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Magnetic semiconductors and half-metals in FeRu-based quaternary Heusler alloys

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ABSTRACT

Phase stability, electronic structure and magnetic properties of the FeRu-based quaternary Heusler alloys, FeRuYZ (Y = Ti, V, Cr, Mn and Z = Al, Ga, In, Si, Ge, Sn), have been investigated theoretically. In one primitive unit cell, these alloys contain 24–26 valence electrons. The formation energy E_f of FeRuYZ increases with increasing atomic number of Z when the Y or Z elements belong to the same group in the periodic table. And in the same period, group-IIIA Z element is not preferable for the stability of FeRuYZ compared with corresponding group-IVA element. This can be explained from the charge density difference. The 24-electron FeRu-based quaternary Heusler alloys are all paramagnets. Among them, FeRuTiSi (Ge, Sn) are all semiconductors with real band gap at the Fermi levels. These alloys may have potential applications as thermoelectric materials. High spin polarization ratio is observed in the 25-electron Heusler alloys, among which FeRuCrAl is predicted to have a 100% spin polarization ratio. The 26-electron FeRuCrSi is found to be a spin gapless semiconductor (SGS) with total spin moment of $2\mu_B$. These materials can be interesting for the development of spintronic materials. The origin of SGS character in FeRuCrSi was discussed and compared with half-metallic Fe_2CrSi, in which Ru and Fe are isoelectronic. These findings can help to design new SGSs in Heusler alloys.

1. Introduction

Half-metals (HMs) and spin gapless semiconductors (SGSs) are of great value for the improvement of the performance of spintronic devices [1–3]. The high spin polarization ratio and variable magnetic properties can elevate the efficiency of spintronic devices and fit applications in different occasions. The HMs have a metal-like conducting band in one spin channel and a semiconductor-like band in the other spin channel, which results in a 100% spin polarization of the conduction electrons at the Fermi level E_F and can be used as spin polarized current sources [4,5]. The SGSs are a specific type of HMs and can be looked on as an intermediate state between the HMs and gapless semiconductors. In SGSs, one spin channel has an open band gap at E_F like a half-metal but the other spin channel has a zero-width gap like a gapless semiconductor [3,6]. All this makes the conducting electrons or holes are 100% spin polarized and easily excited. These unique properties make people take efforts to design and synthesize new HMs and SGSs.

Heusler alloys are a large family of HMs and SGSs, in which varied compositions and changeable atomic ordering have been reported. Traditional Heusler alloys have a highly-ordered cubic structure and a stoichiometric composition of X_2YZ. Here X and Y are transition metal elements, and Z is a main group element. When the composition becomes off-stoichiometric and atomic disorder occurs, more variants can be formed in Heusler alloys. There are four different crystal sites namely A (0, 0, 0), B (0.25, 0.25, 0.25), C (0.5, 0.5, 0.5) and D (0.75, 0.75, 0.75), in the lattice of Heusler alloys. The transition metal elements X, Y enter A, B, C sites and main group element Z always enters D sites in the cubic lattice. The site preference of the transition metal elements is usually determined by the number of their valence electrons: atoms with more electrons tend to occupy the A and C positions while the atoms with fewer electrons prefer the B position [7]. The X and Y atoms can be all of the 3d metals and some 4d/5d metals in the periodic table. So the compositions of half-metallic Heusler alloys are rather diversiform and their magnetic properties are adjustable from zero to $6\mu_B$/f.u. The Curie temperature can be higher than 1100 K [8]. All this makes Heusler alloys quite suitable for technical applications. Till now, different HMs have been synthesized in Mn_2-, Fe_2- and Co_2-based Heusler alloys [9–13].

Now, investigations on Heusler type HMs and SGSs have extended to the quaternary Heusler alloys. When the two X atoms in the chemical formula are different (marked as X and X′), a series of equiatomic quaternary Heusler alloys will be formed, in which the A, B, C, D sites are occupied by X, X', Y and Z atoms with 1:1:1:1 stoichiometry,

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respectively. Recently, different quaternary Heusler alloys have been predicted to be HMs or SGSs theoretically [14–17]. Bainsla et al. reported the SGS character in CoFeMnSi experimentally [18]. CoRu-based alloys were also designed for high Curie temperature applications [19]. A detailed review can be found in Ref. [20].

In this paper, we investigated the electronic structure and magnetic properties of 18 FeRu-based quaternary Heusler alloys, FeRuYZ (Y = Ti, V, Cr, Mn and Z = Al, Ga, In, Si, Ge, Sn), to search for new HMs and SGSs. One specific advantage in FeRu-based Heusler alloys is that many Fe_2YZ (Y = V, Cr, Mn, Z = Al, Ga, Si) and Ru_2YZ (Y = Ti, V, Cr, Mn and Z = Al, Ga, Si, Ge, Sn) Heusler alloys have been synthesized successfully [11,21–25]. Fe and Ru are also in the same group in the periodic table. Thus the formation of FeRuYZ can be looked on as an "isostructural alloying" between Fe_2YZ and Ru_2YZ, which implies that these alloys are quite likely to be synthesized experimentally. In Fe_2RuSi, Ru has been proved to have a strong preference for the A, C sites in Heusler alloys and can retain the highly-ordered structure [26]. This is preferable in practical applications for the HM or SGS characteristic may be destroyed by atomic disorder.

2. Theoretical methods

The electronic and magnetic properties of the quaternary Heusler alloys, FeRuYZ (Y = Ti, V, Cr, Mn and Z = Al, Ga, In, Si, Ge, Sn), were calculated by the CASTEP code [27,28]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential with a plane-wave basis set [29]. The electronic exchange–correlation energy was treated under the generalized-gradient-approximation (GGA) [30]. The plane-wave basis set cut-off energy was 500 eV. A mesh of 20 × 20 × 20 *k*-points was employed for the Brillouin zone integrations in the calculation of FeRuYZ. These parameters ensured good convergences for total energy. The convergence tolerance for the calculations was selected as the difference on total energy within 1×10^{-6} eV/atom.

The formation energy E_f was calculated following the formula $E_f = E_{total} - [E_{Fe\ bulk} + E_{Ru\ bulk} + E_{Y\ bulk} + E_{Z\ bulk}]$. Here E_{total} is the ground state total energy per formula unit of each FeRuYZ alloy, $E_{Fe\ bulk}$, $E_{Ru\ bulk}$, $E_{Y\ bulk}$ and $E_{Z\ bulk}$ are the energies of pure metals in their stable bulk form. For example, Fe, Cr, V and Mn have BCC structure, and Si, Ge Sn have diamond-like structure, while Ti and Ru have hexagonal structure. The magnetic states of these pure metals were considered in the calculation. The *k*-mesh is 24 × 24 × 24 and other parameters are the same as the settings above.

3. Results and discussions

The properties of Heusler alloys X_2YZ are strongly related to the atomic ordering. The site preference of transitional metal X and Y is usually determined by the so-called "valence electrons rule". That is transition metal atoms with more valence electrons prefer entering the A, C sites while atoms with fewer valence electrons prefer the B site [7]. For FeRuYZ (Y = Ti, V, Cr, Mn), both Fe and Ru have more valence electrons than the Y atoms in present work, then in FeRuYZ Fe and Ru enter the A, C sites and Y atom enters the B site. However, some exceptions to "valence electrons rule" were reported in Heusler alloys recently [17,31]. For example, in Zr_2CoAl, two Zr atoms entering the A, C sites are lower in total energy and more stable compared with entering the A, B sites, though Zr has fewer valence electrons compared with Co. Different structures can influence the electronic structure and half-metallic/SGS character obviously [32].

To determine the most stable structure in Heusler alloys FeRuYZ and predict the electronic properties precisely, during the structural optimization, in each FeRuYZ alloy we compared the total energies of three different atomic orderings, in which Fe, Ru and another transition metal Y enters B (0.25, 0.25. 0.25) site, respectively. The supercell models for the three atomic orderings have been presented in Fig. 1 to show more detail. In Fig. 2, we present the structural optimization results for FeRuCrSi as an example. During the calculations, nonmagnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) states have been considered.

In Fig. 2, the curves for Ru entering the B site locate above other curves and are high in total energy, indicating that this configuration is not energetically favored. While the FM/AFM curves for Cr entering B site have the lowest total energy, suggesting that the atomic ordering with Fe, Ru entering the A, C sites and Cr entering the B site is stable in energy compared with others. The results for other FeRuYZ alloys are similar. This agrees with the strong preference of Ru for the A, C sites observed experimentally [26]. The equilibrium lattice constants of FeRuYZ were derived by minimizing the total energy and listed in Table 1. When Z elements belong to the same group in periodic table, the lattice constants of FeRuYZ increase monotonously with increasing atomic number of Z. In the same group, the atomic radii of main group elements Z usually increase with increasing atomic number [33], which leads to the expansion of the lattice.

Now, quite a few quaternary Heusler alloys have been predicted to be half-metal/SGS, however, whether they can be synthesized experimentally or not is still a question. In order to assess the structural stabilities of FeRuYZ, we calculated the formation energies E_f of them. A negative formation energy means that a single Heusler phase may be favored energetically, while a positive E_f has the opposite effect. This information can help to synthesize FeRuYZ alloys effectively.

The calculated E_f was listed in Table 1. In Fig. 3, we presented the variation of E_f as functions of the main group element Z, in which an interesting rule can be observed. When Y element is fixed, the formation energy increases with increasing atomic number of Z element in the same group. Here FeRuYIn (Y = V, Cr, Mn) and FeRuCrSn have positive formation energies and are difficult to be synthesized. But the other ten FeRuYZ Heusler alloys have E_f lower than −1 eV and may have high stabilities from theoretical point of view. It may be found that, group IIIA Z elements are not preferable for the stability of FeRuYZ compared with corresponding group IVA elements. For example, the E_f of FeRuCrAl and FeRuCrGa are higher than those of FeRuCrSi and FeRuCrGe. Considering the variations of lattice constant and formation energy with different Z elements are similar, a possible reason for this rule may be attributed to the atomic size effect. These results can be useful for the design and preparation of new FeRu-based and other related quaternary Heusler alloys.

It is known that the stability of solids (E_f for example) is strongly related to the chemical bonds/hybridization between the valence electrons in them. To investigate the variation of E_f with composition further, we calculated the charge density difference (CDD) of FeRuCrZ (Z = Al, Ga, In, Si, Ge, Sn) as examples and presented the results in Fig. 4. CDD can reflect the charge distribution directly and help to understand the atomic bonding in the lattice [34]. In the CDD maps, the electron excess is depicted by red[1] color and electron deficiency is presented by blue color in units of number of e/Å^3. One can see that in FeRuCrZ, deep red areas representing charge accumulation are mainly observed in the middle of nearest neighbor Fe/Ru-Z and Fe/Ru-Cr, indicating that covalent bonding character has been formed between them. As we know, hybridization between the valence electrons from nearest neighbor atoms is important for the phase stability of Heusler alloys. A strong covalent bonding is quite preferable for the formation of highly-ordered structure [35,36]. When the Z atoms belong to the same group, the red areas in the CDD map become smaller and the red color becomes lighter with increasing atomic number of Z. The change between Fe and Z atoms is especially obvious. For example, in FeRuCrIn and FeRuCrSn, the yellow region is quite obvious between Fe-In and Fe-Sn, which means the covalent bonding is weakened and the phase

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[1] For interpretation of color in Fig. 4, the reader is referred to the web version of this article.