Effect of the main-group elements on the electronic structures and magnetic properties of Heusler alloys Mn$_2$NiZ (Z = In, Sn, Sb)

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Abstract

The magnetic properties and electronic structure of Mn$_2$NiZ (Z = In, Sn, Sb) have been studied. The magnetic structure of these alloys is mainly determined by the main-group element Z instead of the distance between the Mn atoms. Electronic structure calculations suggest that Mn$_2$NiIn and Mn$_2$NiSn are both ferrimagnets with antiparallel alignment between the Mn moments. But this antiferromagnetic coupling is weakened by the increasing number of valence electrons of the Z atoms. When it comes to Mn$_2$NiSb, a ferromagnetic coupling between the Mn atoms is observed. Mn$_2$NiSn and Mn$_2$NiSb have been synthesized successfully. Their $M_s$ at 5 K agree well with the theoretical value.

1. Introduction

In recent years, the Mn-based Heusler alloys have attracted much attention for their potential applications as functional materials. The typical applications are half-metallic materials and ferromagnetic-shape-memory-alloys (FSMAs). Mn$_2$VAl, Mn$_2$VSi, Mn$_2$FeZ (Z = Al, Sb) and also Mn$_2$CoZ (Z = Al, Ga, Si, Sb) have been predicted as half-metallic materials by theoretical and experimental studies [1–4]. Also a series of novel half-metallic antiferromagnets has been developed in Mn-based Heusler alloys [5–7]. Meanwhile, new FSMAs such as Mn$_2$NiGa and MnNiIn have been discovered in Mn-based Heusler alloys [8–10]. All these attract much attention in searching for new functional materials in this series of alloys. Recently, field-induced martensitic transition is observed in Co-doped Mn$_2$NiGa. The cause has been attributed to the “ferromagnetic activation effect” of Co. With the substitution of Co, the moments of the nearest neighboring Mn are aligned ferromagnetically [11]. So it can be meaningful to investigate the effect of alloying on the electronic structure and magnetic properties of Mn-based Heusler alloys.

Recently, a new Mn-based Heusler alloy Mn$_2$NiSb has been reported [12]. It is found that the main-group element Sb may also has a similar “activation effect”. In Mn$_2$NiSb, the two Mn atoms are nearest neighbors and have ferromagnetic coupling between their moments, while other reported Mn-based Heusler alloys like Mn$_2$NiGa all show antiparallel alignment between the two Mn moments [4,8]. So it is the main-group elements that play an important role in the electronic structure and magnetic properties of these alloys. In this paper, the electronic structures and magnetic properties of Heusler alloys Mn$_2$NiZ (Z = In, Sn, Sb) are studied experimentally and theoretically. The influence of main-group elements on the electronic structure has been discussed.

2. Experimental and computational methods

The Mn$_2$NiZ (Z = In, Sn, Sb) ingots were prepared by arc-melting the constituent elements in a high-purity argon atmosphere. The purity of the starting materials was 99.9% or higher. All ingots were melted at least three times for homogenization. The ingots were then wrapped in molybdenum foil and sealed in a quartz tube and annealed at 1073 K for 72 h under protection of...
argon atmosphere. X-ray powder diffraction (XRD) with Cu Kα radiation was used to check the crystal structure and determine the lattice constants. The temperature dependence of the AC susceptibility was measured to determine the Curie temperature \( T_c \). The magnetization curves were measured in a superconducting quantum interference device (SQUID) magnetometer with applied fields up to 5 T.

The electronic structure is calculated using the pseudopotential method with a plane-wave basis set based on density-function theory [13,14]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [15]. The electronic exchange–correlation energy was treated under the local-density approximation (LDA) [16]. The plane-wave basis set cut-off was used as 500 eV for all the cases and 182 \( k \) points are employed in the irreducible Brillouin zone. These parameters ensured good convergences for total energy. The convergence tolerance for 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

Fig. 1 presents the powder XRD pattern of Mn\(_2\)NiZ (Z = In, Sn, Sb). It is clear that a single-phase bcc structure is obtained in Mn\(_2\)NiSn and Mn\(_2\)NiSb. The superlattice reflections (111) and (200) are quite clear in their patterns, indicating that the highly ordered Hg\(_2\)CuTi-type of structure has been formed. The Heusler alloy has a stoichiometric composition X\(_2\)YZ, where X and Y are transition-metal elements, and Z is a main-group element. For Heusler alloys with Hg\(_2\)CuTi-type of structure, the two X atoms occupy different crystal sites namely A (0,0,0), B (\( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \)), respectively, and leave the C (\( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \)) and D (\( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \)) sites to the Y and Z atoms. This is just the case in Mn\(_2\)NiSn or Mn\(_2\)NiGa and has been confirmed by previous studies [8,17]. The lattice constants for Mn\(_2\)NiSn and Mn\(_2\)NiSb are 6.02 and 5.95 Å, respectively. The contraction of the lattice reflects the different atomic radius of Sn and Sb. However, the attempt to synthesize Mn\(_2\)NiIn is not successful, which may be attributed to the larger atomic radius of In compared with that of other main-group elements.

The electronic structure calculations were performed using the experimental lattice constants except for Mn\(_2\)NiIn. The equilibrium lattice constant of it was determined by structural optimization and listed in Table 1. In the calculations, both ferromagnetic and antiferromagnetic configurations were considered.

The calculated total density-of-states (DOS) for Mn\(_2\)NiZ (Z = In, Sn, Sb) are presented in Fig. 2. Due to the same crystal structure and site preference in these alloys, it can be seen that the general shape of their total DOS is quite similar. In both spin directions, the DOS is separated to bonding- and antibonding-states by a dip near the Fermi level (\( E_F \)). The magnetic splitting is obvious, indicating that these alloys have a ferromagnetic ground state. In the majority-spin states, a three-peak structure is identified, which arises from contributions of spin-up bonding and antibonding states of both the Mn and the Ni atoms. However, the majority states are shifted to lower energy as the Z atom varies from In to Sb. It is seen that \( E_F \) is below the antibonding peak in the majority DOS of Mn\(_2\)NiIn, and locates just at the antibonding peak in Mn\(_2\)NiSn. When Z = Sb, the Fermi level is basically above the antibonding peak. This is due to the increasing number of valence electrons from In to Sb. The extra electrons will mainly fill in the majority spin band and introduce more occupied states, which leading to the increase of the total spin moments.

The change of the total DOS mainly arises from the variation of the Mn (A) states. Mn atoms at the A sites and the main-group atoms Z at the D site are nearest neighbors. The Z atom provides s–p states to hybridize with d electrons and determines the degree of occupation of the p–d orbital [18]. So the variation of the Z atoms will influence the DOS of Mn (A) directly. Fig. 3 presents the partial DOS (PDOS) of Mn (A) and Mn (B), respectively. The variation of the Mn (B) DOS is small, which always keeps a two-peak structure (bonding- and antibonding-peak) due to the crystal-field effect. For the DOS of Mn (A), the case is quite different. The majority DOS of Mn (A) is shifted lower on energy scale, agreeing well with the variation of the total DOS. It is worth noting that, for Mn\(_2\)NiIn, the structures of the PDOS of Mn (A) and Mn (B) are 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 high 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, suggesting an antiparallel configuration of their spin moments. However, as the Z atom varies to Sn or Sb, the antibonding peak in the majority DOS of Mn (A) is shifted partly below \( E_F \). This change can weaken the antiferromagnetic coupling between the Mn atoms.
The exchange interactions and magnetic structure of these alloys. And of alloys, it is mainly the main-group elements that influence the weakened though the lattice constant contracts. So in this series and 3.30

\[ M(\text{B}) = 0.60 \text{ and } 3.30 \mu_B, \text{respectively.} \]

\[ M(\text{A}) = 1.03 \mu_B, \text{and } M(\text{B}) = -2.84 \mu_B. \]

\[ T_C = 647 \text{K}. \]

Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice constant (Å)</th>
<th>( M_\text{A} ) (( \mu_B ))</th>
<th>( M_\text{B} ) (( \mu_B ))</th>
<th>( M_{\text{Mn}(\text{A})} ) (( \mu_B ))</th>
<th>( M_{\text{Mn}(\text{B})} ) (( \mu_B ))</th>
<th>( M_\text{Ni} ) (( \mu_B ))</th>
<th>( M_\text{Sn} ) (( \mu_B ))</th>
<th>( T_C ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn2NiIn</td>
<td>5.96</td>
<td>1.03</td>
<td>-2.84</td>
<td>3.62</td>
<td>0.20</td>
<td>0.04</td>
<td>-2.84</td>
<td>3.62</td>
</tr>
<tr>
<td>Mn2NiSn</td>
<td>6.02</td>
<td>2.95</td>
<td>3.35</td>
<td>-0.26</td>
<td>3.34</td>
<td>0.24</td>
<td>0.04</td>
<td>3.30</td>
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<tr>
<td>Mn2NiSb</td>
<td>5.95</td>
<td>4.20</td>
<td>4.21</td>
<td>0.60</td>
<td>3.30</td>
<td>0.30</td>
<td>0.02</td>
<td>6.47</td>
</tr>
</tbody>
</table>

* The lattice constant of Mn2NiIn is a theoretical value.

The calculated total and partial spin moments for Mn2NiZ (Z = In, Sn, Sb) are listed in Table 1. It can be seen that the total spin moment increases as Z varies from In to Sb. The moments for Mn (A) and Mn (B) in Mn2NiIn are -2.84 and 3.62 \( \mu_B \), respectively. The Mn moments partly compensate each other. So Mn2NiIn is a typical ferrimagnet with a total moment of 1.03 \( \mu_B \). Mn2NiSn is also a ferrimagnet, as has been proved by neutron diffraction [17], but the partial moment of Mn (A) is only -0.26 \( \mu_B \), indicating that the antiferromagnetic coupling between the Mn moments is weakened. In Mn2NiSb, a ferromagnetic coupling between the Mn moments is observed. The moment for Mn (A) and Mn (B) is 0.60 and 3.30 \( \mu_B \). In order to testify the calculated results, the magnetization curves of Mn2NiSn and Mn2NiSb were measured at 5 K, as has been presented in Fig. 4. The saturation magnetization \( M_s \) for Mn2NiSn and Mn2NiSb is 2.95 and 4.20 \( \mu_B/\text{f.u.} \), respectively, as has been listed in Table 1. These results fit the theoretical values well. The small division of the Mn2NiSn moment may be related to the antisite disorder in the crystal [19].

In full-Heusler alloys, the exchange mechanism determining the magnetic order is rather complicated and can be understood on the basis of nearest neighbor exchange coupling. According to the study of Sasioglu et al., the nearest neighbor exchange interaction has determining influence on the magnetic order [20]. In normal Heusler alloys, the exchange interaction between the Mn moments is usually influenced by the distance between them. If the Mn atoms are nearest neighbors, the coupling between their moments tends to be antiferromagnetic [21,22]. But in Mn2NiZ (Z = In, Sn, Sb), antiferromagnetic coupling is weakened though the lattice constant contracts. So in this series of alloys, it is mainly the main-group elements that influence the exchange interactions and magnetic structure of these alloys. And the doping of Sb may be a possible way to control the magnetic structure of other Mn-based Heusler alloys. The Curie temperatures of Mn2NiSn and Mn2NiSb are 565 and 647 K, respectively, as have been listed in Table 1. The lower \( T_C \) of the former may be related to the antiferromagnetic coupling of Mn moments in it Fig. 4.

4. Conclusion

The magnetic properties and electronic structures of Mn2NiZ (Z = In, Sn, Sb) have been studied. It is found that the magnetic structures of these alloys are mainly determined by the main-group elements Z instead of the distance between the Mn atoms. Electronic structure calculations suggest that Mn2NiIn and Mn2NiSn are ferrimagnets with antiparallel alignment between the Mn moments. However, this antiferromagnetic coupling is weakened with the increasing number of valence electrons of the Z atoms. When it comes to Mn2NiSb, a ferromagnetic coupling between the Mn moments is observed. The calculated total spin moments also increase with increasing number of valence electrons. Mn2NiSn and Mn2NiSb have been synthesized successfully. Their \( M_s \) at 5 K agree well with the theoretical value. The \( T_C \) of Mn2NiSn is lower than that of Mn2NiSb, which may be related to the antiferromagnetic coupling of Mn moments in the former.

Acknowledgements

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References