Effect of doping and pressure on the electronic and magnetic properties of the quaternary Heusler alloys

Nasrin Estaji and Mahdi Afshar

Department of Physics, Iran University of Science and Technology, Tehran, Iran

E-mail: nasrin.estaji69@gmail.com

Abstract

The effect of doping on the electronic structures and magnetic properties of the quaternary Heusler alloys under pressures is investigated. Electronic structure calculations reveal that ZrCoTiSi is a half-metallic ferromagnet with a total magnetic moment of 3.00 \( \mu_B \), which mostly arises from the 3d electrons of Ti atoms. In order to investigate the doping effects, different proportions of Y, Fe, Sc and Al atoms are substituted for Zr, Co, Ti and Si atoms, respectively. The calculated results on the basis of the density functional theory (DFT) indicate that, except Sc doping for \( x > 0.50 \), other substituted alloys can succeed the widely known Slater–Pauling rule \((M_t = Z_t - 18)\) of the ideal half-metallic materials, and preserve their half-metallic properties with full spin polarization. In addition, the behaviors of alloys with different concentrations of \( x \) under various pressures are investigated. ZrCoTi\( [Si(1-x)Al(x)] \) and [Zr\((1-x)Y(x)CoTiSi\)] alloys keep up their half-metallicity by increasing proportions of \( x \) doping \((0 < x < 1)\) under higher pressure in the range of 3.01 GPa to 17.61 GPa for Al doping and 3.01 GPa to 14.11 GPa for Y doping. However, in the replacement of Fe for Co in Zr\( [Co(1-x)Fe(x)]TiSi\) alloys, the resistance against pressure to conserve half-metallicity decreases from 3.01 GPa to 2.05 GPa. The Sc doping in ZrCo\[Ti(1-x)Sc(x)]Si alloys causes loss of half-metallicity for \( x > 0.50 \), and endures up to 1.67 GPa external pressure to preserve their half-metallic properties.

1. Introduction

Half-metallic materials have played an important role due to their novel practical uses in spintronic, magnetoelectronics and superconductor technologies [1–4]. The electronic band structures of half-metallic ferromagnet (HMF) materials show different behavior for each of the majority and minority spin states. The majority spin band acts as a metal, while the minority one behaves as a semiconductor with a gap around the Fermi level. Due to the special band structure character, HMFs show full spin polarization at the Fermi level, and they may be suitable candidates for technological applications [5].

Heusler alloys as common HMFs are a large family that normally have high Curie temperature and they can also be easily synthesized experimentally [6]. HMF Heusler alloys have received considerable attention since they were predicted by de Groot et al. in 1983 in the half-Heusler NiMnSb alloy [7]. Quaternary Heusler structures with the \((XX'YZ)\) arrangement are obtained, where \( X, X' \) and \( Y \) are the transition metals and \( Z \) is a sp atom [8]. Due to the promising electronic and magnetic properties of quaternary Heusler alloys, a number of experimental and theoretical studies have been reported about them, exhibiting their half-metallicity [9–17], high Curie temperatures [18, 19] and spin gapless semiconducting properties [20, 21]. Among these studies, Özdoğan et al. studied 60 LiMgPdSn-type quaternary Heusler alloys using the density functional theory calculations, finding most of them behave half-metallic [22]. In addition, Singh et al. investigated the magneto-electronic properties of the YCoTiX \((X = Al, Ga, Si, Ge)\) quaternary Heusler alloys [23]. They reported half-metallicity properties of mentioned alloys following the Slater–Pauling rule \( M_t = Z_t - 18 \). They calculated 1.00 \( \mu_B \) total magnetic moment for YCoTiX \((X = Al, Ga)\) and 2.00 \( \mu_B \) for \( X = Si, Ge \). In the same way, M.N. Rasool et al. studied the YCoVZ \((Z = Si, Ge)\) and YCoTiZ \((Z = Si, Ge)\) quaternary Heusler alloys with Slater-
They found that YCoVSi and YCoVGe alloys are spingapless semiconductor, whereas YCoTiSi and YCoTIGe alloys show half-metallic behavior. Idrissi et al. studied the electronic and magnetic properties of the YFeCrZ (Z = Al, Sb and Sn) quaternary Heusler alloys, observing half-metallic behavior with integer total magnetic moment 2.00 $\mu_B$ following the Slater-Pauling rule. Due to the interesting properties of Zr-based Heusler alloys, they have attracted considerable attention in the scientific literatures. LiMgPdSn-type of Zr-based alloys with half-metallic properties normally have large band gap in the minority spin band. Gao et al. showed that ZrCoVIn, ZrCoCrBe, ZrCoFeP, and ZrFeCrIn alloys have large band gaps of 0.98 eV, 0.71 eV, 0.41 eV and 0.80 eV with the Curie temperature higher than room temperature. They found that ZrCoVIn, ZrCoCrBe and ZrFeCrIn alloys follow the Slater-Pauling behavior with 3.00 $\mu_B$ total magnetic moment, while ZrCoFeP obeys the Slater-Pauling rule with 2.00 $\mu_B$.

In recent years, several studies have focused on the effects of defects, dopings, and disorders on the magnetic and electronic properties of Heusler alloys. Mao et al. investigated the effect of electron doping on the electronic structure of the FeCoZrGe Heusler alloy with different proportions of Nb and As doping instead of Zr and Ge, respectively. They found that it is possible to control half-metallicity by different concentrations of doping. Their calculations showed that the doped alloys maintain their half-metallic behavior for different proportions of doping with full spin polarization. They also reported that studied doped alloys would become more suitable for practical uses due to the increase in the Curie temperature. Moreover, Özdoğan et al. studied the electronic and magnetic properties of doped full Heusler alloys Co$_2[Cr(1-x)Mn(x)][Al(1-y)Si(y)]$.[36] They observed that all alloys are half-metal with following the Slater-Pauling rule. Their conclusion is that varying the concentrations of the transition metal and sp atoms may be a suitable way to modify the electronic and magnetic properties of the half-metallic Heusler alloys.

Beside these studies, some other theoretical and experimental investigations have also been devoted to the effects of pressure on the half-metallic properties of Heusler alloys.[37–40]. Seema studied the effect of hydrostatic pressure on electronic and magnetic properties of CoRuFeSi Heusler alloy, indicating that it keeps the full spin polarization up to 30 GPa and beyond this pressure it loses its perfect half-metallicity.[41] Shigeta et al. studied theoretically and experimentally the pressure-dependent magnetic properties of the half-metallic Heusler alloy Co$_7$TiSn.[42] They observed that the band gap of Co$_7$TiSn is open at the Fermi level in the minority spin band under pressure at 6.722 GPa. Moreover, Singh et al. studied the impact of pressure on the electronic properties of YCoTiX (X = Al, Ga, Si, Ge) alloys, observing that these studied alloys preserve their half-metallicity under pressure up to 25 GPa.[23]

As the pressure effects on magnetic properties of doped Heusler alloys are discussed in a limited literature, it is interesting to simultaneously study the implications of doping and applying pressure on Heusler alloys. In this study, by using density functional calculations, the electronic and magnetic properties of ZrCoTiSi-type Heusler...
alloys are investigated. The relations between doping and pressure on these alloys are developed. It aims to evaluate the resistant of doped quaternary Heusler alloys of the ZrCoTiSi-type under various pressures.

2. Computational method

The quaternary Heusler alloy ZrCoTiSi is crystallized in the LiMgPdSn crystal structure [6] which is a space group FB-43m (No. 216) with the Wyckoff positions of Zr: 4a (0 0 0), Co: 4c (1/4 1/4 1/4), Ti: 4d (3/4 3/4 3/4) and Si: 4b (1/2 1/2 1/2) as shown in figure 1. Calculations based on the density functional theory (DFT) on the electronic and magnetic properties of ZrCoTiSi structure are performed based on the full-potential local-orbital scheme using the relativistic version of FPLO-14 package [43, 44]. Calculations related to doping and pressure effects of doped alloys are carried out by using the virtual crystal approximation (VCA). The self-consistent potentials are calculated on a $20 \times 20 \times 20$ K-points in the Brillouin zone for all studied cases with the generalised gradient approximation (GGA) for the exchange-correlation potential [45, 46]. The sets of valence basis in the calculations are selected as (4s, 4p, 5s, 4d, 5p) for Zr, (3s, 3p, 4s, 4p, 3d) for Co and Ti, and (2s, 2p, 3s, 3p, 3d) for Si. All lower states are acted as core states. The convergence of the self-consistent iterations is set to $10^{-6}$ for the density and $10^{-8}$ Hartree for the total energy.
3. Results and discussion

3.1. Electronic and half-metallic behaviors

In order to determine the ground state behavior of ZrCoTiSi, a geometry optimization is performed by calculating the total energy as a function of lattice constant using scalar relativistic approximation as shown in figure 2. The equilibrium lattice constant in the FM state is found 6.24 Å. The total and atomic magnetic moments as well as the number of the valence electrons in the Slater-Pauling rule and spin polarization of ZrCoTiSi are presented in table 1. The spin polarization degree (SPD) at the Fermi level is calculated as follows:

![Figure 4. Equilibrium lattice constant of doped alloys as a function of doping element.](image4)

![Figure 5. Total density of states (DOS) of doped alloys under the VCA.](image5)
where $N^\uparrow(E_F)$ and $N^\downarrow(E_F)$ are the number of majority and minority spin states at the Fermi level \[47\]. The results reveal that ZrCoTiSi is a half-metallic material with a full spin polarization. It is in agreement with the Slater-Pauling rule \[18\] with the total magnetic moment of $3.00\, \mu_B$, which is originated mainly from Ti atoms. Based on the equilibrium lattice constant, the total spin density of states (DOS) and the spin-polarized band structure of the quaternary Heusler alloy ZrCoTiSi are calculated, and the results are depicted in figure 3. It is observed that the majority spin bands are metallic, while the minority spin bands show a semiconducting gap, indicating ZrCoTiSi is a half-metal with $1.303\, \text{eV}$ energy band gap. These results are consistent with the results obtained by Berri \textit{et al} \[48\]. They studied the half-metallic properties of the ZrCoTiZ (Si, Ge, Ga, Al) quaternary Heusler alloys. They reported $1.03\, \text{eV}$, $0.90\, \text{eV}$, $0.68\, \text{eV}$ and $0.59\, \text{eV}$ half-metallic gap for ZrCoTiSi, ZrCoTiGe, ZrCoTiGa and ZrCoTiAl alloys, respectively. They also showed that the hybridization of d-states between transition metal atoms leads to a large half-metallic gap. Among these alloys, ZrCoTiSi and ZrCoTiGe have $3.00\, \mu_B$ total magnetic moment, while ZrCoTiGa and ZrCoTiAl have $2.00\, \mu_B$.

### 3.2. Effects of doping on the electronic and magnetic properties

To simulate the doping of ZrCoTiSi with holes, each of Zr, Co, Ti and Si atoms is substituted with neighbouring chemical elements Y, Fe, Sc, and Al atoms in [Zr(1−$x$)Y($x$)]CoTiSi, [Zr(1−$x$)Fe($x$)]TiSi, [ZrCo(1−$x$)Sc($x$)] Si and ZrCo[Si(1−$x$)Al($x$)] alloys, respectively. The virtual crystal approximation (VCA) is used in the calculations. In the VCA calculations, for instance in ZrCo[Si(1−$x$)Al($x$)] alloys, both Si and Al atoms are substituted by atom with fractional number of electrons $(1−x)Z_{Si} + xZ_{Al}$, where $Z_{Si}$ and $Z_{Al}$ are the number of electrons of Si and Al individual atoms, respectively. The similar way for other alloys is conducted. The DFT equations are solved in the full potential scheme for the unit cell with non-integer electron charges. In the calculations, the equilibrium lattice constant is used for each alloy. It is observed that the equilibrium lattice constant increases with enhancing the amount of Y, Sc and Al doping, whereas it behaves in opposite way for the Fe doping as shown in figure 4. This behavior is related to how valence orbitals of composing elements of doped alloys are filled. In the Fe doping compared to other dopings, the hybridization of valence orbitals increases and the lattice constant decreases.
First, the effects of doping on the electronic properties of alloys are studied. Total DOS calculations of doped alloys with different concentrations of x doping (0 ≤ x ≤ 1) are presented in figure 5. These calculations indicate that there is a gap around the Fermi level in the minority spin, while the majority spin shows a conductive feature. The DOS calculations show that the doped alloys preserve their half-metallic properties in Y, Fe and Al dopings for different concentrations of x, while in Sc doping it is up to x = 0.50. Galanakis et al. studied the effects of Cr and Fe dopings in Co₂Mn₁−xCrₓSi and Co₂Mn₁−xFexSi Heusler alloys, respectively [33]. They observed that the Co₂Mn₁−xCrₓSi alloys keep their half-metallic properties for three different concentrations of Cr doping, while the half-metallicity of the Co₂Mn₁−xFexSi alloys loses in 20 percent of Fe doping.

As the important role of hybridization of d-states of transition metals in half-metallicity, the partial density of states of states of ZrCoTi₆Si(1−x)Al(x) alloys are also studied. The results are shown in figure 6. It is observed that the density of d-states of Ti is more than Co and Zr atoms at the Fermi level in majority spin states, which is related to larger amount of individual magnetic moment of Ti compared to other elements. It is also observed that the valence bands are mainly derived from d-states of Co, while the conductive bands mostly consist of d-states of three transition metals Zr, Co and Ti, while Si has a minor role in the total density of states. It can also be seen that the strong hybridization between d-states of transition metals in the conductive band decreases with increasing of doping.

In table 2 the effects of doping on the total and atomic magnetic moments of the doped alloys are presented. It is shown that total magnetic moments are mainly contribute by Ti atoms. It also indicates that by increasing x concentrations, doping alloys satisfy the Slater-Pauling rule, and their total magnetic moments reduce from 3.00 μᵣ to 2.00 μᵣ, with exception for x > 0.50 in Sc doping. Chen et al. investigated the effect of doping on the electronic and magnetic properties of the TiZrCo₁−x(1−x)Ge(x) alloy Heusler alloy [49]. They reported that Ge doping which is considered as electron doping increases the stability of alloys by increasing the half-metallic gap. Their results showed that the total magnetic moment of doped alloys consistent with the Slater-Pauling rule Mₜ = Zₜ − 18 increased from 2.00 μᵣ to 3.00 μᵣ by increasing Ge concentration.

The values of valence band maximum (VBM), the conduction band minimum (CBM) as well as the energy band gap (Eₓ) of minority spin states of the doped alloys are summarized in table 3. It is noteworthy that by increasing the amounts of x doping of Y, Fe and Al concentrations, the width of energy band gap is decreased slightly, whereas Sc doping exhibits similar behavior only up to x = 0.50. In comparison to the total DOS of ZrCoTi₆Si, it can be seen that, despite decreasing in the band gap width, the positions of the majority spin at the Fermi level are increased considerably. This position in ZrCoTi₆Si is in 0.5 eV that goes up to a range of 4 eV to 5 eV in the cases of alloys with Al and Fe doping, and it rises around 3 eV to 4 eV for alloys with Sc and Y doping. Although half-metals with larger gap signify more stability, higher position of the majority spin at the Fermi level represents greater spin-polarized current in real experiments [36]. Several studies investigated the Heusler alloys with large half-metallic gap [50–53]. Among them, Guo et al. reported large half-metallic gap for ZrFeVZ (Z = Al, Ga, In) quaternary Heusler alloys with 2.00 μᵣ total magnetic moment [52]. These alloys exhibit 0.348 eV, 0.428 eV and 0.323 eV half-metallic gaps in the minority spin band, respectively.

3.3. Effects of pressure on the magnetic and half-metallic properties
As the initial point, by calculating total energy as a function of lattice constant, the equilibrium lattice constants for all doped alloys are obtained. Based on the obtained values, it is found that the total energy E(V) as a function

Table 2. Total and atomic spin magnetic moments (in μB) for the doped alloys under the VCA.

| x   | [Zr(1−x)Y(1−x)]CoTi₆Si | ZrCo[Ti(1−x)Sc(x)]Si | ZrCo[Ti(1−x)Ge(x)]Si | ZrCo[Ti(1−x)Sc(x)]Si | ZrCo[Ti(1−x)Ge(x)]Si |
|-----|------------------------|----------------------|----------------------|----------------------|----------------------|
| 0.00| 0.474                  | 0.031                | 1.996                | 0.017                | 2.000                |
| 0.25| 0.365                  | 0.191                | 1.952                | 0.019                | 2.750                |
| 0.50| 0.274                  | 0.008                | 1.899                | 0.019                | 2.500                |
| 0.75| 0.209                  | 0.003                | 1.839                | 0.019                | 2.250                |
| 1.00| 0.157                  | 0.017                | 1.769                | 0.017                | 2.000                |

| x   | Zr[Co(1−xFex)]Ti₆Si | ZrCo[Ti(1−x)Sc(x)]Si | ZrCo[Ti(1−x)Ge(x)]Si |
|-----|---------------------|----------------------|----------------------|
| 0.00| 0.474               | 0.031                | 1.996                |
| 0.25| 0.365               | 0.191                | 1.952                |
| 0.50| 0.274               | 0.008                | 1.899                |
| 0.75| 0.209               | 0.003                | 1.839                |
| 1.00| 0.157               | 0.017                | 1.769                |
of the volume $V$ has a parabolic form as given in equation (2).

$$ E(V) = aV^2 + bV + c $$  \hspace{1cm} (2)

Determination of constants $a$, $b$ and $c$ from the total energy $E(V)$ results leads to equation (3) for the applying pressure.

$$ P = -\frac{dE(V)}{dV} = -(2aV + b) $$  \hspace{1cm} (3)

The volume changes due to increasing pressure are shown in figure 7 for ZrCoTi[$\text{Si} (1-x)\text{Al}(x)$] alloys. The maximum pressure under which the alloys preserve their half-metallicity are given in table 4, indicating that ZrCoTiSi remain half-metal up to 3.01 GPa with the total magnetic moment 3.00 $\mu_B$. For [Zr(1−x)Y(x)]CoTiSi and ZrCoTi[Si(1−x)Al(x)] alloys, by increasing the amounts of $x$ doping ($0 \leq x \leq 1$), half-metallic behaviors preserve under pressure up to 14.11 GPa and 17.61 GPa, respectively. However, in Zr[Co(1−x)Fe(x)]TiSi alloys with increasing $x$ doping of Fe atom, the ability to preserve half-metallic properties is decreased to 2.05 GPa under pressure. It is noteworthy that the total magnetic moments decrease gradually with respect to the Slater-Pauling rule, and they reach to 2.00 $\mu_B$ with full spin polarization in the cases of Y, Fe and Al doping. For Sc doping, the alloys are full spin polarized up to $x = 0.50$ concentration under pressure of 1.67 GPa. The ZrCo[Ti (1−x)Sc(x)]Si alloys having $x > 0.50$ are not in agreement with the Slater-Pauling rule, therefore they lose their half-metallic properties under pressure.

The variation of total magnetic moments under different pressures for doped alloys are presented in figure 8. It is observed that the magnetic moments of [Zr(1−x)Y(x)]CoTiSi and ZrCoTi[Si(1−x)Al(x)] alloys become less dependent on the pressure by increasing $x$ doping of Y and Al atoms. While for Fe doping, Zr[Co(1−x)Fe(x)]TiSi alloys become more sensitive to pressure. These alloys lose their half-metallicity under pressure up to 2.05 GPa.

Table 3. The values of (VBM), (CBM) and ($E_{\text{gap}}$) in eV of the minority spin under the VCA.

| $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 1 | $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 2 |
|---------|-------|-------|------------------|---------|-------|-------|------------------|
| 0.00    | -1.052| 0.251 | 1.303            | 0.00    | -1.052| 0.251 | 1.303            |
| 0.25    | 0.859 | 0.267 | 1.126            | 0.25    | 0.859 | 0.267 | 1.126            |
| 0.50    | -0.747| 0.311 | 1.058            | 0.50    | -0.747| 0.311 | 1.058            |
| 0.75    | -0.580| 0.306 | 0.886            | 0.75    | -0.580| 0.306 | 0.886            |
| 1.00    | -0.418| 0.277 | 0.695            | 1.00    | -0.418| 0.277 | 0.695            |

Figure 7. $V/V_0$ ratios as a function of pressure for ZrCoTi[$\text{Si} (1-x)\text{Al}(x)$] alloys.

Table 3.

| $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 1 | $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 2 |
|---------|-------|-------|------------------|---------|-------|-------|------------------|
| 0.00    | -1.036| 0.105 | 1.141            | 0.00    | -1.036| 0.105 | 1.141            |
| 0.25    | -1.055| 0.042 | 1.097            | 0.25    | -1.055| 0.042 | 1.097            |
| 0.50    | -1.139| -0.011| 1.150            | 0.50    | -1.139| -0.011| 1.150            |
| 0.75    | -1.178| -0.050| 1.128            | 0.75    | -1.178| -0.050| 1.128            |

| $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 1 | $x$     | VBM 1 | CBM 2 | $E_{\text{gap}}$ 2 |
|---------|-------|-------|------------------|---------|-------|-------|------------------|
| 0.25    | -1.036| 0.105 | 1.141            | 0.25    | -1.036| 0.105 | 1.141            |
| 0.50    | -1.055| 0.042 | 1.097            | 0.50    | -1.055| 0.042 | 1.097            |
| 0.75    | -1.139| -0.011| 1.150            | 0.75    | -1.139| -0.011| 1.150            |
| 1.00    | -1.178| -0.050| 1.128            | 1.00    | -1.178| -0.050| 1.128            |

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Table 4. The total and individual magnetic moments (in $\mu_B$) of studied half-metal alloys under calculated pressures.

| P(GPa) | $M_{tot}$ | $M_{Zr(1-x)Y(x)}$ | $M_{Co}$ | $M_{Ti}$ | $M_{Si}$ |
|--------|-----------|--------------------|----------|----------|----------|
| x = 0.00 | 3.01 | 0.474 | 0.498 | 1.996 | 0.031 |
| x = 0.25 | 8.76 | 2.750 | 0.289 | 0.462 | 1.902 | 0.095 |
| x = 0.50 | 9.69 | 2.500 | 0.200 | 0.388 | 1.825 | 0.085 |
| x = 0.75 | 12.94 | 2.250 | 0.115 | 0.343 | 1.697 | 0.094 |
| x = 1.00 | 14.11 | 2.000 | 0.064 | 0.287 | 1.564 | 0.083 |

| P(GPa) | $M_{tot}$ | $M_{ZrCo(1-x)Fe(x)}$ | $M_{Ti}$ | $M_{Si}$ |
|--------|-----------|----------------------|----------|----------|
| x = 0.25 | 5.40 | 2.750 | 0.306 | 0.530 | 1.849 | 0.063 |
| x = 0.50 | 5.14 | 2.500 | 0.205 | 0.538 | 1.709 | 0.047 |
| x = 0.75 | 2.23 | 2.250 | 0.164 | 0.480 | 1.589 | 0.016 |
| x = 1.00 | 2.05 | 2.000 | 0.147 | 0.364 | 1.478 | 0.008 |

| P(GPa) | $M_{tot}$ | $M_{ZrCoTi(1-x)Sc(x)}$ | $M_{Ti}$ | $M_{Si}$ |
|--------|-----------|----------------------|----------|----------|
| x = 0.25 | 3.42 | 2.750 | 0.429 | 0.553 | 1.682 | 0.084 |
| x = 0.50 | 1.67 | 2.500 | 0.427 | 0.610 | 1.372 | 0.089 |
| x = 0.75 | — | — | — | — | — | — |
| x = 1.00 | — | — | — | — | — | — |

| P(GPa) | $M_{tot}$ | $M_{ZrCoTi(1-x)Al(x)}$ | $M_{Ti}$ | $M_{Si}$ |
|--------|-----------|----------------------|----------|----------|
| x = 0.25 | 8.76 | 2.750 | 0.329 | 0.448 | 1.882 | 0.089 |
| x = 0.50 | 12.63 | 2.500 | 0.246 | 0.376 | 1.780 | 0.095 |
| x = 0.75 | 13.95 | 2.250 | 0.203 | 0.294 | 1.675 | 0.075 |
| x = 1.00 | 17.61 | 2.000 | 0.152 | 0.234 | 1.543 | 0.069 |
in comparison to initial ZrCoTiSi, which preserves its half-metallicity up to 3.01 GPa. In the case of Sc doping, the pressure effect is different from the other alloys due to preserving half-metallicity only up to $x = 0.50$ at 1.67 GPa. Rasul et al. investigated the physical properties of ScNiCrX ($X = \text{Al, Ga}$) Heusler alloys under different pressures [54]. It is observed that the ScNiCrAl remains half-metal up to 6 GPa with full spin polarization at Fermi level, while the ScNiCrGa loses its half-metallic properties for higher pressures than 16 GPa. Similarly, Enamullah et al. studied the effect of pressure on CoMnCrAl and CoFeCrGe Heusler alloys [55]. They found that the former is sensitive to pressure because the alloy experiences transition from half-metal to metal state by applying 10.7 GPa pressure through 2 to 3 percent reduction in equilibrium lattice constant, whereas the latter shows more robustness under pressure since the transition occurs at 54.1 GPa.

It is observed that the resistant against pressure is increasing with doping in [Zr(1$-x$)Y($x$)]CoTiSi and ZrCoTi[$(1-x)$]Al($x$)], while it is decreasing in Zr[Co(1$-x$)Fe($x$)]TiSi and ZrCo[Ti(1$-x$)Sc($x$)]Si alloys. This opposite behavior depends mainly upon the differences in density of states of these doped alloys, as shown in figure 5. The Fermi levels of the former alloys are nearly at the middle of band gap in the minority spin, while the Fermi levels of the latter ones are close to the edge of the conductive bands of minority spin states.

The effects of applying various pressures on the electronic properties of the considered doped Heusler alloys are shown in figure 9. The results are for no pressure, the maximum pressure keeping the half-metallic feature and a high pressure losing half-metallicity. It can be seen that by increasing pressure, both majority and minority bands are shifted toward the Fermi level and their half-metallic properties begin to disappear. The undoped ZrCoTiSi under higher applied pressure than 3.01 GPa acts differently from half-metals. It can be found that the ZrCoTiAl and YCoTiSi alloys are more resistant against pressure by keeping full spin polarization under pressure up to 17.61 GPa and 14.11 GPa, respectively. ZrFeTiSi preserves the half-metallic electronic structure of DOS up to 2.05 GPa, and for higher pressure the gap in minority spin is disappeared at the Fermi level.

4. Conclusions

The electronic and magnetic properties of the quaternary Heusler alloys of types [Zr$(1-x)$Y($x$)]CoTiSi, Zr[Co$(1-x)$Fe($x$)]TiSi, ZrCo[Ti$(1-x)$Sc($x$)]Si and ZrCo[TiSi$(1-x)$Al($x$)] are studied with different concentrations of $x$ ($0 \leq x \leq 1$) doping under various pressures in the framework of the density functional theory. The virtual
crystal approximation (VCA) approach is used in this study. Based on this study, it is found that the ZrCoTiSi quaternary Heusler alloy follows the Slater–Pauling rule $M_z = Z_{\text{eff}} - 18$ with 3.00 $\mu_B$ total magnetic moment and 1.303 eV minority spin states band gap. As a consequence of the large band gap, this alloy is a robust half-metallic ferromagnet, and it can be a promising candidate for spintronic applications. It is shown that the Zr(1$-$x)Y(x)CoTiSi, ZrCo(1$-$x)Fe(x)TiSi and ZrCoTi(Si(1$-$x)Al(x)) alloys are half-metal ferromagnet for all x concentrations. However, ZrCo(Ti(1$-$x)Sc(x))Si alloys remain half-metal only up to equal concentration of Ti and Sc in $x = 0.50$. Following the Slater–Pauling rule, the total magnetic moments of doped alloys decrease and reach from 3.00 $\mu_B$ to 2.00 $\mu_B$ in the case of Y, Fe and Al doping for all x concentrations. In addition, it is found that although the band gap widths become narrower as the x concentration increases, the amounts of majority spin states at the Fermi level are increased. Furthermore, the effects of pressure on electronic and magnetic properties of the doped Heusler alloys are studied. It is found that $[\text{Zr}(1-x)Y(x)\text{CoTiSi}]$ and $[\text{ZrCoTiSi}(1-x)\text{Al}(x)]$ alloys become more resistant against pressure by increasing amounts of x doping of Y and Al atoms. In contrast, in $\text{ZrCo(1-x)Fe(x)TiSi}$ alloys the resistance against pressure is decreased by increasing x doping of Fe atom. In the case of Sc doping, $\text{ZrCo(Ti(1-x)Sc(x))Si}$ alloys preserve their half-metallicity up to $x = 0.50$ with the endurance less pressure compared to the initial state $\text{ZrCoTiSi}$, and for $x > 0.50$ they lose their half-metallic properties. It is shown that it is possible to control the electronic and magnetic properties of ZrCoTiSi-type quaternary Heusler alloys by suitable doping. At the same time, the resistance of doped alloys under pressures can be assessed. These theoretical results may be useful references for experimentalists in this field.

**ORCID iDs**

Nasrin Estaji @ https://orcid.org/0000-0001-6138-7534
Mahdi Afshar @ https://orcid.org/0000-0002-5886-3787

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