Half-metallicity in Fe-based Heusler alloys Fe$_2$TiZ (Z = Ga, Ge, As, In, Sn and Sb)

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**Abstract**

The electronic structure and magnetic properties of new Fe-based Heusler alloys Fe$_2$TiZ (Z = Ga, Ge, As, In, Sn and Sb) have been studied by first-principles calculations. In these alloys, the 24-electron Fe$_2$TiGe, Fe$_2$TiSn are nonmagnetic semiconductors and other compounds are all ferrimagnetic metals. Fe$_2$TiAs and Fe$_2$TiSb are predicted to be half-metals with 100% spin polarization. The spin polarization ratio in Fe$_2$TiGa and Fe$_2$TiIn is also quite high. The calculated total moment ratio for Fe$_2$TiAs and Fe$_2$TiSb is 1.04, which is mainly determined by the Fe partial moment. The half-metallicity of Fe$_2$TiSb is stable under lattice distortion. The spin polarization of Fe$_2$TiSb is found to be 100% for the lattice variation in a range of 5.6–6.1 Å, which is attractive in practical applications.

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1. Introduction

In recent years, the half-metallic ferromagnets (HMFs) have attracted much attention for their potential applications in the field of spintronics [1–3]. The HMFs have an semiconductor-like gap in one spin band around the Fermi level whereas the other spin band is metallic-like, which results in a complete spin-polarization of the conduction electrons at the Fermi level. HMFs are of great interest from both theoretical and technical aspects, for many magnetoelectronic devices rely on an imbalance in the number of majority- and minority-spin carriers [3,4]. The completely (100%) spin-polarized current of HMFs can be used as spin injectors for many spin dependent devices.

Heusler alloys have become a large family of half-metals. Quite a few Heusler alloys, especially Co- or Mn-based are predicted to be half-metallic. In preceding studies, Co$_2$MnX (X = Si, Ge, Sn), Co$_2$CrAl (Ga), Co$_2$FeSi and Co$_2$TiZ [5–11] have been found to exhibit half-metallic character by theoretical and experimental studies. For Mn-based compounds, people have reported the half-metallic properties in Mn$_2$VZ (Z = Al, In, Sn, and Sb) [12], Mn$_2$CrSb [13], Mn$_2$FeZ (Z = Al, Sb) [14] and Mn$_2$CoZ (Z = Al, Ga, In, Sn, and Sb) [15]. Recently, high quality magnetic tunnel junctions (MTJs) based on these alloys have also been prepared [16,17].

Considering the applications of half-metallic Heusler alloys in spintronic devices, design and synthesis of new materials can be a meaningful work. Here, Fe-based compounds are another big family in Heusler alloys. In 2007, Fe$_2$CrSi were predicted to be half-metallic and prepared experimentally [18]. Then many studies have been carried out on this alloy [19,20]. However, compared with Co-based or Mn-based alloys, studies on the half-metallicity of Fe-based Heusler alloys are still not enough. The electronic structures of many other Fe-based Heusler alloys are unclear yet. In this paper, we studied the electronic structure and magnetic properties of Heusler alloys Fe$_2$TiZ (Z = Ga, Ge, As, In, Sn and Sb), in which two half-metals Fe$_2$TiAs and Fe$_2$TiSb are predicted.

2. Calculation methods

The electronic structure was calculated by means of CASETP code based on pseudopotential method with a plane-wave basis set [21,22]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [23]. The electronic exchange–correlation energy was treated under the generalized-gradient-approximation (GGA) [24]. For all cases, a plane-wave basis set cut-off of 500 eV was used and a mesh of $15 \times 15 \times 15$ k-points was employed for Brillouin zone integrations. These parameters ensured good convergences for total energy. The convergence tolerance for the calculations was selected as a difference on total energy within $1 \times 10^{-6}$ eV/atom.

Heusler alloys Fe$_2$TiZ crystallize in Cu$_2$MnAl-type structure, in which two Fe atoms occupy 8c (1/4, 1/4, 1/4) Wyckoff positions and Ti enters 4a (0, 0, 0), finally, the main group element Z enters 4b (1/2, 1/2, 1/2). This crystal model is used for all the following calculations.
3. Results and discussion

3.1. Lattice constant and magnetic structure

To determine the equilibrium lattice constant and stable magnetic structure of Fe$_2$TiZ, structural optimizations were performed on these alloys first for nonmagnetic (NM), ferromagnetic (FM) and ferrimagnetic (AFM) states. It is found that for Fe$_2$TiZ ($Z$ = Ga, As, In, Sn and Sb), the FM calculation also converged to an AFM state and has the same total energy compared with AFM calculation. The energy of the NM states is higher in these four alloys. For Fe$_2$TiGe and Fe$_2$TiSn, the NM state is more stable and both the FM and AFM calculations also give a nonmagnetic ground state. The details of the total energy as functions of lattice parameters can be found in Fig. 1. Considering the similarity between the energy of FM and AFM states, the curve of the FM states is omitted in Fig. 1 for visibility.

The equilibrium lattice constants of Fe$_2$TiZ were derived by minimizing the total energy and listed in Table 1. The relationship between the lattice constant and the main group element Z is presented in Fig. 2. It is clear that, in the same row of the period table, the lattice constant shows a decreasing tendency as Z varies from Ga to As or In to Sb.

![Fig. 1](image1)

**Fig. 1.** Calculated total energy for Fe$_2$TiZ ($Z$ = Ga, Ge, As, In, Sn and Sb) as functions of the lattice parameters for the nonmagnetic (NM) and ferrimagnetic (AFM) states.

![Fig. 2](image2)

**Fig. 2.** The calculated lattice constants and total spin moments of Fe$_2$TiZ ($Z$ = Ga, Ge, As, In, Sn and Sb), the x-axis is the number of valence electrons of the Z atom.

Besides Fe$_2$TiSn [25], there are few data on the formation of other Fe$_2$Ti-based Heusler alloys. In order to investigate the phase stability of Fe$_2$TiZ further, like Ref. [26] we calculated the formation energies

$$
\Delta E = E_{\text{Fe}_2\text{TiZ}} - (2E_{\text{Fe}} + E_{\text{Ti}} + E_{Z})
$$

where $E_{\text{Fe}_2\text{Ti}}$ is the ground state total energy of Fe$_2$TiZ Heusler alloys, $E_{\text{Fe}}$, $E_{\text{Ti}}$ and $E_{Z}$ are the total energies of Fe, Ti, and main group element Z in pure element bulk form. The obtained formation energies are presented in Table 1, from which we can infer the phase stability of Fe$_2$TiZ qualitatively. It can be seen that all the formation energies are negative, suggesting that Fe$_2$TiZ in Heusler structure is favored in energy aspect than phase separation. The $\Delta E$ of Fe$_2$TiSb is $-1.28$ eV, and the $\Delta E$ of other compounds like Fe$_2$TiSb or Fe$_2$TiGe are comparable to which. Since Fe$_2$TiSn has been synthesized successfully, other Fe$_2$TiZ compounds may also be prepared experimentally.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice constant (Å)</th>
<th>$\Delta E$ (eV)</th>
<th>$M_{Fe}$ (μB)</th>
<th>$M_{Ti}$ (μB)</th>
<th>$M_{Z}$ (μB)</th>
<th>$P$ (%)</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$TiGa</td>
<td>5.80</td>
<td>1.05</td>
<td>0.88</td>
<td>0.68</td>
<td>0.46</td>
<td>0.02</td>
<td>89 FM</td>
</tr>
<tr>
<td>Fe$_2$TiIn</td>
<td>6.06</td>
<td>0.22</td>
<td>0.93</td>
<td>0.82</td>
<td>0.66</td>
<td>0.04</td>
<td>93 FM</td>
</tr>
<tr>
<td>Fe$_2$TiGe</td>
<td>5.74</td>
<td>-2.31</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>SC</td>
</tr>
<tr>
<td>Fe$_2$TiSn</td>
<td>6.03</td>
<td>-1.28</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>SC</td>
</tr>
<tr>
<td>Fe$_2$TiAs</td>
<td>5.74</td>
<td>-1.67</td>
<td>1.00</td>
<td>0.66</td>
<td>0.38</td>
<td>0.04</td>
<td>100 HMF</td>
</tr>
<tr>
<td>Fe$_2$TiSb</td>
<td>6.00</td>
<td>-1.12</td>
<td>1.00</td>
<td>0.72</td>
<td>0.46</td>
<td>0.02</td>
<td>100 HMF</td>
</tr>
</tbody>
</table>

**Table 1**
The equilibrium lattice constants, formation energy $\Delta E$, calculated total and partial magnetic moment, together with spin polarization ratio for Fe$_2$TiZ ($Z$ = Ga, Ge, As, In, Sn and Sb) alloys. Here FM is ferromagnetic metal, SC is semiconductor and HFM is half-metallic ferromagnet.
3.2. Electronic structure and magnetic properties

The calculated total and partial density of states (DOS) of Fe₂TiZ are presented in Fig. 3(a)–(c), respectively. It is clear that when the Z atoms belong to the same group, the shape of their DOS is quite similar, while when they belong to the same period, a clear change of the electronic structure is observed. We will begin with Fe₂TiGe and Fe₂TiSn to analyze the electronic structure of Fe₂TiZ alloys. As can be seen in Fig. 3(b), the total DOS of Fe₂TiGe and Fe₂TiSn is symmetrical in majority and minority spin directions. In both spin directions, an energy gap is opened around the Fermi level $E_F$ and divides the total DOS into bonding and antibonding parts. The formation of this gap is related to the hybridization of Fe and Ti $d$ electrons. In Heusler alloys, the covalent hybridization between the lower-energy $d$ states of the high-valent transition metal atom like Fe and the higher-energy $d$ states of the low-valent transition metal like Ti leads to the

![Fig. 3](image_url) Calculated DOS for Fe₂TiZ (Z = Ga, Ge, As, In, Sn and Sb) alloys.

![Fig. 4](image_url) Band structure of Fe₂TiIn (a), Fe₂TiSn (b) and Fe₂TiSb (c). The solid and dashed lines represent the majority and minority spin states, respectively.
energy gap separating the bonding and antibonding peak. Based on which, the \(d-d\) hybridization between the \(d\) states of Fe determined the shape and width of this gap [27].

Both \(\text{Fe}_2\text{TiGe}\) and \(\text{Fe}_2\text{TiSn}\) have 24 valence electrons. These electrons occupy the majority and minority spin bands equally (12 up and 12 down), which results in a nonmagnetic semiconductor-like band structure [28]. These results agree well with preceding studies in \(\text{Fe}_2\text{TiSn}\) [29]. In Fig. 4(b), as an example, we presented the energy bands of \(\text{Fe}_2\text{TiSn}\), the case in \(\text{Fe}_2\text{TiGe}\) is similar. It can be seen that the energy gap in \(\text{Fe}_2\text{TiSn}\) is an indirect \(\Gamma^–X\) gap and the Fermi level locates just above the top of the valence band at the \(\Gamma\) point.

\(\text{Fe}_2\text{TiAs}\) and \(\text{Fe}_2\text{TiSb}\) have one more valence electron than 24. The extra electron fills in the majority spin and spin polarization happens. In Fig. 3(c), it is clear that the majority total DOS of \(\text{Fe}_2\text{TiAs}\) and \(\text{Fe}_2\text{TiSb}\) are shifted to lower energy compared with \(\text{Fe}_2\text{TiGe}\) and \(\text{Fe}_2\text{TiSn}\). The majority energy gap moves from around 0 eV in \(\text{Fe}_2\text{TiSn}\) to \(-0.6\) eV in \(\text{Fe}_2\text{TiAs}\) or \(\text{Fe}_2\text{TiSb}\). So in majority spin, the Fermi level of \(\text{Fe}_2\text{TiAs}\) and \(\text{Fe}_2\text{TiSb}\) moves to the top of an antibonding peak, while in minority spin, the Fermi level is still within the gap. This leads to a 100% spin polarization of the conduction electrons at \(E_F\). We can conclude that Heusler alloys \(\text{Fe}_2\text{TiAs}\) and \(\text{Fe}_2\text{TiSb}\) are half-metallic.

In the PDOS of Fig. 3(c), the width of the half-metallic gap in the DOS of \(\text{Fe}_2\text{TiAs}\) and \(\text{Fe}_2\text{TiSb}\) is mainly determined by the PDOS of Fe, indicating that the half-metallic gap in them is a \(d-d\) gap from the hybridization between the \(d\) states of nearest-nearest Fe [27].

Ti atom has eight Fe atoms as nearest neighbors, so the \(d\) states of Ti are split into a doublet with \(t_{2g}\) symmetry and a triplet with \(e_g\) symmetry in the cubic crystal field. It may be noticed that the PDOS of Ti is quite symmetrical in the two spin direction and the exchange splitting is weak. So the spin moment on Ti site is small. This is different from Mn or Cr atom in Heusler alloys, which usually has a large local spin moment [18] and may relate to the strong itinerant character of Ti \(d\) electrons.

The DOS of \(\text{Fe}_2\text{TiGa}\) and \(\text{Fe}_2\text{TiIn}\) are presented in Fig. 3(a). They have 23 valence electrons, so the down-spin DOS of them are shifted to higher energy compared with \(\text{Fe}_2\text{TiSn}\) (24 valence electrons). The down-spin energy gap moves to \(+0.7\) eV and \(E_F\) locates at the bonding region. In the DOS of \(\text{Fe}_2\text{TiGa}\) and \(\text{Fe}_2\text{TiIn}\), there is still a small amount of states around \(E_F\) in the up-spin gap, so they are not ideal half-metals. The spin polarization ratio is 89% for \(\text{Fe}_2\text{TiGa}\) and 93% for \(\text{Fe}_2\text{TiIn}\). This is also meaningful in technical applications.

In Fig. 4, we also presented the energy bands of \(\text{Fe}_2\text{TiIn}\) and \(\text{Fe}_2\text{TiSb}\) as examples to show the detail of their electronic structures. The cases in \(\text{Fe}_2\text{TiGa}\) or \(\text{Fe}_2\text{TiAs}\) are similar. For \(\text{Fe}_2\text{TiSb}\), the Fermi level locates in the middle of a \(\Gamma^–X\) indirect gap in down-spin (dotted line), and passes through the bottom of the conduction band in up-spin (solid line), which makes \(\text{Fe}_2\text{TiSb}\) a half-metal. But for \(\text{Fe}_2\text{TiIn}\), both the up-spin and down-spin energy bands are continuous at \(E_F\), so it is only a common ferromagnetic metal.

The calculated total and partial spin moments of \(\text{Fe}_2\text{TiZ}\) are listed in Table 1. The variation of the moments with different \(Z\) elements is also presented in Fig. 2(b). It is known that in half-metallic Heusler alloys, the total moments \(M\) of them are integral values and follow the Slater–Pauling curve of \(\text{Fe}_{23/2}\) [27,30]. \(\text{Fe}_2\text{TiGe(Sn)}\) and \(\text{Fe}_2\text{TiAs(Sb)}\) have 24 and 25 electrons, respectively, in Fig. 2, we can see that the calculated moment of them fit the \(Z = 24\) curve quite well. \(\text{Fe}_2\text{TiGa(In)}\) have 23 valence electrons, derived from the \(S\)–\(P\) curve, the total moment of them should be 1 \(\mu_B\). However, since \(\text{Fe}_2\text{TiGa}\) and \(\text{Fe}_2\text{TiIn}\) are not ideal half-metals, the calculated moments are 0.88 \(\mu_B\) and 0.93 \(\mu_B\), respectively.

In Table 1, it can be found that, for \(\text{Fe}_2\text{TiZ}\) \((Z = \text{Ga, Ge, As, In, Sn and Sb})\), besides the nonmagnetic \(\text{Fe}_2\text{TiGe}\) and \(\text{Fe}_2\text{TiSn}\), other compounds are all ferrimagnets. In \(\text{Fe}_2\text{TiZ}\), Fe contributes most to the total moment. The moment of Ti is relatively small and antiparallel to that of Fe. Similar results are also observed in \(\text{Co}_{2}\text{TiSn}\) [11], in which a small negative Ti moment is observed.

### 3.3. Influence of lattice distortion

Finally, we will discuss the effect of uniform lattice distortion on the half-metallicity of \(\text{Fe}_2\text{TiZ}\) alloys. Now, for applications in spintronic devices, half-metals are usually prepared as thin films, then their lattice constants will be influence by the lattice of the substrate strongly and deviate from the equilibrium value. Since the spin polarization in half-metals may be sensitive to the lattice constants, studies on the relationship between the half-metallic character and the lattice constant for a given material are meaningful from both theoretical and technical aspects. In this paper, half-metallic \(\text{Fe}_2\text{TiSb}\) is selected as an example.

In Fig. 5 the DOS of \(\text{Fe}_2\text{TiSb}\) at different lattice constants are presented. In minority spin, with lattice expanding, a clear change of the Fermi level position is observed. From right to left, the Fermi level moves across the half-metallic gap. However, in majority spin, the Fermi level always locates at the Fe antibonding DOS peak. All this retains a high spin polarization ratio of \(\text{Fe}_2\text{TiSb}\) within the range studied (5.6–6.2 Å). The variation of lattice
constants will change the band gradients and the hybridization between the electrons of different atoms. When lattice constant increases, the center and width of the gap will change and the electrons will become more localized [31], which make the majority and minority bands move with respect to the Fermi level.

In Fig. 6, the total spin moment $M$ and spin polarization ratio $P$ of $\text{Fe}_2\text{TiSb}$ are presented as functions of lattice constant. It is clear that between 5.6 and 6.1 Å, the values of $M$ and $P$ remain unchanged. With lattice constant expanding further, the total moment increases to 1.09 $\mu_B$ and the spin polarization decreases slightly (98%). These results agree with preceding discussions on half-metallicity in $\text{Fe}_2\text{TiSb}$ is insensitive to lattice distortion. Within the range studied, the Fermi level locates always in the minority gap, and in majority spin, it locates in a high DOS peak. This kind of configuration helps to stabilize the half-metallicity and high spin polarization ratio when the half-metallic gap is disturbed by atomic disorder or lattice distortion.

4. Conclusions

The electronic structure and magnetic properties of new Fe-based Heusler alloys $\text{Fe}_2\text{TiZ}$ ($Z = \text{Ga, Ge, As, In, Sn and Sb}$) have been studied by first-principles calculations. In these alloys, the 24-electron $\text{Fe}_2\text{TiGe}$, $\text{Fe}_2\text{TiSn}$ are nonmagnetic semiconductors and other compounds are ferrimagnetic metals. $\text{Fe}_2\text{TiAs}$ and $\text{Fe}_2\text{TiSb}$ are predicted to be half-metallic with 100% spin polarization. The spin polarization ratio in $\text{Fe}_2\text{TiGa}$ and $\text{Fe}_2\text{TiIn}$ is also slightly (98%). These results agree with preceding discussions on $\text{Fe}_2\text{TiSb}$ is 100% for the lattice variation in a range of 5.6–6.1 Å, which is attractive in technical applications.

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