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# Electronic structure and half-metallicity of the new Heusler alloys PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}ZrTiAl$

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ABSTRACT

The electronic structure and magnetic properties of the PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}ZrTiAl$ Heusler alloys were investigated using the full-potential linearized augmented plane wave (FPLAPW) within the generalized gradient approximation (GGA). For the PtZrTiAl, and PdZrTiAl alloys, the results showed that these Heusler alloys were stable in the Type I structure. The (Pt, Pd)ZrTiAl Heusler alloys are found to exhibit half-metallic ferromagnetism for both the Type I and Type II structure. The total magnetic moments of the PtZrTiAl and PdZrTiAl alloys were obtained to be 3 $\mu_B$ per formula unit, which are in agreement with the Slater-Pauling rule $m_{tot} = (Nv - 18)$. The half-metalliciy characteristic exists in the relatively wide ranges of 6.06–6.78 Å, and 6.13–6.73 Å for the PtZrTiAl and PdZrTiAl alloys, respectively. To complete the fundamental characteristics of these alloys, $Pt_{0.5}Pd_{0.5}ZrTiAl$ is predicted to be a half-metallic ferromagnet with an energy gap of 0.90 eV in the minority spin and a complete spin polarization at the Fermi level. These new Heusler alloys may become ideal candidate material for future spintronic applications.



## 1. Introduction

Half-metallic ferri- and ferromagnet materials have potential applications as spin polarized current sources for current perpendicular to the plane of giant magnetoresistance [1–3], non-local spin-valve devices [4,5], spin injectors to semiconductors [6], and magnetic tunnel junctions [7,8].

Heusler compounds have been extensively studied, motivated by their increasing importance due to advancements in spintronics [9–13]. These materials behave like metals with respect to the electrons of one spin direction and like semiconductors (or insulators) with respect to the electrons of the other spin direction. The first material which was predicted to be a half-ferromagnet was the half-Heusler alloy NiMnSb found by de Groot and collaborators [14] in 1983.

Many quaternary Heusler compounds are found to possess the half-metallic band structure, as revealed by the ab-initio calculations [15–21]. Rasool et al. [22] calculated the structural, magnetic, and electronic properties of YCoCrZ (Z = Si, Ge, Ga, Al) using the full-potential linearized augmented plane wave (FPLAPW) scheme within the GGA. The electronic structure calculations predicted a HMF band structure for YCoCrZ (Z = Si, Ge, Ga, Al), with half-metallic gaps of 0.70, 0.65, 0.46 and 0.35 eV for YCoCrSi, Ge, Ga and Al, respectively. The calculated total magnetic moment 4.00 $\mu_B$ and 3.00 $\mu_B$ for YCoCrSi, Ge and YCoCrGa, Al respectively were found to agree with the Slater-Pauling rule [23–25]. Wang et al. [26] and Liu et al. [27] also predicted that ZrVTi(Al, Ga) and ZrTiCr( Al, Ga and In) quaternary Heusler compounds were HM ferromagnets. Xie

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**Table 1**
Three non-equivalent structure type configurations.

| | 4a(0,0,0) | 4c(1/4,1/4,1/4) | 4b(1/2,1/2,1/2) | 4d(3/4,3/4,3/4) |
|---|---|---|---|---|
| Type I | Al | Ti | Zr | Pt/Pd |
| Type II | Al | Zr | Ti | Pt/Pd |
| Type III | Zr | Al | Ti | Pt/Pd |

et al. [28] calculated the magnetic and electronic structure of ZrMnVZ and ZrCoFeZ (Z = Si, Ge) using the full-potential local-orbital (FPLO) minimum-basis band-structure method within the GGA. The electronic structure calculations predicted a HMF band structure for ZrMnVZ and ZrCoFeZ (Z = Si, Ge), with half-metallic gaps of 0.14, 0.18 and 0.22 eV for ZrMnVSi, ZrMnVGe and ZrCoFeSi, respectively. Very recently, Wang et al. [29,30] with his colleague have studied the ZrFeVGe, ZrFeCrIn, ZrCoCrBe, ZrCoVIn alloys, which exhibited spin-gapless semiconductor characteristics in their electronic structures based on first-principles calculation.

The Zr-based quaternary Heusler alloys, ZrCoTiZ(Z = Si, Ge, Ga and Al), ZrFeTiZ (Z = Al, Si and Ge) and ZrNiTiAl have been reported to be HMF very recently [16,17]. This is the first prediction of HMF in the 4d transition metal elements for Heusler alloys.

Generally the PtZrTiAl and PdZrTiAl quaternary Heusler alloys crystallize in the LiMgPdSn-type crystal structure [31,32]. The resulting structure has F-43 m symmetry. The atomic coordinates for the PtZrTiAl and PdZrTiAl alloys are listed in Table 1. It is known that PtZrTiAl and PdZrTiAl crystallize in the LiMgPdSn-type structure with three non-equivalent type structures. The calculations were based on the supercell (i.e.,$1 \times 1 \times 1$) where two Pt atoms at (0.75, 0.25, 0.25) and (0.25, 0.25, 0.75) are replaced by Pd atoms.

However, studies on the PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}$ZrTiAl Heusler alloys are not explored well in the existing literature. This motivates us to investigate the electronic, magnetic and mechanical properties of these alloys by performing the band structure calculations using the FP-LAPW method for the PBE-GGA exchange correlation potentials.

## 2. Method of calculations

Full-relativistic calculations of the electronic structure of PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}$ZrTiAl are performed within the spin-polarised density functional theory [33] using the abinitio full-potential linearized augmented plane wave method [34] as implemented in the WIEN2K code by Blaha et al. [35]. In its general form the LAPW method expands the potential in the following form:

$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(r) & inside\, sphere, \\ \sum_{K} V_K e^{iK.r} & outside\ sphere. \end{cases} \quad (1)$$

The Kohn–Sham equations are solved self-consistently using the full-potential linearized augmented plane wave method. In the interstitial region, the plane wave cut-off value was imposed by the condition $R_{MT}K_{max} = 8$, where $K_{max}$ is the plane wave cut-off and $R_{MT}$ is the smallest of all atomic sphere radii. The radii $R_{MT}$ of the muffin tins (MT) are chosen to be approximately proportional to the corresponding ionic radii. Exchange-correlation effects are treated using the GGA as parameterized by Perdew et al. [36]. Self-consistent calculations are considered to be converged when the total energy of the system is stable within $10^{-4}$ *Ry*. The convergence criteria for total energy and force are taken as $10^{-5}$ and $10^{-4}$ eV/Å, respectively. The valence wave functions inside the spheres are expanded up to $l_{max} = 10$, while the charge density was Fourier expanded up to $G_{max} = 12$. The Monkorst-Pack special k-points were performed using 3000 and 1000 special k-points in the Brillouin zone for (Pt,Pd)ZrTiAl and $Pt_{0.5}Pd_{0.5}$ZrTiAl, respectively.

## 3. Results and discussion

As the first step, the total energy versus cell volume calculations were carried out the (Pt, Pd)ZrTiAl alloys in the ferromagnetic (FM) state (Fig. 1). The results indicate that (Pt,Pd)ZrTiAl in the Type-I structure is more stable than in the Type II and Type III structure. Table 2 presents the calculated equilibrium lattice constants for the (Pt, Pd)ZrTiAl quaternary Heusler alloys that are determined by fitting the total energy as a function of volume to the Murnaghan equation of state [37]. Until now, experimental or theoretical lattice parameters, the bulk modulus and its pressure derivative value have not been reported. Table 2 includes these and it also includes the bulk modulus and its pressure derivative *B'* data for CoMnCrSb [19] and CoFeMnSi [38] for comparison purpose.

The following equation defines the formation energy ($E_f$) for PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}$ZrTiAl and determines the thermal stability of the compounds

$$E_f = E^{Tot}_{(Pt,Pd)ZrTiAl} - \left[E^{bulk}_{(Pt,Pd)} + E^{bulk}_{Zr} + E^{bulk}_{Ti} + E^{bulk}_{Al}\right], \quad (2)$$

where $E^{tot}{}_{PtZrTiAl}$, $E^{tot}{}_{PdZrTiAl}$ and $E^{tot}{}_{Pt0.5Pd0.5ZrTiAl}$ are the equilibrium total energy calculated by first principles of the PtZrTiAl, PdZrTiAl and $Pt_{0.5}Pd_{0.5}$ZrTiAl alloys per formula unit and $E^{tot}{}_{Pt}$, $E^{tot}{}_{Pd}$, $E^{tot}{}_{Zr}$, $E^{tot}{}_{Ti}$ and $E^{tot}{}_{Al}$ correspond to the total energy

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