Effect of site preference of 3d atoms on the electronic structure and half-metallicity of Heusler alloy Mn$_2$YAl

Hongzhi Luo$^1$, Zhiyong Zhu$^1$, Li Ma$^1$, Shifeng Xu$^1$, Xiaoxi Zhu$^2$, Chengbao Jiang$^2$, Huibin Xu$^2$ and Guangheng Wu$^1$

$^1$ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China
$^2$ School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, People’s Republic of China

Received 23 October 2007, in final form 15 January 2008
Published 14 February 2008
Online at stacks.iop.org/JPhysD/41/055010

Abstract
The site preference of 3d atoms $Y$ in Mn$_2$YAl ($Y=\text{V, Fe, Co}$) alloys and its influence on their electronic structures and magnetism have been studied by first-principles calculations. The results prove that elements with more valence electrons than Mn tend to enter the A (0, 0, 0) and C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) sites and elements with fewer electrons prefer the B ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) site (Wyckoff positions). Meanwhile, it is found that for Mn$_2$VAl and Mn$_2$FeAl, a high spin polarization can be obtained whether the $Y$ atom enters the (A, C) or the B site. In particular, Mn$_2$VAI is half-metallic whether it forms the Cu$_2$MnAl type or the Hg$_2$CuTi type of structure. And a 100% spin polarization can be retained even when a 25% Mn–V antisite disorder occurs. This is quite preferable in practical applications. It is also found that the higher-valent element such as Co at the B ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) site has opposite effects and tends to close the energy gap. Finally, a systemic summarization on the electronic and magnetic properties of Mn$_2$YAl ($Y=\text{Ti, V, Cr, Mn, Fe and Co}$) alloys was made. All of them except for Mn$_2$TiAl are predicted as half-metals. The calculated total spin moment is an integral value and increases from $-3\mu_B$/f.u. for Mn$_2$TiAl to $+2\mu_B$/f.u. for Mn$_2$CoAl with increasing number of valence electrons. This agrees with the Slater–Pauling curve quite well. All the Mn$_2$YAl alloys studied here are ferrimagnets.

1. Introduction
In recent years, one of the most active fields of research is spin-electronics (spintronics) [1–3], in which it is the electron spin that carries information based on the alignment of a spin relative to a reference. This offers opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects. In particular, most magnetoelectronic devices rely on an imbalance in the number of majority and minority spin carriers, so a material with high spin polarization at the Fermi level is preferred [3]. An ideal choice is the so-called half-metals, which usually have an energy gap in the minority spin states at the Fermi level whereas the majority spin is strongly metallic. This results in a complete spin polarization of the conduction electrons [4].

Within this framework, the first half-metal was predicted by de Groot et al [4], in the half-Heusler alloys in 1983; in succession, some Heusler alloys have been theoretically predicted as half-metals and many experiments have been carried out to testify their magnetic and transport properties [5–9]. High tunnel magnetoresistance (TMR) was also observed in magnetic tunnel junctions (MTJs) based on Co$_2$FeSi [10] and Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al [11] films. Among these alloys, the case in Mn$_2$YZ is particularly interesting. It has been found that, in Mn$_2$YZ, the half-metallic properties are retained whether the $Y$ atoms have less valence electrons, like V and Cr, or more electrons than Mn, like Co [12–15]. So the Mn$_2$YZ alloys may be a promising family for finding new half-metallic materials and are worth studying thoroughly.

The Heusler alloy has a stoichiometric composition of $X_2YZ$, where $X$ and $Y$ are transition metal elements and $Z$ is a main group element. Generally, the Heusler structure can be looked upon as four interpenetrating face-centred-cubic (fcc) lattices, which has four unique crystal sites, namely, A (0, 0, 0),...
Figure 1. Crystal structure of the Heusler alloys. The unit cell has four crystal sites as the basis: A (0, 0, 0), B \( \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \), C \( \left( \frac{1}{2}, \frac{1}{2}, z \right) \) and D \( \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \) in Wyckoff coordinates.

(This figure is in colour only in the electronic version)

B tends to enter the (A, C) sites and form a Cu2MnAl type of structure; the main group elements usually occupy the D sites. For example, in Fe2YSi, the 3d elements Y with fewer d electrons than Fe tend to occupy the B sites whereas elements with more electrons prefer the (A, C) sites and Si occupies the D site [17]. This is also the case in most of the predicted half-metallic Heusler alloys. However, it is also found that Cr2MnZ (\( Z = P, As, S, Bi \)) are half-metallic with the Mn atom entering the B site [18], which is opposite to the normal case and suggests a new way for discovering candidates for half-metallic materials. Meanwhile, there is always a degree of antisite disorder in practical applications, which may strongly affect the half-metallic properties [19].

So the study on the site preference may be meaningful for synthesis of new half-metallic Heusler alloys.

In this paper, we studied the site preference of Y atoms in Mn2YAl (Y = V, Fe, Co) alloys and its influence on the electronic structure and half-metallic properties. Here the V atom has fewer valence electrons than Mn, and the Fe or Co atoms have more electrons than Mn. So they represent two types of elements in the 3d metals. We found that, for Mn2VAI and Mn2FeAl, a high spin polarization can be obtained whether the Y atom enters the (A, C) or the B site. Finally, we make a systemic summarization on the electronic and magnetic properties of Mn2YAl alloys (Y = Ti, V, Cr, Mn, Fe, Co).

2. Computational method

We carried out electronic-structure calculations using the pseudopotential method with a plane-wave basis set based on density-function theory [20, 21]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [22]. The electronic exchange-correlation energy was treated under the generalized-gradient-approximation (GGA) [23]. The plane-wave basis set cut-off was used as 500 eV for all the cases. One hundred and eighty two k points are employed in the irreducible Brillouin zone. These parameters ensured good convergences for the total energy. The convergence tolerance for the calculations was selected as \( 1 \times 10^{-6} \) eV atom\(^{-1} \). The calculations were based on theoretical equilibrium lattice parameters.

3. Results and discussion

To determine the equilibrium lattice constant and testify the site preference, we perform calculations on Mn2YAl (Y = V, Fe and Co) alloys for two different configurations, which are the Y atom enters the B site and the Y atom enters the (A, C) sites. The results are shown in figure 2. There is an obvious difference in the total energy between the two configurations. It can be seen that, for Mn2VAI, the V atom occupying the B sites (Cu2MnAl-type structure) is much lower in energy. While for Mn2FeAl and Mn2CoAl, the Y atom prefers to enter the (A, C) sites (Hg2CuTi-type). This agrees with the previous studies quite well [16]. The calculated equilibrium lattice constants and the energy difference between the two configurations at the equilibrium lattice constant are listed in table 1.

In figures 3(a)–(f) we show the calculated total and partial DOSs for Mn2YAl (Y = V, Fe and Co) alloys with both Cu2MnAl and Hg2CuTi types of structure. First, we will discuss the case in Mn2VAI with the two different structures. It can be seen in figures 3(a) and (b) that the different site preference of the V atom does not change the general shape of their electronic structures. The low energy states below \(-6 \) eV are mainly the s electrons of the Al atoms. The s electrons are relatively small and are separated from the p and d states by a dip in DOS in both spin directions. Thus they are unaffected by the d–d interaction and are not shown in figure 3. The states at around \(-4 \) eV are mainly the p states of the Al atoms in the occupied valence states. Above the p electrons are the d states of Mn and V atoms which extend from \(-4 \) to +2 eV and hybridize with each other. It can be seen that the d states are wide on the energy scale. This is mainly due to the strong hybridization of the 3d metals. It has been found that covalent hybridization between the lower-energy d states of the higher-valent transition metal atom such as Fe and the higher-energy d states of the lower-valent transition metal such as Mn is strong and can lead to the formation of bonding and antibonding bands [24]. Meanwhile, there are also contributions from the p electrons of the Z atoms.

It is clear that there are energy gaps at the Fermi level in the majority spin states of Mn2VAI whether it crystallizes in lower-energy Cu2MnAl type or higher-energy Hg2CuTi type of structure. Meanwhile, there is a large DOS peak in the...
Figure 2. Calculated total energy for Mn$_2$YAl ($Y$ = V, Fe and Co) compounds as functions of lattice parameters for both the Cu$_2$MnAl type and the Hg$_2$CuTi type of structure in the FM state.

Table 1. Calculated equilibrium lattice constants, the energy difference $\Delta E$ between the Cu$_2$MnAl and Hg$_2$CuTi types of structure at the equilibrium lattice constant, the calculated total and partial magnetic moments and spin polarization ratio for Mn$_2$YAl ($Y$ = V, Fe and Co) alloys.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\Delta E$ (eV)</th>
<th>Lattice constant (Å)</th>
<th>$M_{tot}$ ($\mu_B$/f.u.)</th>
<th>$M_{Mn}$ ($\mu_B$)</th>
<th>$M_{Y}$ ($\mu_B$)</th>
<th>$M_{MnAl}$ ($\mu_B$)</th>
<th>$P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$VAl (Cu$_2$MnAl type)</td>
<td>$-0.9$</td>
<td>5.800</td>
<td>$-2.00$</td>
<td>$-1.84$</td>
<td>1.5</td>
<td>0.18</td>
<td>100</td>
</tr>
<tr>
<td>Mn$_2$VAl (Hg$_2$CuTi type)</td>
<td></td>
<td>5.950</td>
<td>$-1.99$</td>
<td>$-3.02$ (A)</td>
<td>$-2.36$</td>
<td>0.2</td>
<td>100</td>
</tr>
<tr>
<td>Mn$_2$FeAl (Cu$_2$MnAl type)</td>
<td>$0.46$</td>
<td>5.725</td>
<td>0.93</td>
<td>$-1.08$</td>
<td>2.92</td>
<td>0.16</td>
<td>86</td>
</tr>
<tr>
<td>Mn$_2$FeAl (Hg$_2$CuTi type)</td>
<td></td>
<td>5.725</td>
<td>1.01</td>
<td>$-2.54$ (A)</td>
<td>0.06</td>
<td>0.08</td>
<td>100</td>
</tr>
<tr>
<td>Mn$_2$CoAl (Cu$_2$MnAl type)</td>
<td>$1.30$</td>
<td>5.700</td>
<td>1.57</td>
<td>1.32</td>
<td>$-0.90$</td>
<td>$-0.18$</td>
<td>7</td>
</tr>
<tr>
<td>Mn$_2$CoAl (Hg$_2$CuTi type)</td>
<td></td>
<td>5.750</td>
<td>2.00</td>
<td>$-2.44$ (A)</td>
<td>0.98</td>
<td>0.04</td>
<td>100</td>
</tr>
</tbody>
</table>

minority spin states. This results in a 100% spin polarization at $E_F$ in their spin states and makes Mn$_2$VAl half-metallic with the two different structures. It is known that in half-metallic Heusler alloys the lower-valent atoms usually prefer to occupy the B site and help to open the energy gap at $E_F$, while higher-valent atoms such as Fe, Co at the B site may have the opposite effect and may destroy the half-metallicity [19, 25]. Here, the majority gap in the DOS of Mn$_2$VAl with higher-valent Mn atom at the B site may be related to the large exchange splitting of Mn atoms, which helps to retain the gap. This is also the case in half-metallic Cr$_2$MnZ with Mn entering the B site as reported in [18]. The calculated $\Gamma$–X indirect band gap for Mn$_2$VAl is 0.24 eV for the Cu$_2$MnAl type and 0.14 eV for the Hg$_2$CuTi type of structure, respectively.

It is known that, in Heusler alloys, the electronic structure and magnetic properties of the 3d atoms are strongly influenced by their chemical surroundings such as the number, distance and symmetry of the nearest neighbours for a given site. So there are still differences between their DOS when the V atom enters the (A, C) or B sites, which are more obvious in the minority spin states. It can be seen in figure 3(b) that in the total DOS of Mn$_2$VAl with Cu$_2$MnAl type of structure, there is a high unoccupied antibonding peak at about 1.6 eV in the minority spin states, but in figure 3(a), the occupied bonding peak is high in the minority total DOS for Mn$_2$VAl with Hg$_2$CuTi type of structure. Meanwhile, the states around at $-1.8$ eV are much lower in the minority total DOS in figure 3(a) compared with those in figure 3(b). The high minority antibonding peak in figure 3(a) is from the contributions of both Mn and V states, while the high spin-down bonding peak in figure 3(a) is composed only of the bonding states of Mn (B). The differences are also seen in the partial DOS. It can be seen in figure 3 that the exchange splitting between the occupied states in one spin direction and the unoccupied states in the other spin direction is larger in the partial DOS in figure 3(a) than that in figure 3(b), which results in larger partial spin moments in Mn$_2$VAl with the Hg$_2$CuTi structure as shown in table 1.

The calculated total and partial DOSs of Mn$_2$FeAl and Mn$_2$CoAl with two different structures are shown in figures 3(c)–(f). Both of them are more stable when crystallizing in the Hg$_2$CuTi type of structure. However, as
seen in figure 3, the site occupation of higher-valent atoms has a different influence on their electronic structures.

For Mn$_2$FeAl, the influence of Fe at different crystal sites on the half-metallicity is not so strong. In the total DOS of the two atomic configurations, the majority DOS is high at $E_F$ and there is a gap in the minority DOS, which result in high spin polarization. For Mn$_2$FeAl with Hg$_2$CuTi type of structure, the spin polarization is 100%. Thus we can say it is a ‘true’ half-metal. For Mn$_2$FeAl with Cu$_2$MnAl type of structure, there is still a small DOS in the minority gap, so it is not half-metallic. However, the spin polarization ratio is still as high as 86%. The states in the minority gap mainly come from the antibonding peak of Fe (B), which suggests that the occupation of higher-valent atoms at the B site tends to destroy the half-metallicity.

The influence of higher-valent atoms is more clearly seen in the electronic structure of Mn$_2$CoAl, which is a half-metallic ferromagnet when the Co atom enters the (A, C) sites and is only a normal ferromagnetic metal when Co enters the B sites. In the DOS of Mn$_2$CoAl with Hg$_2$CuTi type of structure, the Fermi level lies in a dip in both majority and minority spin states, but there is no DOS in the minority gap, which makes Mn$_2$CoAl a half-metal. But for Mn$_2$CoAl with Cu$_2$MnAl type of structure, the DOS at $E_F$ is high in both spin directions, so its spin polarization ratio is rather low. From the partial DOS in figure 3(f), it is clear that the high minority states mainly come from the antibonding peak of Co (B).

The calculated total and partial spin moments for Mn$_2$YAl (Y = V, Fe, Co) alloys are listed in table 1. It is clear that the alloys predicted as half-metals have an integral magnetic moment. All the three alloys are ferrimagnets whether they crystallize in the Cu$_2$MnAl or the Hg$_2$CuTi type of structure. This is also the case in most of the Mn$_2$YZ alloys [13, 26]. Among the three Mn$_2$YAl alloys studied, the case of Mn$_2$VAl is particularly interesting. It is known that in half-metallic Heusler alloys, the antisite disorder between the (A, C) and the B sites can close the energy gap and destroy the half-metallicity [19, 27], which is a big problem in practical applications. Here we found that Mn$_2$VAl is half-metallic whether V occupies the (A, C) or the B site, so it may be expected that the half-metallicity is retained when the Mn–V antisite disorder occurs. To testify this, we calculated the electronic structure of Mn$_2$VAl with 25% Mn–V disorder, which has a chemical formula of \((\text{Mn}_{1.75}\text{V}_{0.25})_4(\text{V}_{0.75}\text{Mn}_{0.25})_4\text{Al}_4\). Similar calculations have been performed on Co$_2(\text{Mn}_{1-x}\text{Fe}_x)_4\text{Si}_4$ [28] which give satisfactory results. The calculated total DOS is shown in figure 4. It is found that a 100% spin polarization is retained when the disorder occurs and that the total magnetic moment is 1.99 $\mu_B$/f.u. which is quite similar to 2.00 $\mu_B$/f.u. in the fine ordered crystal. In practical applications, it is difficult to completely eliminate the atomic disorder, so a material such as Mn$_2$VAl which can keep a 100% P under a degree of disorder is preferred.

Finally, to do a deep study on the Mn$_2$YZ alloys, we will summarize the electronic and magnetic properties of Mn$_2$YAl (Y = Ti, V, Cr, Mn, Fe and Co) in the section given below. All the alloys studied here crystallize in the stable structure, that is the Y atom enters the B site for Y = Ti, V, Cr and Mn and enters the (A, C) site for Y = Fe and Co.

To the best of our knowledge, there are few reports on the structure and magnetic properties of Mn$_2$TiAl, so we first perform structural optimization for it to find the theoretical equilibrium lattice constant and to decide the stable ground...
The results are shown in figure 5. It is clear that the ferrimagnetic (FM) state is lower in energy than the paramagnetic (PM) state in Mn2TiAl. The energy difference between the FM and PM states is 0.53 eV at the equilibrium lattice constant.

Figure 6 gives the calculated total DOS for Mn2YAl alloys. The lattice constants of Mn2CrAl and Mn3Al are from [13, 15]. It is easily seen that their electronic structures are somewhat similar. All of them have an energy gap in one spin direction, which is in the majority DOS for Y = Ti, V, Cr and Mn and is in the minority DOS for Y = Fe, Co. This difference is due to their having a different number of valence electrons less or more than 24. It is worth noting that in Mn3Al there are 12 valence electrons in both spin directions, so it is difficult to distinguish the majority and minority bands by the number of electrons. Here we choose the energy gap located at the majority spin states. All Mn2YAl (Y = Ti, V, Cr, Mn, Fe and Co) alloys are half-metals except for Mn2TiAl, which has a small DOS in the majority gap and does not have complete spin polarization. The loss of the half-metallicity on Mn2TiAl may be attributed to its relatively large lattice constant. For it has been found that the energy gap width is quite sensitive to the lattice parameters and decreases with the expanded lattice [13, 29]. Meanwhile, we found that a small change of the lattice constant reopens the energy gap, so one can restore the half-metallicity in Mn2TiAl by doping with other metals. Another possible cause is the low DOS in the minority spin states at \( E_F \), which is too small to keep high spin polarization when there is a small DOS in the majority gap.

As the Y atom varies from Ti to Co, with increasing number of valence electrons, the majority and minority spin states are shifted to lower energy with respect to the Fermi level, which leads to the change in both their half-metallic and magnetic properties. It is clear in figure 6 that the states at \( E_F \) in the majority or minority DOS first increase with increasing number of valence electrons, then decrease again in the case of Mn2CoAl. Thus there are high DOS peaks in the total DOS of Mn2CrAl, Mn3Al and Mn2FeAl. This high DOS peak at \( E_F \) is preferable in half-metals, for it can be expected that this large peak will retain high spin polarization when a small DOS is introduced into the energy gap owing to some effects such as lattice distortion or atomic disorder. Also a high DOS is important for high efficiency spin projection systems.

The calculated total and partial magnetic moments for Mn2YAl alloys are listed in table 2 and also shown in figure 7, in which the solid line represents the Slater–Pauling curve, that is \( M_{\text{tot}} = Z_t - 24 \), where \( M_{\text{tot}} \) is the total spin magnetic moment per formula unit and \( Z_t \) is the total number of valence electrons. It is clear that all the alloys predicted as half-metals have an integral spin moment and agree with the Slater–Pauling curve quite well. For Mn2YAl (Y = Ti, V, Cr, Mn, Fe and Co), they have 21–26 valence electrons, so \( M_{\text{tot}} \) varies from \(-3\mu_B/\text{f.u.} \) to \(+2\mu_B/\text{f.u.} \), respectively. Meanwhile, our results suggest the Slater–Pauling curve can be used for alloys with valence electrons both more or less than 24. All the Mn2YAl alloys are ferrimagnets and the atoms at the B site have a large spin moment. So doping in Mn2YAl alloys can be a promising way for synthesizing new half-metallic antiferromagnets.

Besides high spin polarization of the conduction electrons at the Fermi level, another important factor for the half-metallic material is a high Curie temperature which should exceed room temperature for realistic applications. For Mn2YAl alloys, theoretical and experimental studies have been carried out.
Table 2. The calculated equilibrium lattice constants and the total and partial magnetic moments in $\mu_B$, spin polarization ratio $P$ for the Mn$_2$YAl ($Y = Ti, V, Cr, Mn, Fe and Co$) alloys with their stable structures. (Here VEN is the valence electron number.)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice constant (Å)</th>
<th>$M_{\text{tot}}$ ($\mu_B$/f.u.)</th>
<th>$M_{\text{Mn}}$ ($\mu_B$)</th>
<th>$M_{\text{Y}}$ ($\mu_B$)</th>
<th>$M_{\text{Al}}$ ($\mu_B$)</th>
<th>$P$ (%)</th>
<th>NVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$TiAl</td>
<td>5.940</td>
<td>−3.01</td>
<td>−2.26</td>
<td>1.32</td>
<td>0.2</td>
<td>35</td>
<td>21</td>
</tr>
<tr>
<td>Mn$_2$VAl</td>
<td>5.800</td>
<td>−2.00</td>
<td>−1.84</td>
<td>1.5</td>
<td>0.18</td>
<td>100</td>
<td>22</td>
</tr>
<tr>
<td>Mn$_2$CrAl</td>
<td>5.710</td>
<td>−1.00</td>
<td>−1.70</td>
<td>2.32</td>
<td>0.08</td>
<td>100</td>
<td>23</td>
</tr>
<tr>
<td>Mn$_2$Al</td>
<td>5.800</td>
<td>−0.001</td>
<td>−1.98</td>
<td>3.76</td>
<td>0.2</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>Mn$_2$FeAl</td>
<td>5.725</td>
<td>1.01</td>
<td>−2.54 (A)</td>
<td>0.06</td>
<td>0.08</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>Mn$_2$CoAl</td>
<td>5.750</td>
<td>2.00</td>
<td>−2.44 (A)</td>
<td>0.98</td>
<td>0.04</td>
<td>100</td>
<td>26</td>
</tr>
</tbody>
</table>

Figure 7. Calculated total spin moments for the studied Mn$_2$YAl ($Y = Ti, V, Cr, Mn, Fe and Co$) alloys. The solid line represents the Slater–Pauling curve.

4. Conclusion

We have studied the site preference of 3d atoms $Y$ in Mn$_2$YAl ($Y = V, Fe, Co$) and its influence on their electronic structures and magnetism by first-principles calculations. The calculations prove that elements with more valence electrons than Mn tend to enter the (A, C) sites and elements with fewer ones prefer the B sites. It is found that for Mn$_2$VAI and Mn$_2$FeAl, a high spin polarization can be obtained whether the $Y$ atom enters the (A, C) or the B site. In particular, Mn$_2$VAI is half-metallic when it crystallizes in either Cu$_2$MnAl type or Hg$_2$CuTi type of structure. And a 100% spin polarization is retained even when a 25% Mn–V type of disorder occurs. This is quite preferable in practical applications. It is also found that the higher-valent element such as Co at the B site has opposite effects and tends to close the energy gap. Finally, we summarize the electronic and magnetic properties of Mn$_2$YAl ($Y = Ti, V, Cr, Mn, Fe and Co$) alloys. All of them except for Mn$_2$TiAl are predicted as half-metals. The calculated total spin moments are integral values and increase from $-3\mu_B$/f.u. for Mn$_2$TiAl to $+2\mu_B$/f.u. for Mn$_2$CoAl with increasing number of valence electrons. This agrees with the Slater–Pauling curve quite well. All Mn$_2$YAl alloys studied are ferrimagnets.

Acknowledgment

This work is supported by the National Natural Science Foundation of China through Grant No 50531010 and Natural Science Foundation of Hebei through Grant No E2006000063.

References