Structural, elastic, electronic and magnetic properties of quaternary Heusler alloy 
\( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x (x = 0 - 1) \): First-principles study

B. Benichou\textsuperscript{a,b,\,*}, Z. Nabi\textsuperscript{c}, B. Bouabdallah\textsuperscript{d} and H. Bouchenafa\textsuperscript{a,e}

\textsuperscript{a}Department of Physics, Faculty of Sciences Exact, Djillali Liabès University, Sidi Bel Abbès 22000, Algeria.
\textsuperscript{b}Department of Physics, Faculty of Sciences Exact and Informatics, Hassiba Benbouali University, Chlef 02000, Algeria.
\textsuperscript{c}Department of Electronics, Faculty of Technology, Physics Department, Djillali Liabès University, Sidi Bel Abbès 22000, Algeria.
\textsuperscript{d}Condensed Matter and Sustainable Development Laboratory, Djillali Liabès University, Sidi Bel Abbès 22000, Algeria.
\textsuperscript{e}Department of Physics, Faculty of Sciences Exact and Informatics, Hassiba Benbouali University, Chlef 02000, Algeria.

\textsuperscript{\,*}e-mail: boucif_benichou@yahoo.fr

Received 27 November 2017; accepted 19 December 2017

We investigate the structural, elastic, electronic and magnetic properties of the Heusler compounds \( \text{Cu}_2\text{MnSi}, \text{Cu}_2\text{MnAl} \) and \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) quaternary alloys, using the full-potential linear-augmented plane-wave method (FP-LAPW) in the framework of the density functional theory (DFT) using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). Our results provide predictions for the quaternary alloys, using the full-potential linear-augmented plane-wave method (FP-LAPW) in the framework of the density functional theory (DFT) using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). Our results provide predictions for the quaternary alloy \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x (x = 0.125, 0.25, 0.375, 0.5) \) in which no experimental or theoretical data are currently available. We calculate the ground state’s properties of \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) alloys for both nonmagnetic and ferromagnetic configurations, which lead to ferromagnetic and metallic compounds. Also, the calculations of the elastic constants and the elastic moduli parameters show that these quaternary Heusler alloys are ductile and anisotropic.

\textbf{Keywords:} Electronic structure; elastic properties; ab-initio calculations; quaternary Heusler alloys.

\textbf{PACS:} 75.10.Hk; 71.45.Nt

\section{1. Introduction}

So far, the Heusler alloys are still interesting due to their potential application in spintronics, such as giant magnetoresistance (GMR), tunneling magnetoresistance (TMR) [1], superconductors [2], ferromagnetic shape memory alloys [3] and magnetic actuator [4]. Besides of Heusler alloys, the intermetallic compounds are also promising materials for automobile, aviation, aerospace and advanced thermoelectric applications.

Many works on \( \text{Cu}_2\text{MnZ} \), especially \( \text{Cu}_2\text{MnAl} \) alloys, have been investigated in both cases, experimentally [5-7] and theoretically [8-10]. Rai \textit{et al.}, [11] showed that \( \text{Cu}_2\text{MnAl} \) is an interesting ferromagnetic and metallic compound in spite of its non-ferromagnetic elements. Hamri \textit{et al.}, [12] illustrated that all the studied ferromagnetic systems \( \text{X}_2\text{MnSn} (\text{X} = \text{Cu, Ni, Pd}) \) exhibit a metallic character and possess an interesting elastic constants. Also, Ghosh \textit{et al.}, [13] found that \( \text{Cu}_2\text{MnGa} \) has metallic and ferromagnetic properties and is thermodynamically as well as mechanically stable alloy. In addition to ternary Heusler studies, there exist several searches on quaternary alloys. Galaknakis [14] investigated quaternary alloys as \( \text{X}_2\text{Y}_{1-x}\text{Y'}_x\text{Z} \), \( (\text{X}_1\text{Z}, \text{X}_2\text{Y})_2\text{YZ} \) and \( \text{X}_2\text{YZ}_{1-x}\text{Z'}_x \), he found that there is a possibility of obtaining half-metallic systems. The spin polarization of \( \text{Co}_2\text{Cr}_{1-x}\text{Fe}_x\text{Al} \) quaternary alloys have been reported by Karthik \textit{et al.}, [15]. Nanto \textit{et al.}, [16] have studied the magnetic properties of nanocrystalline \( \text{Fe}_2\text{Mn}_{0.5}\text{Cu}_{0.5}\text{Al} \) using mechanical alloying technique.

This paper is arranged as follows: In the next section, we give a brief description of the calculation method. Section 3 deals with the crystal structural aspects. In Sec. 4, the results and their comments are presented and the paper is ended after by a conclusion summarizing the study.

\section{2. Computational Details}

The first principles calculations performed within the FP-LAPW method [17] which is implemented in the WIEN2k code [18], based on the DFT theory [19,20], where the GGA approximation [21] has employed to describe the exchange and correlation potential. For the numerics, we estimate the plane wave parameter \( R_{MT} \times K_{\text{max}} \) as 7.0, and to ensure the correctness of the calculations, we have taken \( l_{\text{max}} = 12 \). The \( G_{\text{max}} \) parameter was 12.0. The separation energy between the core and the valence states has chosen as - 6.0 Ry. The self consistent potentials calculated on a \( 21 \times 21 \times 21 \) k-mesh in the Brillouin Zone for ternary alloys and \( 2 \times 2 \times 2 \) k-mesh for quaternary alloys, which correspond respectively, to 286 and 4 k-points in the irreducible BZ. The muffin-tin sphere radii were 2.2, 2.0, 2.0 and 1.9 for \( \text{Cu, Mn, Si and Al} \),
respectively. The energy convergence criterion was taken as $10^{-5}$ Ry.

3. Crystal structure

Full-Heusler alloys have the chemical formula $X_2YZ$, where $X$ and $Y$ denote transition metals and $Z$ is an s-p element. The atomic positions for $X$ (Cu) atoms are $(1/4, 1/4, 1/4)$, $(3/4, 3/4, 3/4)$, while $(1/2, 1/2, 1/2)$ for $Y$ (Mn) and for $Z$ (Si, Al) it is $(0, 0, 0)$. In Fig. 1, we show the crystal structure of $\text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x$ ($x = 0, 0.125, 0.25, 0.375, 0.5, 1$) alloys, where the present structures consist of four interpenetrating face-centered-cubic sublattices, with $L2_1$ phase and Fm-3m, space group no. 225. To simulate $\text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x$ quaternary alloys, we consider a $(2 \times 2 \times 2)$ supercell eight times bigger than $L2_1$ unit cell. The supercell is then constituted of 32 atoms; 16 Cu, 8 Mn and 8 Si/Al, as shown in Fig. 1.

![Figure 1. Crystal structure of Cu$_2$MnSi$_{1-x}$Al$_x$ (x = 0, 0.125, 0.25, 0.375, 0.5, 1).](image)

4. Results and Discussion

4.1. Structural Properties

To obtain the lattice constant, the bulk modulus and its first pressure derivative which are listed in Table I, we have fitted the computed energies to the empirical Murnaghan’s equation of state [22]. In this respect, the optimization of the geometrical structure parameters of $\text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x$ alloys has performed by using nonmagnetic (NM) and ferromagnetic (FM) configurations. The total energy variation, which is taken as function of volume for both non-magnetic and ferromagnetic states with different concentrations, is illustrated in Fig. 2. It can be seen that these alloys are ferromagnetic. The results for $\text{Cu}_2\text{MnAl}$ compound, which are given in Table I, agree with the experimental results [23,24] and other theoretical works [8, 10, 11, 25]. To the best of our knowledge, no comparable studies in literature on $\text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x$ ($x = 0.125, 0.25, 0.375, 0.5$) alloys. The estimated lattice parameters (Å), from the Vegard’s law [26] in Eq. (1), for the

![Figure 2. Calculated total energy as a function of volume curves for Cu$_2$MnSi$_{1-x}$Al$_x$ (x = 0.125, 0.25, 0.375, 0.5) alloy.](image)
Shear modulus (G), Young’s modulus (E), Poisson’s ratio (ν), and those of Rai et al. [23] and those of Rai et al. [23] for Cu$_2$MnSi$_{1-x}$A$_x$ with the exception of Cu$_2$MnSi$_{1-x}$A$_x$ which does not fulfill the stability criteria. Cu$_2$MnSi$_{1-x}$A$_x$ (x = 0, 0.125, 0.25, 0.375, 0.5, 1).

Table I. Calculated lattice parameter (a), bulk modulus (B) and its pressure derivative (B’) for Cu$_2$MnSi$_{1-x}$A$_x$ (x = 0, 0.125, 0.25, 0.375, 0.5, 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>B (GPa)</th>
<th>B’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$MnSi</td>
<td>5.8645</td>
<td>136.137</td>
<td>5.147</td>
</tr>
<tr>
<td>Cu$<em>2$MnSi$</em>{1-0.125}$Al$_{0.125}$</td>
<td>5.87</td>
<td>118.758</td>
<td>6.136</td>
</tr>
<tr>
<td>Cu$<em>2$MnSi$</em>{1-0.25}$Al$_{0.25}$</td>
<td>5.88095</td>
<td>124.910</td>
<td>3.450</td>
</tr>
<tr>
<td>Cu$<em>2$MnSi$</em>{1-0.375}$Al$_{0.375}$</td>
<td>5.8879</td>
<td>126.467</td>
<td>4.229</td>
</tr>
<tr>
<td>Cu$<em>2$MnSi$</em>{1-0.5}$Al$_{0.5}$</td>
<td>5.8918</td>
<td>118.944</td>
<td>6.261</td>
</tr>
<tr>
<td>Cu$_2$MnAl</td>
<td>5.9274</td>
<td>126.689</td>
<td>4.066</td>
</tr>
</tbody>
</table>

For these calculations, we have used the following equations:

\[ G = \frac{G_R + G_V}{2} \]  
\[ G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \]  
\[ G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \]  
\[ E = \frac{9GB}{3B + G} \]  
\[ ν = \frac{3B - 2G}{2(3B + 2G)} \]  
\[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]  
\[ ξ = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \]

Table II too. For these calculations, we have used the following equations:

\[ G = \frac{G_R + G_V}{2} \]  
\[ G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \]  
\[ G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \]  
\[ E = \frac{9GB}{3B + G} \]  
\[ ν = \frac{3B - 2G}{2(3B + 2G)} \]  
\[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]  
\[ ξ = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \]

selected concentrations 0.125, 0.25, 0.375, 0.5, are 5.86875, 5.8775, 5.88625 and 5.895 respectively.

\[ \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x : a(\text{Å}) = 5.86 \times (1 - x) + 5.93 \times x \]  (1)

4.2. Elastic Properties

In order to discuss the mechanical stability of the parent compounds Cu$_2$MnSi, Cu$_2$MnAl and Cu$_2$MnSi$_{1-x}$Al$_x$ quaternary alloy, we have calculated the three independent elastic constants for cubic crystals C$_{11}$, C$_{12}$ and C$_{44}$, by using a numerical first-principles method. The traditional mechanical stability conditions in cubic crystal are expressed as follows: C$_{11}$ - C$_{12}$ > 0, C$_{11}$ > 0, C$_{44}$ > 0, C$_{11}$ + 2C$_{12}$ > 0 and C$_{12}$ < B < C$_{11}$ [28]. The calculated elastic constants C$_{ij}$, given in Table II, show that with the exception of Cu$_2$MnSi which does not fulfill the stability criteria, Cu$_2$MnAl and Cu$_2$MnSi$_{1-x}$Al$_x$ alloys are elastically stable. The obtained results for Cu$_2$MnAl alloy agree with experimental results in Ref. 23 and those of Rai et al., [11] and Jalilian [25].

In addition, other parameters have been calculated as the Shear modulus (G), Young’s modulus (E), Poisson’s ratio (ν), anisotropy factor (A), and Kleinman parameter (ξ), listed in
Pugh [29] proposed an approximate criterion by the ratio B/G to predict the ductility of materials. If B/G ratio is higher than the critical value that separates brittle and ductile materials which is about 1.75, this corresponds to ductile behavior; else, the material is brittle. The calculated values in Table II indicate that the B/G ratios are between 1.866 and 3.027, suggesting the ductile nature of the studied alloys. The Cauchy pressure \( C_{12} - C_{44} \) identifies the type of bonding [30]. Negative Cauchy pressure corresponds to more directional and non-metallic character, while positive value indicates predominant metallic bonding. According to Cauchy pressure, the predominant bonding for \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) Heusler alloys is metallic. The Young’s modulus (E) characterizes the stiffness of a material. A higher value of E, stiffer is the material. It can be seen, from Table II, that \( \text{Cu}_2\text{MnAl} \) is stiffer than \( \text{Cu}_2\text{MnSi} \). Poisson’s ratio (\( \nu \)) indicates the degree of directionality of the covalent bonds. Its value for covalent materials is small (\( \nu < 0.1 \)), whereas the typical value for ionic materials is 0.25 [31]. Our calculated Poisson’s ratios are from 0.279 to 0.319, so the contribution in the intra-atomic bonding for \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) alloys is ionic. For an isotropic material, the anisotropy factor (A) is equal to one, while any different value shows anisotropy. The calculated anisotropy factor indicates that \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) compounds are anisotropic.

**Figure 3.** Total and partial density of states for \( \text{Cu}_2\text{MnSi}_{1-x}\text{Al}_x \) \( (x = 0, 0.125, 0.25, 0.375, 0.5, 1) \) Heusler alloy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( M^{\text{Cu}} )</th>
<th>( M^{\text{Mn}} )</th>
<th>( M^{\text{Si}} )</th>
<th>( M^{\text{Al}} )</th>
<th>( M^{\text{interstitial}} )</th>
<th>( M^{\text{tot}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_2\text{MnSi} )</td>
<td>0.067</td>
<td>3.305</td>
<td>-0.0062</td>
<td>-0.028</td>
<td>0.302</td>
<td>3.735</td>
</tr>
<tr>
<td>( \text{Cu}<em>2\text{MnSi}</em>{1-0.125}\text{Al}_{0.125} )</td>
<td>0.073</td>
<td>3.332</td>
<td>-0.00002</td>
<td>-0.028</td>
<td>0.314</td>
<td>3.790</td>
</tr>
<tr>
<td>( \text{Cu}<em>2\text{MnSi}</em>{1-0.25}\text{Al}_{0.25} )</td>
<td>0.070</td>
<td>3.330</td>
<td>-0.00429</td>
<td>-0.030</td>
<td>0.302</td>
<td>3.762</td>
</tr>
<tr>
<td>( \text{Cu}<em>2\text{MnSi}</em>{1-0.375}\text{Al}_{0.375} )</td>
<td>0.063</td>
<td>3.297</td>
<td>-0.0071</td>
<td>-0.032</td>
<td>0.279</td>
<td>3.686</td>
</tr>
<tr>
<td>( \text{Cu}<em>2\text{MnSi}</em>{1-0.5}\text{Al}_{0.5} )</td>
<td>0.060</td>
<td>3.273</td>
<td>-0.0085</td>
<td>-0.033</td>
<td>0.262</td>
<td>3.636</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{MnAl} )</td>
<td>0.047</td>
<td>3.242</td>
<td>——</td>
<td>-0.034</td>
<td>0.200</td>
<td>3.502</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.56 [11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.51 [23]</td>
</tr>
<tr>
<td></td>
<td>0.073 [33]</td>
<td>3.49 [33]</td>
<td>-0.046 [33]</td>
<td>3.73 [33]</td>
<td></td>
<td>3.6 [34]</td>
</tr>
</tbody>
</table>

Exp. [34]

Rev. Mex. Fis. 64 (2018) 135–140
STRUCTURAL, ELASTIC, ELECTRONIC AND MAGNETIC PROPERTIES OF QUATERNARY HEUSLER ALLOY... 139

4.3. Electronic Properties

To determine the electronic structure’s nature of Cu₂MnSi₁₋ₓAlₓ compounds, we have calculated the total and partial densities of states for spin-up and spin-down, as displayed in Fig. 3. From this figure, one can see that there is no energy gap at Fermi level in both minority and majority spin states, proving the metallic character of the system. The TDOS spectrum of the parent compounds is divided into two main regions. The lowest valence bands below −9 eV for Cu₂MnSi (below −6 eV for Cu₂MnAl) are entirely due to Si and Al s-states, while the bands from −7 to 3 eV for Cu₂MnSi (−5.5 to 3 eV for Cu₂MnAl) are chiefly governed by the Cu and Mn 3d states. A comparison with other studies obtained by Kulkova et al., [8] and Rai et al., [11], our results for Cu₂MnSi show quite good agreement. For Cu₂MnSi₁₋ₓAlₓ quaternary alloy, the principally parts of the total densities of states situated between −5 to 3 eV, are contributed by the 3d states of Cu and Mn atoms.

4.4. Magnetic Properties

The calculated total and partial spin magnetic moments for Cu₂MnSi, Cu₂MnAl and Cu₂MnSi₁₋ₓAlₓ quaternary alloy are quoted in Table III. Obviously, for Cu₂MnSi and Cu₂MnAl alloys, the total magnetic moment, which includes the contribution from the interstitial region, originates mainly from the Mn atom, with a small contribution of Si, Al and Cu sites. Our results agree well with Kulkova et al., [8], Ghosh et al., [13] and Kandpal et al., [32]. For all the considered concentrations x, the positive spin magnetic moment of Cu and Mn means a ferromagnetic coupling between Cu and Mn atoms. The negative magnetic moment for Si and Al leads to an antiferromagnetic alignment of Si and Al ones. The obtained total and partial spin magnetic moment for the Cu₂MnAl alloy are in good agreement with previous theoretical results [8,11,32,33] and experimental ones [34], which are also reported in Table III. To our knowledge, there are no values of the magnetic moments in the literature for the quaternary alloy. In Fig. 4, the variation of the total and partial magnetic moments for Cu₂MnSi₁₋ₓAlₓ (x = 0, 0.125, 0.25, 0.375, 0.5, 1) alloys versus the composition x, are non-linear.

5. Conclusion

In conclusion, using the FP-LAPW based on GGA approximations calculations to predict the structural parameters, elastic, electronic and magnetic properties of the Cu₂MnSi₁₋ₓAlₓ quaternary alloy, we have found that the lattice constants are in excellent agreement with the estimated values by Vegard’s law. The analysis of the electronic band structures and density of states of Cu₂MnSi₁₋ₓAlₓ alloys reveal that they are ferromagnetic and metallic compounds by nature. The large magnetic moment is located on Mn sites. We have also found that the Cu₂MnSi does not fulfill the mechanical stability conditions, where Cu₂MnAl and Cu₂MnSi₁₋ₓAlₓ Heusler alloys are stable and have a ductile behavior. The Young’s modulus, Shear modulus, Poisson’s ratio anisotropy factor and Kleinman parameters, often measured for polycrystalline samples, were also derived. We hope that this simulation may be a guideline for the experimentalists.
22. F.D. Murnaghan, Proc. Natl. Acad. Sci. USA. 30 (1944) 244.