correlation effects were treated within the version of the generalized gradient approximation, namely GGA-PBEsol, which is known to yield better results for solids. In addition, the problem of underestimating the band gap energy is remedied by the use of TB-mBJ approximation which allows one to give a better description of the band-gap energy.

In this method, the unit cell of the crystal is divided into non-overlapping muffin-tin (MT) spheres which are separated by an interstitial region. Inside the non-overlapping spheres of the MT radius, RMT, around each atom, was fixed to be to 2.11, 2.11, 1.99 and 2.0 bohr for Cu, Mn, Al, and Se, respectively. The basis set was split into core and valence subsets, the separation energy of valence and core states (cut-off energy) was chosen as -6.0 Ry.

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The Kohn–Sham equations are solved self-consistently. The core states were treated within the spherical part of the potential only and were assumed to have a spherically symmetric charge density confined inside the MT spheres. The valence part was treated with the potential expanded into spherical harmonics. The valence wave functions in the spheres were expanded to $l_{\max} = 10$ and a plane wave expansion was used in the interstitial region, the value of the cut-off parameters was chosen as $\text{RMT} \times K_{\max} = 8.0$ where K_{\max} is the largest reciprocal lattice vector, and by using the special K -point sampling schemes which have $12 \times 12 \times 6$ grid leading to 63 k -points in the irreducible Brillouin zone (IBZ). A limit value below the chosen value of 10^{-5} eV for total energy convergence allows convergence of self-consistent calculations.

3. Results and discussions

3.1. Structural properties

The CuMnAlSe_3 compound crystallizes in a tetragonal structure [7], space group $P42c$ (No. 112). Figure 1 shows the unit-cell of the studied materials. The obtained equilibrium lattice constants a and c and equilibrium unit-cell volume V_0 , the bulk modulus B_0 and its pressure derivative B' obtained from the E versus V curve fitted to the Murnaghan equations of state [19], and the relaxed atomic coordinates of the investigated compounds are summarized in Table I and Table II along with the available experimental data for the sake of comparison. Our obtained results are in good agreement with the available experimental findings. Our calculated values for a and c deviate by less than 3.16% and 0.52%, respectively, from the measured ones. To the best of our knowledge, these are the first predicted values of the B and B' for the CuMnAlSe_3 compound. With this relatively low B value, the studied material can be characterized as very soft material.

TABLE I

Equilibrium structural parameters a [\AA], c [\AA], c/a , equilibrium volume/f.u. V_0 [\AA^3], bulk modulus B , its pressure derivative B' for CuMnAlSe_3 .

a	c	c/a	V_0	B	B'
5.426	10.92	2.014	321.500	59.394	5.175
5.6034 ^a	10.977 ^a	1.96 ^a	344.66 ^a		

^aRef. [7]

TABLE II

Atomic positions in CuMnAlSe_3 .

Atoms	Site	x/a	y/b	z/c
Cu	2c	0	1/2	1/4
Mn	2e	0	0	0
Al	2b	1/2	0	1/4
Se	8n	0.2509	0.25528	0.12165
		0.257 ^a	0.253 ^a	0.125 ^a

^aRef. [7]

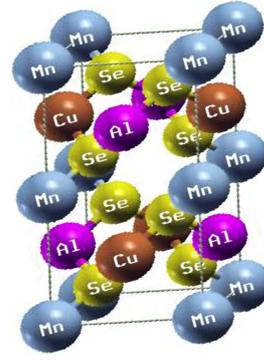


Fig. 1. Representation of the CuMnAlSe_3 -chalcogenide crystal structure.

3.2. Electronic and magnetic properties

In this part we represent the main objective of the actual study, where the electronic and magnetic properties of CuMnAlSe_3 -chalcogenide are presented.

The electronic behavior of a crystal can be described with the calculated electronic band structure and the density of states (DOS) which can give more and detailed information. In Figs. 2–4, the calculated spin-polarized electronic band structures and the total density of states (DOS) of CuMnAlSe_3 -chalcogenide at the theoretical equilibrium lattice structure, along the high symmetry lines in the first Brillouin zone associated to the tetragonal lattice, using the FP-LAPW method within GGA-PBEsol and TB-mBJ approaches, have been plotted for both majority (up) and minority (down) spin channels.

Figures 2 and 3 yield an indication of the valence band (VB) and conduction band (CB) separated by the Fermi levels denoted by blue dashed lines for all figures. The distribution of spin-up (majority) and spin-down (minority) channels are not similar which indicates that the CuMnAlSe_3 system is not paramagnetic. In the majority states, several bands cross the Fermi level E_F . These bands are strongly dispersing and contribute mainly to the large density in the majority states. The situation is different for the minority channel.

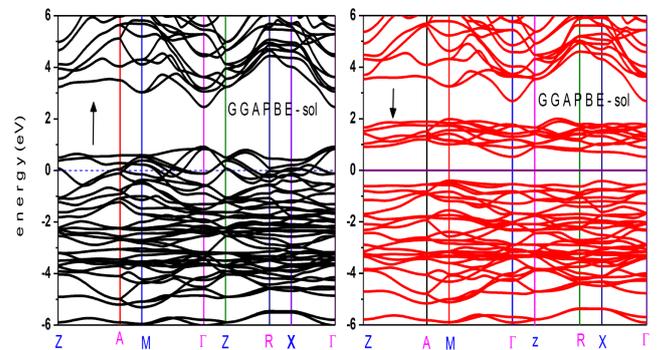


Fig. 2. Electronic band structure of CuMnAlSe_3 -chalcogenide calculated by GGA-PBEsol.

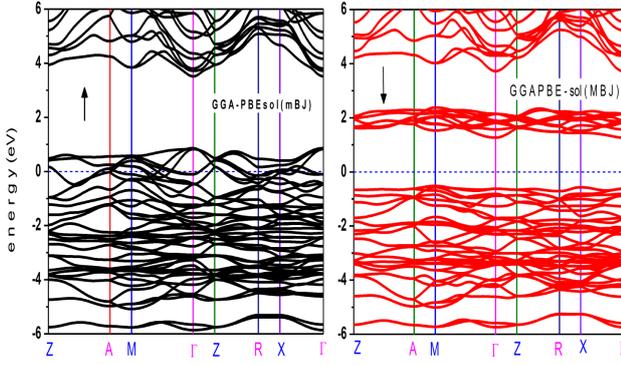


Fig. 3. As in Fig. 2, but calculated by TB-MBJ.

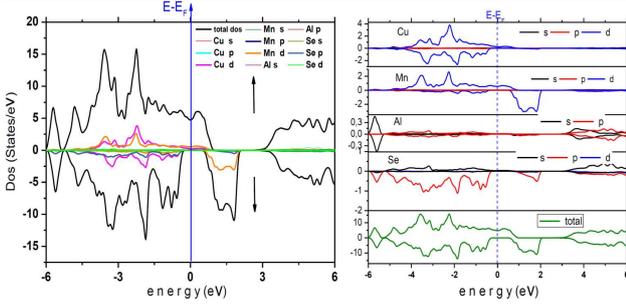


Fig. 4. Calculated partial and total density of states of CuMnAlSe_3 -chalcogenide.

It is obvious that the minority spin channel has a band gap around the Fermi level revealing its semiconducting nature and determining the half-metal character of this chalcogenide quaternary. As shown in the figures, there is no sensible difference between features of the band structures predicted by GGA-PBEsol and TB-mBJ functional. The band gap is found to be indirect and the valence band maximum lies at the M -point and the conduction band minimum occurs at the Γ -point. There is although an important difference between the band gap values yielded by these two approaches. The half-metallic gap, which is defined as the minimum energy required to flip a majority-spin electron from the valence band maximum to the minority-spin Fermi level, is found to be 0.962 eV and 1.825 eV within GGA-PBEsol and TB-mBJ methods, respectively, as listed in Table III.

According to Fig. 4 the top of the valence band is mainly the contribution of Cu $3d$ states (spin-up/spin-down) and Mn $3d$ states (spin-up) with a low contribution of Cu $3p$ and Se $3p$ states (spin-up/spin-down). The conduction bands are dominated by Mn $3d$ states (spin-down) with a very low contribution of the others states.

The energy dependence of the electron spin polarization $P(E_F)$ of a solid material can inform us about its electronic behaviour. Its value is equal to unity (100%) for a half-metallic material [20, 21], and it is given by the following relation:

$$P(E_F) = \frac{\rho_{\uparrow}(E_F) - \rho_{\downarrow}(E_F)}{\rho_{\uparrow}(E_F) + \rho_{\downarrow}(E_F)},$$

TABLE III

Band gap energy E_g [eV], total and partial magnetic moment $[\mu_B]$ for CuMnAlSe_3 -chalcogenide.

	E_g	μ_{Cu}	μ_{Mn}	μ_{Al}	μ_{Se}
GGA-PBEsol	0.962	-0.13675	3.16448	0.02898	-0.07260
TB-mBJ	1.825	-0.25119	3.52761	0.02996	-0.11624

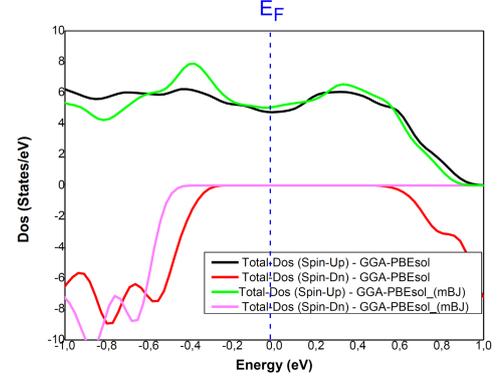


Fig. 5. Total density of states for CuMnAlSe_3 -chalcogenide near the Fermi level calculated by GGA-PBEsol and TB-mBJ.

where $\rho_{\uparrow}(E_F)$ and $\rho_{\downarrow}(E_F)$ are the total density of states for the spin-up and spin-down at the Fermi level. The obtained values by the two used methods are identical. The electrons at the Fermi energy are fully spin polarized (100%) since $\rho_{\downarrow}(E_F) = 0$ as shown in Fig. 5, and confirm that CuMnAlSe_3 is a half-metal.

The total magnetic moment (in μ_B) is just the difference between the number of occupied spin-up states and occupied spin-down states [22]. With the help of the GGA-PBEsol and TB-mBJ schemes, the integer magnetic moments μ_{tot} for CuMnAlSe_3 alloy and atomic magnetic moments for Cu, Mn, Al, and Se atoms are calculated and presented in Table III. In half-metallic materials an important point must be verified which is the fact that the total spin moment μ_{tot} should be an integer number [23]. Our results verify this condition. The calculations give a total spin magnetic moment per f.u. of $6 \mu_B$ for both approaches. The magnetic moment of Mn atom is about $2.7393 \mu_B$ and $3.528 \mu_B$ within GGA-PBEsol and TB-mBJ, respectively, while Cu and Se atoms have a negative moment and the Al atoms possess a very small magnetic moment.

4. Conclusion

In this study, using the first-principles calculations, we investigated the structural, electronic, and magnetic properties of the unexplored half-metal chalcogenide quaternary compound CuMnAlSe_3 . Our calculated structural parameters are in good agreement with the available experimental data. The examined material exhibits a semiconducting behaviour for the minority spin bands.

The gap is found to be indirect and equal to 0.962 eV and 1.825 eV within GGA-PBEsol and TB-mBJ, respectively, and behave as a metal for the majority spin bands indicating the half-metal character. The exploration of the magnetic properties reveals that its total magnetic moment is equal to 6 μ_B for both approaches.

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