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Effect of rapid solidification on the site preference of Heusler alloy Mn$_2$NiSb

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Abstract
The site preference of Mn atoms in Heusler alloy Mn$_2$NiSb can be influenced obviously by different preparing methods. Mn atoms enter the A and B sites after arc-melting and subsequent annealing, and form an Hg$_2$CuTi-type of structure. However, after melt-spinning, the Mn atoms tend to occupy the (A, C) sites and form the Cu$_2$MnAl-type of structure. The electronic structure calculations suggest that the Hg$_2$CuTi-type of structure is lower in energy than the Cu$_2$MnAl one and more stable. The lattice constant of the former is a bit larger than the latter one, agreeing with experimental results. Ferromagnetism is observed in Mn$_2$NiSb with both structures. Calculations give a total moment of 4.21 $\mu_B$ for the Hg$_2$CuTi-type of structure and 3.93 $\mu_B$ for the Cu$_2$MnAl-type one. These results fit the saturation magnetization at 5 K quite well. The difference between the Curie temperatures of the bulk and ribbon samples is about 77 K.

1. Introduction
In recent years, the Mn-based Heusler alloys have attracted much attention for their potential application as functional materials. The studies focus mainly on the half-metallic materials and ferromagnetic shape memory alloys (FMSAs). In 1999, Mn$_2$VAl was predicted to be a half-metal from band theory calculations [1]. In succession, Mn$_2$Ga, Mn$_2$CrZ ($Z = \text{Al, Sb}$) and also Mn$_2$CoZ ($Z = \text{Al, Ga, Si, Sb}$) have also been predicted as half-metallic materials by theoretical and experimental studies [2–4]. Meanwhile, new FMSAs such as Mn$_2$NiGa and MnNiIn have been discovered in Mn-based Heusler alloys [5, 6]. All these attract much attention in searching for new functional materials in this series of alloys. From these studies, it has been found that the site preference and magnetic structure are important for the properties of these alloys. For example, the field-induced martensitic transition in these alloys is strongly related to their magnetic structure especially the magnetic structure of Mn atoms [7]. So it is important to synthesize new Mn-based Heusler alloy and investigate their atomic order and magnetism.

Quite recently, we synthesized a new Mn-based Heusler alloy, Mn$_2$NiSb, which has a ferromagnetic coupling and a large spin moment. This ferromagnetic character has not been reported in other stoichiometric Mn-based alloys and is attributed mainly to the effect of Sb [8]. In this work, we have studied the structure and magnetic properties of the Mn$_2$NiSb melt-spun ribbons. It is known that that melt-spinning technique is a useful way to produce new Heusler alloys and has an obvious influence on the atomic order [9, 10]. Hence, it may be expected that Mn$_2$NiSb ribbons have different site preference and magnetic properties compared with the bulk sample. The results are discussed with the first-principles calculations.

2. Experimental and computational methods
The Mn$_2$NiSb ingots were prepared by arc-melting the constituent elements in a high purity argon atmosphere. The purity of the raw materials was 99.9% or higher. All the 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 873 K for 3 days under the protection of an argon atmosphere. The melt-spun ribbons were prepared by a single wheel technique with a substrate velocity (V_s) of 20 m s⁻¹, under the protection of an Ar atmosphere. Then powder x-ray diffraction (XRD) with Cu Kα radiation was used to verify the crystal structure and to determine the lattice constants. The sample was finely powdered before testing to eliminate the possible texture in the sample. The Curie temperature was determined by high temperature ac susceptibility measurement. The magnetization curves were measured by a SQUID magnetometer with an applied field up to 5 T.

The electronic structure is 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 were described by the ultrasoft pseudopotential [13]. The electronic exchange–correlation energy was treated under the local-density approximation (LDA) [14]. 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 × 10⁻⁶ eV atom⁻¹. The calculations were performed based on the theoretical equilibrium lattice parameters.

3. Results and discussion

3.1. Crystal structure

Usually, the Heusler alloys X₂YZ can be taken as four interpenetrating face-centred-cubic (fcc) lattices, which have four unique crystal sites, namely A (0, 0, 0), B (½, ½, ½), C (½, ½, ½) and D (½, ½, ½) in Wyckoff coordinates. In Heusler alloys, the X and Y atoms are transition metal elements and occupy the (A, C) and B sites, and the main group element Z occupies the D site. Usually, the site preference of different 3d elements in Heusler alloys is determined by the number of their valence electrons [15]. Elements with more valence electrons tend to enter the (A, C) sites; while elements with less electrons prefer the B sites; the main group elements usually occupy the D sites.

The crystal structure of the Heusler alloys can be determined by powder XRD. The ordered Heusler structure can be represented by the existence of the superlattice diffractions of (111) and (200). For the B2 or A2 type of structure, one or two superlattice diffraction peaks will disappear [16]. Meanwhile, the intensities of different lattice reflections are proportional to the square of the structure factor, F². The F (111) and F (200) are order-dependent superlattice reflections, while F (220) is an order-independent principal reflection. So the different superlattices can be distinguished by comparing the intensity ratios of the different lattice reflections I(111)/I(220) and I(200)/I(220) or I(111)/I(200) directly [17, 18].

In figure 1, we present the powder XRD patterns for the bulk and ribbon samples of Mn₂NiSb, respectively. It can be seen that in both patterns the superlattice diffraction peaks (111) and (200) are quite strong, indicating that a highly ordered structure is obtained. However, the relative intensity of the two peaks is quite different. I(111)/I(200) is 1.67 in the bulk sample, while 0.82 for the ribbon. This suggests that annealing and melt-spinning may have different influences on the site preference of Mn in Mn₂NiSb. In order to investigate this further, we stimulated the powder XRD pattern for two models: one is the Mn atoms entering the (A, C) sites, which is also called the Cu₂MnAl-type of structure, as has been observed in most Heusler alloys such as Cu₂MnSi or Cu₂MnAl; and the other is the Mn atoms entering the A and B sites, which is also called the Hg₂CuTi-type of structure. A typical example is Mn₂NiGa [16].

The calculated superlattice diffractions (111) and (200) are shown in the inset of figure 1. I(111)/I(200) are 2.50 and 0.80 for the Hg₂CuTi- and Cu₂MnAl-types of structure, respectively. This agrees with the experimental results and suggests that Mn₂NiSb may have a different site preference due to different synthesizing methods. The derived lattice constant for the two samples are listed in table 1. It can be seen that the lattice constant of the ribbon sample is smaller than that of the bulk one.

3.2. Total energy and electronic structure

In figure 2, we present the total energy as a function of the lattice parameters for Mn₂NiSb with both the Cu₂MnAl- and the Hg₂CuTi-types of structure. It is clear that the Hg₂CuTi-type of structure is lower in energy, suggesting that it is more stable than the Cu₂MnAl one. However, with a small contraction of the lattice, the energy difference decreases and when a < 5.7 Å, the total energy of the Cu₂MnAl-type structure becomes smaller. Hence it may be expected that this structure can be obtained by a metastable preparing method such as melt-spinning. Also it can be expected that the lattice constant of Mn₂NiSb with the Cu₂MnAl-type of structure should be smaller than that of the Hg₂CuTi one, as has been observed in...
Table 1. The lattice constants, Curie temperature $T_C$, saturation magnetization $M_s$, and calculated total and partial spin moments for Mn$_2$NiSb with Cu$_2$MnAl- and Hg$_2$CuTi-types of structure.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lattice constant (Å)</th>
<th>$T_C$ (K)</th>
<th>$M_s$ ($\mu_B$/f.u.)</th>
<th>$M_{Cu}$ ($\mu_B$)</th>
<th>$M_{Mn}$ ($\mu_B$)</th>
<th>$M_{Ni}$ ($\mu_B$)</th>
<th>$M_{Sb}$ ($\mu_B$)</th>
</tr>
</thead>
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<tr>
<td>Mn$_2$NiSb</td>
<td>5.935</td>
<td>570</td>
<td>3.80</td>
<td>3.93</td>
<td>1.92</td>
<td>0.28</td>
<td>-0.16</td>
</tr>
<tr>
<td>Cu$_2$MnAl-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$_2$NiSb</td>
<td>5.954</td>
<td>647</td>
<td>4.20</td>
<td>4.21</td>
<td>0.6 (A)</td>
<td>0.3</td>
<td>0.02</td>
</tr>
<tr>
<td>Hg$_2$CuTi-type</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.3</td>
</tr>
</tbody>
</table>

Figure 2. Calculated total energy for Mn$_2$NiSb as function of lattice parameters for both the Cu$_2$MnAl-type and the Hg$_2$CuTi-type of structure.

Figure 3. The calculated total and partial DOS for Mn$_2$NiSb with the (a) Cu$_2$MnAl-type and (b) Hg$_2$CuTi-type of structure.

experimental patterns. Similar metastable Heusler alloys have also been found in Ni$_2$FeGa and Ni$_2$FeSb [9, 10].

The calculated total and partial density of states (DOS) of Mn$_2$NiSb with two different structures are presented in figures 3(a) and (b), respectively. Both of them present strong magnetic splitting and ferromagnetic character in their total DOS. However, due to the different atomic site preference in the crystal, there is an obvious difference between them. In the majority spin states, the Fermi level $E_F$ locates at the shoulder of a DOS peak for Mn$_2$NiSb with both structures. But in the minority spin states, $E_F$ is on the DOS peak for the Cu$_2$MnAl-type of structure which results in a high value of $N(E_F)$, while it is close to an energy gap for the Hg$_2$CuTi-type of structure, reducing the value of $N(E_F)$ effectively. It is known that a high $N(E_F)$ will decrease the structural stability while a low $N(E_F)$ has the opposite effect [19, 20]. So Mn$_2$NiSb with a Hg$_2$CuTi-type of structure is favoured energetically, agreeing with the preceding discussions from total energy.

The difference between their electronic structures is clearly seen in the partial DOS. For Mn$_2$NiSb with a Cu$_2$MnAl-type structure, the Mn atoms enter the (A, C) sites and have four Ni and four Sb as nearest neighbours. Due to the similar surroundings, their DOS are the same. It can be seen that the Mn and Ni d states are wide on the energy scale. The formation of the bonding and antibonding bands are caused by the strong covalent hybridization between the lower-energy d states of the high-valent transition metal atom such as Ni and the higher-energy d states of the low-valent transition metal such as Mn. The bonding hybrids are localized mainly at the high-valent transition metal atom site while the unoccupied antibonding states mainly at the low-valent transition metal site [21]. It is clear that Mn (A, C) have large antibonding states in the minority spin and unoccupied, while in the majority spin, the states are basically below $E_F$ and occupied. This results in a large spin moment on the Mn site. For Mn$_2$NiSb with Hg$_2$CuTi-type of structure, the Mn atoms occupy the A sites and have four Mn and four Sb as nearest neighbours. There is a large bonding peak far below the Fermi level, which weakens the exchange splitting and makes the Mn (A) moment smaller than that in the Cu$_2$MnAl-type of structure. However, the Mn atom at the B site is in a bcc crystal field, which causes an $e_g-t_{2g}$ splitting and a large spin moment. As will discussed below, the large Mn (B) moment compensates the decrease in the Mn (A) moment and makes the Hg$_2$CuTi-type of sample have a larger total moment than that of the Cu$_2$MnAl one.
The states of Ni are similar and basically below the Fermi level in the DOS for the two kinds of structures. It can be seen that they are quite symmetric in both the up- and down-spin directions and equally populated, so their contributions to the total spin moment will be small. Meanwhile, due to the change in chemical surroundings, the Ni states for the Cu$_2$MnAl-type of structure are shifted to higher energy in both the majority and the minority spin states.

The calculated total and partial spin moments for Mn$_2$NiSb with both the Cu$_2$MnAl- and the Hg$_2$CuTi-types of structure are presented in table 1. It is clear that Mn$_2$NiSb with two structures are both ferromagnets. The spin moment for the Hg$_2$CuTi-type of structure is 4.21 $\mu_B$ and larger than the 3.93 $\mu_B$ of the Cu$_2$MnAl one. The total moment comes mainly from the partial moments of Mn atoms, and the contributions from Ni are small.

Figure 4(a) gives the magnetization curves for the bulk and ribbon samples of Mn$_2$NiSb measured at 5 K. The saturation magnetization $M_s$ of the bulk sample is 4.20 $\mu_B$/f.u, higher than the 3.80 $\mu_B$ for the ribbon sample, as been listed in table 1. This coincides with the preceding theoretical calculation well and is due to the different site preference of Mn in the lattice. The $M_s$ of the ribbon sample is slightly smaller than the calculated one, which may be attributed to the crystal defects in the ribbons.

Temperature dependence of the ac susceptibility for the bulk and the ribbon Mn$_2$NiSb samples is shown in figure 4(b). There is only one ferromagnetic–paramagnetic transition observed from the magnetic measurements, indicating the sample is a single phase. This agrees with the XRD pattern quite well. The Curie temperatures of the two samples are quite different. The $T_C$ of the ribbon sample is about 77 K lower than that of the bulk one, suggesting different exchange interactions in the two samples. It is known that in Mn$_2$NiSb with the Cu$_2$MnAl-type of structure, the Mn atoms enter the (A, C) sites, so they have four Ni and four Sb atoms as nearest neighbours. According to the study in Mn$_2$VAI, its Curie temperature is determined mainly by the exchange interaction between the nearest Mn–V atoms [22]. The case in the Cu$_2$MnAl-type Mn$_2$NiSb may be the same. However, in the Hg$_2$CuTi-type Mn$_2$NiSb, the (A, C) sites are occupied by one Mn and one Ni atom, the other Mn enters the B site and is the nearest neighbour to the (A, C) ones. Hence, the exchange interaction between the nearest Mn atoms is dominant, which determines the Curie temperature. So the different Curie temperatures reflect the different atomic configurations in the crystal.

4. Conclusions

The structure and magnetic properties of Mn$_2$NiSb prepared by arc-melting and melt-spinning have been investigated both theoretically and experimentally. It is found that different methods of preparation have an obvious influence on the site preference of Mn in the lattice. After arc-melting and subsequent annealing, Mn atoms enter the A and B sites, respectively, and form an Hg$_2$CuTi-type of structure. However, after melt-spinning, the Mn atoms tend to occupy the (A, C) sites and form the Cu$_2$MnAl-type of structure. The electronic structure calculations suggest that the Hg$_2$CuTi-type of structure is lower in energy than the Cu$_2$MnAl one and more stable. The lattice constant of the former is a bit larger than the latter one. Calculations give a total moment of 4.21 $\mu_B$ for the Hg$_2$CuTi-type of structure and 3.93 $\mu_B$ for the Cu$_2$MnAl one. These results fit the saturation magnetization at 5 K quite well. There is a difference of 77 K between $T_C$ of the bulk and ribbon samples, which arises from different exchange interactions in different atomic site preferences.

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