Theoretical study of phase stability, electronic and magnetic properties of Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0, 0.25, 0.50, 0.75$ and $1$) Heusler alloys by FP-LAPW method

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First-principle calculations were performed within the framework of the density functional theory (DFT) using FP-LAPW method as implemented in WIEN2k code to determine the structural stability, electronic and magnetic properties of Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0, 0.25, 0.50, 0.75$ and $1$). The results showed that for Rh$_2$CrAl and Rh$_2$CrGe, the Cu$_2$MnAl-type structure is energetically more stable than Hg$_2$CuTi-type structure at the equilibrium volume. The calculated densities of states for Rh$_2$CrAl and Rh$_2$CrGe show half-metallic and nearly half-metallic behavior, respectively. Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0.25, 0.50, 0.75$) these alloys show a half-metallic character, and these compounds are predicted to be good candidates for spintronic applications.

Key words: Heusler alloys, structural properties, electrical properties, magnetic properties

1. Introduction

Heusler alloys have been a subject of unprecedented research since their discovery in 1903 by the German engineer F. Heusler [1,2]. The experimental works showed that the majority of Heusler alloys are ferromagnetic ordered in stoichiometric compositions [3,4]. In the very recent past, Heusler compounds have received a great deal of interest, due to their potential applications in many fields. In particular, magnetic Heusler alloys are mostly used in spin-based electronic devices [5], thermoelectric [6, 7] and superconductors [8]. Both high-spin polarizations and half-metallicity are lately considered as the key factors in such type of materials [9, 10]. It is well known that most of Heusler alloys have the spin polarization near Fermi level which is as high as 100% [11]. Some of the Heusler alloys have only one spin channel for conduction at the Fermi level, while for the other spin channel, a semiconducting gap appears between the valence band and the conduction band [9, 12, 13].

The possibility of tuning the electronic and magnetic properties, especially the spin polarization, many of $X_2YZ$ full, half and inverse Heusler compounds have been explored. For example, Rh$_2$YZ represent an interesting family in the world of Heusler compounds which has been intensively studied during the recent decades. The crystal structure and magnetic properties have been determined for a new series of compounds of the form Rh$_2$T$_2$Sn for $T$ = Mn, Ni, or Cu [11]. In their work, M. Pugaczowa-Michalska and A. Jeżierski et al. studied the magnetic properties of Rh$_2$T$_2$Sn Heusler alloys ($T$=Mn, Fe, Co, Ni and Cu) [14]. Mohammed El Amine Monir et al. studied half-metallic ferromagnetism in the novel Rh$_2$-based...
The basic functions are expanded in combinations of spherical harmonic functions. In this context, the space is divided into non-overlapping muffin-tin (MT) spheres separated by an interstitial region. Functional theory (DFT) with the generalized gradient approximation (GGA-PBE) is used. In this method, the space is divided into non-overlapping muffin-tin (MT) spheres separated by an interstitial region. The space is divided into non-overlapping muffin-tin (MT) spheres separated by an interstitial region. The valence wave functions inside the MT spheres are expanded in terms of spherical harmonics up to $l_{\text{max}} = 10$. We set the parameter $RMT$, $K_{\text{max}} = 7$ (where $RMT$ is the average radius of the MT spheres and $K_{\text{max}}$ is the largest reciprocal lattice vector used in the plane wave expansion). The magnitude of the largest vector in charge density Fourier expansion ($G_{\text{max}}$) was 14 (a.u.)$^{-1}$. Both the plane wave cut-off and the number of k-points were varied to ensure total energy convergence. Our calculations for valence electrons were performed in a scalar-relativistic approximation, while the core electrons were treated relativistically. The self-consistent calculations were considered to converge only when the calculated total energy of the crystal converges to less than 10$^{-4}$ Ry.

In order to simulate the Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0.25$, 0.50, 0.75) quaternary alloy, we generate a supercell with 16 atoms. For $x = 0.25$, we substituted one atom of Ge by one atom of Al; for $x = 0.50$, we substituted two atoms of Ge by two atoms of Al; for $x = 0.75$, we substituted three atoms of Ge by three atoms of Al.

3. Results and discussion

3.1. Structural properties

The total energy as a function of the cell volume curves was fitted to the Murnaghan equation of [25]. In order to determine the ground state properties

$$E(V) = E_0(V) + \frac{B V}{B'(V' - 1)} \left[ B \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B'} - 1 \right]. \quad (3.1)$$

Here, $E_0$, $V_0$, $B$ and $B'$ are the equilibrium energy, volume, bulk modulus and its first derivative,
Phase stability, electronic and magnetic properties

Figure 1. (Colour online) Variation of the total energy as a function of the unit-cell volume of Rh$_2$CrGe, Rh$_2$CrAl for both Hg$_2$CuTi and Cu$_2$MnAl type structure.

respectively. The equilibrium structural parameters ($a$, $B$ and $B'$) of Rh$_2$CrGe$_{1-x}$Al$_x$ Heusler alloys in both Hg$_2$CuTi and Cu$_2$MnAl phases are given in table 1.

Note that for the present Heusler alloys [Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0.25$, $0.5$, $0.75$)], there are no experimental or theoretical data accessible to get our calculations started. In order to obtain their approximate lattice parameters, we have applied a linear combination of the lattice constants of the Rh$_2$CrGe$_{1-x}$Al$_x$ alloys and the associated concentration $x$ of Al incorporated atom allowing for the so-called Vegard’s law [26–28].

Rh$_2$CrGe$_{0.75}$Al$_{0.25}$: $a = (6.088 \times 0.75) + (6.044 \times 0.25) = 6.077$ Å,
Rh$_2$CrGe$_{0.5}$Al$_{0.5}$: $a = (6.088 \times 0.5) + (6.044 \times 0.5) = 6.066$ Å,
Rh$_2$CrGe$_{0.25}$Al$_{0.75}$: $a = (6.088 \times 0.25) + (6.044 \times 0.75) = 6.055$ Å.

The obtained lattice parameter values for the Rh$_2$CrGe$_{0.75}$Al$_{0.25}$, Rh$_2$CrGe$_{0.5}$Al$_{0.5}$ and Rh$_2$CrGe$_{0.25}$Al$_{0.75}$ Heusler alloys are well accorded with Vegard’s law values, which are higher by 0.34%, 0.32% and 0.3%, respectively.

By analyzing the present results, we can see the direct proportion between the lattice parameters
Table 1. Structural parameters ($a$, $B$ and $B'$) of Rh$_2$CrGe, Rh$_2$CrAl and Rh$_2$CrGe$_{1-x}$Al$_x$ ($x$ = 0.25, 0.5 and 0.75).

<table>
<thead>
<tr>
<th>Rh$_2$YZ</th>
<th>a(Å)</th>
<th>B(GPa)</th>
<th>$B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh$_2$CrGe</td>
<td>Cu$_2$MnAl Type</td>
<td>FM</td>
<td>6.936</td>
</tr>
<tr>
<td></td>
<td>Hg$_2$CuTi Type</td>
<td>FM</td>
<td>6.046</td>
</tr>
<tr>
<td>Rh$_2$CrAl</td>
<td>Cu$_2$MnAl Type</td>
<td>FM</td>
<td>6.306</td>
</tr>
<tr>
<td></td>
<td>Hg$_2$CuTi Type</td>
<td>FM</td>
<td>6.0468</td>
</tr>
<tr>
<td>Rh$<em>2$CrGe$</em>{0.25}$Al$_{0.75}$</td>
<td>FM</td>
<td>6.0580</td>
<td>199.0289</td>
</tr>
<tr>
<td>Rh$<em>2$CrGe$</em>{0.50}$Al$_{0.50}$</td>
<td>FM</td>
<td>6.0692</td>
<td>200.0788</td>
</tr>
<tr>
<td>Rh$<em>2$CrGe$</em>{0.75}$Al$_{0.25}$</td>
<td>FM</td>
<td>6.0804</td>
<td>199.6756</td>
</tr>
</tbody>
</table>

[obtained by GGA for the Cu$_2$MnAl (L21) structure and calculated by Vegard’s law] of the three Heusler alloys and the concentration ($x$) of Al atom. This occurs owing to the Ge (125 pm) large atomic radius compared to the Al (118 pm) radius, respectively. It is clearly seen that the GGA offers greater values than the Vegard’s law ones. At the same time, the corresponding bulk modulus values are 199.6756 GPa, 200.0788 GPa and 199.0289 GPa, respectively. We can conclude that Rh$_2$CrGe$_{0.25}$Al$_{0.75}$ is the most compressible full Heusler alloy.

3.2. Electronic and magnetic properties

The calculated densities of states for Rh$_2$CrGe and Rh$_2$CrAl are presented in figure 2, the responsibility of transition metals $3d$-states is very significant in the description of density of sates calculations. The magnetic moments of the materials depend on the interactions of $3d$-band structure with other states [29]. Coey et al. [30] have proposed a large classification scheme for half-metallic ferromagnets: A material with conducting electrons (metallic behavior) at one for the spin channels and an integer moment at $T = 0$ is a good candidate for A type-I half-metallic ferromagnet. This is the phenomenon described by de Groot et al. [31]. Type-IA half-metals are metallic in spin up, and semiconducting in spin down; the opposite is true for the type-IB half-metals [32]. For the Rh$_2$CrGe Heusler alloy, the majority-spin bands are metallic due to the overlap between the conduction and valence bands around $E_F$, but the minority-spin bands are nearly semiconductors because the conduction band minimum cut little the $E_F$ at the $\Gamma$ symmetry point. Thus, Rh$_2$CrGe is nearly half-metallic.

For Rh$_2$CrAl full Heusler alloys, we can see that spin up present a metallic behavior while spin down is semiconductor which indicates a half-metallic behavior. Slater and Pauling [33, 34] had exposed that for a binary magnetic alloy, when we add one valence electron in the compound, this occupis spin-down states only and the total spin magnetic moment decreases by about 1 μB. For L21 full-Heusler, the relation between the total spin magnetic moment in the unit cell $M_t$ and total number of valence electrons $Z_t$ is $M_t = Z_t - 24$ [35]. The number “24” in this formula comes from the number of completely occupied minority states which consist of one $s$, three $p$ and eight $d$ states and gives total 12 states [35]. These Slater and Pauling rules join the electronic properties directly to the magnetic properties, and present a powerful tool to the study of HM Heusler compounds. The number of valence electrons $Z_t$ for Rh$_2$CrAl and Rh$_2$CrGe is 27 [$Z_t = (9 \times 2) + 6 + 3 = 27$] and 28 [$Z_t = (9 \times 2) + 6 + 4 = 28$], respectively, their total spin magnetic moments are 3.000 μB (integer value which confirms a half-metallic behavior) and 3.97579 μB (nearly integer which confirms a nearly half-metallic behavior), respectively. The basis of the HM gap is discussed in herein below. The HM gaps frequently take place from three aspects [36]: 1) charge transfer band gap [36] which is frequently seen in CrO$_2$ and double perovskites [36], 2) covalent band gap which is present in the half-Heusler with $C1b$ structure, and 3) $d$ $d$ band gap, that is the origin
of the HM band gap in the full-Heusler alloys with Cu2MnAl structure. In the latter case, there is a quite strong hybridization between $d$ orbitals of transition metals which makes the $d$-orbitals split into bonding $e_g$ and $t_{2g}$ orbitals below the Fermi level and anti-bonding $e^*_g$ and $t^*_{2g}$ orbitals above the Fermi level. This hybridization is known as $d - d$ hybridization [37].

The calculated total and partial densities of state of Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0.25, 0.5, 0.75$) compounds within the GGA approach are shown in figure 3. One can observe the absence of the gap at Fermi level in the spin ($\uparrow$) and its presence in spin ($\downarrow$), which confirms the metallic behavior for spin ($\uparrow$)

Figure 2. (Colour online) Densities of states of Rh$_2$CrGe and Rh$_2$CrAl.
**Figure 3.** (Colour online) Total and partial densities of states of $\text{Rh}_2\text{CrGe}_{1-x}\text{Al}_x$ ($x = 0.25, 0.5$ and 0.75) compounds.
Table 2. The calculated total and partial magnetic moments (in μB) for Rh₂CrGe, Rh₂CrAl and Rh₂CrGe₁₋ₓAlₓ (x = 0.25, 0.5 and 0.75) compounds.

<table>
<thead>
<tr>
<th></th>
<th>M(Rh₂)</th>
<th>M(Ge)</th>
<th>M(Al)</th>
<th>M_{tot}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh₂CrGe</td>
<td>0.30055</td>
<td>0.03681</td>
<td>−0.00748</td>
<td>3.03681</td>
</tr>
<tr>
<td>Rh₂CrAl</td>
<td>0.19516</td>
<td>0.0059</td>
<td>−0.0256</td>
<td>0.29814</td>
</tr>
<tr>
<td>Rh₂CrGeₐₓAl₀.₇₅</td>
<td>0.24261</td>
<td>2.69551</td>
<td>−0.0059</td>
<td>0.24537</td>
</tr>
<tr>
<td>Rh₂CrGe₀.₃₅Al₀.₇₅</td>
<td>0.29814</td>
<td>2.81287</td>
<td>−0.0041</td>
<td>0.35669</td>
</tr>
<tr>
<td>Rh₂CrGe₀.₇₅Al₀.₂₅</td>
<td>0.35669</td>
<td>2.91783</td>
<td>−0.00014</td>
<td>0.35055</td>
</tr>
</tbody>
</table>

and the semi-conducting behavior for spin (↓). As a result, the Rh₂CrGe₀.₂₅Al₀.₇₅, Rh₂CrGe₀.₅Al₀.₅ and Rh₂CrGe₀.₇₅Al₀.₂₅ are full Heusler are half-metallic compounds. The DOS is characterized by a large domination of the Cr-3d states, which leads to the large spin moments at their sites, which are around 12.99983 μB, 14.00174 μB and 15.00682 μB for the Rh₂CrGe₀.₂₅Al₀.₇₅, Rh₂CrGe₀.₅Al₀.₅ and Rh₂CrGe₀.₇₅Al₀.₂₅ compounds, respectively as shown in table 2. It is seen that the total magnetic moment per unit cell decreases as a function of x concentration (4 μB, 15.00682 μB/16 atoms, 14.00174 μB/16 atoms, 12.990μB/16 atoms, and 3 μB, for x = 0, 0.25, 0.50, 0.75, and 1, respectively), for Rh₂CrGe₁₋ₓAlₓ (x = 0, 0.25, 0.5, 0.75 and 1). The calculated spin magnetic moments for the Rh₂CrGe₀.₂₅Al₀.₇₅, Rh₂CrGe₀.₅Al₀.₅ and Rh₂CrGe₀.₇₅Al₀.₂₅ alloys show that the total magnetic moment which includes the contribution from the interstitial region, comes mainly from the Cr ion with a small contribution of Rh sites. The Ge and Al atoms have a small anti-parallel spin moment to that of the Rh atom occupying the X sites in the lattice.

4. Conclusion

In this paper, we have presented theoretical results of structural, electronic and magnetic properties of Rh₂CrGe₁₋ₓAlₓ Heusler alloys. Calculations were performed using the FP-LAPW method as implemented in WIEN2k code within GGA-PBE. The most important results are as follows:

The alloys studied are more stable in Cu₂MnAl (L2₁) structure.

The ground state properties of the materials studied are determined in the two phases.

The calculated density of state of the ferromagnetic configuration for Rh₂CrGe and Rh₂CrAl show that the first one is nearly half-metallic and the second one is half-metallic.

For x = 0.25, 0.50 and 0.75, the materials have a metallic behavior for spin-up and a semi-conducting behavior for spin-down, so these materials are half-metallic compounds which are most functional in spintronic.

The magnetic moments were mostly contributed by the 3d orbital of Cr and 4d orbital of Rh ions. In the absence of experimental and theoretical works, the present results for the alloys studied provide an estimate of these materials which can be useful for further studies.

References

Теоретичне дослідження фазової стійкості, електронних і магнітних властивостей сплавів Хеслера Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0, 0.25, 0.50, 0.75$ i 1) методом FP-LAPW

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Проведено першопринципні обчислення в рамках теорії функціоналу густини з використанням методу лініаризованих приєднаних плоских хвиль з повним потенціалом та коду WIEN2k з метою визначення структурної стійкості електронних і магнітних властивостей Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0, 0.25, 0.50, 0.75$ і 1). Результати показали, що для Rh$_2$CrAl і Rh$_2$CrGe, структура типу Cu$_2$MnAl є енергетично більш стійкою, ніж структура типу Hg$_2$CuTi при рівноважному об'ємі. Обчислені густини станів для Rh$_2$CrAl і Rh$_2$CrGe показали, відповідно, напівметалеву та майже металеву поведінку. Rh$_2$CrGe$_{1-x}$Al$_x$ ($x = 0.25, 0.50, 0.75$) цих сплавів показали напівметалеву поведінку. Ці сполуки можна вважати хорошими кандидатами для спінтронних застосувань.

Ключові слова: сплави Хеслера, структурні властивості, електричні властивості, магнітні властивості