Magnetic instability in Mn$_2$NiSb

Hongzhi Luo,$^{a,b,*}$ Fanbin Meng,$^a$ Guodong Liu,$^a$ Heyan Liu,$^a$ Shijie Li,$^a$ Enke Liu$^b$ and Guangheng Wu$^b$

$^a$School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China

$^b$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

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Mn$_2$NiSb can exist in both ferromagnetic and antiferromagnetic states because there is only a small total energy difference between the two states. In its electronic structure, two different types of energy gaps exist and are close to the Fermi level. The relative position of the Fermi level to the gap determines the ferromagnetic or antiferromagnetic state. That is the origin of the magnetic instability in Mn$_2$NiSb. A 70% decrease of the total moment is predicted between the ferromagnetic and antiferromagnetic Mn$_2$NiSb.

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In recent years, the Mn-based Heusler alloys have attracted much attention for their interesting physical properties and potential applications as ferromagnetic shape memory alloys [1–3] and half-metals [4–8] in the fields of magnetic actuators and spintronic devices.

Until now, all of the Mn$_2$-based Heusler alloys have been ferrimagnets with antiparallel aligned Mn spin moments, except for Mn$_2$NiSb. The latter is predicted to be a ferromagnet with a parallel aligned Mn moment. The calculated total moment of ferromagnetic Mn$_2$NiSb is 4.21 $\mu_B$, which agrees with the experimental result quite well [9]. However, the detailed mechanism of this ferromagnetic character still needs further investigation.

For example, In Ref. [9], calculations also give a ferrimagnetic state in Mn$_2$NiSb, which has similar total energy compared with the ferromagnetic one and a total moment of 1.33 $\mu_B$. If a ferrimagnetic state does exist, we can expect that under some conditions a ferromagnetic–antiferromagnetic transition will occur in Mn$_2$NiSb or compounds with a similar composition. This phenomenon can be important in searching for materials with a high magnetocaloric effect or a large magnetoresistance.

In this paper, the electronic structure and possible magnetic transition are discussed.

Ordinarily, it is accepted that Mn$_2$NiSb crystallizes in a highly ordered Hg$_2$CuTi-type of structure, in which one Mn (denoted as Mn (A)) and one Ni occupy the 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2) (Ni (C)) Wyckoff positions, and the other Mn (Mn (B)) enters the 4c (1/4, 1/4, 1/4) site. The main group Sb enters the 4d (3/4, 3/4, 3/4) position. This is different from regular Heusler alloys, which crystallize in a Cu$_2$MnAl-type structure. In the Cu$_2$MnAl-type structure, the two Mn atoms will enter the 8c (1/4, 1/4, 1/4) sites [10,11]. In Ref. [12], the site preference and its influence on the XRD pattern in Mn$_2$NiSb have been studied. The Hg$_2$CuTi-type structure is found to be preferable. So, to be accurate, Mn$_2$NiSb should be called “Heusler-like” alloy. In the following paragraphs, we refer to it as the Heusler alloy for the sake of convenience. It should be noted that there may exist a degree of atomic disorder between Mn (A) and Ni in Mn$_2$NiSb, as has been observed in Mn$_2$NiSn [13]. So, in this paper, the influence of Mn (A)–Ni disorder on the magnetic structure has also been considered.

The electronic structure of Mn$_2$NiSb is calculated using the CASTEP code [14,15]. The interactions between the atomic core and the valence electrons were described by the ultrasoft pseudopotential [16]. The electronic exchange–correlation energy was treated under the local-density approximation (LDA) [17,18].
The plane-wave basis set cut-off was 500 eV for all the cases and 408 $k$ points are employed in the irreducible Brillouin zone.

Structural optimization has been made on Mn$_2$NiSb first to determine the equilibrium lattice constant. In the calculation, we considered the non-magnetic (NM) state, the ferromagnetic state (FM, in which the Mn moments at 4a and 4c sites are in parallel alignment) and the antiferromagnetic state (AFM, in which the Mn moments are in antiparallel alignment). For the FM and AFM calculations, different starting spin configurations are considered [11,19].

It is clear that the total energy of the NM state is $\sim$100 meV per atom above the FM or AFM curve while the energy difference between the FM and AFM states is only 5 meV per atom. This value is rather small, and is different from the usual Mn-based Heusler alloys. For example, the energy difference between FM and AFM Mn$_2$NiSn is 75.55 meV per atom in Mn$_2$NiSn [11], which is $\sim$25 times larger than Mn$_2$NiSb. The small difference in total energies of Mn$_2$NiSb confirms that the ferromagnetic Mn$_2$NiSb can be synthesized, as has been observed in experimental studies [9], although its energy is slightly higher. The derived equilibrium lattice constants for the FM and AFM states are 5.88 and 5.90 Å, respectively, which are slightly smaller than the experimental value of 5.95 Å [9] (see Fig. 1). We also find that the energy difference between the FM and AFM states increases notably with increasing lattice constants, which means that the AFM state becomes more stable. The antiferromagnetic Mn$_2$NiSb may thus also be prepared by expanding its lattice to some degree (doping elements with larger atomic radius, for example). Furthermore, ferromagnetic-to-antiferromagnetic transition may occur in samples with the proper composition, accompanied by a large change in magnetic moment.

In Figure 2 the calculated total and partial density of states (DOS) of Mn$_2$NiSb in FM and AFM states are presented. It is clear that the general shape of the FM and AFM DOS are quite similar; the main difference is the relative position of them with respect to the Fermi level. In the majority spin, a similar three-peak structure is observed in both FM and AFM DOS. However, compared with the AFM DOS, the majority FM DOS is shifted to lower energy with respect to the Fermi level $E_F$. For example, the majority antibonding peak is basically above $E_F$ in the AFM DOS and below $E_F$ in the FM DOS.

In the minority spin of the AFM DOS, two energy gaps are opened around the Fermi level: a narrow gap 0.2 eV above $E_F$ and a wide gap 1 eV below $E_F$. The two gaps are separated by a DOS peak from 0.1 to –0.7 eV. The Fermi level $E_F$ is just located at the right side of this peak, close to the narrow gap. In the FM minority DOS, the two gaps still exist, but is shifted to higher energies. Then the $E_F$ is located at the left side of the DOS peak and is close to the wide gap at –0.5 eV (corresponding to the –1 eV gap in AFM DOS). It has been found that the low-DOS region at $E_F$ helps to lower the total energy while the high DOS peak has the opposite effect [20,21]. Thus the electronic structures of both the FM and AFM states are stable, with their Fermi level close to the energy gap. That explains why the energy difference between the FM and AFM states is so small.

As can be observed in Figure 2, the difference between the FM and AFM DOS is mainly related to the PDOS of Mn (A). For the AFM state, 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 far below the Fermi level and occupied, and in the minority PDOS the antibonding peak is high above $E_F$ due to the large exchange splitting. In contrast, an opposite trend is observed in the majority and minority DOS of Mn (A). Therefore, the contributions to the total DOS from Mn (A) and Mn (B) are opposite, indicating an antiparallel configuration of their spin moments [6] in AFM Mn$_2$NiSb. Compared with the AFM state, the majority PDOS of Mn (A) of the FM state moves to lower energy and the minority PDOS moves to higher energy. This will help to relieve the antiparallel coupling between Mn spin moments.

From discussions above, we can conclude that the relative position of the minority energy gaps to the Fermi level...
level is important for the magnetic properties of Mn$_2$NiSb. An investigation of the origin of these gaps would thus help to understand the magnetism of Mn-based Heusler alloys and to explore new materials.

In Figure 3 we present the calculated integrated DOS (number of states, NOS) of Mn$_2$NiSb in FM and AFM states; as examples, the NOS of Mn$_2$CoSb and Mn$_2$CuSb are also presented in Figure 3 for comparison. It is known that an energy gap in the band structure will be presented as a platform in a NOS pattern. Within the range of this platform, the number of electrons remains a constant and this number is related to the origin of the energy gap. In the minority spin channel of Mn$_2$NiSb, one wide platform and a narrow platform are observed below and above the Fermi level for both the FM and AFM states, which contain 12 and 14 valence electrons, respectively. In the FM state, the Fermi level is close to the 12-electron gap, according to the studies of Galanakis et al. This 12-electron gap (Mn$_2$CoSb for example) is an $e_g-t_{1u}$ gap and is mainly determined by the hybridization between the next-nearest Mn (A) and Ni states [22]. In the AFM states, the Fermi level is close to the 14-electron gap. Different from the $e_g-t_{1u}$ gap, the 14-electron gap (Mn$_2$CuSb for example) is an $e_g-t_{2g}$ gap and mainly determined by the hybridization between Mn (A) and Mn (B) states. Details can be found in Ref. [23].

Considering the discussions above, we can find that in Mn$_2$YSb (Y = Cr, Mn, Fe, Co, Ni, Cu, Zn) Heusler alloys, Ni can be a turning point of their electronic and magnetic properties. On the left of Ni, the Mn$_2$YSb compounds all have a 12-electron $e_g-t_{1u}$ gap around $E_F$ and on the right a 14-electron gap of $e_g-t_{2g}$ is observed. For Mn$_2$NiSb itself, in the band structure both the $e_g-t_{1u}$ and $e_g-t_{2g}$ gaps exist near the Fermi level. When $E_F$ is located in a different gap, different magnetic structures will be induced. That is the origin of the magnetic instability in Mn$_2$NiSb. By adjusting the composition of Mn–Ni–Sb properly (doping with elements with fewer electrons like Ga for example) we can control the electronic structure of Mn$_2$NiSb near $E_F$ and increase the energy difference between the FM and AFM states; then transitions between the FM and AFM states can be expected in this series of compounds. To search for materials with a high magnetocaloric effect or large magnetoresistance, the findings in Mn$_2$NiSb can be of great value.

To understand the magnetic instability of Mn$_2$NiSb further, in Figure 4 we compare the calculated magnetic moments and lattice constants of Mn$_2$YSb (Y = Fe, Co, Ni, Cu, Zn) Heusler alloys. The lattice constants of Mn$_2$YSb increase monotonically when the Y atom varies from Fe to Zn. There is a 0.34% increase of the lattice between the FM and AFM Mn$_2$NiSb. Thus, Mn$_2$NiSb has the potential to be used as a magnetic actuator material if this transition can be driven by an external field.

The magnetic moments of Mn$_2$YSb can be divided into two groups: Mn$_2$FeSb, Mn$_2$CoSb and FM Mn$_2$NiSb belong to one of these groups. Their total moments basically follow the Slater–Pauling curve of $M_t = Z - 24$, where $M_t$ is the total magnetic moment per formula unit and $Z$ is the total number of valence electrons. The reason why the moment of FM Mn$_2$NiSb is smaller than 5 $\mu_B$ is that the Fermi level of it is not complete in the gap. For AFM Mn$_2$NiSb, Mn$_2$CuSb and Mn$_2$ZnSb, their total moments are 1.25 $\mu_B$, 2.00 $\mu_B$ and 2.85 $\mu_B$, respectively. This second group of alloys is close to another S–P curve of $M_t = Z - 28$.

As a turning point, there is a drastic decrease of 70% between the total moment of FM and AFM Mn$_2$NiSb. This decrease is related to the different coupling between Mn spin moments in Mn$_2$NiSb. In Table 1, for the FM state, the moments on Mn (A) and Mn (B) site are 0.60 $\mu_B$ and 3.22 $\mu_B$, respectively. This second group of moments and lattice constants of Mn$_2$YSb (Y = Fe, Co, Ni, Cu, Zn) Heusler alloys. The lattice constants are determined by the hybridization between Mn (A) and Mn (B), antiparallel to each other.

The magnetic instability may be expanded to other Mn$_2$Ni-based Heusler alloys. This can be a possible way to synthesize new functional materials.

Finally, we calculated the total energies and magnetic moments of Mn$_2$NiSb with Mn and Ni occupying the A and the C site randomly. The calculations were performed at 5.88 and 5.90 Å, which are the equilibrium lattice constants of the FM and AFM states, using the

Figure 3. Integrated DOS (NOS) of Mn$_2$NiSb in the FM and AFM states; the NOS of Mn$_2$CoSb and Mn$_2$CuSb are also presented for comparison.

Figure 4. Comparison of the lattice constants and magnetic moments of Mn$_2$YSb (Y = Fe, Co, Ni, Cu, Zn).
The saturation magnetization \( M_s \) of Mn\(_2\)NiSb at 5 K is presented for comparison.

### Table 1. The equilibrium lattice constants, total and partial magnetic moments of the Mn\(_2\)NiSb Heusler alloy in FM and AFM states.

<table>
<thead>
<tr>
<th>Lattice constant (Å)</th>
<th>( M_{\text{total}} ) (µB)</th>
<th>( M_{\text{Mn(A)}} ) (µB)</th>
<th>( M_{\text{Mn(C)}} ) (µB)</th>
<th>( M_{\text{Ni}} ) (µB)</th>
<th>( M_{\text{Sb}} ) (µB)</th>
<th>( M_{\text{S}} ) (µB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.88</td>
<td>3.28</td>
<td>-0.11</td>
<td>-0.11</td>
<td>0.21</td>
<td>0.21</td>
<td>3.24</td>
</tr>
<tr>
<td>5.90</td>
<td>3.27</td>
<td>-0.15</td>
<td>-0.15</td>
<td>0.21</td>
<td>0.21</td>
<td>3.24</td>
</tr>
</tbody>
</table>

### Table 2. The total and partial magnetic moments calculated by the KKR–CPA–LDA method for Mn\(_2\)NiSb with atomic disorder between Mn (A) and Ni site.

<table>
<thead>
<tr>
<th>Lattice constant (Å)</th>
<th>( M_{\text{total}} ) (µB)</th>
<th>( M_{\text{Mn(A)}} ) (µB)</th>
<th>( M_{\text{Mn(C)}} ) (µB)</th>
<th>( M_{\text{Ni}} ) (µB)</th>
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</tr>
</tbody>
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KKR–CPA–LDA method [24]. It is found that the total energy of the disorder structure is only \(-2.5\) meV per atom lower than the Hg\(_2\)CuTi type structure. However, the exact mechanism for the atomic site swapping and its influence on the overall magnetic properties need further theoretical considerations and atomic disorder cannot be completely excluded in Mn\(_2\)NiSb.

Table 2 shows the calculated magnetic moments. For both lattice constants, a total moment of \(-3.27\) µB has been observed, which is 22% smaller than the experimental value. The moment of Mn (B) is 3.2 µB, while Mn (A) and Mn (C) have only small negative moments. It can thus be inferred that Mn–Ni disorder will result in an intermediate state between FM and AFM states. Though the Mn (A, C) and Mn (B) moments are still located in the \( t_2g \) gap, the AFM state is stabilized. This is the origin of the magnetic instability in Mn\(_2\)NiSb. If Mn–Ni disorder exists, an intermediate state between the FM and AFM states can be obtained. By doping and alloying in Mn\(_2\)NiSb, we can design its electronic structure and make the FM and AFM states coexist in one material. Transitions between the two states, driven by temperature or magnetic field, may occur.

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