The effect of boron substitution for Sb in the Heusler alloys Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$\textsubscript{x}Co\textsubscript{1−x}B\textsubscript{x} (x = 0, 0.5, 1.0, 1.5) has been studied. The substitution with B reduces the Curie temperature of both the martensite and austenite phases. The saturation magnetization $M_s$ decreases monotonically with increasing B content. The doping of B increases the martensitic transformation temperature effectively. When x = 1.0 and 1.5, an orthorhombic four-layered (4O) martensite is observed at room temperature.

In recent years, Ni–Mn–X (X = In, Sn, Sb) Heusler alloys have attracted much interest because of their magnetic shape memory effect and magnetic field-induced martensitic transformation [1–5]. The magnetic field-induced martensitic transformation is usually accompanied by large magnetic entropy changes and a magnetoresistance effect, which is of great importance for technical applications. The Ni–Mn–X (X = In, Sn, Sb) system was reported by Sutou et al. [1]. Since then, these alloys have been the subject of many experiments, often involving doping. By introducing Co to the Ni–Mn–X lattice, enhanced magnetic field-induced martensitic transformation is observed [2,6,7]. By substituting Fe for In, the compressive strength and maximum compressive strain are greatly increased [8].

Besides the doping of transition metal elements, the doping of main group elements with a small atomic radius, like boron, has also attracted much attention [9–12]. Boron is a small atom and may occupy either the crystal lattice site or the interstitial site. Gautam et al. [9] studied the magnetic properties of Ni$_2$Mn(GaB).

They found that, with the substitution of B for Ga, the martensitic transformation temperature ($T_m$) increases rapidly. They attributed this to the reduction of the cell parameters when B enters the lattice. Xuan et al. [11] studied the effect of interstitial boron atoms in Ni$_{43}$Mn$_{46}$Sn$_{11}$ alloy and found that $T_m$ increases remarkably with increasing B content. However, the cell parameters of Ni$_{43}$Mn$_{46}$Sn$_{11}$B$_x$ become larger when B enters the interstitial site. This is different from the case in Ni$_2$Mn(GaB). All this suggests that the role of boron in the martensitic transformation and magnetic properties of the Heusler alloys is complex. Further studies on the effect of B could help in the search for new functional materials.

In this paper, we synthesized a series of Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$\textsubscript{x}Co\textsubscript{1−x}B\textsubscript{x} (x = 0, 0.5, 1.0, 1.5) alloys and investigated the effect of B substitution for Sb on their martensitic transformation and magnetic properties.

Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$\textsubscript{x}B\textsubscript{x} ingots were prepared by arc-melting methods from pure elemental Ni, Mn, Sb and B. The purity of the raw materials was 99.9% or higher. All the ingots were melted at least three times for homogenization. The purity of the raw materials was 99.9% or higher. The ingots were then wrapped in molybdenum foil, sealed in a quartz tube and annealed at 1173 K for 3 days under a protective argon atmosphere. X-ray powder diffraction (XRD) with Cu $K\alpha$ radiation was then...
used to verify the crystal structure and to determine the lattice constants. The temperature dependence of the AC susceptibility was measured to determine the Curie temperature and the phase transformation temperature. The magnetization curves were measured with a SQUID magnetometer at 5 K in a field up to 5 T. The phase transformation temperatures above room temperature were determined by differential thermal analysis (DTA) with a cooling/heating rate of 10 K min\(^{-1}\).

The crystal structure of the alloys was determined by XRD at room temperature. In Figure 1 we present the XRD patterns of Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5}\)\(x\)B\(_x\) (\(x = 0, 0.5, 1.0, 1.5\)) alloys. The pattern of Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5}\) is a single body-centered cubic phase with a highly ordered L2\(_1\) structure. Superlattice diffraction peaks (1 1 1) and (2 0 0) are clear in the pattern. The sample with a B concentration of \(x = 0.5\) is also an L2\(_1\) phase. However, a small orthorhombic peak from the martensitic phase appears at 43.3\(^\circ\), suggesting that the martensitic transformation temperature of this sample is not far from room temperature. The lattice parameters are calculated to be 5.979 and 5.968 Å for \(x = 0.0\) and 0.5, respectively. When the B content is increased to \(x = 1.0\) and 1.5, the XRD pattern clearly changes. An orthorhombic four-layered (40) structure can be identified by indexing all of the diffraction peaks. The space group of this structure is \(Pnma\). The 40 martensite basically consists of the modulated and four-layered (2 2 0) sheets along the [1 1 0] direction of the parent L2\(_1\) structure [13]. A similar structure has also been observed in Ni\(_{50}\)Mn\(_{38}\)Sb\(_{12}\) [14]. The appearance of this structure indicates that the martensitic transformation temperature of these samples is above room temperature. The derived lattice parameters \(a, b\) and \(c\) are 8.593, 5.662 and 4.350 Å for \(x = 1.0\) and 8.579, 5.660 and 4.341 Å for \(x = 1.5\), respectively. It is seen that in both the martensite and austenite phases the lattice parameters decrease with increasing B content. The reason for this reduction is the smaller radius of the B atom compared with that of Sb.

In Table 1 we list the volume change in Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\) with B substitution. It is seen that the substitution of B for Sb leads to a quite regular decrease in the cell volume. If the boron atoms occupy both the substitutional sites and the interstitial ones, the change of volume may not be so regular: when the B content is small, most boron atoms will fill the interstitial sites, so the volume contraction will be small, but as the B content increases further, more boron atoms will enter the substitutional sites, so the volume contraction will be large. This does not agree with the experimental results. We can assume that in Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\), the boron atoms mainly occupy the substitutional sites, as has been observed in Ni\(_2\)Mn(GaB) [9].

The magnetization curves (M–H curves) of Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\) were measured at 5 K in a field up to 5 T. The results are presented in Figure 2. All of the samples are in the martensitic state at that temperature, as will be presented below. It is clear that the Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\) compounds exhibit ferromagnetic behavior at 5 K. The saturation magnetizations (\(M_s\)) are derived from the M–H curves and are listed in Table 1. One can see from the table that \(M_s\) decreases monotonically with increasing B concentration. One possible reason for the decrease can be attributed to the reduction in the crystal lattice parameters with B substituting for Sb. It is known that in Ni\(_{50}\)Mn\(_{25-x}\)Sb\(_{25-x}\) alloys, because the contribution of Ni to the total moment is rather small, its total moment is mainly determined by the spin moment of Mn. In Ni\(_{50}\)Mn\(_{25+}\)Sb\(_{25-x}\), with the Mn content greater than 25, Mn will occupy the Sb site and its spin moment will be antiparallel to that of other Mn atoms at Mn sites [15]. When B substitutes for Sb, the lattice contraction will shorten the distance between the Mn atoms at the Sb and Mn sites, which will tend to strengthen the antiferromagnetic coupling between the Mn moments and lead to a decrease in the saturation magnetization. Similar results have also been reported in Ni\(_2\)Mn(GaB), in which \(M_s\) decreases almost linearly with increasing B content [9]. The contraction of the lattice leads to the decrease in the Mn–Mn distance and changes the hybridization of the Mn d states. Besides the decreasing lattice parameters in Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\), another possible cause for the decrease in \(M_s\) is that B has fewer valence electrons compared with Sb. It is known that the main group elements in Heusler alloys also provide p states to hybridize with the 3d states of transition metal atoms and determine the occupation degree of the p–d orbitals [16]. Since B has fewer valence electrons, when it substitutes for Sb, more d–holes will be introduced to the majority density of states (DOS) and will decrease the total spin moment.

Figure 3 presents the temperature dependence of the AC susceptibility of Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5-x}\)B\(_x\) alloys. The results of different samples are plotted separately in Figure 3 for better comprehensibility. The magnetic transformation temperatures are derived from the AC susceptibility curves and are listed in Table 1. It can be seen that the behaviors of these curves are quite different. For \(x = 0\) and 0.5, the AC susceptibility curve is quite typical for common ferromagnetic shape memory alloys (FSMAs).

Above 325 K, there is a sharp decrease in the AC susceptibility, which corresponds to a ferromagnetic PARA-magnetic transition of the austenitic phase. The Curie temperatures of the austenite (\(T_{CA}\)) are 335 K for \(x = 0\) and 332 K for \(x = 0.5\). When the temperature is lowered there is an abrupt drop in the AC susceptibility curves, which indicates the occurrence of an austenite–martens-
The martensitic start ($T_{\text{ms}}$), martensitic finish ($T_{\text{mf}}$), austenitic start ($T_{\text{as}}$) and austenitic finish ($T_{\text{af}}$) temperatures have been derived and are listed in Table 1. It can be seen in that table that the substitution of B for Sb leads to an obvious increase in the phase transformation temperature. Meanwhile, thermal hysteresis between the martensitic and austenitic phase transformations is reduced by almost 50% as the B content increases from 0 to 0.5. When $x$ increases further, the shape of the AC susceptibility curve changes dramatically. Below the austenite to martensite transformation temperature, another magnetic transition – at 300 K, corresponding to the Curie temperature of the martensitic phase ($T_{\text{CM}}$) – is observed. The $T_{\text{CA}}$ for $x = 1.0$ also decreases to 324 K. For $x = 1.5$, the Curie temperature of the martensitic phase is 288 K, and no trace of the martensitic transformation is observed in the AC susceptibility curve. The decrease in the Curie temperatures in both the austenite and martensite phases is mainly due to the contraction of the lattice parameters with increasing B content. It tends to enhance the antiferromagnetic coupling between the Mn atoms and weaken the exchange interaction between them. In Figure 3 we can also see that there is an decrease in AC susceptibility with decreasing temperature and a thermal hysteresis below $T_{\text{CM}}$ for $x = 1.0$ and 1.5. It is known that in martensitic Ni–Mn–Sb, ferromagnetic and antiferromagnetic (AFM) phases coexist with each other, and the AFM interaction may be strengthened by the martensitic transformation [17]. This could be the reason for the decrease in susceptibility in the pure martensitic region.

Considered together with the XRD pattern in Figure 1, it can be inferred that the phase transformation temperatures of Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 0, 0.5, 1.0, 1.5$ alloys are higher than room temperature. In order to confirm this, the thermal properties of this sample were studied by DTA measurement to determine the phase transformation temperatures. The DTA curves in the heating and cooling cycles are presented in Figure 4, in which a first-order structural transformation is identified. The phase transition temperatures are listed in Table 1. A clear tendency for the martensitic transformation temperature to increase is observed.

In the Ni–Mn–Ga system, the electron concentration dependence of the martensitic transformation temperature, another magnetic transition – at 300 K, corresponding to the Curie temperature of the martensitic phase ($T_{\text{CM}}$) – is observed. The $T_{\text{CA}}$ for $x = 1.0$ also decreases to 324 K. For $x = 1.5$, the Curie temperature of the martensitic phase is 288 K, and no trace of the martensitic transformation is observed in the AC susceptibility curve. The decrease in the Curie temperatures in both the austenite and martensite phases is mainly due to the contraction of the lattice parameters with increasing B content. It tends to enhance the antiferromagnetic coupling between the Mn atoms and weaken the exchange interaction between them. In Figure 3 we can also see that there is an decrease in AC susceptibility with decreasing temperature and a thermal hysteresis below $T_{\text{CM}}$ for $x = 1.0$ and 1.5. It is known that in martensitic Ni–Mn–Sb, ferromagnetic and antiferromagnetic (AFM) phases coexist with each other, and the AFM interaction may be strengthened by the martensitic transformation [17]. This could be the reason for the decrease in susceptibility in the pure martensitic region.

Considered together with the XRD pattern in Figure 1, it can be inferred that the phase transformation temperatures of Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 0, 0.5, 1.0, 1.5$ alloys are higher than room temperature. In order to confirm this, the thermal properties of this sample were studied by DTA measurement to determine the phase transformation temperatures. The DTA curves in the heating and cooling cycles are presented in Figure 4, in which a first-order structural transformation is identified. The phase transition temperatures are listed in Table 1. A clear tendency for the martensitic transformation temperature to increase is observed.

In the Ni–Mn–Ga system, the electron concentration dependence of the martensitic transformation tempera-

Table 1. The lattice constants, volume change, Curie temperature of the austenitic ($T_{\text{CA}}$) and martensitic phases ($T_{\text{CM}}$), saturation magnetization $M_s$ at 5 K, and martensitic start ($T_{\text{ms}}$), martensitic finish ($T_{\text{mf}}$), austenitic start ($T_{\text{as}}$) and austenitic finish ($T_{\text{af}}$) temperatures for Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 0, 0.5, 1.0, 1.5$ alloys.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume change (%)</th>
<th>$T_{\text{CA}}$ (K)</th>
<th>$T_{\text{CM}}$ (K)</th>
<th>$M_s$ (emu g$^{-1}$)</th>
<th>$T_{\text{ms}}$ (K)</th>
<th>$T_{\text{mf}}$ (K)</th>
<th>$T_{\text{as}}$ (K)</th>
<th>$T_{\text{af}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.979</td>
<td>5.979</td>
<td>5.979</td>
<td>–</td>
<td>335</td>
<td>–</td>
<td>45.5</td>
<td>232</td>
<td>221</td>
<td>251</td>
<td>263</td>
</tr>
<tr>
<td>0.5</td>
<td>5.968</td>
<td>5.968</td>
<td>5.968</td>
<td>0.55</td>
<td>332</td>
<td>–</td>
<td>41.4</td>
<td>249</td>
<td>235</td>
<td>253</td>
<td>270</td>
</tr>
<tr>
<td>1.0</td>
<td>8.593</td>
<td>5.662</td>
<td>4.350</td>
<td>0.98</td>
<td>324</td>
<td>300</td>
<td>33.0</td>
<td>313</td>
<td>292</td>
<td>309</td>
<td>319</td>
</tr>
<tr>
<td>1.5</td>
<td>8.579</td>
<td>5.660</td>
<td>4.341</td>
<td>1.38</td>
<td>–</td>
<td>288</td>
<td>29.2</td>
<td>343</td>
<td>329</td>
<td>347</td>
<td>361</td>
</tr>
</tbody>
</table>

Figure 2. Magnetization curves at 5 K for Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 0, 0.5, 1.0, 1.5$ alloys.

Figure 3. Temperature dependence of the AC susceptibility for Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 0, 0.5, 1.0, 1.5$ alloys.

Figure 4. The DTA curve of Ni$_{50}$Mn$_{36.5}$Sb$_{13.5}$ for $x = 1.5$.
ture \( T_m \) is usually treated based on the Hume–Rothery mechanism. Generally, \( T_m \) will increase with increasing \( e/a \) value in Ni–Mn–Ga systems \([18,19]\). However, in Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5}\)\(_x\)B\(_x\), the opposite trend is observed. \( T_m \) increases with increasing B content, and B has only three valence electrons compared with the five in Sb. Similar results have also been observed in Ni\(_2\)Mn(GaB) \([9]\), Mn\(_2\)FeNiGa \([20]\) and Mn-rich NiMnGa \([21]\). In these alloys, the martensitic phase transformation temperatures decrease with increasing \( e/a \) value. It should be noted that the saturation magnetizations of the martensitic phase of these alloys show the opposite tendency with the variation of \( T_m \), increasing as \( T_m \) decreases to a low temperature. We can thus assume that the magnetism in Mn-rich FSMAs may also influence their martensitic transformation temperatures. It can also influence the magnetic energy and change the stability of the martensitic phase.

In summary, the effect of boron substitution for Sb in Heusler alloys (Ni\(_{50}\)Mn\(_{36.5}\)Sb\(_{13.5}\)\(_x\)B\(_x\)) has been studied. The substitution of B reduces the Curie temperatures of both the martensite and austenite phases. The saturation magnetization \( M_s \) decreases monotonically with increasing B content. This is mainly due to the smaller atomic radius of B compared with that of Sb, which shortens the distance between the Mn atoms and enhances the antiferromagnetic coupling between them. The martensitic transformation temperatures \( T_m \) clearly increases with increasing B content. When \( x = 1.0 \) and 1.5, an orthorhombic 4O martensite was identified at room temperature. The increase in \( T_m \) may be attributed to the variation in the magnetism of the martensite and is worth further investigation.

This work was supported by National Natural Science Foundation of China Grant No. 50901028 and Natural Science Foundation of Tianjin Grant No. 08JCYBJC09700.


