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Composition dependent phase stability of Ni–Mn–Ga alloys studied by *ab initio* calculations

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ABSTRACT

Composition dependent phase stability of Ni–Mn–Ga magnetic shape memory alloys was studied by first-principles density-functional calculations. It is demonstrated that the three kinds of doping (Ni substitution for Mn, Ni for Ga, and Mn for Ga) destabilize all the three structures. However, Ni-doping relatively stabilizes the non-modulated martensite (NM) with simple tetragonal crystal structure, whereas proper Mn-doping relatively stabilizes the monoclinic seven-layered modulated (7M) martensite with monoclinic structure. Comparing the energy difference between the parent and the product phases, we found that martensitic transformation experiences much larger driving force than that of the intermartensitic transformation. Chemical bonds between Ni and Mn are observed not only with the stoichiometric Mn, but also with the excess ones. Bonds between Ni and Mn in modulated martensite is stronger than that of the non-modulated martensite, which is beneficial to the stability of the modulated martensite. The present result provides useful information for further development of magnetic shape memory alloys that is difficult to be obtained from experiments.

1. Introduction

Ni–Mn–Ga magnetic shape memory alloys are promising candidates for applications as actuators and sensors, since large output strain can be driven by external magnetic fields due to the reorientation of the martensite variants [1–7]. The large field driven shape change was observed mostly in modulated martensite [8–12]. However, it has been experimentally evidenced that the modulated martensite has a tendency to further transform to non-modulated martensite (NM) that has a simple tetragonal crystal structure [13–16]. This will lead to the loss of the field induced shape memory effect and may cause aging of the materials as actuators and sensors during service.

It has been revealed that the martensitic transformation temperatures (T_M) of Ni–Mn–Ga alloys is very sensitive to composition [17–24]. It increases gradually with increasing e/a value ($e/a = \frac{10\times Ni_{at\%}+7\times Mn_{at\%}+3\times Ga_{at\%}}{Ni_{at\%}+Mn_{at\%}+Ga_{at\%}}$, where 10, 7 and 3 represent the number of valence states for Ni($3d^8 4s^2$), Mn($3d^6 4s^1$), and Ga($4s^2 4p^1$)). For stoichiometric Ni_2MnGa ($e/a = 7.5$), as the T_M (220 K) is far below room temperature, the application is hindered [25,26]. In order to increase the T_M (or the e/a value) in view of practical applications, three typical substitutions are addressed (Ni substitution for Mn, Ni substitution for Ga, and Mn substitution for Ga). Recently, we selectively studied the martensitic transformation behaviors of three off-stoichiometric alloys, i.e. $Ni_{53}Mn_{22}Ga_{25}$ (Ni substitution for Mn with respect to the stoichiometric composition), $Ni_{52}Mn_{25}Ga_{23}$ (Ni for Ga), and $Ni_{50}Mn_{30}Ga_{20}$ (Mn for Ga), to explore the composition dependence of the ground state of Ni–Mn–Ga alloys [27]. It was found that for the three alloys austenite (A) transformed first to the monoclinic seven-layered modulated (7M) martensite on cooling. For $Ni_{53}Mn_{22}Ga_{25}$ and $Ni_{52}Mn_{25}Ga_{23}$ alloys, the 7M martensite further transformed into the NM martensite (the so-called intermartensitic transformation) at 225 K and 250 K, respectively, indicating that the 7M martensite is thermodynamically metastable. For $Ni_{50}Mn_{30}Ga_{20}$, the 7M martensite remained stable down to 120 K. It is not clear for this composition whether the 7M martensite would further transform to NM martensite, as the detection of transformation at ultralow temperature is not possible experimentally. In addition to this interesting phenomenon, we found in the experiments that the

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Table 1
Doping amount of the corresponding elements.

Doping scheme	Alloy formula	Doping amount
Ni substitution for Mn	$Ni_{2+x}Mn_{1-x}Ga$	$0.05 \leqslant x \leqslant 0.25$
Ni substitution for Ga	$Ni_{2+x}MnGa_{1-x}$	$0.05 \leqslant x \leqslant 0.10$
Mn substitution for Ga	$Ni_2Mn_{1+x}Ga_{1-x}$	$0.05 \leqslant x \leqslant 0.20$

existing temperature range of the 7M martensite is also very sensitive to the composition, indicating that the stable existing range of the 7M martensite can be tuned by composition. This feature could be beneficial to practical applications [27].

As an efficient and economical alternative to experimental trying errors, *ab initio* could be used to thoroughly explore the optimum alloy compositions in order to obtain systematic information on composition dependence of phase stability [28–33]. Under such a background, we conducted *ab initio* calculations on the constituent phases of three series of Ni–Mn–Ga alloys (Ni substitutes for Mn, Ni for Ga, and Mn for Ga) in order to predict an optimum composition doping scheme with an expectation to provide useful information for further development of magnetic shape memory alloys.

2. Computational details

All of the calculations have been carried out based on the density functional theory using the Vienna *ab initio* simulation package [34,35]. The interaction between ions and electrons is described by ultra-soft pseudopotentials (USPP) [36], and the exchange correlation potential is treated by the generalized gradient approximation in the Perdew and Wang formulation (GGA) [37]. Pseudopotentials with $3d^84s^2$, $3d^64s^1$, and $4s^24p^1$ are used as valence states for Ni, Mn and Ga, respectively. The kinetic energy cutoff is 250 eV. Because of the incommensurate superstructure of 7M martensite [38], an 80-atom supercell (10 subcells) is selected for each phase for a convenient comparison between the calculated results. A Monkhorst–Pack grid [39] is employed to sample the Brillouin zone of the supercell: $8 \times 6 \times 1$ k-points. The lattice parameters and atomic positions are further optimized for all structures until the total energy decrease is less than 1 meV and the total-force is smaller than 0.02 eV/Å.

In the present work, taking stoichiometric Ni_2MnGa as a prototype, Ni substitution for Mn, Ni substitution for Ga and Mn substitution for Ga represent three basic types of the composition adjusting schemes to enhance the *e/a* value, i.e. using the elements with higher number of valence electrons to substitute elements with lower number of valence electrons [40–42]. The doping amount of the corresponding elements in each type of doping is given in Table 1.

As reported in a recent study [43], for most of the off-stoichiometric Ni_2MnGa (including $Ni_{2+x}Mn_{1-x}Ga$, $Ni_{2+x}MnGa_{1-x}$, and $Ni_2Mn_{1+x}Ga_{1-x}$ in our present work), the normal site occupation is favorable, i.e., the excess atoms of the rich component occupy the sublattice(s) of the deficient component(s). Hereafter, we focus on the formation energy [44] of the austenite, which is usually used to measure the phase stability in solid states. We substitute

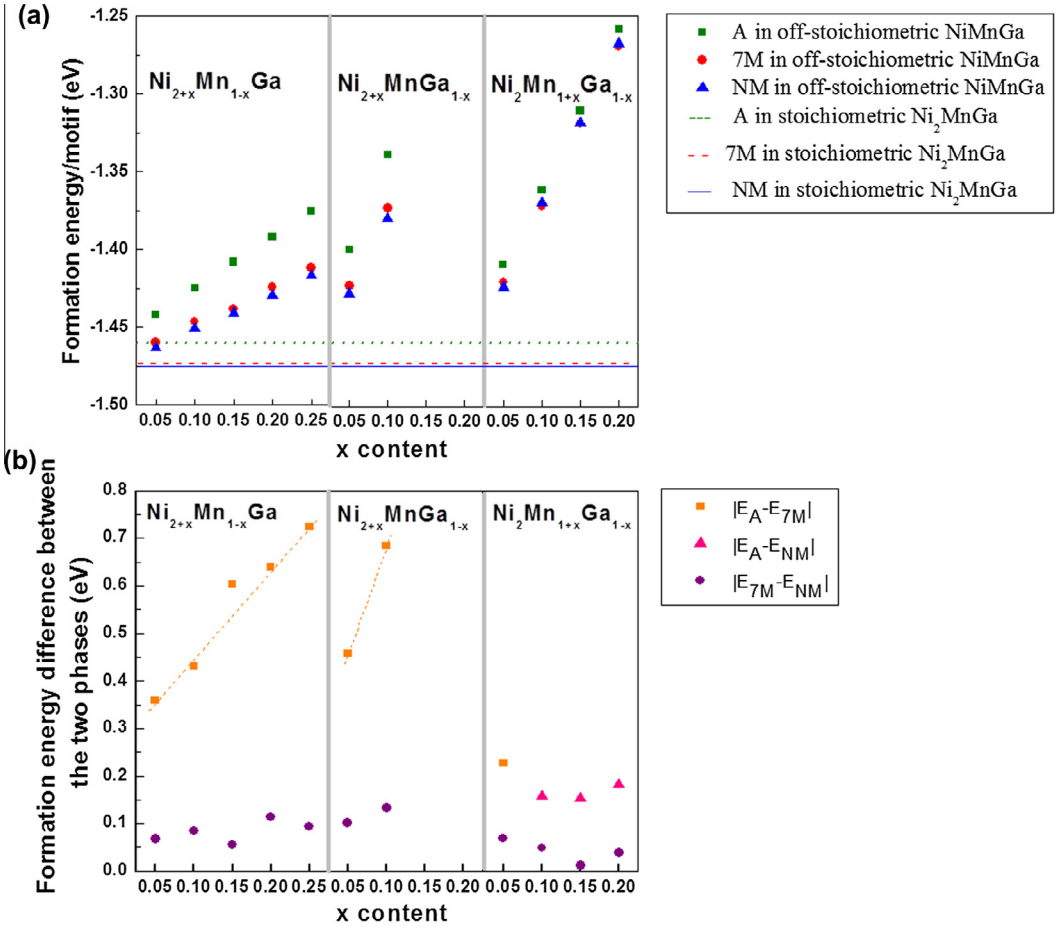

Fig. 1. (a) Formation energy of austenite, 7M and NM martensite and (b) formation energy difference between the parent and the product phases for the two steps of transformations in $Ni_{2+x}Mn_{1-x}Ga$, $Ni_{2+x}MnGa_{1-x}$,and $Ni_2Mn_{1+x}Ga_{1-x}$, respectively.