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Theoretical Investigations of Electronic Structures, Magnetic Properties and Half-metallicity in Heusler Alloys Zr_2VZ (Z = Al, Ga, In)

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The electronic structures, magnetic properties and half-metallicity of Zr_2VZ (Z = Al, Ga, In) bulk materials were investigated through first-principles calculations. Band structure calculations showed that Zr_2VZ (Z = Al, Ga, In) alloys with an $AlCu_2Mn$-type structure were conventional ferrimagnents. However, Zr_2VZ (Z = Al, Ga, In) alloys with a $CuHg_2Ti$-type structure were predicted to be half-metallic ferrimagnets that were quite robust against hydrostatic strain and tetragonal deformation. The total magnetic moment of the Zr_2VZ (Z = Al, Ga, In) alloys with a $CuHg_2Ti$-type structure was 2 μ_B per formula unit and followed the conventional Slater-Pauling rule: $M_t = 18 - Z_t$. (M_t is the total magnetic moment per unit cell and Z_t is the valence concentration) Furthermore, the origin of the band gap in the Zr_2VZ (Z = Al, Ga, In) alloys was also well studied. All of these results indicate that these alloys, when they are successfully prepared, are good candidates for practical applications in spintronics.

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I. INTRODUCTION

A new trend is to use the electron spin in future electronic devices. Half-metallic materials exhibit a 100% spin polarization around the Fermi surface [1], and the considerable difference in the bands of half-metallic materials for both spin channels make them very promising in many aspects (such as tunneling magnetoresistance, spin-injection, spin-manipulation and so on) [1–5]. Since the first half-metallic (HM) magnet NiMnSb, a half-Heusler alloy, was predicted by de Groot *et al.* in 1983 [1], many alloys have been predicted to be half-metallic materials. In fact, till now, investigations and searches for new HM materials have mainly focused on the Heusler alloys because they are likely to have a high Curie temperature T_c, and structural compatibility with the wide-band-gap semiconductors used in spintronic industry.

Previous investigations of half-metallicity focused mainly on the Heuser alloys containing two transition metals of group VIIB, group VIIIA or Cu [6–10]. However, we note that few reports exist on Heusler alloys containing two or three low-valence transition metals, especially Zr. Based on our knowledge, the Zr_2CoZ (Z = Al, Ga, In, Si) and Zr_2RhZ (Z = Al, Ga, In) alloys were investigated only by Birsan [11], Birsan and Kuncser [12], Yan *et al.* [13] and Wang *et al.* [14]. They predicted by using first-principle calculations that the Zr_2CoZ (Z = Al, Ga, In, Si) and the Zr_2RhZ (Z = Al, Ga, In) alloys should be half-metallic materials. Recently, based on ab initio calculations, quaternary Heusler alloys ZrCoFeSi, ZrMnVSi and ZrMnVGe were reported to have robust HM properties [15, 16]. Thus, Zr-based Heusler alloys deserve further exploration.

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Table 1. Valence-band maximum (VBM), conduction-band minimum (CBM), size of the gap (Gap) and of the half-metal gap (HM Gap), the formation energy (E_f), and the lattice constant (a) of Zr_2VZ (Z = Al, Ga, In) alloys with both $AlCu_2Mn$ and $CuHg_2Ti$-type structures at their equilibrium lattice constants.

Zr_2VZ	Structure	a (Å)	VBM (eV)	CBM (eV)	Gap (eV)	HM Gap (eV)	E_f (eV)
Zr_2VAl	$AlCu_2Mn$	6.73	-	-	-	-	−0.12
	$CuHg_2Ti$	6.71	−0.217	0.4868	0.703	0.217	−0.09
Zr_2VGa	$AlCu_2Mn$	6.68	-	-	-	-	−0.06
	$CuHg_2Ti$	6.68	−0.216	0.5598	0.77	0.216	−0.05
Zr_2VIn	$AlCu_2Mn$	6.68	-	-	-	-	−0.04
	$CuHg_2Ti$	6.90	−0.217	0.60	0.82	0.217	−0.02

Table 2. Calculated molecular and atomic magnetic moments (M) for the Zr_2VZ (Z = Al, Ga, In) alloys with both $AlCu_2Mn$ and $CuHg_2Ti$-type structures at their equilibrium lattice constants.

Zr_2VZ	Structure	M_{total} (μ_B)	M_{Zr} (μ_B)	M_V (μ_B)	M_Z (μ_B)
Zr_2VAl	$AlCu_2Mn$	1.79	Zr(A) = −0.3 Zr(C) = −0.3	2.52	−0.12
	$CuHg_2Ti$	2	Zr(A) = −0.78 Zr(B) = 0.04	2.84	−0.08
Zr_2VGa	$AlCu_2Mn$	1.73	Zr(A) = −0.24 Zr(C) = −0.24	1.73	−0.14
	$CuHg_2Ti$	2	Zr(A) = −0.70 Zr(B) = 0.04	2.78	−0.12
Zr_2VIn	$AlCu_2Mn$	1.62	Zr(A) = −0.20 Zr(C) = −0.20	2.16	−0.14
	$CuHg_2Ti$	2	Zr(A) = −0.90 Zr(B) = −0.12	3.12	−0.10

In this work, a series of new full-Heusler Zr-based alloys with both $AlCu_2Mn$ and $CuHg_2Ti$-type structures, Zr_2VZ (Z = Al, Ga, In), were theoretically investigated by using first-principles calculations. To our best knowledge, studies on the electronic structures, magnetic properties and half-metallicity of these alloys have not been done by others, and the lack of experimental results is due to difficulties in synthesizing stoichiometric compositions. However, theoretical studies are still desirable and helpful for enlarging the scope of HM Heusler alloys.

II. COMPUTATIONAL DETAILS

The CASTEP code was used to calculate the electronic structures, magnetism and the total energy. The CASTEP code is based on the density functional theory (DFT) plane-wave pseudo-potential method [17, 18]. In this calculation, an ultrasoft pseudo-potential [19] was used to describe the interactions between the valence electrons and the atomic core, and the exchange-correlation potential was dealt with by using the generalized-gradient approximation (GGA) in the of Perdew - Burke - Ernzerh (PBE) scheme [20, 21]. The cut-off energy of the plane wave basis set was 450 eV for all of the cases, and a mesh of 12 × 12 × 12 k-points in the full Brillouin zone was employed. The calculations continued to ensure good convergence until the energy deviation was less than 0.00001 eV/atom.

III. RESULTS AND DISCUSSION

From the composition point of view, Heusler alloys are intermetallic compounds with a highly-ordered atomic arrangement and consist of four face-centered cubic sublattices interpenetrating along the space diagonal. There are two kinds of highly-ordered atomic arrangements for the alloys: $AlCu_2Mn$ - and $CuHg_2Ti$-type structures. In the $AlCu_2Mn$-type structure, the atomic sites are shown as follows in Wyckoff coordinates: Zr (A) (0, 0, 0), V (B) (0.25, 0.25, 0.25), Zr (C) (0.5, 0.5, 0.5) and Z (D) (0.75, 0.75, 0.75); in the $CuHg_2Ti$-type structure, they are Zr

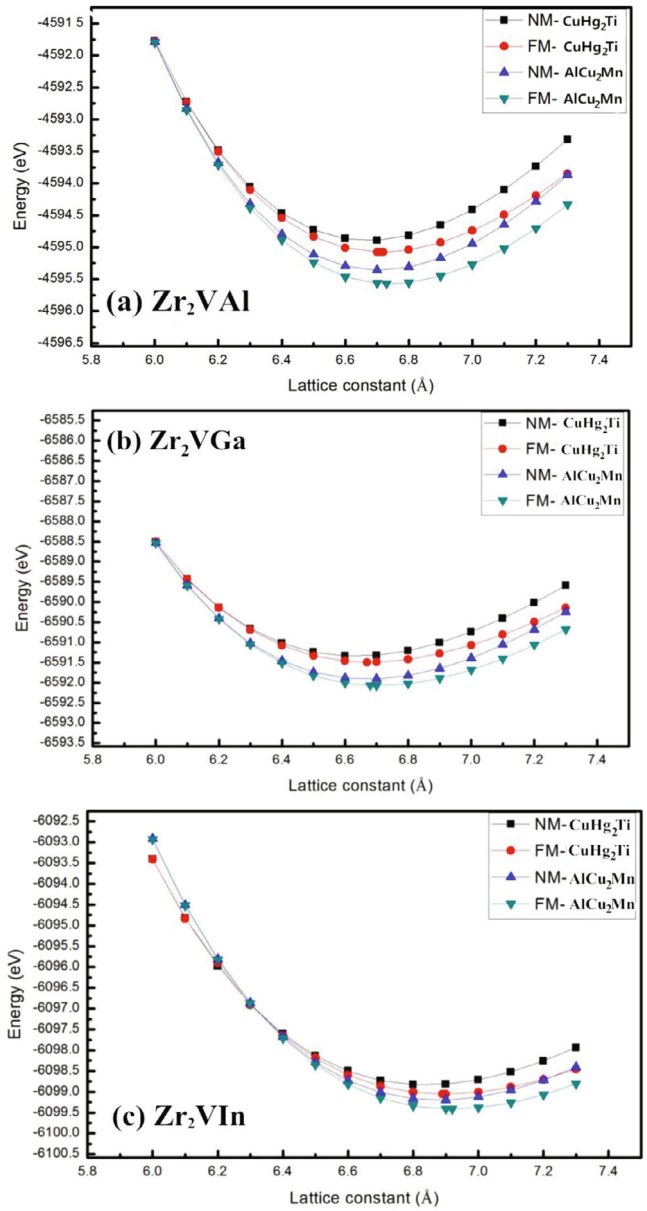

Fig. 1. (Color online) Total energy as a function of the lattice constant for the Zr_2VZ (Z = Al, Ga, In) alloys with $AlCu_2Mn$ and $CuHg_2Ti$-type structures in both FM and NM states: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

(A) (0, 0, 0), Zr (B) (0.25, 0.25, 0.25), V (C) (0.5, 0.5, 0.5) and Z (D) (0.75, 0.75, 0.75).

To perform structural optimizations, we first calculate the total energy of the Zr_2VZ (Z = Al, Ga, In) alloys as a function of the lattice constant for both $AlCu_2Mn$ and $CuHg_2Ti$-type structures in two different magnetic configurations: ferromagnetic (FM) and nonmagnetic (NM). The total energy-lattice constant curves for the Zr_2VZ (Z = Al, Ga, In) alloys are shown in Figs. 1(a), (b), and (c), respectively. We can see the AlCu2Mn-type structure in the FM state is energetically the most stable structure at the equilibrium lattice constant for these three alloys. The achieved equilibrium lattice constants are also shown in Table 1, *i.e.*, 6.71 Å, 6.68 Å and 6.90 Å, respectively, for Zr_2VAl, Zr_2VGa, and Zr_2VIn.

We note that not all of Heusler alloys can be synthesized and form stable phases. In order to demonstrate that the Zr_2VZ (Z = Al, Ga, In) alloys with $AlCu_2Mn$- and $CuHg_2Ti$-type structures could be synthesized with stable phases, we calculated the formation energy E_f by subtracting the sum of equilibrium total energies for the constituent elements from the equilibrium total energies of corresponding alloys under current study by using the formula [22]: $E_f = (E_{tol} - 2E_{Zr} - E_V - E_Z)$. We find that the E_f of the Zr_2VZ (Z = Al, Ga, In) alloys are −0.12 eV for Zr_2VAl with the $AlCu_2Mn$-type structure, −0.09 eV for Zr_2VAl with the $CuHg_2Ti$-type structure, −0.06 eV for Zr_2VGa with the $AlCu_2Mn$-type structure, −0.05 eV for Zr_2VGa with the $CuHg_2Ti$-type structure, −0.04 eV for Zr_2VIn with the $AlCu_2Mn$-type structure and −0.02 eV for Zr_2VIn with the $CuHg_2Ti$-type structure. The calculated formation energies turn out to be negative, and their values are comparable to these for the same kinds of compounds [23]. A negative formation energy indicates that these alloys can easily be synthesized in both structures.

The calculated total (M_t) and atomic magnetic moments at equilibrium lattice constants for Zr_2VZ (Z = Al, Ga, In) alloys in both the $CuHg_2Ti$ and the $AlCu_2Mn$-type structures are given in Table 2. Zr_2VZ (Z = Al, Ga, In) alloys in the $CuHg_2Ti$-type structure have integer magnetic moments of 2 μ_B while the total magnetic moments of Zr_2VZ (Z = Al, Ga, In) alloys in the $AlCu_2Mn$-type structure are 1.79 μ_B, 1.73 μ_B, and 1.62 μ_B, respectively. As we know, an integer value of the total magnetic moment is characteristic of half-metallic materials. Thus, the non-integer values of M_t for Zr_2VZ (Z = Al, Ga, In) in the $AlCu_2Mn$-type structure show that they are not half-metallic materials at the equilibrium lattice constant. Furthermore, the total magnetic moments M_t of Zr_2VZ (Z = Al, Ga, In) alloys in the $CuHg_2Ti$-type structure have a linear relationship to the number of valence electrons Z_t, $M_t = 18 - Z_t$, which is similar to some Ti_2-based and Sc_2-based alloys [24–26]. The atomic magnetic moment of Zr (A) / Zr (B) are −0.78 μ_B / 0.04 μ_B, −0.70 μ_B / 0.04 μ_B, and −0.90 μ_B / −0.12 μ_B for Zr_2VZ (Z = Al, Ga, In), respectively, and the atomic magnetic moments of V are, respectively, 2.84 μ_B, 2.78 μ_B, and 3.12 μ_B. The atomic magnetic moments of Zr (A) and Zr (B) are different from each other, indicating different atomic environments, and the atomic magnetic moment of V is antiparallel to that of the Zr (A) or the Zr (B) atom, so Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure are HM ferrimagnets. In Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure, the atomic magnetic moments of the Z atoms are very small (see Table 2) and only make a small contribution to the total spin moment. Also, the main contribution to Mt comes from the V (C) atom in these three alloys due to a large exchange splitting be-

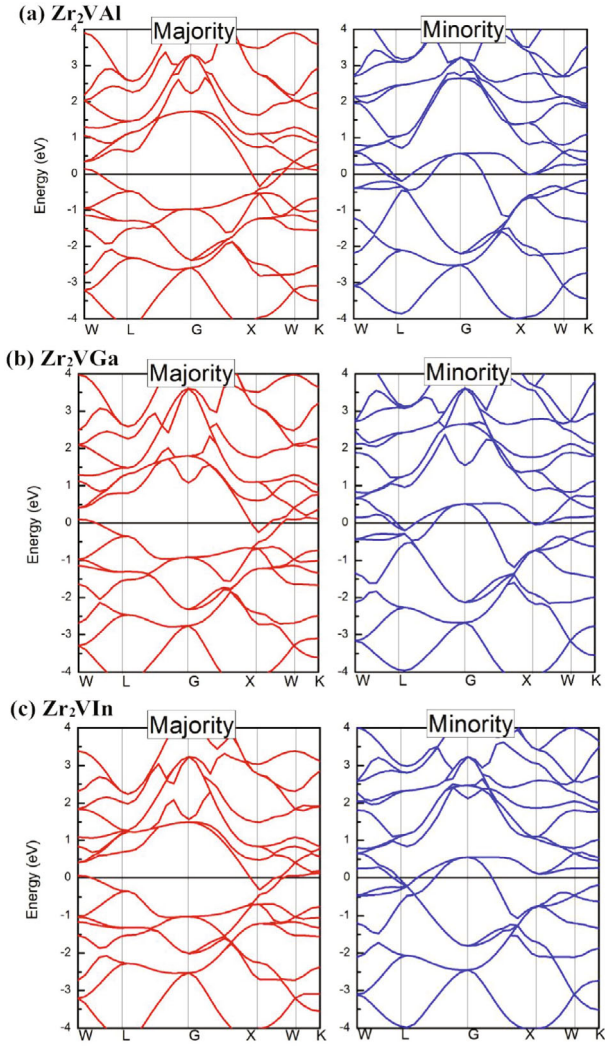

Fig. 2. (Color online) Band structures for Zr_2VZ (Z = Al, Ga, In) alloys with the $AlCu_2Mn$-type structure at their equilibrium lattice constants: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

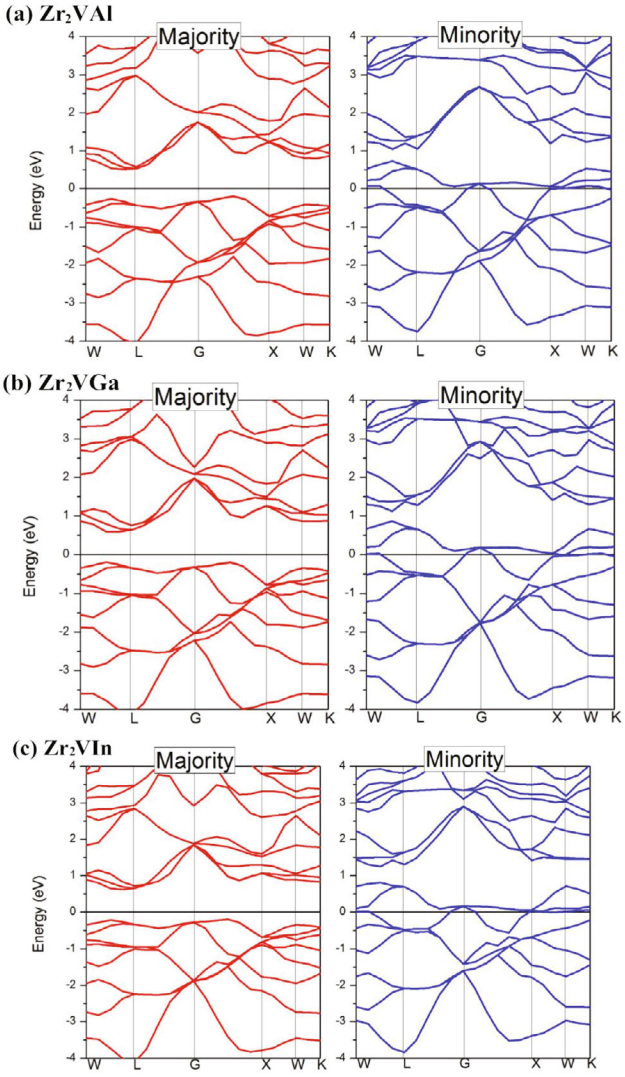

Fig. 3. (Color online) Band structures for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure at their equilibrium lattice constants: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

tween the spin-up and the spin-down channel states of V (C) atoms.

The calculated band structures of Zr_2VZ (Z = Al, Ga, In) alloys for the spin-up channel and the spin-down channel are shown in Fig. 2 for the $AlCu_2Mn$-type structures and in Fig. 3 for the $CuHg_2Ti$-type structures. We can see that in the $AlCu_2Mn$-type structure, the Fermi level crosses energy bands in both spin channels. The density of energy bands near the Fermi level in the spin-down channel is higher than it is in the spin-up channel. This means that the Zr_2VZ (Z = Al, Ga, In) alloys in the $AlCu_2Mn$-type structure are conventional ferrimagnets [23]. However, the Zr_2VZ (Z = Al, Ga, In) alloys in the $CuHg_2Ti$-type structure are half-metals. In detail, in the spin-down direction, the energy bands show a metallic overlap with the Fermi level while in the spin-up direction, an indirect energy gap is opened around the Fermi level. According to Fig. 3, the energy bands in the spin-down channel state are very similar to those in the spin-up channel state, but they are slightly shifted toward higher energies. The splitting exchange effect in the spin-down channel state shifts the energy bands toward the Fermi level and causes the bonding states to cross the Fermi level.

Further calculations mainly focus on the Zr_2VZ (Z = Al, Ga, In) alloys in the $CuHg_2Ti$-type structure. For these three alloys, there is a band gap at the Fermi level in the spin-up channel, which is known as the spin-up band gap. The spin-up band gap is a significant factor in half-metallic materials. The spin-up band gap is calculated by using the highest occupied and the lowest unoccupied bands in the spin-up channel. The results show that the spin-up band gaps of these alloys are quite large

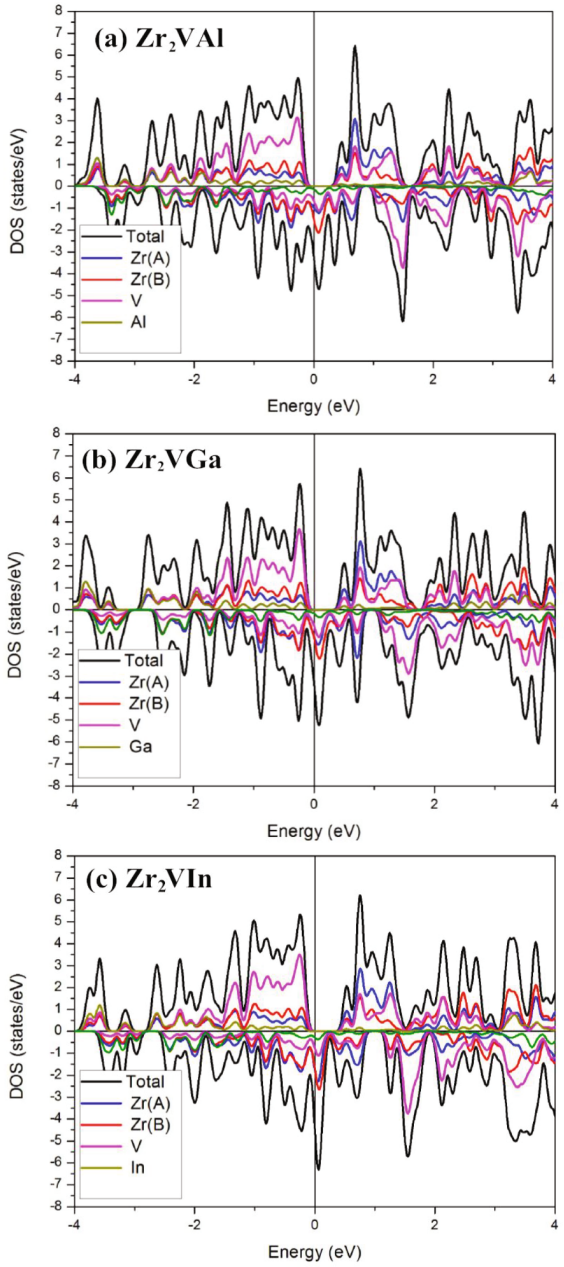

Fig. 4. (Color online) Calculated total and atom-projected DOSs for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure at their equilibrium lattice constants: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

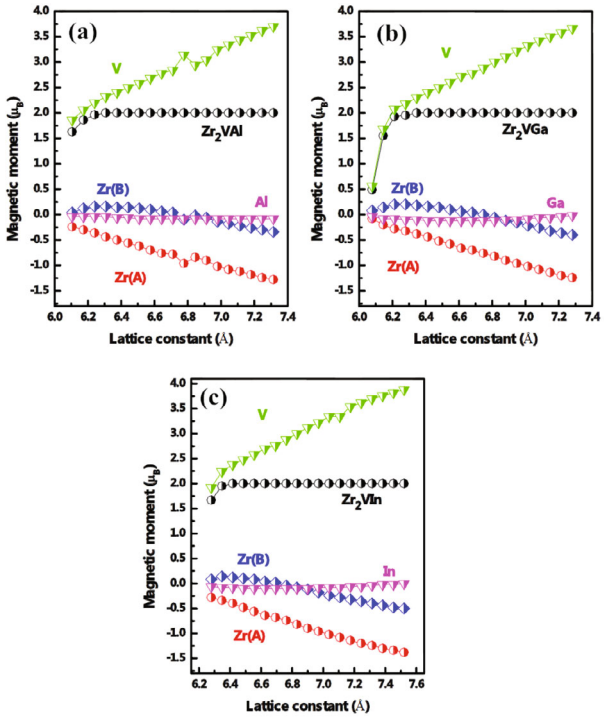

Fig. 5. (Color online) Total and site-projected magnetic moments as functions of the lattice constant for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

and are 0.703 eV, 0.77 eV, and 0.82 eV for Zr_2VZ (Z = Al, Ga, In), respectively. Moreover, the spin-flip gap (HM gap), which is the minimum energy required to flip a minority-spin electron from the valence band maximum edge to the majority-spin Fermi level, is another important parameter for half-metallic materials. The HM gaps of Zr_2VZ (Z = Al, Ga, In) alloys are 0.217 eV, 0.216 eV, and 0.217 eV, respectively. The non-zero HM gaps suggest that these three alloys are true HM materials. Figure 4 presents the spin-polarized total densities of states (DOSs) and atom-projected DOSs of Zr_2VZ (Z = Al, Ga, In) alloys at their equilibrium lattice constants. We treat the spin-up and the spin-down channels for these alloys as positive and negative, respectively. We can see that the main contributions in the energy regions between −4 eV and −2 eV come from the Z-p state and that slight contributions come from the Zr-4d and the V-3d states. The energy range from −2 eV to 4 eV includes mostly Zr-4d and V-4d states.

Here, the origin of the half-metallic band gap for these three alloys with the $CuHg_2Ti$-type structure will be discussed. In this part, we will focus on the origin of the band gap in the spin-up channel. Such a band gap is a very important feature of a half metal. As explained in Refs. 24, 27, and 28, firstly, we start with a discussion of the possible d-d hybridizations between the transition-metal atoms for the Zr_2VZ (Z = Al, Ga, In) inverse Heusler alloys. Based on the classical molecular orbital approach, we consider the hybridization between the Zr (A)-4d state and the V (C)-3d state within octahedral symmetry. The Zr (A)-V (C) bonding gives five bonding d hybrids ($2 \times e_g$ and $3 \times t_{2g}$) and five non-bonding d hybrids ($3 \times t_u$ and $2 \times e_u$) below and above the Fermi level, respectively. Then, the resulting five bonding d hybrids ($2 \times e_g$ and $3 \times t_{2g}$) in their turn hybridize with the orbitals of the Zr (B)-4d orbitals, forming again five bounding d hybrids ($2 \times e_g$ and $3 \times t_{2g}$) and five non-bonding d hybrids ($3 \times e_g$ and $2 \times t_{2g}$) below and above

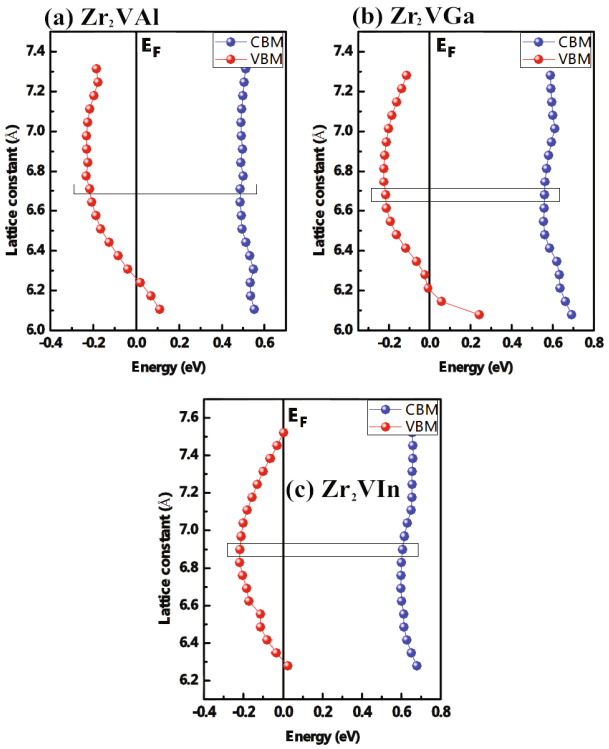

Fig. 6. (Color online) CBM and VBM of the spin-down band as functions of the lattice constant for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

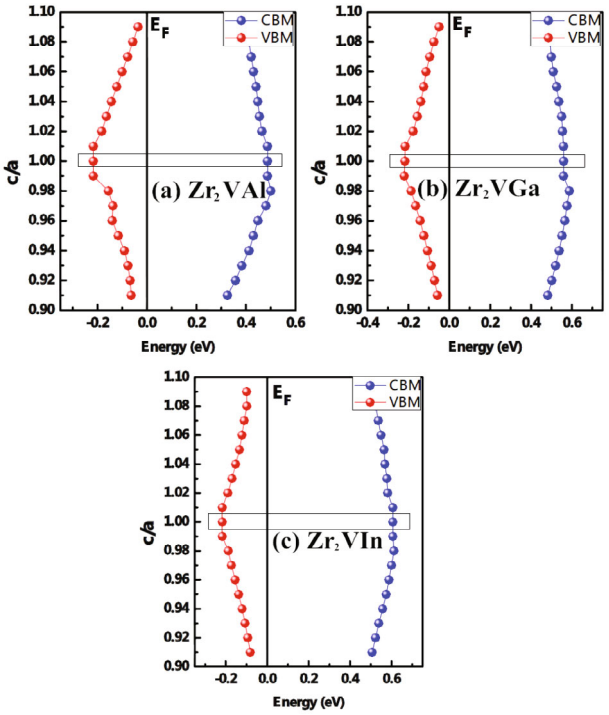

Fig. 7. (Color online) CBM and VBM of the spin-down band as functions of the c/a ratio for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

the Fermi level, respectively. Hence, the Fermi level is located in the spin-up channel band gap between the Γ_{15} and the Γ_{25} bands corresponding to the t_{1u} and the t_{2g} states, as shown in Fig. 3. Thus, during our current work, the d-d band gap was found in the spin-up channel of these three alloys.

To illustrate how the atomic magnetic moments change when the lattice constants is changed, we calculated the atomic magnetic moments of Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure. The relationship between the atomic magnetic moment and the lattice constant is shown in Fig. 5. In the $CuHg_2Ti$-type structure, an integer vaule of M_t can be maintained over a wide range of lattice constants. With decreasing lattice constant, M_t decreases to values lower than 2 μ_B, and half-metallicty breaks. Furthermore, the atomic magnetic moments of the Zr (A), Zr (B) and V (C) atoms are all quite sensitive to lattice distortion. With decreasing pressure, the atomic magnetic moment of the V (C) atom increases while the atomic magnetic moments of the Zr (A) and the Zr (B) atoms decrease, which results in a fixed M_t in a unit cell. Also, the negative magnetic moments of the Zr (A) and the Zr (B) atoms and the positive magnetic moment of the V (C) atom confirm a ferrimagnetic arrangement of Zr_2VZ (Z = Al, Ga, In) with a $CuHg_2Ti$-type structure, as observed in some Heusler alloys [29]. When we extend the lattice constant, which means that we have decreased the hybridization between neighboring atoms, as well as increased their atomic-like property and accordingly reinforced their spin moments.

To discuss the stability of the half-metallicity for changes in the lattice parameter, we calculated the electronic structures at different lattice constants for Zr_2VZ (Z = Al, Ga, In) alloys with a $CuHg_2Ti$-type structure. The valence band maximum (VBM) and the conduction band minimum (CBM) in the spin-up direction were used to represent the half-metallic property due to their electronic structures, except for the band gap, being quite similar for different lattice constants. The CBM and the VBM as functions of the lattice constant are shown in Fig. 6. From Fig. 6, we can see that half-metallicity is maintained in the ranges of $6.30 - 7.31$ Å for Zr_2VAl, $6.34 - 7.28$ Å for Zr_2VGa, and $6.41 - 7.52$ Å for Zr_2VIn, which means Zr_2VZ (Z = Al, Ga, In) alloys can maintain their half-metallicity when their lattice constants are changed by -6% to 9%, -5% to 9%, and -7% to 9% relative to the equilibrium lattice constants for Zr_2VAl, Zr_2VGa, and Zr_2VIn, respectively.

As we known, the growth of thin-film materials is an important technique in practical applications in which tetragonal deformation is most likely to occur because films tends to adjust their in-plane lattice constants to the substrate while changing the out-of-plane lattice constant to keep the volume of the unit cell almost the same as that for the equilibrium bulk lattice constant. For

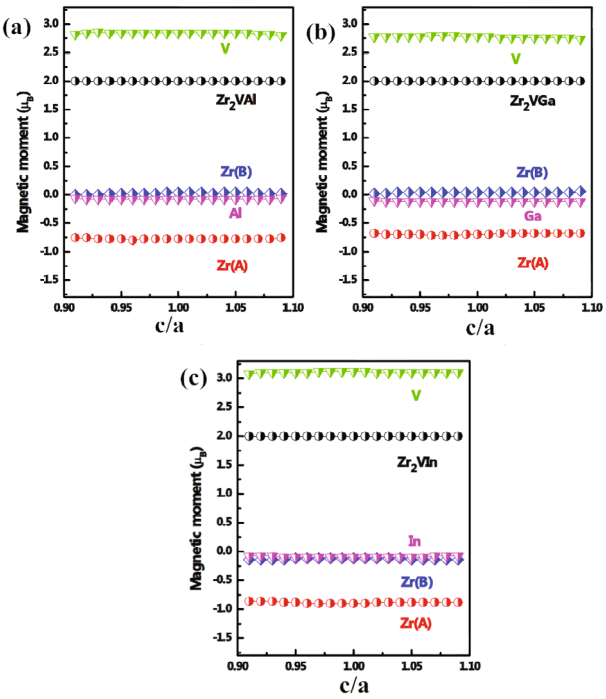

Fig. 8. (Color online) Total and site-projected magnetic moments as functions of the c/a ratio for Zr_2VZ (Z = Al, Ga, In) alloys with the $CuHg_2Ti$-type structure: (a) Zr_2VAl, (b) Zr_2VGa, and (c) Zr_2VIn.

simulating the case of tetragonal deformation, we fix the unit-cell volume to the equilibrium bulk volume and then change the c/a ratio. That is to say, the relationship between the unit-cell volume and the equilibrium lattice constant is as follow: $V = a \times a \times a = a^3$. The calculated CBM and VBM and the calculated total and atomic magnetic moments as functions of the c/a ratio in the range of $0.91 - 1.09$ for Zr_2VZ (Z = Al, Ga, In) alloys are shown in Fig. 7 and Fig. 8, respectively. As shown in Fig. 7, Zr_2VZ (Z = Al, Ga, In) alloys can maintain their HM states when the c/a ratio is changed in the range of $0.91 - 1.09$. The HM character of Zr_2VZ (Z = Al, Ga, In) alloys appears to exhibit a low sensitivity to tetragonal deformation. Next, we focus on the magnetic properties as shown in Fig. 8. Either the total or the atomic magnetic moment exhibits a low sensitivity to tetragonal deformation. The value of the total or the atomic magnetic moment remained almost unchanged over the entire c/a range considered.

IV. CONCLUSION

First-principles calculations were used to investigate the electronic structures, magnetism and half-metallicity of the Zr_2VZ (Z = Al, Ga, In) alloys with both $AlCu_2Mn$ and $CuHg_2Ti$-type structures. The results showed that the Zr_2VZ (Z = Al, Ga, In) alloys with an $AlCu_2Mn$-type structure were conventional ferrimagnets while the Zr_2VZ (Z = Al, Ga, In) alloys with a $CuHg_2Ti$-type structure were half-metallic ferrimagnets. The spin-up channel band gap in half-metals was due to d-d hybridizations among the Zr (A), Zr (B) and V (C) atoms.

The total magnetic moments of $CuHg_2Ti$-type Zr_2VZ (Z = Al, Ga, In) were 2 μ_B per unit cell and followed the SP rule $M_t = 18 - Z_t$. For these alloys, the half-metallicity was robust against hydrostatic strain and tetragonal deformation, making these alloys very stable with respect to their polarization properties. Further, a small mismatch was noted between the equilibrium lattice constant of these alloys and that of semiconductors, which makes possible the growth of these alloys on suitable substrates for spintronics applications.

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