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Electronic, magnetic, and structural properties of ZrRhTiZ (Z = Al, Ga) Heusler Compounds using DFT Studies

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ABSTRACT

The electronic, magnetic, and structural properties were investigated for ZrRhTiZ (Z = Al, Ga) quaternary Heusler compounds by using first-principles calculations framed fundamentally within density functional theory (DFT). The electronic structures obtained revealed that both compounds have half-metallic characteristics by showing 100% spin polarization near the Fermi level. The half-metallicity is robust to the tetragonal distortion and uniform strain of the lattice. The total magnetic moment is 2 μB per formula unit and obeys the Slater-Pauling rule, Mt = Zt − 18 (Mt and Zt represent for the total magnetic moment and the number of total valence electrons in per unit cell, respectively). The ferromagnetic ground state and thermodynamical ground stability of the compound are are supported by relative total energies. The investigated Curie temperatures of the compounds exceed room temperature indicating that these compounds are promising candidates for beyond room temperature spintronics and magneto-electronics applications.

1. INTRODUCTION

Half-metallic materials (HMMs) can provide completely spin-polarized conducting electrons due to their unique electronic band structure which shows metallic characteristics in one spin channel and semiconducting/insulating properties in the other spin channel. Hence, HMMs are very much appreciated as key materials for providing high spin polarized carriers for spintronics devices. As one of the important HMM families, Heusler compounds have a special importance due to their

high Curie temperature, tunable electronic structure, and wide change of lattice constant. Moreover, from the previous reports concerning pseudo-quaternary or ternary Heusler compounds with half-metallicity, it was found that the materials containing 4d or 5d transition metal elements generally demonstrate a wide band gap implying a robust half-metallicity in a quite uniform strain or tetragonal distortion, which is quite suitable for practical applications. Therefore, in recent years, the investigations on the Heusler compounds containing 4d or 5d transition metal elements have become the research focus. Although many ternary Heusler compounds containing 4d transition metal elements have been reported in the literature, the quaternary Heusler compounds containing 4d or 5d transition metal elements, especially, the stoichiometric quaternary Heusler (SQH) compounds with half-metallicity have been rarely reported. Hence, it is important to further investigate and search for new half-metallic SQH materials containing 4d or 5d transition metal elements. In this work, we investigate two new SQH compounds, ZrRhTiAl and ZrRhTiGa, for the first time. Our prime aim in this work is to investigate the electronic and magnetic properties of both compounds and their half-metallic (HM) stability under uniform strain and tetragonal distortion. The elastic constants, formation energy, and cohesive energy were also presented to help understand the possibility of experimental synthesis of these two compounds.

II. METHOD OF CALCULATIONS

In this work, the calculations were performed by employing CASTEP computational code framed fundamentally within DFT. In all the calculations, the ultra-soft pseudo-potential approach with plane wave basis set was used, and the generalized-gradient-approximation (GGA) was adopted for the exchange– correction energy functional part of the total energy. For the expansion of electronic wave functions, the plane wave basis set expansion approach was used. To truncate the plane wave basis set expansion to attain the required convergence criterion, an energy cut-off of 450 eV and a mesh of 12 × 12 × 12 k-points for the Brillouin zone sampling was used. Within our above said applied parameters, calculations ensured a high-level total energy convergence with less than a tolerance of 1 × 10− 6 eV per atom for both ZrRhTiZ (Z = Al, Ga) compound.

III. RESULTS AND DISCUSSIONS

There are four crystallographic sites in Heusler compounds. For quaternary Heusler compounds, there are three possible atomic arrangements depending on each crystallographic site occupation. In this present study, the atomic arrangement properties of ZrRhTiZ (Z = Al, Ga) compounds were investigated by calculating the total energy in ferromagnetic (FM) and non-ferromagnetic (NM) states. The calculated results show that for the ZrRhTiZ (Z = Al, Ga) compound, the most stable case is that Zr and Ti atoms with less valence electrons enter into the Wyckoff sites 4a(0, 0, 0) and 4c(0.25, 0.25, 0.25), Rh atoms with more valence electrons occupy the 4b(0.5, 0.5, 0.5) site, and the main group of atoms, Z atoms, tend to locate at the 4d(0.75, 0.75, 0.75) site. The corresponding simulated crystal structure is shown in Figure 1. The stable arrangement of ZrRhTiZ (Z = Al, Ga) Heusler compounds is like the combination of inverse Zr2RhZ and Ti2RhZ (Z = Al, Ga) Heusler

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compounds and found to be similar to the other Zr-based SQH compounds.

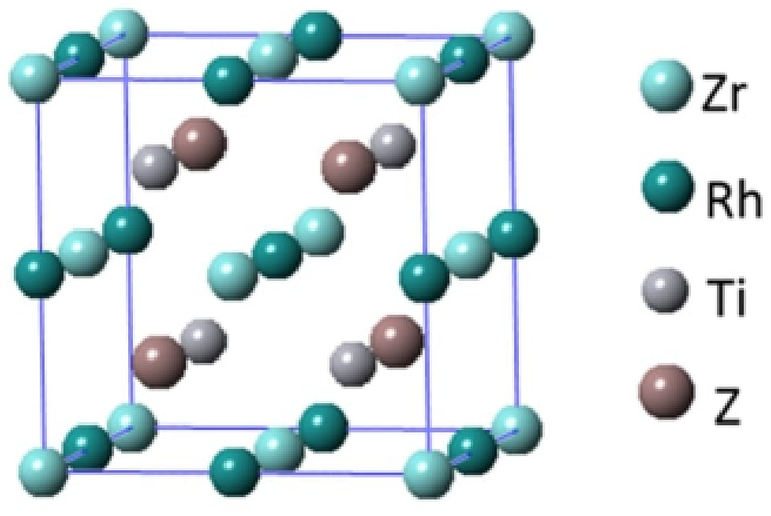

Figure 1. Crystal structure of ZrRhTiZ (Z = Al, Ga) quaternary Heusler compounds.

Figure 2 shows the dependence of the total energy on the lattice parameters in FM and NM states for ZrRhTiZ (Z = Al, Ga) compounds. One can see that both compounds are more stable in FM than NM states according to the viewpoint of the total energy minimization. The equilibrium lattice constants corresponding to the ground state energy are 6.47 Å and 6.45 Å for ZrRhTiAl and ZrRhTiGa, respectively.

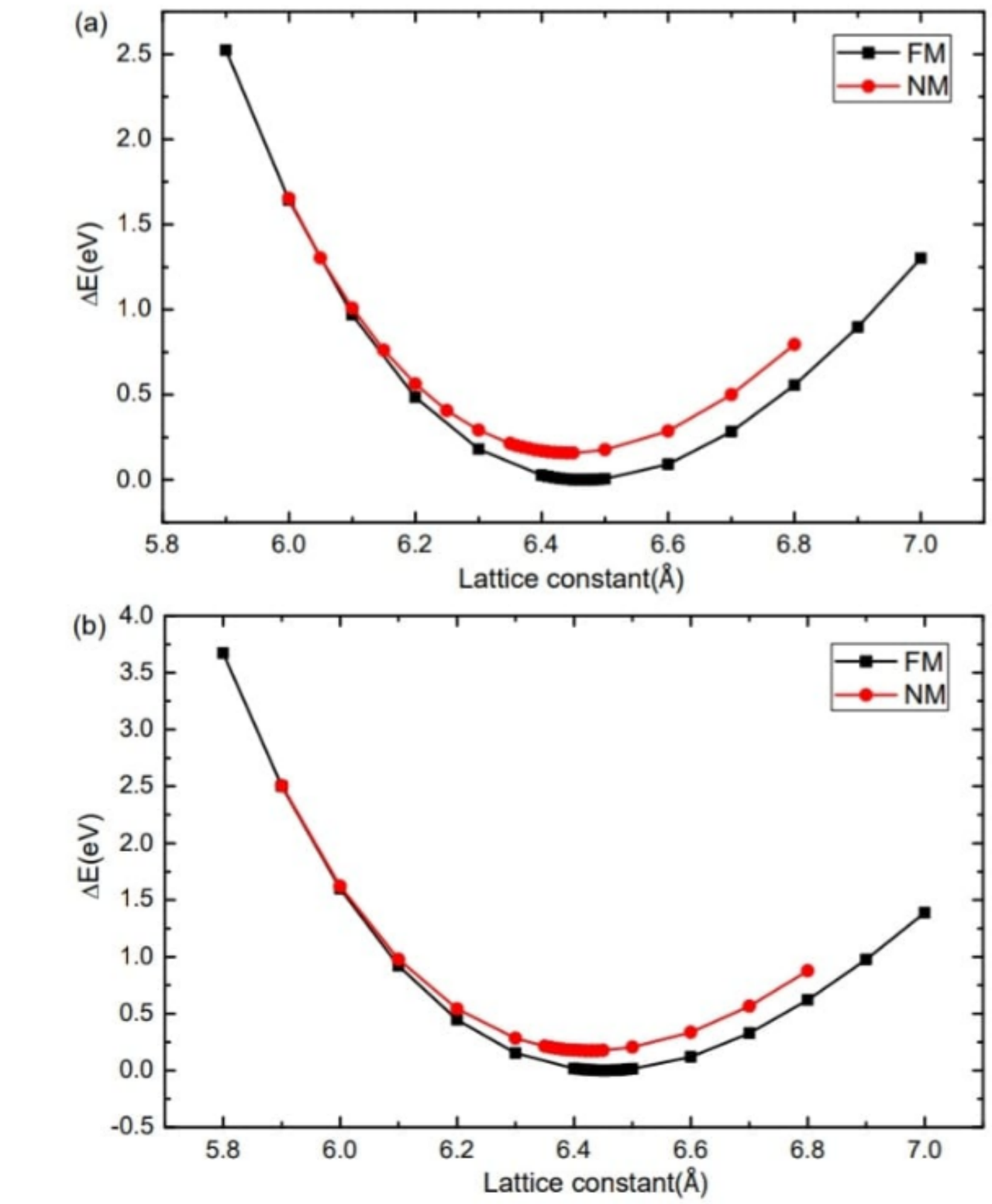

Figure 2. Total energy as a function of the lattice constant in the non-ferromagnetic (NM) and ferromagnetic (FM) states for ZrRhTiAl (**a**) and ZrRhTiGa (**b**) compounds. The lowest energy in the FM state is set as zero point.

The spin-projected band structures in the reduced Brillouin zone along the high symmetry directions were calculated under the equilibrium lattice constant and plotted in Figure 3 for ZrRhTiAl and ZrRhTiGa compounds. From Figure 3, an indirect band gap can be clearly observed in the spin-down channel, and the Fermi level is located within the band gap. In the spin-up channel, the valence and conduction bands are overlapping, and the Fermi level is intersecting them for ZrRhTiZ (Z = Al, Ga) compounds, which indicates that both compounds are half-metallic materials. The band gap (Ebg) and HM band gap (EHM) in the spin-down channel are listed in Table 1. The HM band gap is the minimum energy required to flip a minority of spin electrons from the valence band maximum (VBM) to the majority spin Fermi level. The Ebg is 0.432 eV for ZrRhTiAl and 0.541 eV for ZrRhTiGa. Usually, the large Ebg can be considered as evidence of the robustness of half-metallicity to lattice distortion.

The Mulliken atomic populations quantify the charge transfer from one atom to another one and are listed in Table 2 for ZrRhTiZ (Z = Al, Ga) compounds. It is clear that the charge transfer from Ti to Rh is 0.69e and Zr to Al is 0.08e in ZrRhTiAl, and the charge transfer from Ti to Zr is 0.27e and Ga to Rh is 0.93e in ZrRhTiGa. Appl. Sci. 2018, 8, x 4 of 14 The spin-projected band structures in the reduced

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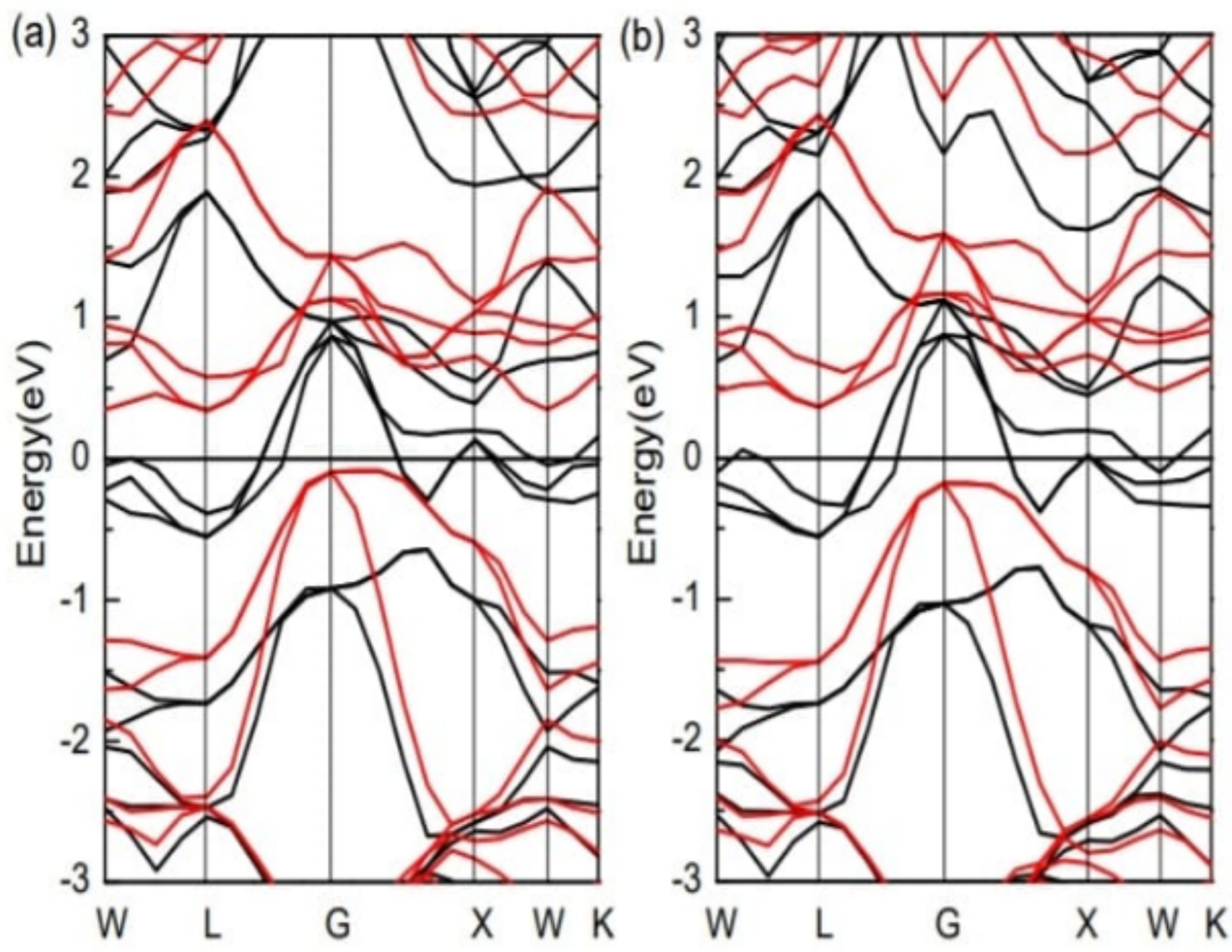

Figure 3. The calculated band structures for ZrRhTiAl (**a**) and ZrRhTiGa (**b**). (The black lines represent the spin-up channel, and the red lines the spin-down channel.).

Table 1. The equilibrium lattice constants (Å), total magnetic moments (μ_B), atomic magnetic moments (μ_B), valence band maximum (eV), conduction band minimum (eV), band gap (eV), half-metallic (HM) band gap (eV), and the number of valence electrons for ZrRhTiZ (Z = Al, Ga) compounds.

Compound	Total	Zr	Rh	Ti	Z	a (Å)	*CBM*	*VBM*	E_{bg}	E_{HM}	Z_t	S-P rule	P (%)
ZrRhTiAl	2.00	1.26	−0.32	1.18	−0.14	6.47	0.350	−0.082	0.432	0.082	20	$M_t = Z_t - 18$	100
ZrRhTiGa		1.22	−0.32	1.32	−0.22	6.45	0.360	−0.181	0.541	0.181			

Table 2. Mulliken population analysis of ZrRhTiAl and ZrRhTiGa.

Species	Atom	s	p	d	Total	Charge(e)
ZrRhTiAl	Zr	2.54	6.37	3.02	11.93	0.07
	Rh	0.89	0.60	8.20	9.69	−0.69
	Ti	2.53	6.12	2.65	11.30	0.70
	Al	1.05	2.03	0.00	3.08	−0.08
ZrRhTiGa	Zr	2.64	6.67	2.96	12.27	−0.27
	Rh	0.97	0.76	8.20	9.93	−0.93
	Ti	2.70	6.37	2.65	11.73	0.27
	Ga	−0.17	2.26	9.99	12.08	0.92

Structural stability: In order to understand the structural stability of the considered compounds, we have optimized the crystal structure from total energy minimization procedure (Fig. 3). The optimizations have been performed for FM and nonmagnetic (NM) cases. The total energy calculations with AFM (1x1x2 super-cell) showed higher energies as compared to FM and NM energies confirming the FM ground states in these materials. The obtained equilibrium lattice constants corresponding to the FM states are 6.46 ˚A and 6.64 ˚A for ZrRhTiAl and ZrRhTiIn compounds, respectively.

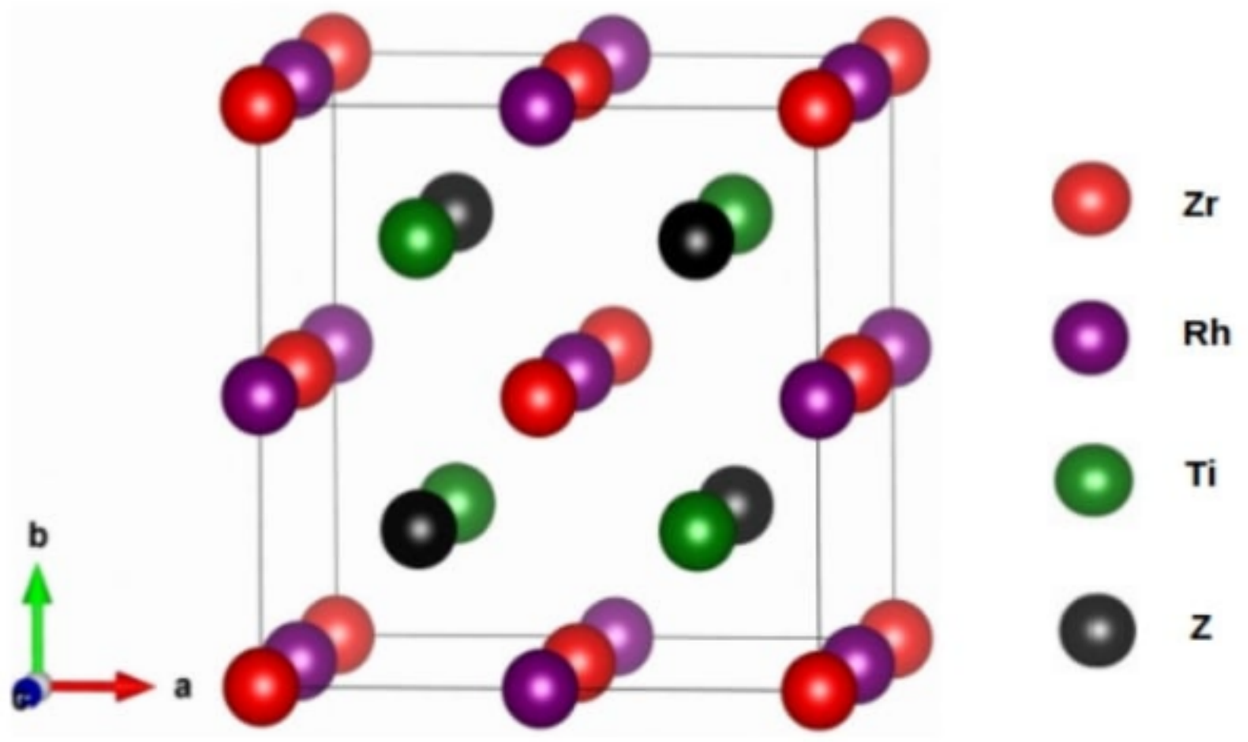

FIG. 3. (Color online) Crystal structure ($F\bar{4}3m$, space group 216) of ZrRhTiZ (Zr = Al, In).

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Further cohesive and formation energies are calculated to confirm the chemical stability of ZrRhTiZ (Z = Al,In) compounds using the following equations

$E_f = E^{total}_{ZrRhTiz} - (E^{bulk}_{Zr} + E^{bulk}_{Rh} + E^{bulk}_{Ti} + E^{bulk}_{Z})$, Z= Al, In

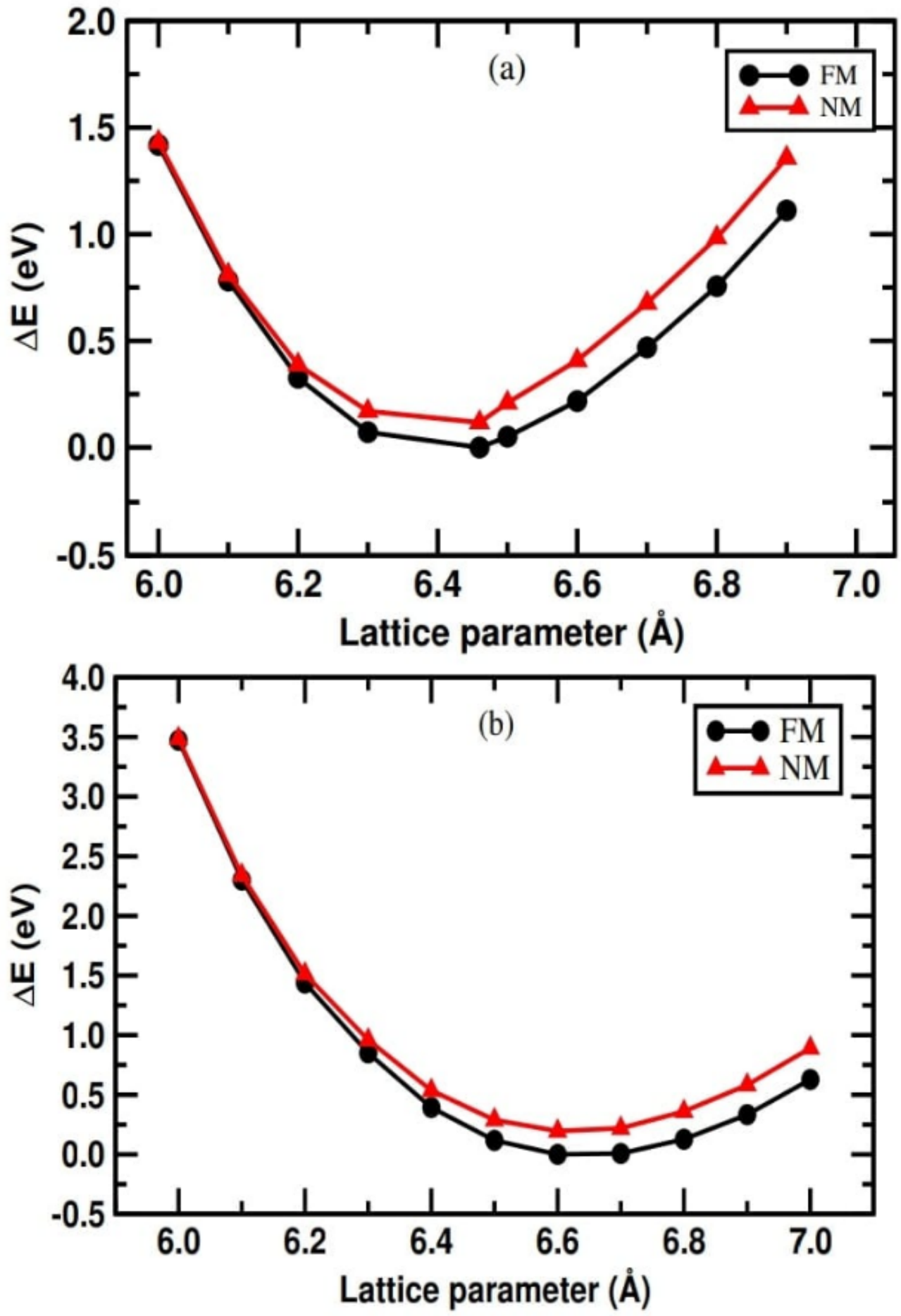

FIG. 4. (Color online) Total energy as a function of lattice constants in the non-magnetic and ferromagnetic configurations of (a) ZrRhTiAl and (b) ZrRhTiIn compounds.

and $Ec = E^{total}_{ZrRhTiZ} - (E^{iso}_{Zr} + E^{iso}_{Rh} + E^{iso}_{Ti} + E^{iso}_{Z})$, Z= Al, In

where $E^{total}_{ZrRhTiZ}$ $F\bar{4}3m$ is the equilibrium total energy of ZrRhTiZ (Z = Al) per formula unit, and E^{bulk}_{Zr} , E^{bulk}_{R} E^{bulk}_{Ti} and E^{bulk}_{Z} are the equilibrium total energies per atom for bulk Zr(HCP), Rh(FCC), Ti(HCP), and Al/In(FCC/tetragonal) respectively. E^{iso}_{Zr}, E^{iso}_{Rh} , E^{iso}_{Ti} and E^{iso}_{Z} are the isolated atomic energies of the elements Zr, Rh, Ti and Z, respectively. The calculated values of formation and

cohesive energies of ZrRhTiAl have -0.492 eV/atom and -6.523 eV/atom; and for ZrRhTiIn have -0.289 eV/atom and -6.062 eV/atom, respectively. The formation energies from our calculations are comparable (Table I) with the values extracted from Open Quantum Materials Database (OQMD)56,57. The differences are due to the use of different DFT methods. The negative values of formation and cohesive energies indicate that these two compounds are thermodynamically stable and can be synthesized experimentally (Table I)

TABLE I. Lattice parameters (a), formation, E_f (eV/atom), and cohesive energies, E_c (eV/atom) of ZrRhTiZ (Z = Al, In).

Compounds	Ref.(Å)	a(Å)	E_f	E_f*	E_c
ZrRhTiAl	6.47[89]	6.46	-0.492	-0.697	-6.523
ZrRhTiIn	6.66[90]	6.64	-0.289	-0.586	-6.062

IV. CONCLUSION

In this paper, the electronic structures, magnetic structures and structural stability are calculated for ZrRhTiZ (Z = Al, Ga) quaternary Heusler compounds by using first principles calculations. Based on the obtained results, we predicted that ZrRhTiZ (Z = Al, Ga) quaternary Heusler compounds are half-metallic materials. These two compounds are among the rare SQH compounds with half-metallicity that contain 4d transition metal elements. The investigations on the effects of US and TD show that the half-metallicity is robust to US and TD. The half-metallicity can be sustained over a wide lattice constant range of 6.09 Å– 6.61 Å for ZrRhTiAl and 6.03 Å– 6.75 Å for ZrRhTiGa

The calculations of formation and cohesive energies reveal that these compounds are stable due to favorable energetics and chemical bonding and can be synthesized for experimental measurements. The calculated optimized lattice parameters for the compounds ZrRhTiAl are 6.46 ˚A , which agree well with the available literature. The Curie temperatures of these compounds exceed the room temperature, indicating that these compounds are promising candidates for spintronics applications.

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