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# The effects of alloying elements Al and In on Ni–Mn–Ga shape memory alloys, from first principles

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## Abstract

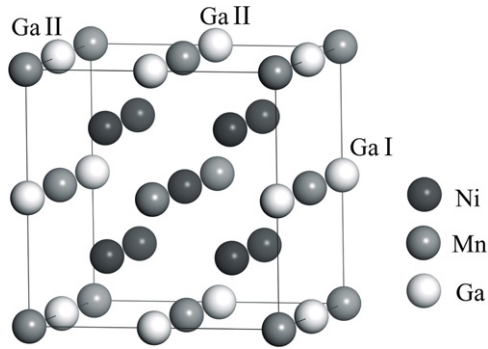
The electronic structures and formation energies of the  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys have been investigated using the first-principles pseudopotential plane-wave method based on density functional theory. The results show that both the austenite and martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy are stabilized by Al alloying, while they become unstable with In alloying. According to the partial density of states and structural energy analysis, different effects of Al and In alloying on the phase stability are mainly attributed to their chemical effects. The formation energy difference between the austenite and martensite phases decreases with Al or In alloying, correlating with the experimentally reported changes in martensitic transformation temperature. The shape factor plays an important role in the decrease of the formation energy difference.

## 1. Introduction

Ni–Mn–Ga shape memory alloys have attracted considerable attention as candidate magnetic actuator materials in the last few years (Ullakko *et al* 1996). Upon cooling,  $\text{Ni}_2\text{MnGa}$  alloy experiences a martensitic transformation from a high symmetry  $L2_1$  austenite phase to a low symmetry martensite phase around 200 K (Webster *et al* 1984). Experimental results have shown that the martensitic transformation temperature ( $T_m$ ) of Ni–Mn–Ga based alloys is very sensitive to the composition, ranging from liquid helium temperature up to over 350 °C (Chernenko *et al* 1995, Jiang *et al* 2003). So it is realizable that the  $T_m$  can be adjusted by alloying in order to meet the changing needs of practical applications. For example, some Ni–Mn–Ga alloys with high Ni content have been developed as promising thermoactuating high temperature shape memory alloys (HTSMAs) (Chernenko *et al* 2003, Xu *et al* 2003, Ma *et al* 2003). Therefore, understanding the mechanism of the composition dependence of  $T_m$  is very important to future research and practical applications.

It is generally acknowledged that the valence electron concentration, i.e. the valence electrons per atom ( $e/a$ ), plays an important role in the martensitic transformation of Ni–Mn–Ga based alloys (Jin *et al* 2002, Pons *et al* 2000, Zayak *et al* 2005, 2006), and in general the  $T_m$  increases with the increasing of the  $e/a$ . However, the investigations on  $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21-x}\text{Al}_x$  (Xin *et al* 2005) and  $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{In}_x$  (Kokorin *et al* 1989) alloys have shown that the  $T_m$  decreases almost linearly with the increasing of Al or In substitution for Ga. Since Al, In as well as Ga are IIIA elements, the substitution of Al or In for Ga atoms in  $\text{Ni}_{54}\text{Mn}_{25}\text{Ga}_{21-x}\text{Al}_x$  and  $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{In}_x$  alloys has no effect on  $e/a$ .

As we know, the alloying elements influence both the electronic and the geometry structures and hence the stability of austenite and martensite phases. Therefore, knowledge of the effects of alloying elements is of great importance for understanding the composition dependence of  $T_m$ . Investigations have shown that the size factor, i.e. the unit-cell volume ( $V$ ) (Kokorin *et al* 1989, Jiang *et al* 2003), and the shape factor, i.e. the ratio between lattice parameters



**Figure 1.** The unit cell of the Heusler ( $L2_1$ ) structure for the parent phase of the  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy.

$c$  and  $a$  ( $c/a$ ) (Ayuela *et al* 1999, 2002, Godlevsky and Rabe 2001, Pons *et al* 2000, Chen *et al* 2006, Lanska *et al* 2004), have an effect on the phase stability and the  $T_m$ . Theoretical and experimental results have shown that the austenite and martensite phases become unstable and the second phase which has a detrimental effect on the shape memory effect precipitates when the Ni content exceeds 57% for  $\text{Ni}_{50+x}\text{Mn}_{25}\text{Ga}_{25-x}$  alloy (Chen *et al* 2006, Ma *et al* 2007). Therefore, systematic theoretical study is needed to further improve our understanding of how alloying elements change the stability of austenite and martensite phases and the martensitic transformation temperature.

In this work, we focus on  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and  $3$ ) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and  $3$ ) alloys. The formation energies of these alloys have been calculated from first principles. According to the formation energy calculation, we find that Al alloying and In alloying have different effects on the phase stability. The formation energy differences between austenite and martensite phases for the Al or In doped alloys have also been calculated, and the relationship between the formation energy difference and the shape factor is discussed.

## 2. Computational method and models

First-principles calculations were performed within the density functional theory (DFT) using the Cambridge serial total energy package (CASTEP) (Segall *et al* 2002). CASTEP uses a plane-wave basis set for the expansion of the single-particle Kohn–Sham wavefunctions, and pseudopotentials to describe the computationally expensive electron–ion interaction, in which the exchange–correlation energy in the generalized gradient approximation (GGA) of Perdew was adopted for all elements in our models (Perdew *et al* 1992). Ultrasoft pseudopotentials (Vanderbilt 1990) were used. In the present calculations, the cut-off energy was set at 500 eV. The  $k$  points in the Brillouin zone for self-consistent field cycles and density of states (DOS) calculations were generated with  $4 \times 4 \times 4$  and  $5 \times 5 \times 4$  meshes for austenite and martensite phases, respectively. We use different  $k$ -point meshes for different phases to ensure the same  $k$ -point separations for all the phases in our calculations. A finite basic set correction and the Pulay scheme of density mixing (Hammer *et al* 1999) were

applied for the evaluation of energy and stress. The lattice constants and all atomic positions have been fully relaxed with experimentally determined lattice constants as primary settings until the forces were less than  $0.03 \text{ eV } \text{\AA}^{-1}$ . More precise testing calculations with a plane-wave cut-off energy of 700 eV and  $k$  points generated with  $7 \times 7 \times 7$  and  $8 \times 8 \times 6$  meshes for austenite and martensite phases, respectively, have been performed, and the result shows that the more precise calculation has little influence on our results. Therefore, the current parameter settings are precise enough for the systems studied in the present paper.

Figure 1 shows the unit cell of the Heusler ( $L2_1$ ) structure for the parent phase of  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy which belongs to the space group of  $Pm\bar{3}m$ . The structure of the martensite phase for  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy belongs to the space group of  $P4/mmm$  and can be expressed via the tetragonal distortion of the  $L2_1$  structure. It is reported that upon cooling,  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy experiences a martensitic transformation from paramagnetic austenite (PA) phase to paramagnetic martensite (PM) phase and then a Curie transition from paramagnetic martensite (PM) phase to ferromagnetic martensite (FM) phase (Ma *et al* 2007). Since the FM phase is the most stable phase at low temperature, the lattice constants and all atomic positions were relaxed in the ferromagnetic state by considering spin polarization. Then the total energy calculations for ferromagnetic and paramagnetic states were performed with and without consideration of spin polarization, respectively. Energetic calculation results indicate that the alloying Al and In atoms in the  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  unit cell prefer to occupy the Ga site since Al, In and Ga are all IIIA elements. So the situations in which the alloying Al and In occupy the Ni or Mn sites are not considered in the present paper. It can be determined according to the atomic geometry positions that there are two groups of Ga atoms in the unit cell of the martensite phase, denoted by Ga I and Ga II, as shown in figure 1. There are one Ga I and two Ga II atoms in the unit cell. Thus, for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys, there are two different substituted sites (Ga I and Ga II) when one Ga atom is substituted by the alloying elements; and the substituted sites can be Ga I and one of Ga II or two Ga II when two Ga atoms are substituted.

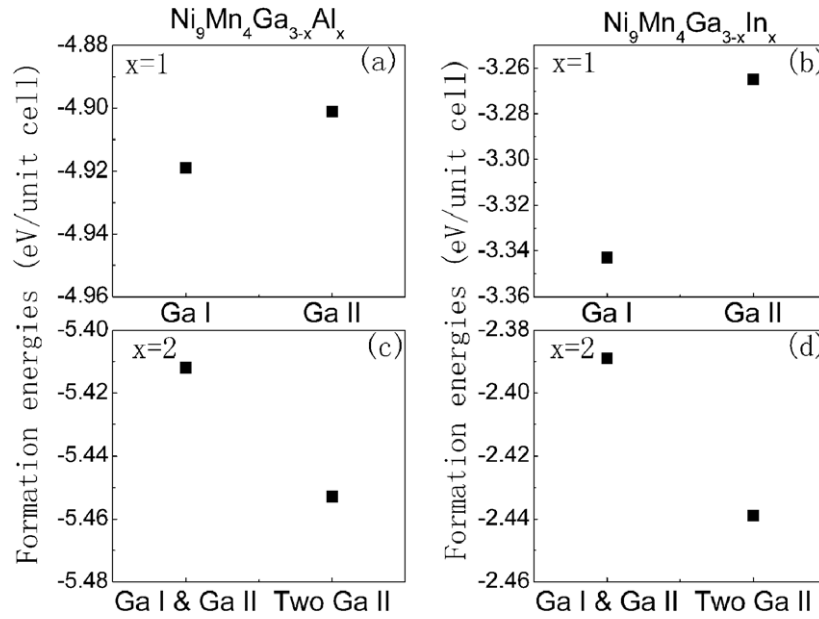
## 3. Results and discussion

### 3.1. Site preference of alloying elements and lattice parameters of martensite phase

In a first step, the formation energies of the ferromagnetic martensite phases are calculated in order to study the site preference of the alloying elements in  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy, since the ferromagnetic martensite phase is the lowest temperature phase and the most stable phase. The formation energy  $E_f$  is a measure of the phase stability in solid states and is defined as the total energy of the compound minus the total energies of the constituent atoms in their bulk structures:

$$E_f = E_{\text{tot}}(\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{X}_x) - 9E_{\text{tot}}^{\text{bulk}}(\text{Ni}) - 4E_{\text{tot}}^{\text{bulk}}(\text{Mn}) - (3-x)E_{\text{tot}}^{\text{bulk}}(\text{Ga}) - xE_{\text{tot}}^{\text{bulk}}(\text{X}). \quad (1)$$

Here X represents Al or In,  $E_{\text{tot}}(\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{X}_x)$  is the total energy of a unit cell for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{X}_x$ ,  $E_{\text{tot}}^{\text{bulk}}(\text{Ni})$ ,



**Figure 2.** The formation energies of alloying Al and In at different sites in the ferromagnetic martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 1, 2$ ) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 1, 2$ ) alloys, respectively.

$E_{\text{tot}}^{\text{bulk}}$  (Mn),  $E_{\text{tot}}^{\text{bulk}}$  (Ga) and  $E_{\text{tot}}^{\text{bulk}}$  (X) are the total energies per atom of Ni, Mn, Ga and X in their bulk structures, respectively.

The formation energies of Al and In at different sites in the ferromagnetic martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 1, 2$ ) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 1, 2$ ) alloys have been calculated. The results for our calculated formation energies are summarized in figure 2. The alloying elements prefer to occupy the site with the lower formation energy. It can be seen from figure 2 that Al and In atoms prefer to occupy the Ga I site for  $x = 1$  and two Ga II sites for  $x = 2$ . The site occupancy behaviours of alloying Al and In in the martensite phase are understandable through geometrical symmetry: the tetragonal symmetry of the unit cell is destroyed if Al or In go to the Ga II site for  $x = 1$  as well as Ga I and one of the Ga II sites for  $x = 2$ , and this may lead to a higher formation energy.

Our calculations yield the equilibrium lattice constants of the ferromagnetic martensite phases (the alloying elements occupy their most preferable sites), as shown in table 1. It is seen from table 1 that the unit-cell volume of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  alloys decreases slightly with the increasing of the Al content, while the unit-cell volume of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys increases with the increasing of the In content. This result is in good consistency with the experiment results that the unit-cell volume of Ni–Mn–Ga varies little when Ga is substituted by Al (Xin *et al* 2005) and it increases when Ga is substituted by In (Kokorin *et al* 1989). The effects of alloying elements on the unit-cell volume are understood through the atomic radius. Al, Ga and In are all IIIA elements, the atomic radius increases with the increasing of the atomic number, and hence the atomic radius of Al is smaller than that of Ga and that of In is larger. For  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  alloys, the lattice parameter  $a$  increases and  $c$  decreases with the increasing of the Al content. For  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys, both  $a$  and  $c$  increase with the increasing of the In content. It is worth noting that the  $c/a$

**Table 1.** Equilibrium lattice parameters of the ferromagnetic martensite phases for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and 3) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and 3) alloys.

	$x$	$a = b$ (Å)	$c$ (Å)	$c/a$	$V$ (Å <sup>3</sup> )
$\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$	0	5.315	6.880	1.294	194.36
	1	5.319	6.835	1.285	193.36
	2	5.317	6.804	1.280	192.37
	3	5.331	6.739	1.264	191.54
$\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$	0	5.315	6.880	1.294	194.36
	1	5.409	6.888	1.274	201.52
	2	5.523	6.842	1.239	208.68
	3	5.566	6.953	1.249	215.43

ratios decrease with the increasing of the alloying element content for both the  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys. All the martensite phases are stabilized with  $c/a > 1$ , showing consistency with some previous studies (Ayuela *et al* 1999, 2002, Godlevsky and Rabe 2001).

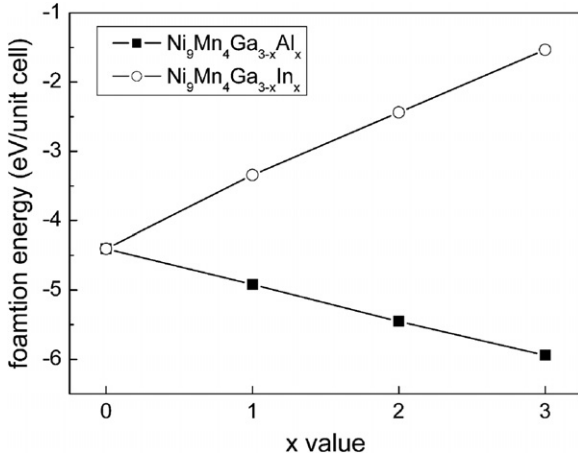
### 3.2. The effects of alloying elements on phase stability

To study the effects of alloying elements on the phase stability, the formation energies of the ferromagnetic martensite phases are calculated for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys. The results for the calculated formation energies are plotted in figure 3.

As was pointed out, the formation energy is a measure of the phase stability in the solid state. The lower the formation energy is, the more stable the phase is. It is seen from figure 3 that the formation energy of ferromagnetic martensite phase decreases with the increasing of the alloying element content for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  alloys, while it increases for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys. Hence, the  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy is stabilized by Al alloying, while it becomes unstable with In

**Table 2.** Formation energies (in eV/unit cell) under the chemical and geometry effects of alloying elements for the ferromagnetic martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$  alloys.

		$\text{Ni}_9\text{Mn}_4\text{Ga}_3$	$\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$	$\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$
Chemical effect			-4.81	-3.00
Geometry effect	Shape factor ( $c/a$ )		-4.80	-2.99
	Size factor ( $V$ )		-4.81	-3.14
Optimized result		-4.32	-4.81	-3.30

**Figure 3.** The formation energies of the ferromagnetic martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and  $3$ ) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and  $3$ ) alloys.

alloying. It is interesting that alloyings with the IIIA elements Al and In have different effects on the stability of the martensite phase.

To further investigate the different effects of Al and In alloyings on the phase stability, we take the  $x = 1$  alloys ( $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$ ) as examples. We know that the effect of alloying elements is composed of two parts, i.e. the chemical effect and the geometry effect (Shang and Wang 2001). To obtain a good understanding of the different alloying effects of Al and In, it may be useful to clarify the roles of the chemical effect and the geometry effect. The chemical effect refers to the effect induced by the substitution of Al (In) for Ga, without considering structure relaxation. However, in the geometry effect, only the structure relaxation contribution is considered. We divide the geometry effect into the effect of the shape factor ( $c/a$ ) and the effect of the size factor ( $V$ ). In the shape factor only the change of  $c/a$  is considered and in the size factor only the change of  $V$  is considered for the impurity doped alloys.

The formation energies of the alloys under the influence of these effects are calculated and the results are summarized in table 2. In our calculation, the influence of the geometry effect is on the premise of the chemical effect, that is, structure relaxation is performed after Ga is substituted by Al or In. It can be seen in table 2 that the formation energies under the chemical effect decrease from  $-4.32$  to  $-4.81$  eV when Ga is substituted by Al, and increase to  $-3.00$  eV when Ga is substituted by In. However, the formation energies under the effects of the shape factor and size factor do not change much:

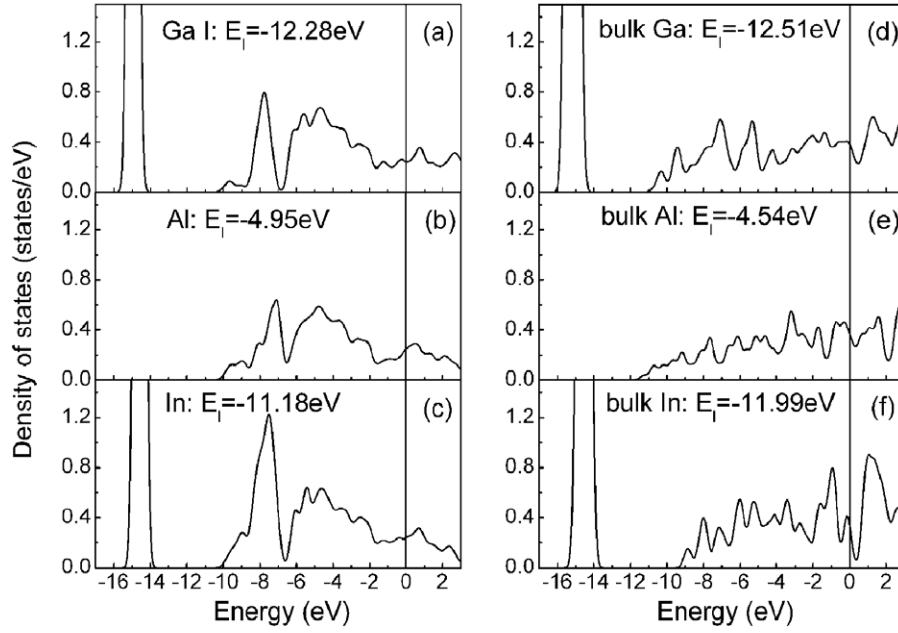
for  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$ , they change from  $-4.81$  eV to  $-4.80$  eV and  $-4.81$  eV, respectively; for  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$ , they change from  $-3.00$  eV to  $-2.99$  eV and  $-3.14$  eV, respectively. This result suggests that it is mainly the chemical effects of Al and In alloyings that result in the decrease of the formation energy for  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  and the increase of the formation energy for  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$ . Therefore, the chemical effects of Al and In play major roles in the higher phase stability of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  alloys and the lower phase stability of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys as compared with  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$ . In addition, the geometry effect of In alloying is stronger than that of Al alloying. This is because In alloying induces more lattice distortion than Al alloying.

In order to further understand the chemical effect of alloying elements on the phase stability, we calculate the projected density of states (PDOS) of Ga in  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$ , Al in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  and In in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$  for the ferromagnetic martensite phase, compared with those for bulk Ga, bulk Al and bulk In, respectively. From the PDOS, the structural energies  $E_l$  of these atoms can be calculated. The structural energy  $E_l$  of an atom is defined as (Wang *et al* 1988, Shang *et al* 2008)

$$E_l = \frac{\int_{-\infty}^{E_F} E \rho dE}{\int_{-\infty}^{E_F} \rho dE} \quad (2)$$

where  $\rho$  is the PDOS of an atom,  $E$  is the eigenenergy, and  $E_F$  is the Fermi energy. The smaller the structural energy  $E_l$ , the more stable the atom in the system.

The calculated PDOS and structural energies  $E_l$  are shown in figure 4. It can be seen from figures 4(d)–(f) that the sp states of the three atoms in their bulks are greatly delocalized from about  $-10$  eV to the  $E_F$  level. From figures 4(a)–(c), it is seen that the PDOS of the sp states splits into two peaks and the states generally move in the lower energy direction, which indicates that the sp states of these atoms in compounds have lower energy and are more stable than those for bulks. Then the stabilization of  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  can be understood via the stabilization of Al atom in the compound since Al has only sp states. Besides, the structural energy  $E_l$  of the Al atom in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  has a smaller value than that for bulk Al, which also demonstrates the higher stability of the Al atom in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$ . However, the structural energy  $E_l$  of Ga in  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  has larger values than that for bulk Ga, and the structural energy  $E_l$  of In in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$  also has larger values than that for bulk In, which means that Ga and In atoms are less stable in compounds. Then we calculate the differences in structural energy between the compound and the bulk. The results are  $0.23$  eV for Ga,  $-0.41$  eV for Al and  $0.81$  eV for In, which means that Al alloying stabilizes the NiMnGa alloy



**Figure 4.** The PDOS and structural energies  $E_f$  of Ga in  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  (a), Al in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{Al}$  (b) and In in  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$  (c) for the ferromagnetic martensite phase, compared with those for bulk Ga (d), bulk Al (e) and bulk In (f), respectively. The vertical line denotes the Fermi level.

while In alloying does not. This result shows good consistency with the formation energy results.

As analyses show that the sp states of Ga and In are more stable in compounds, we focus on the d states of Ga and In. For both compound and bulk cases, the d states of Ga and In are greatly localized around  $-15$  eV. We calculate the structural energies of d states, which are  $-14.92$  eV in the compound and  $-15.16$  eV in the bulk for Ga,  $-13.60$  eV in the compound and  $-14.53$  eV in the bulk for In. The d states in compounds have higher energy than those in the bulk and the differences are  $0.24$  eV for Ga and  $0.93$  eV for In. So the higher energy of the d states of In in the compound is the main cause of the lower stability of  $\text{Ni}_9\text{Mn}_4\text{Ga}_2\text{In}$  alloy. This result suggests that the d states of Ga and In have an important influence on the phase stability and shows consistency with the above structural energy result.

### 3.3. The effects of alloying elements on martensitic transformation

It is known that phase transformation is due to the different phase stabilities of the phases. So the stability changes of austenite and martensite phases have an important influence on the martensitic transformation. To study the stability changes of the two phases, we calculate the impurity formation energies of the paramagnetic austenite (PA) and martensite (PM) phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys. The impurity formation energy is defined as

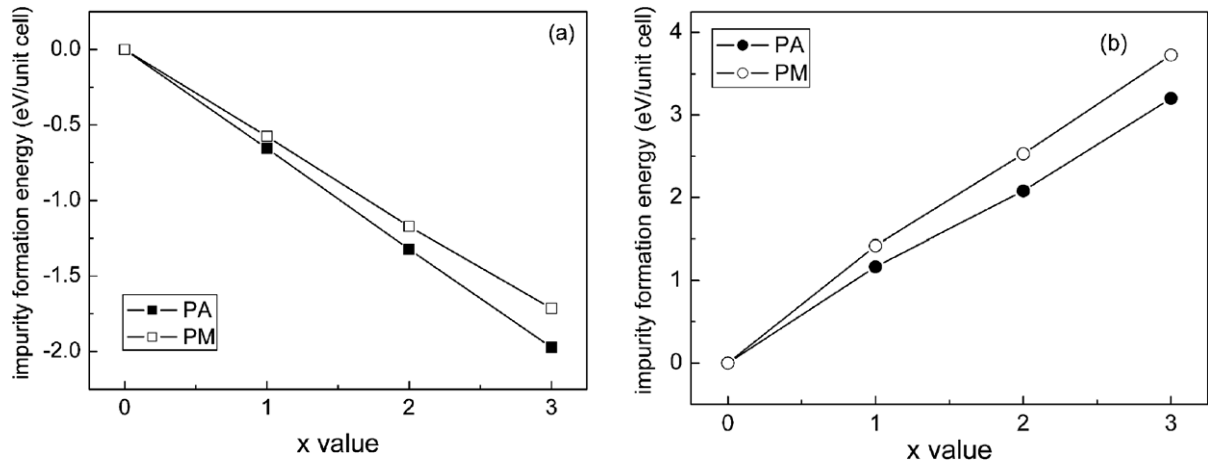
$$E_{f-\text{im}}^{\text{M-im}} = E_f^{\text{M-im}} - E_f^{\text{M}} \quad (3)$$

where M denotes the  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  alloy;  $E_f^{\text{M}}$  and  $E_f^{\text{M-im}}$  refer to the formation energies of the  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  and Al or In doped  $\text{Ni}_9\text{Mn}_4\text{Ga}_3$  systems at their equilibrium lattice constants.

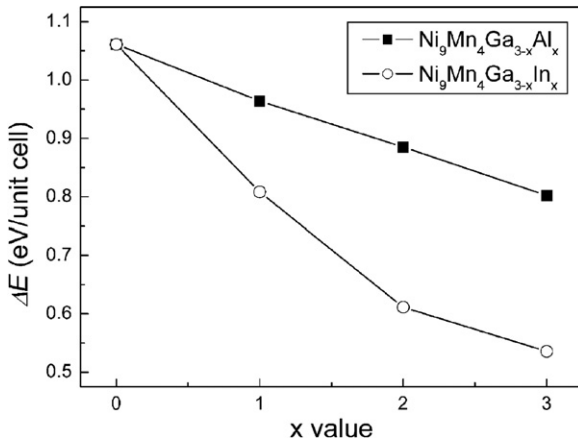
The negative impurity energy means that the doping system is more stable than the clean system. The lower the impurity formation energy is, the more stable the doped phase is.

The results for the calculated impurity formation energies are plotted in figure 5. It is seen from figure 5(a) that the impurity formation energies of both PA and PM phases decrease with the increasing of the Al content. From figure 5(b) it is seen that the impurity formation energies of both phases increase with the increasing of the In content. This result is similar to that for the ferromagnetic martensite (FM) phases and is due to the chemical effect of the alloying elements. It is worth noting that the value of the PA phase decreases faster than that of the PM phase for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  alloys and it increases more slowly than that of the PM phase for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys.

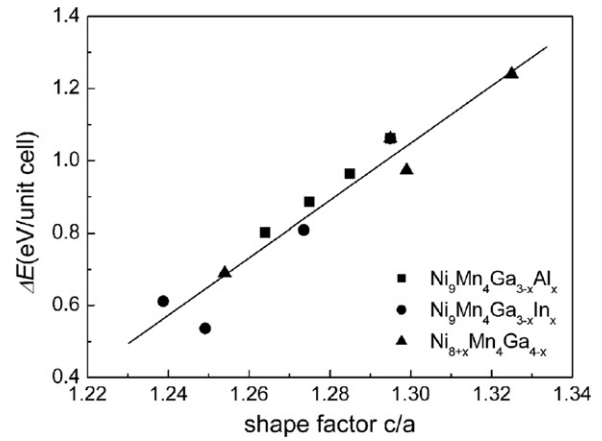
Since the phase stability can be measured via the formation energy, the difference in formation energy between the austenite and the martensite phases must have an important influence on the martensite transformation temperature. To investigate the effects of alloying elements on the martensitic transformation, the differences in formation energy ( $\Delta E$ ) between the PA and PM phases are calculated. The calculated  $\Delta E$ , as a function of Al content in  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and In content in  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys, is plotted in figure 6. The positive values of  $\Delta E$  for all the alloys indicate that the martensite phase has a higher stability than the austenite phase and the phase transformation occurs from the austenite to the martensite phase upon cooling. From figure 6 we can see that  $\Delta E$  decreases with the increasing of the Al or In content, and the reduction of  $\Delta E$  caused by Al alloying is lower than that caused by In alloying. These results show good consistency with the experimental results, that the  $T_m$  decreases upon the



**Figure 5.** The impurity formation energies of the paramagnetic austenite and martensite phases of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and  $3$ ) (a) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and  $3$ ) (b) alloys.



**Figure 6.** Plot of  $\Delta E$  as a function of Al and In content for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and  $3$ ) and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and  $3$ ) alloys, respectively.



**Figure 7.** Plot of  $\Delta E$  as a function of shape factor  $c/a$  for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  ( $x = 0, 1, 2$  and  $3$ ),  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  ( $x = 0, 1, 2$  and  $3$ ) as well as  $\text{Ni}_{8+x}\text{Mn}_4\text{Ga}_{4-x}$  ( $x = 0, 0.5, 1$  and  $2$ ) (Chen *et al* 2006) alloys. The solid line presents the linear regression result for all data.

addition of Al or In elements, and the decreases of  $T_m$  are about 7 K/at.% (Xin *et al* 2005) and 18 K/at.% (Kokorin *et al* 1989) for Al and In doping, respectively. Although the martensitic transformation temperature in a real Ni–Mn–Ga system is complicated and related to many factors, such as long-range order structure (modulation), disorder, magnetism, we can still deduce from our theoretical calculations that the reduction of  $\Delta E$  is relevant to the decrease of  $T_m$  for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys, which is in accordance with previous theoretical works (Ayuela *et al* 1999, Chen *et al* 2006, Chakrabarti *et al* 2005).

We further investigate the alloying effect on  $\Delta E$ . The chemical effect has similar influences on the PA and PM phases, so its influence on  $\Delta E$  is likely to be slight. Moreover, since the volume changes very little during the martensitic transformation, the difference in  $V$  between PA and PM phases is not considered in our calculation. To investigate the relation between the shape factor  $c/a$  and  $\Delta E$ , we plot  $\Delta E$  as a function of shape factor  $c/a$  for  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$ ,

$\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  as well as  $\text{Ni}_{8+x}\text{Mn}_4\text{Ga}_{4-x}$  alloys (Chen *et al* 2006) in figure 7. Obviously,  $\Delta E$  increases with the increasing of  $c/a$  and there is a good linear correlation between  $\Delta E$  and  $c/a$ . This result indicates that the shape factor  $c/a$  plays an important role in the decrease of  $\Delta E$  and then  $T_m$ . The role of  $c/a$  in the reduction of  $\Delta E$  can be understood as follows: a smaller  $c/a$  ratio of the martensite phase indicates less lattice deformation during the martensitic transformation and thus a lower energy is involved.

#### 4. Conclusions

On the basis of the first-principles method within the framework of density functional theory, the alloying effects of Al and In on the phase stability and martensitic transformation of the  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and the  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$  alloys are investigated. Alloyings with IIIA elements Al and In have different effects on the stabilities of austenite and martensite

phases: the phases are stabilized by Al doping, while they become unstable with In doping. According to our analyses on formation energies, PDOS and structural energies, the chemical effect of the alloying elements is the main cause: the lower energy of the sp states is responsible for the higher stability of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{Al}_x$  and the higher energy of d states is responsible for the lower stability of  $\text{Ni}_9\text{Mn}_4\text{Ga}_{3-x}\text{In}_x$ . The formation energy difference  $\Delta E$  between austenite and martensite phases decreases with the increasing of the Al or In content, in accordance with the experimental  $T_m$  results. The shape factor  $c/a$  plays an important role in the decrease of  $\Delta E$  and thus the  $T_m$ . To conclude, this systematic theoretical study of the alloying effects of Al and In elements could help us in doing calculations at elevated temperatures to understand the microscopic mechanism of phase stability and to estimate the martensitic transformation temperature in Ni–Mn–Ga alloys.

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