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First-principles study of four quaternary Heusler alloys ZrMnVZ and ZrCoFeZ (Z = Si, Ge)

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ABSTRACT

We investigate the electronic structure and magnetic properties of four quaternary Heusler alloys ZrMnVZ and ZrCoFeZ (Z = Si, Ge) by using first-principle calculations. It is shown that ZrMnVSi, ZrMnVGe and ZrCoFeSi are half-metallic ferromagnets with considerable half-metallic gaps of 0.14, 0.18 and 0.22 eV, respectively. ZrCoFeGe is nearly half-metallic with a spin polarization of 98.99% at equilibrium lattice constant. Meanwhile, the changes of its properties under pressure are investigated.

1. Introduction

Heusler alloys consist of a large family of intermetallic compounds which attract considerable attention due to the variety of magnetic phenomena which they present [1]. Half-metallic (HM) magnets are seen as the most promising candidates of high-spin-polarization materials, because their band structure is metallic in one of the two spin channels and semiconducting or insulating in the other one, which results in complete (100%) spin polarization of electrons at the Fermi level. A number of new half-metallic materials, such as CrAs, NiMnSb, and Co_2MnAl [2,3], have been initially predicted theoretically by first-principle calculations and later verified by experiments. Among these materials, the ones with Heusler structure have widely concerned, because they can be synthesized easily and have high Curie temperature [4–6].

Recently, half-metallic ferromagnetism (HMF) has been found in Co_2ZrSn, Ni_2ZrSn [7], Ni_2ZrAl [8], ZrNiSn [9], $Ti_{1-x}Zr_xNiSn$ [10] and ZrCoSb [11]. HMF meets most of the requirements of spintronics, as a result of their exceptional electronic structure. Zr-based quaternary Heusler ferromagnets, ZrFeTiAl, ZrFeTiSi, ZrFeTiGe and ZrNiTiAl, with large HM gaps have been reported lately [12].

Usually, Heusler alloys have the structural formulas of X_2YZ with $L2_1$ structure and XYZ with $C1_b$ structure, where X and Y are transition metals and Z is a main-group element. Many X_2YZ [13–16] and XYZ Heusler alloys have been found to be HM ferromagnets or ferrimagnets [17]. As for quaternary Heusler compounds, XX′YZ generally they crystallize in the LiMgPdSn-type crystal structure [18,19].

In this paper, we explore the electronic structures and magnetic properties of four quaternary Heusler alloys by means of band structure calculations. The results reveal that ZrMnVSi, ZrMnVGe and ZrCoFeSi are half-metals, while ZrCoFeGe is a nearly half-metal.

2. Method of calculations

We have carried out density functional calculation using the scalar relativistic version of the full-potential local-orbital (FPLO) minimum-basis band-structure method [20,21]. For the present calculations, the site-centered potentials and densities are expanded in spherical harmonic contributions up to $l_{max} = 12$. The Perdew–Burke–Ernzerhof 96 of the generalized gradient approximation (GGA) is used for exchange–correlation (XC) potential [22]. 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.

3. Results and discussions

Quaternary Heusler alloys XX′YZ have the space group of $F\bar{4}3m$ (No. 216), and they have three possible structures [23–25]. We calculate the spin-polarization and non-spin-polarization total

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energies as a function of lattice constants for both the ZrMnVZ and ZrCoFeZ in the three possible structures. From the calculated total energies at equilibrium lattice constants we find that, all the ZrMnVZ and ZrCoFeZ have the most stable structure where Zr, Mn(Co), V(Fe) and Z occupy the (000), $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$, $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$, and $(\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4})$ positions, respectively. Spin-polarization is more stable than non-spin-polarization. Table 1 presents the optimized lattice constants and the calculated total magnetic moments per formula unit at equilibrium lattices with the most stable structure for ZrMnVZ and ZrCoFeZ. It is shown that ZrMnVSi, ZrMnVGe and ZrCoFeSi are half-metallic ferromagnets, while ZrCoFeGe is a nearly half-metallic ferromagnet.

The calculated total magnetic moment is 1.00 μ_B per formula unit for ZrCoFeSi (Table 1). There are 25 valence electrons in ZrCoFeSi, and the total magnetic moment of 1.00 μ_B per formula unit complies with the Slater-Pauling behavior of HM quaternary Heusler alloys

$$M_{tot} = (Z_{tot} - 24)\mu_B, \quad (1)$$

where Z_{tot} and M_{tot} are the number of total valence electrons and the total magnetic moment respectively. As for the other two HM compounds, there are 20 valence electrons in ZrMnVSi and ZrMnVGe. The total magnetic moment of 2 μ_B per formula unit complies with the Slater-Pauling behavior of HM quaternary Heusler alloys

$$M_{tot} = (Z_{tot} - 18)\mu_B, \quad (2)$$

here Z_{tot} and M_{tot} have the same meanings as previous.

The total magnetic moment contains four parts (Table 2). As for ZrCoFeSi, the magnetic interaction is ferromagnetic between Co and Fe, antiferromagnetic between Zr and Co as well as between Zr and Fe. Different to ZrCoFeSi, the magnetic interaction is ferromagnetic between Zr and V, antiferromagnetic between Zr and Mn as well as between V and Mn for both ZrMnVSi and ZrMnVGe.

Fig. 1 shows the calculated spin-polarized total density of states (DOS) for ZrMnVSi, ZrMnVGe and ZrCoFeSi at their equilibrium lattice constants. From it, one can see that these three HM ferromagnets have considerable HM gaps of 0.14, 0.18 and 0.22 eV, respectively. Near the Fermi level, the spin-up DOS show a metallic property, while the spin-down DOS have a wide gap, so these three quaternary Heusler alloys keep an ideal 100% spin-polarization of conduction electrons at Fermi level.

Fig. 2 shows the calculated band structure of ZrCoFeSi at equilibrium lattice constant as a representation of the three HM compounds. Definitely, ZrCoFeSi exhibits a HM characteristic: the spin-up band structure is metallic, and the energy gap is about 0.64 eV in the spin-down band structure. Fig. 3 shows the calculated results of total and partial DOS of ZrCoFeSi. It can be seen that the total DOS are mainly contributed by the 3d states of Co and Fe atoms in the range of −4 to 2 eV. Near the Fermi level, the 3d states of Co and Fe atoms make a main contribution to the total DOS. Around the Fermi level the 4d states of Zr atoms make the most contribution of the Zr atoms while the 3p states of Si make the most contribution of the Si atoms. We can also see that there is a hybridization between the Co-3d state and Fe-3d state near the Fermi level.

Now, we investigate the HM stability for ZrMnVSi, ZrMnVGe and ZrCoFeSi under uniform strains. Because HM materials are usually used in spintronic devices in the form of thin films or multilayers, the lattice constant will have a change when the films or multilayers are grown on appropriate substrates, and correspondingly the half-metallicity may be destroyed. In order to study the effect of uniform strain (i.e. corresponding to hydrostatic pressure), we calculate the total magnetic moments as a function of lattice constants for ZrMnVSi, ZrMnVGe and ZrCoFeSi. It indicates that the half-metallicity can be retained and the total magnetic moments can be kept an integral number of Bohr magneton (Fig. 4) until the lattice constants are contracted to be 5.86, 5.87 and 5.50 Å for ZrMnVSi, ZrMnVGe and ZrCoFeSi, respectively. The

Table 1
The calculated equilibrium lattice constants (a) in Å, total magnetic moments (m) in μ_B, half-metallic gap (E_g) in eV, and physical nature for the four quaternary Heusler alloys at equilibrium lattice constants.

Compounds	a (Å)	m (μ_B)	E_g (eV)	Physical nature
ZrMnVSi	6.128	2.00	0.14	Half-metal
ZrMnVGe	6.219	2.00	0.18	Half-metal
ZrCoFeSi	5.973	1.00	0.22	Half-metal
ZrCoFeGe	6.056	1.00	0.00	Nearly half-metal

Table 2
The partial magnetic moments of the Heusler alloys ZrMnVSi, ZrMnVGe and ZrCoFeSi under the equilibrium lattice constant.

XX′YZ	m_X (μ_B)	$m_{X'}$ (μ_B)	m_Y (μ_B)	m_Z (μ_B)	m_{tot} (μ_B)
ZrMnVSi	0.01	−0.05	2.10	−0.06	2.00
ZrMnVGe	0.09	−0.28	2.31	−0.12	2.00
ZrCoFeSi	−0.17	0.56	0.65	−0.04	1.00

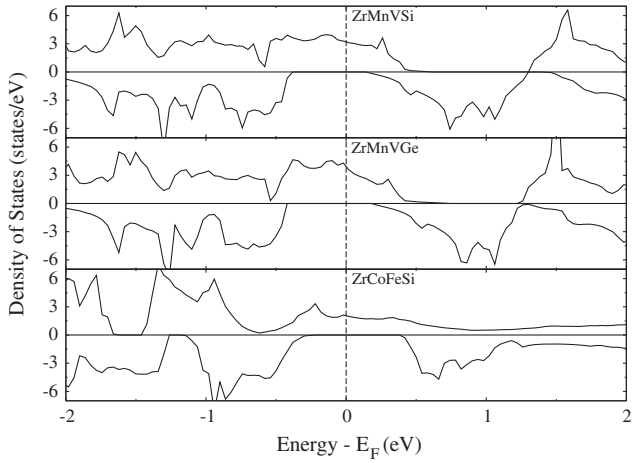

Fig. 1. The total density of states for ZrMnVSi, ZrMnVGe and ZrCoFeSi at equilibrium lattice constants.

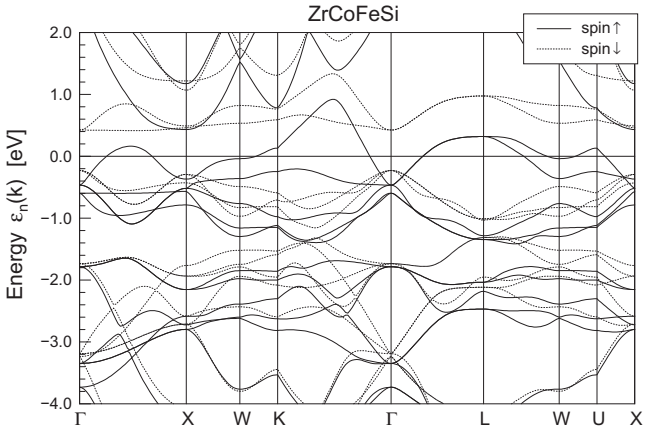

Fig. 2. Spin-up and spin-down band structure for ZrCoFeSi at the equilibrium lattice constant of 5.973 Å. Arrows ↑ and ↓ represent the spin-up and spin-down states respectively.