Half-metallic Characteristics of the Novel Half Heusler Alloys XCrSb (X = Ti, Zr, Hf)

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Abstract

Ab-initio calculations are performed to examine the structural, mechanical, electronic, magnetic and thermodynamic properties of the half-Heusler ternary alloys XCrSb (X = Hf, Ti, Zr). In this study, the spin-polarized density functional theory (DFT) method that is spin-polarized with generalised gradient approximation (GGA) are used to perform ab-initio calculations to investigate the physical properties of a novel half-Heusler ternary alloys XCrSb (X = Hf, Ti, Zr). It was confirmed that the alloys are stable mechanically and exhibit ferromagnetic states (FM). The study reveals that the alloys portray half-metallic character with narrow energy gaps. And it also shows that they have a total magnetic moment of approximately $3\mu_B$. From the formation energy calculation, it shows that the alloys can be synthesized experimentally. Also, it was observed that they are mechanically stable. The heat capacities and Debye temperatures were also computed and they show high thermodynamic stability.

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Keywords: Half-Heusler Alloys, Half-metallic ferromagnet (HMF), Spin-polarization, Band Structure, Density of state, Quasi-Harmonic Approximation (QHA)

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1. Introduction

The Heusler alloys have been studied extensively in the recent past, and one of the major results is that they are among the best half-metallic ferromagnets (HMF) to achieve 100% spin polarization at room temperature. Density Functional Theory (DFT) has proven to be a reliable tool for calculating electronic structures for many decades, this is due to its simple and useful approach in approximating the ground state functionals of real many-body electrons. The theory is built on the fact that the properties of many-body interacting system can be seen as a functional of the ground state electron density [1]. From the works of Mehmood et al [2-3], it was gathered that the half-Heusler alloys YZSb (Z = Cr, Mn) and RhCrZ (Z = Si, Ge) exhibit half-metallic properties within the framework (DFT) among others. Also, the electronic, magnetic and optical properties were equally studied. The field of spintronics is quite different from the conventional electronics in which charges are responsible for transfer of information, whereas in spintronics spins are responsible for the transfer of information. Some of these enhancements and advantages are; increasing the speed of the data processors, drop in the consumption of electric power and the increase in integration density [4 - 6]. The study of half Heusler (HH) alloys present interesting and different magnetic occurrences, and this have attracted researchers in re-

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and the kinetic energy cut-off. The Monkhorst Pack format with 8 x 8 x 8 framework was used, for the energy cut-off for the alloys XCrSb (used for the structural optimization and static SCF calculations ensuring the accuracy of the calculations [34]. The k-points are essential flags (in the input-file) in International Table of Crystallography. The crystal structures of ZrMnAs [27], PtXBi (X = Fe, Co, Mn and Ni) [28], ZrNiPb [29], and XVSB (X = Fe, Ni, Co) [30]. The works of Rogl and coworkers [31] provides an extensive review on the mechanical, electronic/phonon dispersion and as well as thermodynamic properties using First-Principles calculations. Among them are: ZrMnAs [27], PtXBi (X = Fe, Co, Mn and Ni) [28], ZrNiPb [29], and XVSB (X = Fe, Ni, Co) [30]. The works of Rogl and coworkers [31] provides an extensive review on the mechanical, electronic/phonon dispersion and as well as thermodynamic properties using First-Principles calculations. Among them are: ZrMnAs [27], PtXBi (X = Fe, Co, Mn and Ni) [28], ZrNiPb [29], and XVSB (X = Fe, Ni, Co) [30].

2. Methodology

The ab-initio total energy calculations were executed employing the QUANTUM ESPRESSO (QE) as applied in the works of Giannozzi [32]. The Projected Augmented Wave pseudo potential was used in the computation [33]. The exchange inter-relationship between electrons, bonding and magnetic features were treated with the GGA-PBE approach. The (HH) alloy XYZ, has an fcc structure, in space group F-43m No. 216 with its Strukturbericht designation of C1 b as recorded in the International Table of Crystallography. The crystal structures for the three alloys are presented in Figure 1. We use the spin-polarized density funtional theory (DFT). The energy cut-off value and the k-points are essential flags (in the input-file) in ensuring the accuracy of the calculations [34]. The k-points are used for the structural optimization and static SCF calculations for the alloys XCrSb (X = Hf, Ti and Zr). Convergence tests for the energy cut-off and the k-points are carried out before determining their appropriate values for the calculations. The Monkhorst Pack format with 8 x 8 x 8 framework was used, and the kinetic energy cut-off were fixed to 60Ry for HfCrSb and ZrCrSb, 65Ry for TiCrSb alloys. The Pseudo-atomic configurations used as valence electrons, in this study, are Hf 5d^2 6s^2 , Ti 3d^2 4s^2 , Zr4d^2 5s^2 , Cr 3d^6 4s^1 , and Sb 4d^{10} 5s^2 5p^3 respectively. The (X = Hf, Ti and Zr), Sb and Cr occupy the atomic positions 4a(0, 0, 0), 4b(1/2, 1/2, 1/2) and 4c(1/4, 1/4, 1/4) respectively.

3. Results and Discussions

3.1. Structural and Mechanical Properties

Investigating the structural properties of the ground state configuration of the XCrSb compounds (where X = Ti, Zr and Hf), firstly, the structural/geometry optimisation was carried out by minimizing the total energy of the alloys with respect to the variation of the lattice parameters. The lattice constant a, the bulk modulus B and its pressure derivative B' were obtained when the energy-lattice parameter was fitted to the Birch Mur-naghan equations of state. These results are presented in Table 1 and the obtained energy-lattice curves for the various alloys are shown in Figure 2. The three HH alloys in different magnetic states were studied in order to ascertain the true nature of the alloys. The results for the ferromagnetic (FM) states, non-magnetic (NM) states as well as for the anti-ferromagnetic (AFM) states were presented in Fig. 3. It is observed that the (FM) states posses the lowest ground state energy for the three HH alloys, hence they are all ferromagnets. It is the ferromagnetic states of these alloys that have been used to compute the other properties in this work. In solids, the elastic constants and some structural features play vital roles in determining the mechanical stability of the material [35]. For cubic phases, the stability is measured by the following criteria C_{11} + 2C_{12} > 0, C_{11} - C_{12} > 0, and C_{11} > 0 [36]. The alloys are mechanically stable since all the necessary conditions were satisfied, see Table 2. The bulk modulus B, Young Modulus E and shear modulus G are parameters used to quantify the mechanical properties of solids. From Table 1, the results of the B and E show that the deformation resistance decreases in trend from HfCrSb to ZrCrSb to TiCrSb alloys, except for the shear modulus that has a contrary behaviour. An expression to establish the plasticity of a material is given by the $\frac{B}{G}$ ratio. The threshold value for distinguishing between ductility and brittleness of materials is about 1.75 [37].

![Figure 1. The crystal structure of XCrSb where X=Ti, Zr and Hf.](image-url)
From our results presented in Table 2, it is obvious that the alloys are ductile in nature since the values of the B/G ratio are more than 1.75. Although, there was no available experimental or theoretical reports on the XCrSb series for comparison, but our results for B, E, and the elastic properties are still within appreciable range when compared with the XCoSb series in literatures [31, 38]. It is observed that the values of the mechanical properties obtained for XCoSb HH alloys are higher than that of XCrSb obtained in this work. This is due to the fact that the bonding during the hybridization of the d-orbital of Cr atom and the d-orbital of X(Ti, Zr and Hf) atom is weak as shown in Figures 7–9. The present calculated results of Zener anisotropy A, shows that the three alloys are anisotropic, since the values are approaching 1, which is an indication of high elastic anisotropy. These results were obtained using the relation, from equation (1), as recorded in [39].

\[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]  

(1)

Another factor that can affect the stability of a material against shear stress is the Poisson’s ratio \(\nu\). It reveals the nature of the bonding forces in materials. The value range is of the order 0 \(<\nu<0.5\) [39]. From the results of \(\nu\) in Table 2, it shows that the three alloys are of good plasticity. The Cauchy relation is another parameter which expresses the ductility and brittleness of materials. When the value is positive, the material is considered ductile, otherwise it is brittle. The alloys under consideration are ductile as reported in Table 2. The formation energy \(\Delta H\) of the alloys were investigated to verify whether they can be synthesized experimentally. The calculation was done using Equation 2:

\[ \Delta H = E_i - \left( \frac{E_{b1}^{e_1}}{N_a} + \frac{E_{b2}^{e_2}}{N_b} + \ldots \right) \]  

(2)

where \(E_i\) is the total energy of the alloy, \(E_{b1}^{e_1}\) and \(E_{b2}^{e_2}\) are the total energies of the constituent elements respectively, and \(N_a\) represents the number of atom per cell. From the calculations, the formation energies of XCrSb (X = Hf, Ti, and Zr) are -1.49eV, -1.10eV and -1.0eV respectively. These results confirm that the alloys can be synthesized easily because the enthalpies have negative values.
3.2. Electronic and Magnetic Properties

From the crystal structure of the (HH) compounds in Figure 1, the X\((X = Ti, Zr\) and Hf\) atom forms a tetrahedral position with the Cr atom as the cation at the center. The zincblende sublattice \([CrX]^{3+}\) formed hybridizes with the \([Sb]^{-3}\) ion. With this configuration the Cr atom gains one extra electron added to its initially six valence electrons thereby resulting to seven electrons that occupy the \(d\)-orbital. During the filling of the \(d\)-orbital, three electrons are left unpaired which constitute the magnetic moment of the alloys. The spin magnetic moment for each of the alloys is approximately 3\(\mu\) as shown in Table 3. This satisfies the spin magnetic moment predicted by the Slater-Pauling rule [40]. The rule asserts that the total spin magnetic moment per formula unit \(M_{\text{tot}}\) is given by \(M_{\text{tot}} = |N_v - 18|\) for (HH) compounds, where \(N_v\) is the sum of electrons at the valence. The sum of electrons at the valence for Ti, Zr and Hf are 4 each while that of Cr and Sb are 6 and 5 respectively. Hence the total number of electrons at the valence for each compounds is 15. The total and partial magnetic moments are presented in Table 3.

In order to obtain quantitative results to reveal the half metallic character from the electronic band structure calculations, the spin polarization \(P\) was computed for the minority and majority bands. From the three alloys, we have 0ev, 0.25ev for the up and down DOS at the Fermi level respectively. Using Equation (3) for spin polarization [41], we obtained 100% spin polarization in the alloys.

\[
P = \frac{\text{Dos}(E_f(\text{up})) - \text{Dos}(E_f(\text{down}))}{\text{Dos}(E_f(\text{up})) + \text{Dos}(E_f(\text{down}))} \times 100\%
\]  

(3)

The electronic properties of the three (HH) alloys have been computed in the form of band structures and are presented in Figures 4 – 6. The (HH) alloys XCrSb \((X = Ti, Zr\) and Hf\) are found to posses the half-metallic properties since their band structures with the majority spin channels have indirect band gaps while their band structures for the minority spin channels show metallic behaviour. The measured band gaps for TiCrSb, ZrCrSb and HfCrSb are 0.31eV, 0.49eV and 0.42eV respectively. The PDOS for the three compounds have also been computed and are presented in Figures 7 – 9. The purpose of the PDOS plot is to give insight into the nature of bonding between the orbitals of the individual atoms. The PDOS of the three half
Heusler alloys are some how similar this is due to the fact that they have similar atoms inhabiting the Y and Z atomic sites and the three different atoms inhabiting the X atomic site are in the same group. From the minority-spin channels of the three HH alloys, the $t_{2g}$ states of Cr atom dominate the region below the Fermi energy while the $e_g$ states dominate in the region above the Fermi energy. Since both states are occupied around the Fermi energy, hence they show metallic character. The gaps seen around the Fermi energy in the majority spin straits for the three half-Heusler compounds are due to the crystal field splitting of the $d$-orbital of Cr atom into $t_{2g}$ and $e_g$. Due to the exchange interactions between the Cr $d$-orbital and the X(Ti, Zr and Hf) $d$-orbital, there is depletion of electrons in the majority spin states leading to unoccupied states. This results to the development of half-metallic gap around the Fermi energy. We also observed the bonding states between the Cr $d$-orbital and the X(Ti, Zr and Hf) $d$-orbital just below the Fermi energy and the anti-bonding states between the Cr $d$-orbital and the X(Ti, Zr and Hf) $d$-orbital just above the Fermi energy. This observation is in line with observations by other researchers who worked on half Heusler alloys. It is also important to investigate the relationship between the magnetic moment and the lattice constant in order to determine the range of lattice constants at which the magnetic moment is preserved. From Figure 10, it is observed that the magnetic moment of $3\mu_B$ is preserved within the range of 11.2a.u to 14a.u for three HH alloys.

### 3.3. Thermodynamic Properties

In Solid State Physics, the Debye temperature $\Theta_D$ is one basic factor in describing phenomena associated with many physical properties, like melting points, lattice vibration, specific heat, thermal expansion etc. The $\Theta_D$ is used for delineating high temperature regions from low temperature regions in solids. Basically, the $\Theta_D$ depends on the elastic constants. The $\Theta_D$ can be calculated from the average sound velocity, $V_m$ by the expression $[42, 43]$

$$\Theta_D = \frac{h}{k_B} \left( \frac{3n}{4\pi V_a} \right)^{1/2}$$  \hspace{1cm} (4)

$$V_m = \left[ \frac{1}{3} \left( \frac{1}{V_t^3} + \frac{2}{V_s^3} \right) \right]^{1/3}$$  \hspace{1cm} (5)

$$V_t = \left( \frac{3B + 4G}{3\rho} \right)^{1/2}$$  \hspace{1cm} (6)

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**Table 1.** The Structural properties: the $a$ (Å), $B$ (GPa), and $B'$, energy of formation $\Delta H$ (eV), band gap near Fermi energy $E_g$ (eV) and magnetic ground state $M_g$.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$a$</th>
<th>$B$</th>
<th>$B'$</th>
<th>$\Delta H$</th>
<th>$E_g$</th>
<th>$M_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCrSb</td>
<td>6.197</td>
<td>84.96</td>
<td>4.43</td>
<td>-1.10</td>
<td>0.31</td>
<td>FM</td>
</tr>
<tr>
<td>ZrCrSb</td>
<td>6.383</td>
<td>95.80</td>
<td>4.65</td>
<td>-1.00</td>
<td>0.49</td>
<td>FM</td>
</tr>
<tr>
<td>HfCrSb</td>
<td>6.341</td>
<td>99.66</td>
<td>4.75</td>
<td>-1.49</td>
<td>0.42</td>
<td>FM</td>
</tr>
</tbody>
</table>

**Table 2.** The mechanical/elastic properties: the $C_{11}$, $C_{12}$ and $C_{44}$ (GPa), $B / G$ ratio, $E$ (Gpa), Poisson’s ratio $\nu$, Zener anisotropy $A$, and the Cauchy relation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$G$</th>
<th>$B / G$</th>
<th>$E$</th>
<th>$\nu$</th>
<th>$A$</th>
<th>$C_{12} - C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCrSb</td>
<td>108.80</td>
<td>73.02</td>
<td>33.70</td>
<td>27.38</td>
<td>3.10</td>
<td>74.17</td>
<td>0.35</td>
<td>1.88</td>
<td>39.32</td>
</tr>
<tr>
<td>ZrCrSb</td>
<td>112.76</td>
<td>69.87</td>
<td>30.98</td>
<td>27.17</td>
<td>3.53</td>
<td>73.58</td>
<td>0.35</td>
<td>1.44</td>
<td>38.89</td>
</tr>
<tr>
<td>HfCrSb</td>
<td>128.29</td>
<td>85.33</td>
<td>32.33</td>
<td>27.99</td>
<td>3.56</td>
<td>76.76</td>
<td>0.37</td>
<td>1.51</td>
<td>53.00</td>
</tr>
</tbody>
</table>

**Table 3.** The total and partial magnetic moments of the half-Heusler alloy XCrSb (X=Hf, Ti, Zr).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$M_x(\mu_B)$</th>
<th>$M_{Cr}(\mu_B)$</th>
<th>$M_{Sb}(\mu_B)$</th>
<th>$M_{tot}(\mu_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCrSb</td>
<td>0.2899</td>
<td>2.7133</td>
<td>-0.0025</td>
<td>3.0007</td>
</tr>
<tr>
<td>ZrCrSb</td>
<td>0.1835</td>
<td>2.8653</td>
<td>-0.0386</td>
<td>3.0102</td>
</tr>
<tr>
<td>HfCrSb</td>
<td>0.1900</td>
<td>2.7696</td>
<td>0.0001</td>
<td>2.9597</td>
</tr>
</tbody>
</table>

**Table 4.** The specific heat capacity $C_v$, Debye temperature $\Theta_D$, Zero Point energy $E_o$, and Debye sound velocity $V_s$.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$C_v$(J/Nmol.)</th>
<th>$\Theta_D$(K)</th>
<th>$E_0$(kJ/Nmol.)</th>
<th>$V_s$(m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCrSb</td>
<td>72.33</td>
<td>253</td>
<td>7.11</td>
<td>2302</td>
</tr>
<tr>
<td>ZrCrSb</td>
<td>72.63</td>
<td>238</td>
<td>6.69</td>
<td>2232</td>
</tr>
<tr>
<td>HfCrSb</td>
<td>73.16</td>
<td>209</td>
<td>5.87</td>
<td>1946</td>
</tr>
</tbody>
</table>
where $B$, $G$ and $\rho$ are the bulk modulus, shear modulus and densities of the various alloys respectively. The calculated specific heat capacity, Debye temperatures, Zero Point energy and the Debye sound velocity for the various alloys are presented in Table 4. The Debye temperatures computed in this work are in reasonable range when compared with other half Heuslers [31, 38].

The Debye temperature is related to the strength of the covalent bonds in solids, that is, the higher the $\Delta_D$ of a compound indicates a stronger covalent bond which leads to high melting point. Also, a strong covalent bond is associated with the hardness of the material 44. The other thermodynamic properties such as the enthalpy $H$, Free energy $F$, heat capacity at constant volume $C_v$ and the entropy $S$ of the alloys are evaluated by using the QHA. The results are shown in Figure 8. We can see that the $C_v$ of the alloys increases swiftly as the temperature increases, such that at very high temperature it tends to reach the Dulong-Petit terminal point. It was also observed that at very low temperature, $C_v$ is proportional to $T^3$. The entropy and enthalpy graphs show that as the temperature increases the values of the properties increased, while the reverse is observed for that of Free energy.
The physical properties of a novel (HH) compounds XCrSb (where X = Hf, Ti, and Zr) have been investigated using ab-initio calculations. The ferromagnetic state is found to be more stable and favourable than the antiferromagnetic and non-magnetic states structurally in term of total energy. The alloys are found to be stable from the mechanical stability conditions. Also, the B/G ratio and the Cauchy-relation reveals that the alloys satisfied the Slater-Pauling rule. The alloys are ductile. The electronic band structure and the DOS calculations reveal that the alloys exhibit half metallic ferromagnetic property and having approximately $3\mu_B$ magnetic moment. The total magnetic moment of these alloys is produced through remarkable exchange splitting between the majority-spin states and the minority-spin states of Cr orbital. From Table 3, the Cr atom is found to be the major contributor. Furthermore, the alloys satisfied the Slater-Pauling rule. The alloys are half-metallic in nature with energy-gaps of 0.4196eV, 0.309eV, 0.4946eV for HfCrSb, TiCrSb, and ZrCrSb respectively. Theoretically, it is shown that these new alloys can be synthesized easily experimentally because of their negative formation energies. Finally, $\Delta_D$ and $C_v$ computed for the three HH alloys are within acceptable range when compared with other HH alloys in that series. Finally, the half-metallicity, the stability in the ferromagnetic phase and the 100% spin-polarization around the Fermi energy make these alloys promising candidates for future spintronics applications.

**References**


