Role of covalent hybridization in the martensitic structure and magnetic properties of shape-memory alloys: The case of Ni$_{50}$Mn$_{5+x}$Ga$_{35-x}$Cu$_{10}$

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The influence of covalent hybridization on the martensitic structure and magnetic properties of Ni$_{50}$Mn$_{5+x}$Ga$_{35-x}$Cu$_{10}$ shape-memory alloys has been investigated. It is found that the lattice distortion ($c/a$) of L1$_0$ martensite linearly increases upon substitution of Mn for Ga, showing a change of slope at Ga $= 25$ at. %, which is ascribed to a weakened covalent hybridization between main-group and transition-metal atoms. Moreover, due to the competition between the covalent hybridization and the magnetic ordering of the substituted Mn atoms, the magnetic moment per formula unit and the Curie temperature show maxima at Ga $= 25$ at. % as well. This behavior is closely associated with the corresponding changes of the strength of the covalent hybridization. The results, therefore, suggest that a careful control of the concentration of main-group atoms in Heusler alloys may serve as a tuning parameter for finding multifunctional materials. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4791701]

Heusler alloys are ternary compounds with the formula X$_2$YZ, where X and Y are transition metals and Z a main-group metal. In these alloys, the p-d orbital hybridization between the main-group and the transition-metal atoms determines the phase stability, the magnetic properties, and the atomic site occupations. Previously, Zayak et al.,12 Roy et al.,13 and Bhobe et al.4,5 have found that in the Ni$_2$MnZ (Z = Ga, In, Sn) and Cu-doped Ni$_2$MnGa ferromagnetic (FM) shape-memory Heusler alloys, the p-d orbital hybridization changes the density of states near the Fermi level, modifying the phase stability.11 It is well known that the martensitic structure is sensitive to the composition. Upon changing composition, the well-studied NiMnGa alloys may exhibit a five-layer modulated (5M), seven-layer modulated (7M), or a non-modulated (L10) martensitic structure.11,14 Therefore, so far, there are only few reports on the effect of covalent hybridization on the crystal structure and the magnetic properties of martensite.

In the present study, we have selected Ni$_{50}$Mn$_{5+x}$Ga$_{35-x}$Cu$_{10}$ alloys as representative to study the effect of covalent hybridization on the martensitic structure and the magnetic properties. Previously, several physical properties of Ni$_2$Mn$_{1-x}$Cu$_x$Ga alloys have been investigated by means of first-principles calculations and experimentally as well. Roy et al.4,5 have suggested that, in Ni$_2$Mn$_{1-x}$Cu$_x$Ga alloys, the introduction of Cu enhances the covalent hybridization between Ni and Ga, which leads to a higher martensitic-transformation temperature. Therefore, Ni-Mn-Ga-Cu alloys with a high Cu-content are very convenient to investigate the martensitic structure at room temperature.

Polycrystalline ingots of Ni$_{50}$Mn$_{5+x}$Ga$_{35-x}$Cu$_{10}$ ($x = 0–15$) alloys were prepared by arc-melting appropriate amounts of high-purity Ni, Mn, Ga, and Cu metals under argon atmosphere. All ingots were annealed for 3 days in evacuated quartz tubes filled with argon at 1073 K and then quenched into ice water. X-ray diffraction (XRD) with Cu-K$_\alpha$ radiation was used to characterize the crystal structure and to determine the lattice parameters. The martensitic-transformation temperatures were determined by differential scanning calorimetry (DSC). The saturation magnetization and Curie temperature of the alloys were measured in a superconducting quantum interference device (SQUID) magnetometer. The Korringa-Kohn-Rostoker coherent-potential approximation and local density approximation (KKR-CPA-LDA) method19–21 were used to calculate the magnetic structures of the Ni$_{50}$Mn$_{5+x}$Ga$_{35-x}$Cu$_{10}$ ($x = 0–15$) alloys. The lattice parameters for the first-principles calculations were obtained by linearly fitting the experimental results. The valence-electron localization function was calculated by the CASTEP package.22

In order to investigate the covalent hybridization in Heusler alloys, the important thing is to analyze the electronic distribution. Here, we prefer to simplify the landscape by plotting the valence-electron localization function contour map in the (100) plane of Ni$_2$MnGa in the martensitic state, which is displayed in Fig. 1(b). There is strong p-d covalent hybridization between the nearest-neighbor Ni and Ga atoms, similar to the MnNiGe:Fe system.23 It has been shown, experimentally and theoretically, that this hybridization determines the martensitic-transformation temperature in both NiMnGa and NiMnGaCu alloys.3,14,24 The effect of

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FIG. 1. (a) Crystal structure of the Heusler alloy Ni$_3$MnGa in the L1$_0$ martensite state. (b) Valence-electron localization function contour map in the (100) plane. The scale bar at the bottom right corner shows the increasing covalent bonding when the color changes from blue to red.

Different from the L1$_0$ martensitic structure of Ni$_{50}$Mn$_{17.5}$Ga$_{22.5}$Cu$_{10}$, the Cu-free Ni$_{50}$Mn$_{27.5}$Ga$_{22.5}$ alloy possesses the 5M martensitic structure. This L1$_0$ structure can result from the substitution of a smaller Cu atom (0.157 nm radius) for the larger Mn atom (0.179 nm), which causes other atoms around the newly introduced Cu to shift slightly and consequently destroy the periodic arrangement of the atoms. Furthermore, the introduced Cu atoms provide more electrons to serve as the media of the covalent hybridization between Ni and Ga atoms. As a result, the hybridization between Ni and Ga is enhanced, which results in an increase of the martensitic-transformation temperature. This explains why the martensitic-transformation temperature of Ni$_{50}$Mn$_{17.5}$Ga$_{22.5}$Cu$_{10}$ is higher than that of Ni$_{50}$Mn$_{27.5}$Ga$_{22.5}$.

The inset shows the atomic sites on the (010) plane. The scale bar at the bottom right corner shows the increasing covalent bonding when the color changes from blue to red.

FIG. 2. Composition dependence of the lattice parameters and the lattice distortion (c—a)/a of Ni$_{50}$Mn$_{x}$Ga$_{35—x}$Cu$_{10}$ alloys. The straight lines are linear fits to the experimental data. The inset shows the atomic sites on the (010) plane. The scale bar at the bottom right corner shows the increasing covalent bonding when the color changes from blue to red.

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Figure 3 shows the Ga content dependence of the magnetic moment of Ni$_{50}$Mn$_{5—x}$Ga$_{35—x}$Cu$_{10}$ alloys. The magnetic moment per formula unit first increases upon decreasing Ga content, reaches a maximum value for Ga = 25 at. %, and then decreases again with further substitution of Mn for Ga atoms. In order to understand this anomalous variation of the magnetic moment, we should first determine the atomic occupation during the substitution. The atomic sites in Heusler alloys, indicated by A, B, C, and D, are shown in Fig. 3. Generally, the main-group atoms mainly occupy D sites, the transition-metal atoms with relatively more valence electrons will preferentially occupy the A and/or C sites, while those with relatively less valence electrons occupy the B sites.

In Ni$_{50}$Mn$_{5—x}$Ga$_{35—x}$Cu$_{10}$ alloys, the valence-electron number of Cu(3d$^1$4s$^1$) is larger than those of Ni(3d$^8$4s$^2$), Mn(3d$^5$4s$^2$), and Ga(4s$^2$4p$^1$). The details of the preferential atomic-site occupation of the atoms in Ni$_{50}$Mn$_{5—x}$Ga$_{35—x}$Cu$_{10}$ alloys are presented in Fig. 4. The atomic occupations in the tetragonal martensite structure are the same as in cubic austenite structure, consistent with the diffusionless martensitic transformation.

The atomic-site occupation and magnetic properties discussed above indicate that, in Ni$_{50}$Mn$_{5—x}$Ga$_{35—x}$Cu$_{10}$ alloys, the magnetic properties are a balance between the magnetic interaction between the Mn moments and the covalent hybridization between Ga and the transition metal atoms. For Ga > 25 at. %, the calculations show that the stronger covalent hybridization causes all Mn atoms to...
They are the main contributors to the magnetism of Ni₅₀Mn₅₀Cu₁₀ alloys. The calculated data are also plotted in Fig. 3, the moment of the atoms at A/C sites will be most sensitive to variation of the covalency. Thus, in Ni₅₀Mn₅₀Cu₁₀ alloys, the variation of the Ni(C) moments can be ascribed to the changes of the covalent hybridization between Ga and the transition-metal atoms.

Ga < 25 at.%, these moments of Ni and Mn(B) atoms are antiparallel to the moments of the newly introduced Mn(D) atoms. (iii) The Ni(A,C) moments vary in a similar way with the Ga-content as the magnetic moment per formula unit of Ni₅₀Mn₅₀Ga₃₅Cu₁₀, both reaching a maximum value at Ga = 25 at.%. Because the atoms at A/C sites are nearest-neighbors of the atoms at B/D sites, as shown in the inset of Fig. 3, the moment of the atoms at A and/or C sites will be most sensitive to variation of the covalency. Thus, in Ni₅₀Mn₅₀Ga₃₅Cu₁₀ alloys, the variation of the Ni(A,C) moments can be ascribed to the changes of the covalent hybridization between Ga and the transition-metal atoms.

Figure 5 shows the structural and magnetic phase diagram of Ni₅₀Mn₅₀⁺ₓGa₃₅⁻ₓCu₁₀. The Curie temperature T⁰Μ first increases from 24 K for Ga = 35 at. % with decreasing of Ga content, showing a maximum value of 269 K at Ga = 25 at. %, and then decreases again upon further substitution of Ga for Mn. This behavior of T⁰Μ reveals the variation of the exchange interaction in Ni₅₀Mn₅₀⁺ₓGa₃₅⁻ₓCu₁₀ alloys. For Ga > 25 at.%, as a consequence of the preferential occupation of the lattice sites and the magnetic order, the number of magnetic atoms on the FM sublattice increases upon substitution of Mn for Ga. The FM interaction between the magnetic atoms becomes gradually stronger, which results in an increase of T⁰Μ. However, for Ga < 25 at.%, anti-ferromagnetic interactions occur in the Mn(D) sublattice, which leads to a decrease of T⁰Μ. Similar results have been reported for Mn₂CoNiₓGa¹₋ₓ alloys.²⁶

TABLE I. Composition dependence of the calculated atomic moments (in μₜₜ), the corresponding moments per formula unit (in μₜₜ/f.u.), and the measured moments (in μₜₜ/f.u.) for Ni₅₀Mn₅₀⁺ₓGa₃₅⁻ₓCu₁₀ alloys.

<table>
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<tr>
<th>Ga (at.%)</th>
<th>Ni(A,C)</th>
<th>Cu(A,C)</th>
<th>Ni(B)</th>
<th>Mn(B)</th>
<th>Mn(D)</th>
<th>Gal(B)</th>
<th>Ga(D)</th>
<th>Mₜₜ,calc.</th>
<th>Mₜₜ,exp.</th>
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<tr>
<td>30</td>
<td>0.17</td>
<td>0.03</td>
<td>0.11</td>
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<td>0.0003</td>
<td>-0.03</td>
<td>1.62</td>
<td>1.63</td>
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<tr>
<td>27</td>
<td>0.21</td>
<td>0.04</td>
<td>0.12</td>
<td>3.24</td>
<td>...</td>
<td>-0.0012</td>
<td>-0.04</td>
<td>2.06</td>
<td>2.07</td>
</tr>
<tr>
<td>25</td>
<td>0.25</td>
<td>0.08</td>
<td>0.09</td>
<td>3.04</td>
<td>...</td>
<td>...</td>
<td>-0.04</td>
<td>2.28</td>
<td>2.24</td>
</tr>
<tr>
<td>22.5</td>
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<td>0.12</td>
<td>3.42</td>
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<tr>
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<td>-3.51</td>
<td>-0.04</td>
<td>1.66</td>
<td>1.67</td>
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In summary, we combined of experiments and theoretical calculations to investigate the influence of covalent hybridization on the martensitic structure and the magnetic properties of Ni$_{50}$Mn$_{50−x}$Ga$_{35−x}$Cu$_{10}$ ($x = 0$–15) alloys. We have shown that, as a result of $p-d$ orbital hybridization between Ga and transition-metal atoms, the lattice parameters ($a = b$) decrease while the lattice distortion ($c/a$) increases with decreasing Ga content, showing a kink at Ga $= 25$ at.%. This behavior can be attributed to the weaker covalency upon decreasing Ga atoms. The competition between the covalent hybridization and the magnetic interaction of the moments with those of the newly introduced Mn atoms makes that the magnetic moment per formula unit and the Curie temperature both reach maximum values at Ga $= 25$ at.%. Higher martensitic transformation temperatures and large temperature hysteresis are observed for Ga-poor alloys, making the Ni$_{50}$Mn$_{50−x}$Ga$_{35−x}$Cu$_{10}$ ($x ≥ 15$) alloys interesting single-phase wide-hysteresis high-temperature shape-memory alloys.

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27. See supplementary material at http://dx.doi.org/10.1063/1.4791701 for the typical X-ray diffraction patterns, DSC curves, magnetic-field and temperature dependence of the magnetization for Ni$_{50}$Mn$_{50−x}$Ga$_{35−x}$Cu$_{10}$ alloys. We show here the experimental results of the valence-electron concentrations (c/a), characteristic martensitic-transformation temperatures, temperature hysteresis ($\Delta T$), latent transformation heat ($\Delta Q$) and Curie temperature of the martensite for Ni$_{50}$Mn$_{50−x}$Ga$_{35−x}$Cu$_{10}$ alloys.