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Unusual lattice constant changes and tunable magnetic moment compensation in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys


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We report on unusual lattice parameter changes and tunable magnetic moment compensation in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ (x = 0–25) Heusler alloys by substituting Ga for Mn. The observed lattice parameter first increases with increasing Ga content x, showing a maximum at x = 12.5, and then abnormally decreases due to the enhanced covalence effect between transition-metal and main-group atoms. Moreover, a tunable magnetic moment compensation was also observed due to the diversification in role of the main magnetic contributor when the structure varies from Hg$_2$CuTi-type Mn$_2$CoGa to Cu$_2$MnAl-type CoMnGa$_2$. These results provide an alternative way to simultaneously tune both the structural and magnetic properties of Heusler alloys, which is particularly important for developing flexible spintronics devices.

Since the discovery of ferromagnetic shape memory effects, half metallic properties, and magnetic compensation behavior, Mn$_2$-based Heusler alloys with Hg$_2$CuTi-type (space group 216) structure have attracted considerable interest recently. Among them, Mn$_2$CoGa shows a high Curie temperature of about 718 K and possesses a total molecular magnetic moment of 2 $\mu_B$, following the Slater-Pauling rule for half metals. By substituting Mn for Co atoms in Mn$_2$CoGa, Aljiani et al. found that the molecular magnetic moment of Mn$_2$Co$_{0.4}$Ga alloy can be significantly reduced down to 0.49 $\mu_B$, which is useful for spin transfer torque applications. As shown in Fig. 1(a), the atomic sequence in Mn$_2$CoGa along [111] direction is Mn(A)Mn(B)Co(C)Ga(D). The Mn (A)–Mn (B) and Mn (B)–Co (C) atom pairs are in the nearest neighbor distance, and the atomic magnetic moment of Mn (A) antiparallelly aligns with those of Mn (B) and Co (C). By substituting Ga for Mn atoms in Mn$_2$CoGa alloy, according to the atomic preferential occupation rule in Heusler alloy, the newly introduced Ga atoms preferentially occupy Mn (B) sites. As shown in Fig. 1(a), the final substitution generates Cu$_2$MnAl-type Heusler alloy CoMnGa$_2$. Correspondingly, with the decrease of Mn (B) atom in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys, the main magnetic contributor can transfer from Mn (B)/Co (C) sublattice to Mn (A) sublattice. Therefore, the competition between the magnetic moment of the two sublattices will cause a magnetic moment compensation behavior in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys. Unlike the case of substitution of Mn for Co atoms in Mn$_2$CoGa, the cubic structure can be still persisted over the whole substitution of Ga for Mn atoms in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$. Meanwhile, with the increase of Ga content, the covalence effect between transition-metal and main-group atoms can be largely enhanced. In this Letter, a series of Heusler alloys Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ (x = 0–25) have been prepared. The covalence effect induced abnormal lattice behavior and tunable magnetic moment compensation in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys have been systematically studied.

Polycrystalline ingots of Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ (x = 0–25) alloys were prepared by arc-melting high-purity metal Mn, Co, and Ga under argon atmosphere. Based on the DSC results (supplementary Fig. S1), all the ingots were subsequently annealed in evacuated quartz tubes with argon for homogenizing at 1073 K for two days and then for atomic ordering at 973 K for one day. Finally, all the samples were quenched into ice water. The x-ray diffraction (XRD) with Cu-K$_\alpha$ was employed with step-scan method to characterize the crystal structure and to determine the lattice parameter. The saturation magnetizations of all samples were measured by a superconducting quantum interference device (SQUID) magnetometer at 5 K. The Curie temperatures were measured by SQUID in a temperature range from 5 K to 400 K and vibrating sample magnetometer (VSM) with a high-temperature facility. The Korringa-Kohn-Rostoker coherent-potential approximation and local density approximation (KKR-CPA-LDA) method was applied to calculate the magnetic structures of Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys. The ideal lattice parameters for first-principles calculations were obtained by linearly fitting the experimental results.

Figure 1(b) shows the powder XRD patterns of three typical samples measured at room temperature. All samples crystallized in body centered cubic (BCC) structure without other detectable second phases. The observed superlattice reflection peaks indicate the Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys dominantly state in high-ordered structure (supplementary Fig. S2 and Table S1). Furthermore, the CoMnGa$_2$ shows very clear superlattice reflection peaks of (111), (200) (311), and (222), which are much more obvious than those of Mn$_2$CoGa and other alloys as well. This should be attributed to the large difference of atomic scattering factor between Mn and Ga.

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radius, because the radius of Ga (0.181 nm) is larger than that of Mn (0.179 nm). However, with the further substituting Ga for Mn atoms, the lattice parameter gradually decreases and presents a local maximum at composition dependence of the lattice parameters of Mn50 alloys. This is due to the domination of atomic radius, because the radius of Ga (0.181 nm) is larger than that of Mn (0.179 nm). However, with the further substitution of Ga for Mn atoms, the lattice parameter starts to decrease and presents a local maximum at x = 12.5. This unusual decrease obviously conflicts the atomic radius rule and strongly suggests that another physical mechanism should be responsible for this abnormal lattice behavior.

TABLE I. Calculated molecular magnetic moments ($M_{\text{calc.}}$) and measured molecular magnetic moments ($M_{\text{exp.}}$) (in $\mu_B$/f.u.), as well as the calculated atomic magnetic moments (in $\mu_B$/atom) for Mn50-xCo25Ga25+x alloys with various compositions.

<table>
<thead>
<tr>
<th>x</th>
<th>Mn(A)</th>
<th>Mn(B)</th>
<th>Co(C)</th>
<th>$M_{\text{calc.}}$</th>
<th>$M_{\text{exp.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-1.69</td>
<td>2.89</td>
<td>0.88</td>
<td>2.03</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>-1.76</td>
<td>2.95</td>
<td>0.71</td>
<td>1.26</td>
<td>1.24</td>
</tr>
<tr>
<td>10</td>
<td>-1.81</td>
<td>2.93</td>
<td>0.56</td>
<td>0.48</td>
<td>0.56</td>
</tr>
<tr>
<td>12.5</td>
<td>-1.83</td>
<td>2.94</td>
<td>0.49</td>
<td>0.12</td>
<td>0.20</td>
</tr>
<tr>
<td>15</td>
<td>1.81</td>
<td>-2.90</td>
<td>-0.42</td>
<td>0.24</td>
<td>0.22</td>
</tr>
<tr>
<td>20</td>
<td>1.78</td>
<td>-2.89</td>
<td>-0.29</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>25</td>
<td>1.76</td>
<td>—</td>
<td>-0.19</td>
<td>1.55</td>
<td>1.51</td>
</tr>
</tbody>
</table>

In fact, as shown in Fig. 1(a), the Hg2CuTi-type Mn2CoGa can be considered as a layered structure, where Mn(A)/Co(C) layers and Mn(B)/Ga(D) layers sandwich each other with a distance of one fourth of the lattice parameter. While Cu3MnAl-type CoMnGa2 composes of the Mn(A)/Co(C) layers and Ga(B)/Ga(D) layers. Due to the p-d orbital hybridization between main-group and transition-metal atoms, the pure Ga/Ga layers will cause much stronger covalent effect than Ga/Mn layers in Mn50-xCo25Ga25+x alloys. Thus, it is reasonable to believe that the decrease of the lattice constant originates from the enhanced covalent effect due to the increase of Ga content in the system.

Figure 2(a) shows the composition dependence of molecular magnetic moment and the saturation magnetic field of Mn50-xCo25Ga25+x alloys. The experimental molecular magnetic moments are quite consistent with the values from calculations, which indicate the high-ordered structure is dominant in Mn50-xCo25Ga25+x alloys. Interestingly, a magnetic moment compensation behavior occurred in the inter-alloys. The molecular magnetic moment first decreases and reaches a near zero value at x = 12.5, and then turns to increasing. This magnetic moment compensation phenomenon has been reported in Mn1-xCoGa (x = 0–1) experimentally and (Mn1-xCo)xVA theoretically, respectively. In these two serials of alloys, the magnetic moments belonging to different sublattices align in a collinear but antiparallel style and counteract each other. However, in our Mn50-xCo25Ga25+x alloys, as shown in Fig. 2(a), the...
composition dependence of saturation magnetic field also shows a v-shaped behavior with a minimum value of 0.3829 Tesla at $x = 12.5$, coincidently consistent with the compensation point. Therefore, the saturation magnetic field minimum behavior may be attributed to turning point between Hg$_2$CuTi-type and Cu$_2$MnAl-type structures at the middle composition of Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys. As there usually exists a morphotropic phase boundary (MPB), which minimums the energy barrier of the magnetization. Here, the minimum value of $dM(H)/dH$ curve was chosen as the saturation magnetic field. In the quasi-linear part above the threshold filed, the contribution of conduction-electron magnetic moment should be included because the conduction-electron magnetic moment can be also aligned along the external magnetic field, especially in MnCoGa$_2$ alloy.

Table I lists the calculated atomic magnetic moments of Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys with various composition. One may see that the atomic magnetic moment of Mn ($B$) keeps almost constant during the composition changes. By contrast, the magnetic moments of Co ($C$) and Mn ($A$) atoms dramatically change with the increase of Ga content. In Fig. 2(b), we plot the calculated magnetic moments of Co ($C$) and Mn ($A$) atoms as a function of Ga content $x$. We found that the magnetic moment of Co ($C$) atom linearly decreases with the increase of Ga content. Turning to the magnetic moment of Mn ($A$) atom, however, it does not monotonously decrease like that of the Co ($C$) atom in the same strong covalent environment. It first increases and reaches a local maximum at $x = 12.5$, and then decreases when $x > 12.5$. Because the nature of localized $d$-electrons in Mn atom, the magnetic moment of Mn ($A$) is not easily influenced by the weak $p$-$d$ hybridization at $x < 12.5$. As a result, an abnormal increase in atomic magnetic moment of Mn ($A$) can be observed, which may be qualitatively explained by the reduction of Mn ($B$) atoms. However, at $x > 12.5$, the enhanced covalent effect makes the atomic magnetic moment of Mn ($A$) decrease in Ga-rich alloys. Not uniquely, the kink in the composition dependence of the atomic magnetic moment of Mn ($A$) has also been observed at $x = 12.5$, as shown in Fig. 2(b). Again, this observation proves the domination behavior of the covalent effect when it is strong enough. It has been known that, in Fe$_3$Al and Fe$_{3-x}$Si alloys, the degree of partial filling of 3$d$ band by electrons transferring from $sp$ atoms can result in a decrease of the magnetic moment of Fe atoms at the $A$ and $C$ sites. In our Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys, such covalent effect is further enhanced by increasing the content of Ga.

Hg$_2$CuTi-type Mn$_2$CoGa is a typically ferrimagnetic Heusler alloy, in which the magnetic moment of Mn($A$) atom is relatively small and antiparallelly aligns to those of Mn($B$) and Co($C$) atoms. Therefore, the Mn($B$) and Co($C$) atoms are the main contributors of magnetism in Mn$_2$CoGa. However, Cu$_2$MnAl-type CoMnGa$_2$ is another ferrimagnetic alloy, in which the Mn($A$) atom has larger magnetic moment than Co($C$) atom (see Table I). Thus, the Mn($A$) atom turns to be the main contributor of magnetism in CoMnGa$_2$. By substituting Ga for Mn atoms in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys, as shown in Fig. 3, the Mn($B$) atoms are replaced gradually by the newly introduced Ga atoms and the conversion of role for the main contributor of magnetism occurs in the off-stoichiometric alloys between Mn$_2$CoGa and CoMnGa$_2$. The compensation point with near zero value observed in this work strongly suggests that, in these Heusler alloys, the magnetic structures are in a collinear style.

Figure 4 shows the composition dependence of Curie temperature ($T_C$) of Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys. The $T_C$ linearly decreases from 710 K (for the sample Mn$_2$CoGa) to 192 K (for the sample CoMnGa$_2$). The $T_C$ is mainly determined by the 3$d$ exchange interaction among transition-metal atoms in Heusler alloys. In Mn$_2$CoGa, the Mn($A$)-Mn($B$) and Mn($B$)-Co($C$) atom pairs are in the nearest neighbor distance, which determine a strong exchange interaction and result in a high $T_C$. On the other hand, in CoMnGa$_2$ alloy, only the next-nearest-neighbor Mn($A$)-Co($C$) atom pairs provide a relatively weak exchange interaction. During the substitution of Ga for Mn($B$), the number of Mn($B$) decreases and the exchange interaction between Mn($B$)-Co($C$) and Mn($A$)-Mn($B$) atom pairs is weakened gradually, which leads the $T_C$ to decrease.

Finally, we should point out that the tunable magnetic moment compensation behavior observed in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys probably gives rise to potential application in spintronics. Especially for Mn$_{37.5}$Co$_{25}$Ga$_{37.5}$ alloy, it possesses the near zero molecular magnetic moment, very low saturation magnetic field and the high spin polarization (supplementary Fig. S3). These features make Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys as the potential candidate materials to serve as the electrodes of spin-transfer torque devices in the next-generation data storage technique.

In summary, the structural variation from Hg$_2$CuTi-type Mn$_2$CoGa to Cu$_2$MnAl-type CoMnGa$_2$ has been realized by substituting Ga for Mn. The lattice parameter changes and magnetic moment compensation have been investigated in
Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$ alloys. We found that with increasing Ga content, the lattice parameter first increases and then normally decreases, showing a maximum at $x = 12.5$. This abnormal behavior can be attributed to the enhanced covalent effect due to the $p$-$d$ orbital hybridization between Ga and the transition metals. Moreover, the impact of covalence effect on the magnetic moments of transition-metal atoms was also investigated. As a result, we observed tunable magnetic moment compensation behavior in Mn$_{50-x}$Co$_{25}$Ga$_{25+x}$. A very low saturation magnetic field and near zero magnetic moment were observed at the turning point of two structures, making Mn-based Heusler alloys appealing for developing flexible spintronics devices.

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