Comprehensive DFT Investigation of Structural, electronic and magnetic properties of CoRhYSi (Cr, Mn) QHA.

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Abstract

In this paper we were reported structural, electronic and magnetic properties of CoRhYSi (Y = Cr, Mn) QHA. Computational methods are infallible in predicting the ground state and numerous other properties of materials. There have been copious efforts to design high spin-polarized ferromagnetic materials for utilizing the electron spin to revolutionize conventional electronics.

We study the structural, electronic and magnetic properties of Co-based Quaternary Heusler compounds CoRhCrSi and CoRhMnSi using Density Functional Theory (DFT). The full-potential linearized augmented plane Wave is used in the calculations. The exchange-correlations are addressed using Perdew–Burke And Ernzerhof's generalized gradient approximation (GGA-PBE). With the exception of CoRhCrSi and CoRhMnSi, which are simple ferromagnets that are approximately half metallic In nature, electronic structure calculations demonstrate that these compounds have a gap in the Minority states band and are obviously half-metallic ferromagnets. The magnetic moments of the CoRhCrSi and CoRhMnSi compounds match relatively well with the Slater-Pauling rule, Indicating half metallicity and high spin polarization for these compounds.

Keywords. Density functional theory, QHA, Half Metallicity ,spin polarization, Curie temperature.

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Introduction

The first half-metallic ferromagnetic (HMF) Materials, the half-Heusler alloy NiMnSb, was discovered by de Groot using first-principles calculation's [1]. In recent years, HMF materials have been intensively investigated because they exhibit Metallic character for majority spin and semiconducting behavior for minority spin. Therefore, they are good

candidates for spintronic applications, In which tunneling magnetoresistance (TMR) and Giant magnetoresistance (GMR) are required [2].

Up to now an Immense collection of materials from different fields such as perovskites, chalcogenides, and Heusler alloys were reported to display half-metallicity. Among all of them, Heusler alloys are regarded as a novel due to high spin polarization, magnetism, and high Curie temperature. One of the important aspects of these alloys is that they are almost all ferromagnetic .These alloys come in a variety of forms, including recently developed quaternary alloys and half, full, and inverse versions. Quaternary Heusler alloys (QHA) with 4d and f-electrons are the least studied of the aforementioned varieties. CoFeCrAs, CoMnVAs, CoFeCrZ (Z = Si, As, Sb), and CoFeCrX (X = Si, Ge) are a few of the theoretical and experimentaly synthesised QHA [3-5]. These half-metallic alloys have high Curie temperatures as well as high thermoelectric efficiencies. Inspired by these novel functionalities we will analyze the new QHA family CoRhYSi (Y= Cr, Mn) and will analyze the effect on various physical properties such as electronic, magnetic, mechanical, and thermoelectric properties. Our findings will serve as guidelines for future theoretical and experimental works.

Computational Methodology

Density functional theory (DFT), as implemented in VASP code [6], is used to do the calculations. 520 eV was chosen as the cut-off energy, while 10^{-8} eV was chosen as the total energy tolerance. For unit-cell structures, the formation energy was computed using a 22 x 22 x 22 Γ- centered k-point mesh.. The total energy was then calculated using the full-potential linearized augmented plane Wave (FP-LAPW) method implemented in WIEN2k code [7] using the optimized structural Parameters acquired by VASP code [8]. The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) [9] was used to treat the exchange–correlation potential. K_{max} RMT= 9 was used to define the wavefunctions in the interstitial area, where RMT is the smallest atomic Muffin tin radius and Kmax is the largest reciprocal lattice vector of the plane wave expansion. For Co, Cr, Mn, Rh, and Z (Z = Si) atoms, RMT values of 2.4, 2.2, 2.0, and 1.7 atomic units (a.u.) were chosen, respectively. 10^{-4} Ry, 10^{-4} e, and 1 mRy/au were chosen as the total energy, charge density convergence tolerances, and force tolerances, respectively.

Structural Properties

CoRhYSi (Y = Cr, Mn) QHAs have a stoichiometry of 1:1:1:1 and a chemical formula of

XX′YZ, where X, X′, and Y are transition metal elements and Z is a main group element with s-p orbitals. The QHAs crystallize in a face-centered cubic LiMgPdSn (Y-type) structure with the space group F43m (no. 216). The atomic configurations of this sort of structure are Y-type-I, Y- type-II, and Y-type-III, as shown in Figure 1. The element's Wyckoff positions in the three types are 4a (0,0,0), 4c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4d (3/4, 3/4, 3/4), as shown in Table 1. The Y-type-I crystal structure was found to be the most stable crystal structure based on total energy calculations (see Table 2). The formation energy (Eform) is calculated using the following formula to determine the thermodynamic stability of these QHAs [10]

$$E_{\text{form}} = E_{\text{tot}} - \left(E_{Co}^{\text{bulk}} + E_{Rh}^{\text{bulk}} + E_{Y}^{\text{bulk}} + E_{Z=Si}^{\text{bulk}}\right),$$

where E_{tot} represents the equilibrium total energy per formula unit of CoCrRhSi, CoMnRhGe alloys, and ECo^{bulk}, $^{ER^{h}bulk}$, EYb^{ulk}, and $EZ{=}Si^{bulk}$ refer to the equilibrium total energies per atom in their individual bulk structures. Table 4 shows that the formation energy values are negative, indicating that CoYRhSi (Y = Cr, Mn) QHAs are thermodynamically stable. Table 3 also shows the optimized lattice parameter for each alloy. It is noticeable from this table that the increase in the atomic number of Z (Z = Si) atoms increases the lattice parameters. The calculated lattice parameter values are in agreement of the experimental results, see Table 3 [10]. It calculated the total energy as a function of volume of all three possible atomic configurations to determine the most stable structure, taking into account the paramagnetic (NM) and ferromagnetic (FM) phases [11]. It's worth noting that the majority of magnetic Heusler compounds are stable in their ferromagnetic state [11]. The equilibrium structural parameters can then be determined by minimizing the energy.

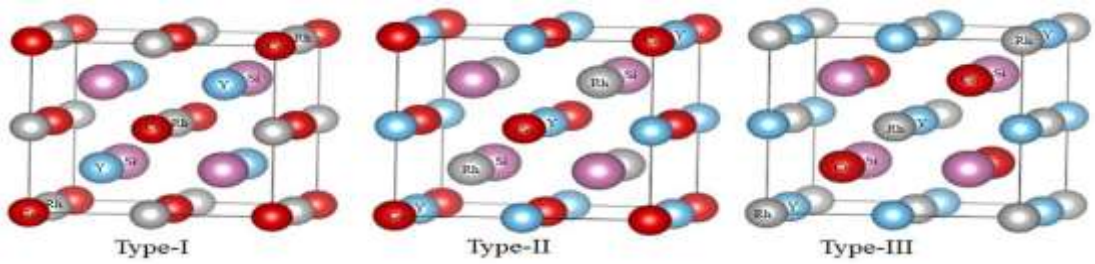

Figure 1. Three different types of the primitive cell of the quaternary Heusler compounds.

Table 1. The Wyckoff positions 4a, 4c, 4b, 4d of the atoms in CoYRhSi (Y = Cr, Mn) quaternary Heusler alloys for three types of configurations

Y	4a (0,0,0)	4b (1/2, 1/2, 1/2)	4c (1/4, 1/4, 1/4)	4d (3/4, 3/4, 3/4)
Type-I	Co	Rh	Y	Z
Type-II	Co	Y	Rh	Z
Type-III	Rh	Co	Y	Z

Table 2. The total energy in eV of CoYRhSi (Y = Cr, Mn) QHAs in the three types of configurations

Alloys	Type-I	Type-II	Type-III
CoCrRhSi	-29.719	-30.633	- 30.145
CoMnRhSi	- 29.187	-30.749	- 29.918

Table 3. Lattice constant a (Å), elastic constants Cij (GPa), bulk modulus B (GPa), Young's modulus E (GPa), isotropic shear modulus G (GPa), Poisson's ratios ν, anisotropy factor A, Pugh's ratio B/G, and the melting temperature Tmelt (K) of CoRhYSi (Y = Mn, Cr) quaternary Heusler compounds

Physical Parameter	**CoCrRhSi**	**CoMnRhSi**
$E_{form}(eV)$	-1.321	-1.914
a	5.786	5.839
	5.786[a)]	5.839[c)]
C11	335.898	334.408
C12	145.233	141.947

C44	58.916	72.14
B	216.881	211.453
	234.569[b)]	
E	185.233	216.135
G	68.357	81.295
v	0.358	0.330
A	0.618	0.749
Cp	86.317	69.0547
B/G	3.173	2.601
Tmelt	2624	2574

(a, b)Ref [11],[12].

Electronic and Magnetic Properties

The band structure, total density of states (TDOS), projected density of states (PDOS), and magnetic characteristics of CoRhYSi (Y = Mn, Cr), quaternary Heusler alloys are presented in this section. The band structure and TDOS of CoRhYSi (Y = Mn, Cr), alloys are shown in Figure 2. For CoRhYSi (Y = Mn, Cr) quaternary Heusler compounds, the spin polarized band structure was calculated along the high symmetry paths of the first Brillouin zone. From Figure 2, the CoRhYSi (Y = Mn, Cr) alloys were found that they have half-metallic behavior. The minority spin channel in these structures behaves as semiconducting, with band gap values of 0.542 and 0.576 eV along the Γ and X symmetry line, respectively, whereas the majority spin channel behaves metallically. The positive and negative values correspond to the DOS of the spin-up and spin-dn states, respectively. The hybridized state of Cr, Mn, and Rh as they cross the Fermi level is responsiblefor the metallic behavior in the spin-up channel [11]. The separation between these anti-bondingstates forms the spin-dn semiconducting band gap, as seen in several EQH compounds [13],[17]. From Equation 1, the electric spin polarization of CoRhYSi (Y = Mn, Cr) quaternary Heusler compounds was calculated at the Fermi energy. CoRhYSi (Y = Mn, Cr) quaternary Heusler compounds express a 100% electron spin polarization due to the absence of minority-spin density of state at Ef . Thus, these compound are showing a promising materials for spintronic application [14]. At Γ and X, the Valence band maximum (VBN) and the conduction band minimum (CBN) are located, respectively, and the Fermi energy is near (VBN). Therefore, CoCrRhSi and CoMnRhSi reveal an indirect band gap of 0.542 eV

and 0.576 eV, respectively, in the minority-spin channel. These results are in agreement with the other studies as follow in Table 3. These results are consistent with previous ab initio investigations of CoFeCuZ quaternary Heusler alloys (Z = Al, As, Ga, In, Pb, Sb, Si, Sn) [85]. Furthermore, the occurrence of flat energy levels in the conduction bands along the Γ and X symmetry line, as well as significantly dispersive bands in other directions, could indicate a high Seebeck coefficient and thermoelectric properties [15].

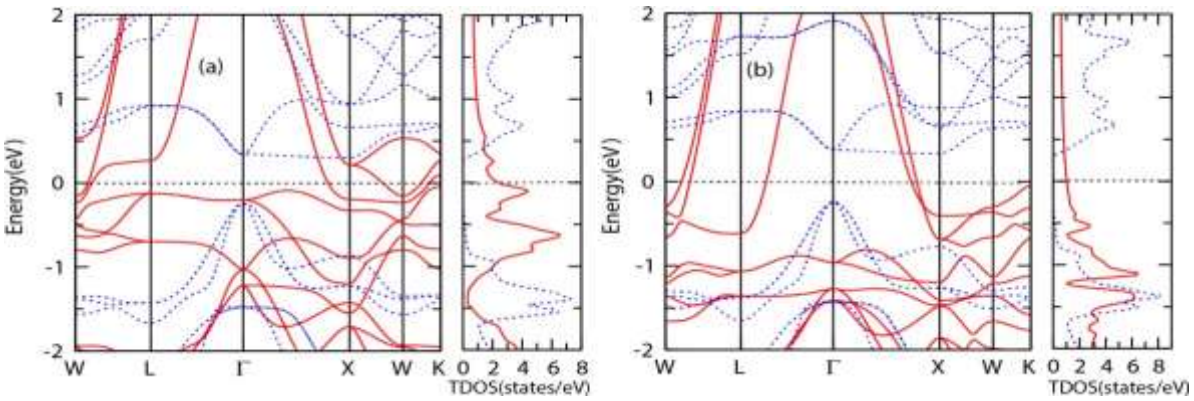

Figure 2. The electronic band structures and total density of states (TDOS) of a) CoCrRhSi, b)CoMnRhSi. The solid and dotted lines represent the majority and minority spin channels, respectively.

The following formula can be used to calculate the spin-polarization [18]:

$$P = \frac{\rho_{\uparrow}(E_f) - \rho_{\downarrow}(E_f)}{\rho_{\uparrow}(E_f) + \rho_{\downarrow}(E_f)} X100 \qquad \text{Equation 1}$$

where $\rho_{\mathrm{t}}(E_f)$ and $\rho_{\downarrow}(E_f)$ are the majority and minority spin density of states, respectively, at the Fermi level (E_f) [18]. Table 3 shows that the CoCrRhSi and CoMnRhSi alloys have a perfect spin-polarization of 100 percent, corresponding to half-metallic behavior. CoFeMnGe QHAs have a similar high spin-polarization value [16].

Table 4. The calculated band gap values Eg (eV), spin polarization P (%), total magnetic moment Mtotal (μB), local magnetic moments per atom Mi (μB) (i = Co, Cr, Mn Rh, Z) for CoRhYZ (Y= Cr,Mn) (Z = Si) alloys

Compound	E_g(eV)	P (%)	$m_{Co}\,[\mu_B]$	$m_{Rh}[\mu_B]$	$m_Y[\mu_B]$	$m_{Si}[\mu_B]$	$m_{total}\,[\mu_B]$
CoRhCrSi	0.54 (minority)	100	1.15	0.36	2.41	-0.02	4.00
					2.390[b)]		4.00[a)]
CoRhMnSi	0.57 (minority)	100	1.25	0.44	3.31	-0.02533	5.00

a, b) [11]

In Table 4, the calculated local and total magnetic moments under the equilibrium lattice constant of CoRhYSi (Y = Mn, Cr) compounds are given. CoCrRhSi compound displays a ferromagnetic behavior,

that is appeared from the total magnetic moment of 4.00 μ_B. Also, CoMnRhSi compound expresses a ferromagnetic behavior with total magnetic moment of 5.00μ_B. From the local magnetic moments of Cr, Mn and Co atoms, the major benefaction comes of the total magnetic moment of CoCrRhSi and CoMnRhSi. To the total magnetic moments, the metalloid atom (Si) reveals a negligible contribution. The half-metallicity of material is stated by the Slater-Pauling rule, and its total magnetic moment. Also, the half-metallic behavior is depending in the integer value of total magnetic moment. For the CoRhYSi (Y = Mn, Cr) compounds, the Slater-Pauling rule is given by the following equation [19], [20]:

$$M_{tot} = (Z_{tot} - 20)\mu_B \qquad \text{Equation 2}$$

Where M_{tot} is the total magnetic moment, and Z_{tot} is the accumulated number of valence

electrons. The integer values of 4.00 and 5.00 μ_B for CoRhYSi (Y = Mn, Cr) alloys are shown in this table 4, confirming the half-metallic behavior of these QHAs. As a result, these QHAs appearto be potential candidates for future spintronic applications [23]. In the cases of CoCrRhSi and CoMnRhSi alloys, however, the Cr and Mn atoms have local magnetic moments of 2.41 and 3.31μ_B, respectively. In the case of CoCrRhSi and CoMnRhSi alloys, the coupling between the local magnetic moments of Cr and Mn atoms and those of Co and Rh atoms is ferromagnetic. Rh atoms in CoCrRhSi and CoMnRhSi, with local magnetic values of 0.36 and 0.44 μ_B, respectively. The linear relationship between Curie temperature (TC) and total magnetic moments is acknowledged to be one of the methods that has been used to estimate the Curie temperature [10], [15], [21], [22]:

$T_C = 23 + 181M_{tot}$ Equation 3

The value of Curie temperature for CoCrRhSi and CoMnRhSi alloys is found to be 747 and 928 K, respectively.

CONCLUSION

DFT computations are used to investigate the structural electronic and magnetic properties of CoCrRhSI and CoMnRhSi Quaternary Heusler Alloys. The Y-Type-11 structure was found to be the most stable configuration for these Quaternary Heusler Alloys based on total energy calculations. These CoCrRhSi and CoMnRhSi alloys exhibit half-metallic behaviour with band gaps of 0.542 and 0.576 eV respectively. With an integer total magnetic moments of 4.00 and 5.00 μ_B and a spin polarization of 100%, they show half-metallic ferromagnetic properties. Because of their half-metallic ferromagnetic properties, they appear to be good for spintronic applications.

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