Electronic structure and magnetism of the Heusler alloy Mn$_2$NiAl: A theoretical study of the shape–memory behavior

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Article info
Article history:
Received 9 April 2010
Accepted 13 April 2010

Keywords:
Heusler alloy
Band structure
Martensitic transformation

1. Introduction

In recent years, Mn-based Heusler alloys have received much attention because of their potential application as half-metallic materials, ferromagnetic shape–memory alloys (FSMAs) and other functional materials. Half-metallic materials can act as a spin filter providing a current with a high degree of spin polarization, which is of great importance in spin-dependent devices [1]. Mn$_2$VAl, Mn$_3$Ga, and also Mn$_2$CoZ ($Z$=Al, Ga, Si, Sb) have been predicted to be half-metallic materials by theoretical and experimental studies [2–5]. Meanwhile, new FSMAs have also been discovered among Mn-based Heusler alloys [6–8]. FSMAs are magnetic materials that exhibit a martensitic transformation together with large magnetic-field-induced strains. They can serve as magnetic actuator material.

In studies of FSMA, it is found that most FSMAs among the Heusler alloys are Ni–Mn based alloys, which can be obtained by substitution of some main group elements for Ni or Mn in NiMn alloys [9]. Besides experimental studies on the Ni–Mn system, theoretical calculations also play an important role in the search for new FSMAs. Chakrabarti and Barman [10] have predicted by first-principles calculations the martensitic transformation behavior in the stoichiometric Heusler alloy Mn$_2$NIn, in which the main group element In has been substituted for 50% of the Ni in NiMn. Accordingly, a martensitic transformation has been observed in Mn$_2$Ni$_{60}$In$_{40}$ ribbons at about 200 K [7]. So, to synthesize new FSMAs, theoretical calculations may be of essential importance.

In this paper, the electronic structure and magnetic properties of the Heusler alloy Mn$_2$NiAl with bcc and with tetragonal structure are studied by first-principles calculations. The possibility of martensitic transformation behavior in Mn$_2$NiAl is predicted.

2. Computational methods

The electronic structure has been calculated using the pseudopotential method with a plane-wave basis set based on density-functional theory [11,12]. The interactions between the atomic core and the valence electrons are described by the ultrasoft pseudopotential [13]. The electronic exchange-correlation energy has been treated under the local-density approximation (LDA) [14,15]. For all cases, a plane-wave basis set cut-off of 500 eV was used and 182 $k$ points were employed in the irreducible Brillouin zone. These parameters ensured good convergence of the total energy. The convergence tolerance in the calculations was selected as $1 \times 10^{-6}$ eV/atom. The calculations were performed based on the theoretical equilibrium lattice parameters.
3. Results and discussion

The Heusler alloy crystallizes in a highly-ordered bcc structure and has a stoichiometric composition \( X_2YZ \), where \( X \) and \( Y \) are transition-metal elements, and \( Z \) is a main-group element. Generally, the Heusler-alloy structure can be looked upon as four interpenetrating fcc lattices, in which the transition-metal atoms occupy the \( A(0, 0, 0), B(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), C(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), \) and \( D(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}) \) sites, respectively. The main-group-element occupies the \( D \) site, and \( A \), \( B \), \( C \) sites are occupied by transition metals. This is called the Hg\(_2\)CuTi-type of structure [16] as has been reported for Mn\(_2\)NiSn [17] or Mn\(_2\)NiGa [6]. This structure is different from the Cu\(_2\)MnAl type of structure, which is usual for Heusler alloys. In the Cu\(_2\)MnAl type of structure, the two Mn atoms occupy the \( A(, C) \) sites equally and leave the \( B \) site to Ni.

To determine the theoretical lattice parameter, and test the site preference on Mn\(_2\)NiAl, calculations have been performed with Mn\(_2\)NiAl with the Hg\(_2\)CuTi- and with the Cu\(_2\)MnAl-type of structure in both the non-magnetic (PM) and the ferromagnetic (FM) states. The results are presented in Fig. 2. It can be seen that, in both structures, the FM states are lower on the energy scale and thus more stable. The energy difference between the Hg\(_2\)CuTi- and the Cu\(_2\)MnAl-type of structure is 5.336 eV, which is a bit smaller than that of Mn\(_2\)NiGa [6], due to the smaller atomic radius of Al compared with that of Ga.

Fig. 3 presents the calculated total and partial density of states (DOS) of Mn\(_2\)NiAl in the austenitic phase. The total DOS of Mn\(_2\)NiAl consists of a low-energy part (below \(-6 \) eV), which is mainly made up of the s-states of Al, and a high-energy part (above \(-5 \) eV), which mainly arises from the contributions of the d-states of Mn and Ni atoms, together with the p-states of Al. The general properties of the total DOS are dominated by Ni and Mn 3d states in the bonding and antibonding region.

In both the majority- and minority-spin directions, the total DOS is separated into bonding and antibonding states by an energy gap below the Fermi level \((E_F)\). The majority-spin shows a three-peak structure, which arises from the contributions of the spin-up bonding and antibonding states of both the Mn and the Ni atoms. In the minority DOS, the states below the energy gap are mainly composed of the bonding peaks of Mn \((A)\) and Ni, and the states above the gap come from the antibonding peak of Mn \((B)\). In the majority-spin states, the energy gap is located around \(-0.33 \) eV, while in the minority-spin states, the gap is shifted to \(-0.65 \) eV due to the magnetic splitting.

It should be noted that, in the total DOS of austenitic Mn\(_2\)NiAl, \(E_F\) is located at the shoulder of a DOS peak in both spin directions, resulting in a relatively high \(N(E_F)\). It has been reported that a high \(N(E_F)\) will decrease the structure stability while low \(N(E_F)\) has the opposite effect [18,19]. So, this may result in the possibility of a structural transformation with lowering temperatures. The electronic structure of the martensitic phase will be discussed in the next section.

In Fig. 3, the PDOS of Mn\((B)\) shows a two-peak structure (bonding and antibonding peak) due to the crystal-field effect, which results in a large local spin moment at the Mn\((B)\) site. It may be noted that,
for Mn$_2$NiAl, the structure of the PDOS of Mn(A) and Mn(B) is opposite to each other. In the majority states of Mn (B), the two peaks are basically below the Fermi level and occupied and, in the minority PDOS, the antibonding peak is high above $E_F$. In contrast, the partial DOS of Mn(A) lies mainly below $E_F$ in the minority-spin states and, above $E_F$ in the majority-spin states. Therefore, the contributions to the total DOS from Mn(A) and Mn(B) are opposite to each other, indicating an antiparallel configuration of their spin moments [4]. This agrees well with reported results on Mn$_2$NiGa [10]. In Mn$_2$NiAl, the two Mn atoms are nearest neighbors with a distance of 1.991 Å. The small distance may cause strong direct Mn–Mn interaction and result in the antiparallel orientation of Mn (A) and Mn (B) spin moments [20].

The PDOS of Ni in Fig. 3 lies basically below the Fermi level and is quite symmetric in the majority- and minority-spin direction. The contribution of Ni to the total spin moment is small. The p states of Al also hybridize with the 3d states of Mn and Ni. This hybridization will induce a small spin moment at the Al site. The details can be explained from the feature of covalent magnetism, as introduced in Ref. [21].

Experimental lattice constants of martensitic Mn$_2$NiAl are still unavailable. We perform a structural optimization for it first. In the optimization of the martensitic phase, for convenience sake, we assume that there is no volume difference between the austenitic and martensitic phases. That is also the case in many other FSMAs such as Mn$_2$NiGa, Mn$_2$NiIn or Ni$_2$MnGa [10,20,22]. For example, in Mn$_2$NiGa, the experimental volume difference between the two phases is only 0.6% [6]. The minimum of the total energy $E_{tot}$ was obtained by varying $c/a$ as a function of a volume-fixed tetragonal lattice. The results are presented in Fig. 4. It can be seen that there are two local energy minima in the $E_{tot}= c/a$ curve. The shallow one is at $c/a=0.97$ and the deeper one at $c/a=1.222$. This is quite similar to the case of Ni$_2$MnGa [22]. The minimum at $c/a=1.222$ is lower on the energy scale, indicating that the martensite with $c$-axis lattice expansion and $a$, $b$-axis lattice contraction is more stable. The equilibrium lattice constants are $a=b=5.43$ Å and $c=6.88$ Å and the $c/a$ ratio is 1.222, similar to the experimental result of 1.214 for Mn$_2$NiGa [6].

Fig. 5 presents the calculated total and partial DOS for martensitic Mn$_2$NiAl. It is seen that tetragonal distortion does not affect the general shape of the total DOS. A main change is that the majority DOS peak in the austenitic phase at $-1.0$ eV splits into two peaks in the martensitic phase at $-1.26$ and $-0.69$ eV, respectively. Meanwhile, an interesting difference in the total DOS around $E_F$ is observed: the energy gap moves to the high-energy end in the martensitic DOS. In the austenitic phase, $E_F$ is located at the shoulder of the antibonding peak, but in the martensitic phase, $E_F$ moves to the bottom of the energy gap, which reduces the value of $N(E_F)$ effectively. The total energy difference between the martensitic and the austenitic phase is $-0.07$ eV/unit. This indicates that the tetragonal phase is more stable and that a martensitic transformation may occur at lowering temperature. Similar results have also been observed in Ni$_2$MnGa and are known as the Jahn–Teller effect, in which the DOS peak at $E_F$ in the austenitic phase is divided into two peaks below and above $E_F$ with tetragonal distortion, resulting in a lowering of the total energy and causing the martensitic transformation [23].

With the martensitic transformation, the majority antibonding peak at $0.25$ eV in the austenitic phase is shifted to $0.6$ eV. The variation of the total DOS indicates a charge transfer from the occupied to the unoccupied states. This transfer will introduce more d-holes in the majority states and make the total spin moment of the martensite smaller than that of the austenite.

The martensitic transformation does not change the configuration between the PDOS of Mn(A) and Mn(B). As a result, their spin moments are also antiparallel like in the austenite. The calculated total and partial spin moments of Mn$_2$NiAl are listed in Table 1. The total spin moments are 1.48 and 1.14 μB/f.u. for the austenite and martensite, respectively. The variation of the total moment is mainly due to the change of the Mn spin moments. The Mn(A) moment is $-1.48$ μB in the austenitic phase and $-1.66$ μB in the martensitic phase, while the Mn(B) moment decreases from $2.72$ to $2.58$ μB in the martensitic phase. This all leads to a decrease of the total spin moment. In both the austenitic and the martensitic phase, the Ni moment is small ($0.22$ μB in the austenitic phase and $0.24$ μB in the martensitic phase) and contributes little to the total spin moment. These results agree quite well with earlier discussions on Mn$_2$NiGa and Mn$_2$NiIn [10,20]. In these compounds, there is a ferrimagnetic coupling between the Mn(A) and the Ni or Mn(B) moment.

![Fig. 4. Total energy as a function of the c/a ratio for Mn$_2$NiAl in the martensitic phase.](image)

![Fig. 5. Calculated spin-projected total and partial DOS of Mn$_2$NiAl in the martensitic phase.](image)

### Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>$M_{total}$ (μB/f.u.)</th>
<th>$M_{Mn(A)}$ (μB)</th>
<th>$M_{Mn(B)}$ (μB)</th>
<th>$M_{Ni}$ (μB)</th>
<th>$M_{Al}$ (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenite</td>
<td>1.48</td>
<td>-1.48</td>
<td>2.74</td>
<td>0.22</td>
<td>-0.02</td>
</tr>
<tr>
<td>Martensite</td>
<td>1.14</td>
<td>-1.66</td>
<td>2.58</td>
<td>0.24</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
4. Conclusions

The electronic structure and magnetic properties of the Heusler alloy Mn$_2$NiAl have been studied by first-principles calculations. It is found that the phase transformation from cubic to tetragonal structure lowers the total energy effectively, indicating the possibility of a martensitic phase transition at low temperatures. After the martensitic phase transformation, the Fermi level is shifted from the shoulder of the antibonding peak in the austenitic phase to the bottom of an energy gap, which reduces the value of $N(E_F)$ and increases the phase stability of the martensite. Thus, ferromagnetic shape memory effect may be discovered in Mn$_2$NiAl or in alloys with some adjustment of the composition. Mn$_2$NiAl is a ferrimagnet in both the austenitic and the martensitic phases. The total spin moments are 1.48 and 1.14 $\mu_B$/f.u. for the austenite and the martensite, respectively. The total moment is mainly determined by the antiparallel aligned Mn(A) and Mn(B) spin moments because the contribution of Ni to the total moment is small.

Acknowledgements

This work is supported by National Natural Science Foundation of China in Grant no. 50901028 and Natural Science Foundation of Tianjin Grant no. 08JCYBJC09700.

References