

**Abstract**

Employing ab initio electronic structure calculations, we have investigated electronic and magnetic properties of the Zr-based quaternary Heusler alloys: VZrCoIn, VZrFeGe, FeZrCoP, CrZrCoBe and CrZrFeZ (Z=In and Ga). Our ab initio calculation results show that all the alloys are (or nearly) spin-gapless semiconductors. All the alloys have large band gaps, indicating the stability of them at room temperature. The Slater-Pauling behaviours of these alloys are discussed as well. The values of Curie temperature of all the alloys are estimated. And it is found that the values of the Curie temperature for all our calculated quaternary Heusler alloys are higher than that of room temperature.

**Keywords:** Ab initio, Spin-gapless semiconductors, Quaternary Heusler alloys, Curie temperature,

**1. Introduction**

Efficient spin injection from a ferromagnet to a semiconductor is very meaningful for the development of the performance of spintronic devices [1]. Since the prediction of HM ferromagnetism of Heusler alloy NiMnSb by ab initio calculations in 1983 [2], half metallic ferromagnetism (HMF) has attracted great interest. And the half metallic ferromagnetic Heusler alloys

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are good candidates for the application of spintronic devices, as these alloys often have high spin polarization, high Curie temperature compatible lattice structure. The improvement of computer science makes it possible to design materials on computers, which is efficient and less cost [3, 4, 5]. Especially, computational material science enables the study of the new materials [4, 5], which is useful to the experiments and practical applications.

Recent studies have shown that there is a new class of materials, namely, spin-gapless semiconductors (SGS) [6, 7, 8]. SGS was first predicted in diluted magnetic semiconductors PbPdO$_2$ by *ab initio* calculations [6]. The excited carriers can be 100% spin polarized with tunable capabilities, and the SGS may be more practical in the use of spintronic applications than half metals (HM). But there is a drawback that the Curie temperature ($T_C$) of this material is almost 180 K [6, 10]. As is known the Heusler alloys often have high $T_C$, the Heusler alloys may be a realization of SGS. And the Heusler compound Mn$_2$CoAl was first predicted to be a SGS with a high $T_C$ of 720 K [7]. So the Heusler alloys are promising candidates for the future SGS use.

There are many investigations on the half metal Heusler alloys [11, 12, 13, 14]. In recent reports [15, 16, 17, 18, 19, 20], some so-called LiMgPdSn or Y-type structure Heusler alloys with a formula of $X_1X_2YZ$ have been discovered to be HMs by density function theory (DFT). Among the new structure Heusler alloys, MnCrVAl, MnCrTiSi, CoFeCrAl, CoFeTiAs, CoMnCrSi, Mn-VTiAs, FeVTiAs, FeCrTiAl CrVTiAl, CoVTiAl, CoFeMnSi, CoFeCrAl and CoFeVSi are (or nearly) SGSs [21, 22]. As reported in Refs. [7, 23, 24, 25], the ternary Heusler alloys Ti$_2$ MnZ (Z=Al, Ga and In), Mn$_2$CoAl, Ti$_2$CoSi and Ti$_2$VAs are (or nearly) also SGSs.

The Zr-Ti coupling quaternary Heusler alloys, ZrFeTiZ (Z=Al, Si and Ge) and ZrNiTiAl have been reported to be HMF very recently [26]. This is the first prediction of HMF in the 4d-3d transition metal elements coupling quaternary Heusler alloys. As reported, these alloys have large half metallic band gaps and spin flip gaps. But they are just normal HMFs not SGSs.

It is very interesting that the Zr-Ti coupling quaternary Heusler alloys have large HM band gaps and spin flip gaps, which means these alloys may be stable at room temperature. And there may be other Zr-based quaternary Heusler alloys with large HM band gaps, some probably being SGSs. Motivated by the above, we have designed the new Zr-based quaternary Heusler alloys: VZrCoIn, VZrFeGe, FeZrCoP, CrZrCoBe and CrZrFeZ (Z=In and Ga). The electronic and magnetic properties of the alloys are investigated
by ab initio calculations. VZrCoIn, CrZrCoBe, FeZrCoP and CrZrFeIn also have large HM band gaps of 0.98 eV, 0.71 eV, 0.41 eV and 0.80 eV. CrZrFeGa and VZrFeGe are semiconductors. The calculation results show that VZrCoIn, CrZrCoBe, VZrFeGe, FeZrCoP, CrZrFeIn and CrZrFeGa are (or nearly) SGSs. The values of Curie temperature of all the alloys are estimated. It is found that the values of the Curie temperature for all our calculated quaternary Heusler alloys are higher than that of room temperature. This means that all the calculated quaternary Heusler alloys keep being SGSs at room temperature and they may be practical in the future SGS use.

2. Computational method

The lattice optimization, electronic density of states (DOS), magnetic moment and band structure of the new Zr-based quaternary Heusler alloys are calculated by employing ab initio method. All our ab initio calculations are performed by using the full-potential local-orbital minimum-basis band structure scheme (FPLO) with generalized gradient approximation (GGA). For the irreducible Brillouin zone, we use the $k$ meshes of $20 \times 20 \times 20$ for all the calculations. The convergence criteria of self-consistent iterations is set to $10^{-6}$ to the density and $10^{-8}$ Hartree to the total energy per formula unit.

As described in Refs. [15, 16], the quaternary Heusler alloys has a so-called LiMgPdSn or Y-type structure (space group No.216, F43m). So all our calculations are performed in this lattice structure.

3. Results and discussions

In general, the quaternary Heusler alloys have a formula of $X_1X_2YZ$. In our calculations, the $X_2$ atom is Zr atom and Z is a main group element atom. $X_1$ and $Y$ are the 3d transition metal element atoms, which the atomic number $X_1$ is smaller than that of $Y$. According to group theory, the LiMgPdSn or Y-type structure quaternary Heusler alloys have four Wychoff positions: $4a$ ($0, 0, 0$), $4c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), $4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and $4d$ ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$). The lattice structure is face centered cubic (FCC). In principle, the $X_1$, $X_2$, $Y$ and $Z$ atoms can occupy one of the $4a$, $4c$, $4b$ and $4d$ positions. By interchanging the positions of atoms in LiMgPdSn or Y-type structure quaternary Heusler alloys, three possible types of atom arrangement are formed: Y-type (I),
Y-type (II) and Y-type (III). \(X_1, X_2, Y\) and \(Z\) atoms are arranged at different positions Y-type (I)=(4a, 4c, 4b, 4d), Y-type (II)=(4a, 4c 4d, 4b) and Y-type (III)=(4b, 4c, 4d, 4a). In order to get the equilibrium structures of the Zr-based quaternary Heusler alloys, the geometry optimization are firstly performed in their three different configurations by calculating the total energies as a function of lattice constants. From the calculated results of total energies at equilibrium lattice constants, we find that Y-type (I) is the most stable one of the three structures for both spin-polarization (FM phase) and non-spin-polarization (NM phase). And FM phase is more stable than NM phase in Y-type (I). This is in agreement with the previous papers [15, 16, 17, 18, 26]. The obtained equilibrium of lattice results in Y-type (I) are presented in Table 1 for the FM phases. So we will only discuss the quaternary Heusler alloys in Y-type (I) structure for the FM phases.

3.1. Slater-Pauling behaviours

Table 2 shows the magnetic moment of all our calculated alloys under the equilibrium lattice constants.

All the calculated quaternary Heusler alloys have very large band gaps. It means they may keep their magnetic properties at room temperature.

We will have a brief discussion of the Slater-Pauling behaviours based on the values of total magnetic moment in Table 2. The calculated total magnetic moment per formula unit, 3 \( \mu_B \) for the quaternary Heusler alloys VZrCoIn, CrZrCoBe, CrZrFeIn, CrZrFeGa and VZrFeGe, obeys the Slater-Pauling behaviour which can be expressed by,

\[ M_{\text{tot}} = (Z_{\text{tot}} - 18) \mu_B \]  

here \( M_{\text{tot}} \) and \( Z_{\text{tot}} \) are the total magnetic moment per formula unit and the number of total valence electrons in each the above alloys. \( Z_{\text{tot}} \) is 21 for VZrCoIn, CrZrCoBe, CrZrFeIn and CrZrFeGa. The values of magnetic moment per formula unit is 2 \( \mu_B \) for the calculated quaternary Heusler alloys FeZrCoP. The Slater-Pauling behaviour which is obeyed by FeZrCoP can be expressed by,

\[ M_{\text{tot}} = (Z_{\text{tot}} - 24) \mu_B \]  

here \( M_{\text{tot}} \) and \( Z_{\text{tot}} \) have the same meaning as previous. The investigations of the Slater-Pauling behaviours of usual \( X_2YZ \) full Heusler alloys can be found in Refs. [32, 33]. Similar to the discussions in Refs. [6, 7, 22, 25], we should focus on the total density of states (DOS) in Figure 1 for each
There are 26 valence electrons in FeZrCoP. The minority spin-down band structure is similar to the usual full-Heusler alloys in Refs. [32, 33] and 3d-3d coupling quaternary Heusler alloy CoFeTiAs described in Ref. [22]. There are 12 electrons in the minority spin-down band structure. The remaining 14 electrons in the majority spin-up band structure occupy the \( e_u \) states and the non-bonding \( e_u \) states don’t overlap with the antibonding \( e_g \) states. As a result, a spin-gapless semiconductor (SGS) is formed and this alloy obeys the Slater-Pauling behaviour expressed by Equation (2). Similar to Ref. [22], in the case of VZrCoIn, CrZrCoBe, CrZrFeIn, CrZrFeGa and VZrFeGe, there are 21 electrons in each of them. In the minority spin-down band structure, the \( t_{1u} \) states are unoccupied and the minority-spin band gap is created between non-bonding \( t_{1u} \) and the bonding \( t_{2g} \) states. In the majority spin-up band structure, the \( t_{1u} \) states are occupied while the \( e_u \) states are above the Fermi levels. So there are 12 occupied majority spin-up states and 9 minority spin-down states. Thus the the values of the total magnetic moment for VZrCoIn, CrZrCoBe, CrZrFeIn, CrZrFeGa and VZrFeGe are all 3 \( \mu_B \) and they obey the Slater-Pauling behaviour expressed by Equation (1).

### 3.2. Electronic structure properties

In this section, we will discuss the properties of spin-gapless semiconductors (SGS). Figure 1 shows the total and partial density of states (DOS) under the equilibrium lattice constants of all our calculated quaternary Heusler alloys. Figure 2 shows the corresponding band structures.

Firstly, we focus on the total DOS. In each of the cases, there is a large gap in the spin down band structure and the Fermi level falls within this gap. In the spin up band structure, for VZrCoIn and CrZrFeIn, the valence and conduction bands touch each other and the Fermi level falls within a zero-energy gap, which forms a valley in the spin up band structure. As described in Refs. [6], VZrCoIn and CrZrFeIn can be classified as SGSs. So no energy is required to excite electrons from the valence band to the conduction band, which is the same phenomenon that can be seen for the Hg-based gapless semiconductors and graphene [6]. And more interesting is that for an excitation energy up to the band gap energy of the spin channel and the holes can also be 100% spin polarized. So the carriers two can be possible fully polarized in the two SGSs. Therefore they can be used as spintronic materials with superior performance to half metals and diluted magnetic semiconductors [6, 7]. In the cases of CrZrCoBe and FeZrCoP, in
the spin up band structure, there is a small overlap of the band being located and above and below the Fermi level although no band-crossing occurs. So the quanternary Heusler alloys CrZrCoBe and FeZrCoP are almost SGSs. In the case of CrZrFeGa, it is clear to see there is a large band gap in the spin-down channel. And a close look at the band structure reveals that there is a very narrow band gap of 0.02 eV. In the spin up band structure, the valence and conduction bands touch each other but the Fermi level falls within a narrow band gap. So CrZrFeGa is very close to a SGS. In the case of VZrFeGe, there is a large band gap in both spin down and up channels but the two gaps are not located at the same energy region. And a close look at the band structure reveals that there is a band gap below the Fermi level in the spin up band which touches the Fermi level resulting in an almost vanishing DOS below the Fermi level. So the Fermi level slightly crosses the spin-down conduction band and the spin-up valence band. As a result, the quanternary Heusler alloy VZrFeGe can be classified as an indirect spin-gapless semiconductor.

Next the partial density of states (PDOS) will be discussed. From the PDOS, we can get that for all our calculated quanternary Heusler alloys, the 3d states of X1 and Y atoms make the most contributions to the total DOS near the Fermi levels. The 4d states of Zr make the most contributions to the total DOS of the Zr states near the Fermi levels. And the np (the values of n for In, Be, Ga, Ge and P are 5, 2, 4, 4 and 3) states of Z states make the most contributions to the total DOS near the Fermi levels of the Z states. From the PDOS, it can be seen there are hybridizations between X1-3d, Zr-4d and Y-3d states around the Fermi levels.

3.3. Curie temperature

As is known, the Curie temperature, $T_C$, of the magnetic materials is crucial for the practical applications. So in this section, we would comment on the expected Curie temperature.

The previous investigations on multi-sublattice half-metallic Heusler compounds have shown that Curie temperature is more or less proportional to total spin magnetic moment (or the sum of the absolute values of the atomic spin magnetic moments in the case of ferrimagnets) since Curie temperature is mainly determined by the nearest neighbor inter-sublattice exchange interactions \cite{34, 35, 36, 37, 38, 39}. As described in Refs. \cite{40, 23}, it is found experimentally that the $T_C$ of Mn$_2$CoAl is 720 K and the the sum of the absolute values of the spin moments is 5.47 $\mu_B$. Based on the empirical
value and according to Table 2, we can estimate that the value of $T_C$ for the quaternary Heusler alloy FeZrCoP is 320 K. As the sum of the absolute values of the atomic spin magnetic moments for FeZrCoP is the lowest of all our calculated quaternary Heusler alloys, the values of $T_C$ for all our calculated quaternary Heusler alloys are higher than that of room temperature. So the SGSs may probably be stable at room temperature. And they may be candidates for the future spin-gapless semiconductors applications.

4. Conclusions

In conclusion, we have investigated some Zr-based quaternary Heusler alloys by employing \textit{ab initio} calculations. It is found that the Zr-based quaternary Heusler alloys VZrCoIn, CrZrCoBe, VZrFeGe, FeZrCoP, CrZrFeIn and CrZrFeGa are (or nearly) SGSs with large band gaps by studying the DOS. The Slater-Pauling behaviours of these alloys are discussed briefly. The Curie temperature for these alloys have also been estimated, and the results show that the values of the Curie temperature for these alloys are higher than that of room temperature. So these alloys can be the potential candidates for the future SGS applications.
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Table caption

1. **Table 1**: The results of the lattice optimization of all our calculated quaternary Heusler alloys in Y(I) structure for FM phase.

2. **Table 2**: The partial and total magnetic moments of all our calculated Heusler alloys in type (I) structure under the equilibrium lattice constant. $M_{abs}$ is the sum of magnetic moments of all the atoms for each alloy.
Figure Caption

1. **Figure 1**: The total density of states and partial states for each our calculated quaternary Heusler alloy under the equilibrium lattice constants. The black blue, red, green and cyan curves represent the total states, 3d states of $X_1$, 4d states of Zr, 3d states of Y and np states of Z respectively.
Figure 1:
Table 1: The results of the lattice optimization of all our calculated quaternary Heusler alloys in Y(I) structure for FM phase.

| X1ZrYZ       | \(a_{opt}\) (Å) | \(E_{tot}\) (Ry)       | band gap (eV) |
|--------------|-----------------|------------------------|---------------|
| VZrCoIn      | 6.468           | -23650.670779          | 0.98          |
| CrZrCoBe     | 6.013           | -12116.709912          | 0.71          |
| CrZrFeIn     | 6.419           | -23612.431029          | 0.80          |
| CrZrFeGa     | 6.184↑          | -15734.120866↑         | 0.71↑         |
| VZrFeGe      | 6.210↑          | -15840.940640↑         | 0.81↑         |
| FeZrCoP      | 5.944↑          | -13215.295374↑         | 0.41↑         |

Table 2: The partial and total magnetic moments of all our calculated Heusler alloys in type (I) structure under the equilibrium lattice constant. \(M_{abs}\) is the sum of magnetic moments of all the atoms for each alloy.

| X1ZrYZ       | \(M_{X_1}\) (\(\mu_B\)) | \(M_{Zr}\) (\(\mu_B\)) | \(M_{Y}\) (\(\mu_B\)) | \(M_{Z}\) (\(\mu_B\)) | \(M_{tot}\) (\(\mu_B\)) | \(M_{abs}\) (\(\mu_B\)) |
|--------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|
| VZrCoIn      | 2.89 0.19 0.04 -0.12     | 3.00                      | 3.25                      |
| CrZrCoBe     | 3.21 -0.17 0.14 -0.18    | 3.00                      | 3.72                      |
| CrZrFeIn     | 3.45 -0.27 -0.03 -0.15   | 3.00                      | 3.91                      |
| CrZrFeGa     | 3.12 -0.29 0.32 -0.15    | 3.00                      | 3.88                      |
| VZrFeGe      | 2.58 0.00 0.57 -0.15     | 3.00                      | 3.32                      |
| FeZrCoP      | 1.19 -0.24 0.99 0.06     | 2.00                      | 2.49                      |