Effect of Co on magnetic property and phase stability of Ni–Mn–Ga ferromagnetic shape memory alloys: A first-principles study*

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The effect of Co content on magnetic property and phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic shape memory alloys has been investigated using first-principles calculations. The total energy difference between paramagnetic and ferromagnetic state of austenite plays an important role in the magnetic transition. The high Curie temperature can be attributed to the stronger Co–Mn exchange interaction as compared to the Ni–Mn one. The phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite increases with increasing Co content, which is discussed based on the electronic structure.

Keywords: ferromagnetic shape memory alloys, magnetic properties, martensitic transformations, electronic band structure

PACC: 7115A, 7115M, 8130K

1. Introduction

Ni–Mn–Ga alloy has attracted considerable attention in recent years because it exhibits both ferromagnetism and shape memory effect.[1−4] The large magnetic-field-induced strain, giant magnetocrystalline anisotropy, large saturation magnetization, and giant magnetic memory effect have been reported for Ni–Mn–Ga alloy.[5−10] These make it an ideal candidate in magnetically controlled shape memory applications. From the application point of view, high Curie temperature (T_c) is required for developing ferromagnetic shape memory alloys (FSMAs) with large magnetocrystalline anisotropy at high temperatures. However, the highest T_c is only about 380 K observed in the stoichiometric Ni_2MnGa, which is a too low temperature for some applications.[11] Moreover, it is reported that the T_c of these alloys is less composition-dependent.[6] Therefore, great efforts have been devoted to alloying this system with a fourth element to increase the T_c. Recent investigations show that substitution of Co for Ni is an effective way to increase T_c.[12−16] Replacing Ni by Co in Ni–Mn–Ga alloy with Co content up to 14 at% causes the T_c to increase from 377 K to 519 K and the martensitic transformation temperature to decrease. In addition, the addition of Co increases the compressive strength and decreases the yield stress. These interesting properties make Ni–Mn–Ga–Co alloys promising high-temperature FSMAs. However, there has not been any indication as to why Co should display these effects. It is our goal that first-principles calculations could provide some insights on the role of Co in Ni–Mn–Ga alloys. This paper reports the results on the effect of Co on the magnetic property and phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ (x = 0, 6.25, 12.5, 18.75) FSMAs.

2. Calculation method

The calculations presented in this study are performed with the CASTEP code,[17] based on density functional theory, using Vanderbilt-type ultrasoft pseudopotentials[18] and a plane-wave expansion of the wave functions. We use the generalized gradient approximation (GGA) to describe the

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exchange and correlation potential. The structure is optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method, and convergence is assumed when the forces on atoms are less than 0.03 eV/Å (1 Å=0.1 nm). The plane-wave cutoff energy of 350 eV is employed. The calculations are done using a 8×8×8 Monkhorst–Pack grid; the calculations have been performed for $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ($x = 0$, 6.25, 12.5, 18.75) paramagnetic and ferromagnetic austenite. For the Ni_2MnGa austenite, the $Fm\bar{3}m$ space group is used with atomic positions 8*c* (Ni), 4*b* (Mn) and 4*a* (Ga).[1,19] The crystal structure of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite is taken as the $L2_1$ structure of Ni_2MnGa, in which appropriate Ni is replaced by Co. In every case, the geometrical optimization is always made, based upon which the total energy, heat of formation, magnetic moments and electronic structure are then calculated. The total energy is defined as the sum of kinetic energy, electron–electron interaction energy and exchange–correlation energy. The heat of formation is defined as $\Delta E = \frac{1}{16}[E_{\rm tot} - mE_{\rm Ni} - nE_{\rm Co} - 4E_{\rm Mn} - 4E_{\rm Ga}]$, where $E_{\rm tot}$ is the total energy of the cell; $E_{\rm Ni}$, $E_{\rm Co}$, $E_{\rm Mn}$ and $E_{\rm Ga}$ are the single-atom energies of Ni, Co, Mn and Ga atoms in their elemental crystals; and m and n are the atomic numbers of Ni and Co in the cell, respectively.

3. Results and discussion

Figure 1 shows the lattice constant as a function of Co content in $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite. It can be seen that the lattice constant decreases slightly with increasing Co content, which agrees well with the experimental results.[20] However, the atomic size of Co is bigger than that of Ni. This abnormal decrease of lattice constant is related to the change of phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite. In addition, we find that the error in the calculated lattice constant compared with the experimental data for Ni_2MnGa austenite is less than 1%,[1,19] demonstrating that the pseudopotentials used here and geometry are reliable.

For $Ni_{50-x}Mn_{25}Ga_{25}Co_x$, the experimental results show that the martensitic transformation temperature is lower than $T_{\rm c}$. Therefore, the magnetic transition of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ occurs in the austenite. Since Ni–Mn–Ga and Ni–Mn–Ga–Co alloys satisfy the Stone condition of ferromagnetism,[21] the $T_{\rm c}$ can be taken to be proportional to the total energy difference between the paramagnetic and the ferromagnetic states.[22,23] Although this approximation gives a much higher value of $T_{\rm c}$, it still could be used to find the relative variation.[24] Figure 2 shows the effect of Co content on the total energy difference between paramagnetic and ferromagnetic states of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite. It is noted that the total energy difference increases with increasing Co content. This indicates that the $T_{\rm c}$ increases with the increase of Co substitution for Ni, which explains the experimental data.[12,16]

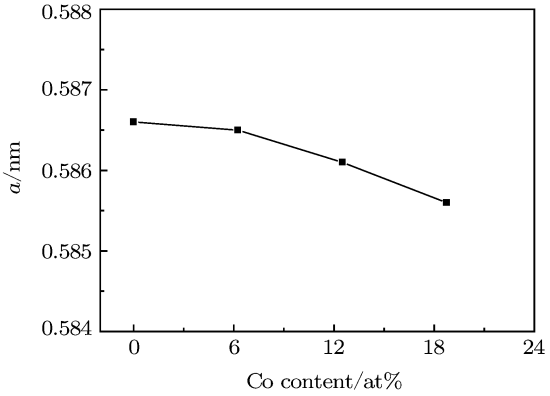


Fig. 1. The lattice constant dependence of Co content for $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite.

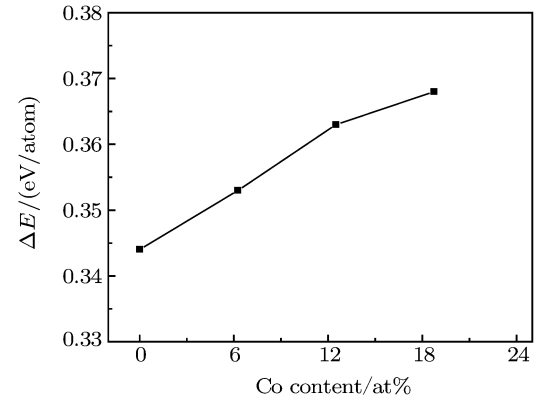


Fig. 2. Effect of Co content on total energy difference (ΔE) between paramagnetic and ferromagnetic states of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite.

In order to further investigate the effect of Co on the magnetic property and the $T_{\rm c}$, the total and local magnetic moments of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic austenite are calculated and shown in Fig. 3. It is found that the total magnetic moment of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite is due to the Mn, Co and Ni magnetic moments in order of importance. The total magnetic moment increases with increasing Co content. This can account for the larger magnetic moment of Co than that of Ni. Although the magnetic ordering of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ is mainly attributed

to the Mn–Mn exchange interaction, the Ni–Mn and Co–Mn exchange interactions also play an important role in establishing magnetic properties. In particular, the magnetic moment of Co is larger than that of Ni, leading to the stronger Co–Mn direct exchange interaction as compared to the Ni–Mn one. Thus, the addition of Co increases the magnetic exchange interaction in $Ni_{50-x}Mn_{25}Ga_{25}Co_x$. Therefore, the origination that the T_c increases with the increase of Co content can be attributed to the stronger Co–Mn exchange interaction as compared to the Ni–Mn one.

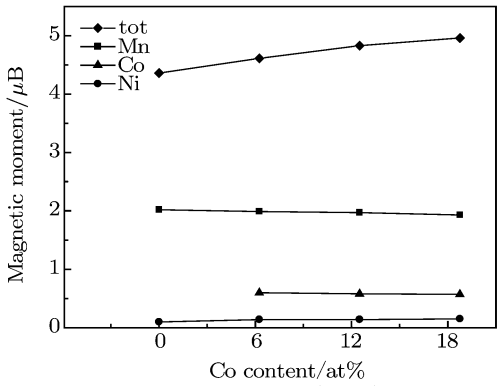


Fig. 3. The total and local magnetic moments of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic austenite as a function of Co content.

In order to study the effect of Co content on the phase stability, the heats of formation of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic austenite are calculated as a function of Co content, as shown in Fig. 4. It can be seen that the heat of formation decreases with increasing Co content. This suggests that the phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite increases with the increase of Co content.

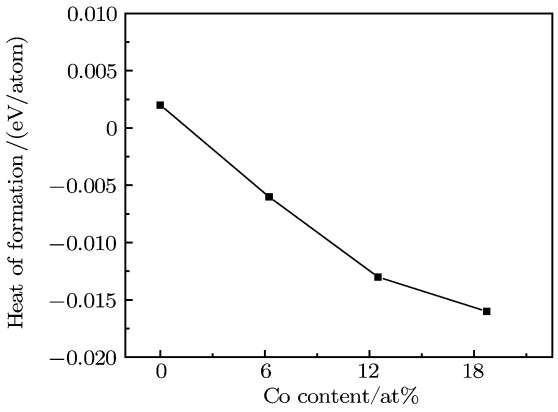


Fig. 4. Heat of formation of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic austenite as a function of Co content.

The effect of Co content on the phase stability can be understood thoroughly on the basis of density of states (DOS). Figure 5 shows the total DOS of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ ferromagnetic austenite. It can be seen that Co content has little effect on majority-spin DOS at the Fermi level. All the minority-spin DOS has a sharp peak close to the Fermi level. The most interesting feature is that the peak of the minority-spin DOS at the Fermi level decreases with increasing Co content. For $Ni_{31.25}Mn_{25}Ga_{25}Co_{18.75}$, the Fermi level lies exactly at the minimum, giving the largest magnitude of heat of formation, and therefore the largest stabilizing effect for the austenite. This is actually a typical pseudogap effect[25] and the stability effect of the pseudogap can be explained in more details in partial DOS. As an example, partial DOS for Ni, Co and Mn 3d in $Ni_{37.5}Mn_{25}Ga_{25}Co_{12.5}$ austenite are shown in Fig. 6. It is noted that the minority-spin DOS below the Fermi level is mostly 3d states contributed by the Ni and Co, while the minority-spin DOS above the Fermi level is mainly 3d states in the Mn site. There are significant intensities for Ni and Co sites at the low energy side, and Mn site at the high energy side, demonstrating 3d–3d hybridization between Ni (Co) and Mn. Furthermore, we observe that the minority-spin Ni 3d partial DOS has a peak at the Fermi level. In contrast, the minority-spin Co 3d partial DOS does not exhibit any peak. These indicate that the hybridization between Co 3d and Mn 3d states is stronger than that between Ni 3d and Mn 3d states, resulting in the above-mentioned austenite-stabilizing effect of Co.

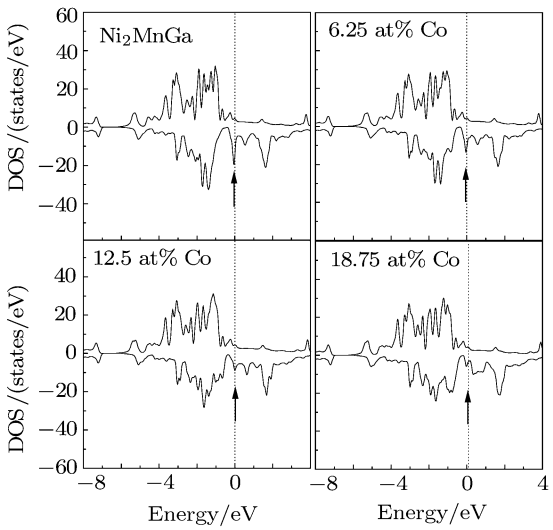


Fig. 5. Total DOS of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite. The Fermi level is shown by the vertical dashed line. The arrow denotes the peak of the minority-spin DOS near the Fermi level.

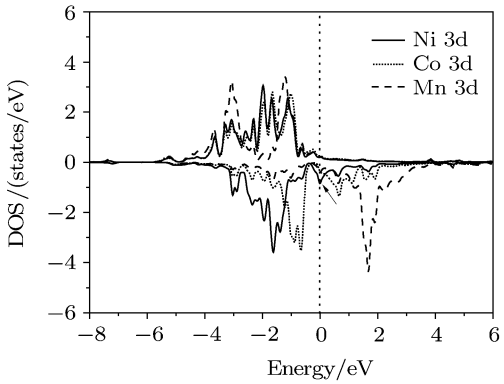


Fig. 6. The Ni, Co and Mn 3d partial DOS of $Ni_{37.5}Mn_{25}Ga_{25}Co_{12.5}$ austenite. The Fermi level is shown by the vertical dashed line. The arrow denotes the peak of Ni 3d partial DOS at the Fermi level.

Furthermore, the comparison of Ni–Mn and Co–Mn hybridization can be revealed in a more direct manner by charge density. In general, high charge accumulation between neighbouring atoms indicates a strong hybridization between the orbitals of the atoms and thus a strong bonding interaction. As an example, figure 7 shows the charge density of $Ni_{43.75}Mn_{25}Ga_{25}Co_{6.25}$ ferromagnetic austenite in the (110) plane. It is clearly seen that the charge accumulation between Ni and Mn is much less than that between Co and Mn, indicating a weaker Ni–Mn bonding interaction as compared to the Co–Mn one. This is consistent with the above analysis of the phase stability.

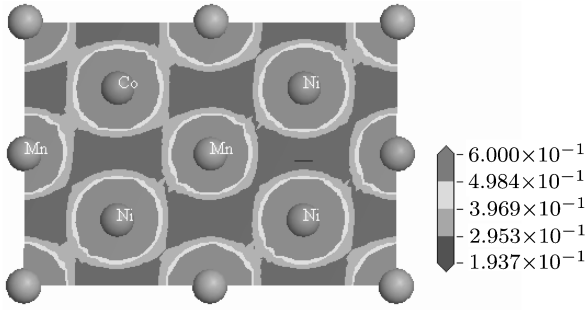


Fig. 7. The charge density of $Ni_{43.75}Mn_{25}Ga_{25}Co_{6.25}$ austenite in the (110) plane.

4. Conclusions

We have used the first-principles calculations to study the effect of Co on magnetic property and phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ FSMAs. It is found that the total energy difference between paramagnetic and ferromagnetic states of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite increases with increasing Co content, which brings about the enhancement of the T_c. A higher T_c can be attributed to the stronger Co–Mn exchange interaction as compared to the Ni–Mn one. The calculated heat of formation and DOS show that the phase stability of $Ni_{50-x}Mn_{25}Ga_{25}Co_x$ austenite increases with increasing Co content. The mechanism of austenite-stabilizing effect of Co is due to a stronger hybridization between Co 3d and Mn 3d states than that between Ni 3d and Mn 3d states.

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