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Structure stability and magnetic properties of Ni_2XGa (X = Mn, Fe, Co) Ferromagnetic Shape Memory Alloys by DFT approach

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Abstract
In this paper, we report some ab initio calculation results of three perfect stoichiometric alloy systems Ni_2XGa (X = Mn, Fe, Co). The calculations have been performed on optimizing the crystal structures in both austenitic and martensitic phases, the electronic density of states (DOS), the magnetic properties and the difference of charge distributions on considering that Mn, Fe, Co are adjacent to each other within one period in the periodic table of elements, and they are all ferromagnetic. We have shown the impact of these magnetic elements on several properties of each alloy. Study on these three Heusler alloy systems is important in view of property prediction.

Introduction

Since large magnetic field induced strains (MFIS) were discovered in the ferromagnetic martensitic phase of near-stoichiometric Ni_2MnGa alloys [1], there has been an increasing interest in research and development of such alloys due to the wide applications. Our group is involved in determining the crystal structure [2] and the twinning relationship between martensitic variants [3] in a Ni-Mn-Ga ferromagnetic shape memory alloy. Furthermore, theoretical prediction of martensitic transformation crystallography by crystallographic phenomenological theory in such material had been conducted [4]. However, the high brittleness of Ni-Mn-Ga alloy imposes difficulties for its practical applications. In addition, the large MFIS effect appears in the vicinity of room temperature. Therefore, the high instability limits the use of such materials. Addition of other elements could be a potential alternative to improve these disadvantages. So the study of the substitution of one element by another and the addition of the fourth element have been experimentally started. Many new types of ferromagnetic shape memory alloys have been developed in order to increase toughness, for example Ni–Fe–Ga [5, 6] Ni–Co–Ga [7, 8], etc. Near-stoichiometric Ni_2FeGa alloys seem to be a promising system as they undergo, on cooling, a martensitic transformation (MT) from $L2_1$ -Heusler-structure to ferromagnetic martensite with layered structures (i.e. five-layered, 5M, or seven-layered, 7M [5, 6]), which are good candidates to show large MFIS. Recently intermetallic Ni–Co–Ga alloys are recognized as new ferromagnetic shape memory material due to their good ductility [9], magnetic-controlled two-way shape memory effect [10] and high martensitic starting transformation temperatures [11]. However, experimental studies have some shortages: long study period, limited scope, high costs, etc. The theoretical calculation can simulate substitution or addition elements with any desired composition and accordingly select the most reasonable composition, which can provide useful guidance for experiments.

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Calculation method

The ab initio calculations were performed based on the density functional theory (DFT), using the Vienna ab initio software package [12-15] (VASP). The interaction between ions and electrons is described by ultra-soft Vanderbilt pseudopotentials [16,17] (USPP) and by the projector-augmented wave (PAW) method. Both USPP and PAW method in VASP code allow for a considerable reduction of the number of plane-waves per atom for transition metals. The pseudopotentials used were generated within the generalized gradient approximation (GGA) in Perdew and Wang parametrization [18] to describe the exchange-correlation energy. In the pseudopotential approach, core electrons that do not participate in the bonding of the material are frozen and only the valence electrons are taken into account. For the pseudopotentials used, the electronic configurations were Ni ($3d^8 4s^2$), Mn ($3d^6 4s^1$), Fe ($3d^7 4s^1$), Co ($3d^8 4s^1$), Ga ($4s^2 4p^1$), respectively. In this work, the kinetic energy cutoff chosen was 275 eV for PAW-GGA and 250eV for USPP-GGA. A Monkhorst-Pack [19] grid was used to sample the Brillouin zone. The dimension of the *k* points grid varies with the cell size in order to keep a constant *k* points density in the Brillouin zone. So for a 4-atoms primitive cell, we used a 12×12×12 *k* points grid, and for a 16-atoms conventional cell, 10×10×10 *k* points grid was chosen. The calculation is semi-relativistic and the spin polarization was taken into account. All structures were relaxed using the conjugate gradient algorithm. Both the atomic position and volume were optimized. After relaxation, the forces on the atoms were checked to be lower than 0.02 eV/Å and the external pressure in the cell should be close to zero. From these calculations, energies, magnetic moments, and relaxed structures have been analyzed. In addition, the total density of states as well as the partial density of states (PDOS) were determined. To calculate the PDOS, the projection of the electronic density onto the atomic orbital requires defining radius of the projection sphere. The following atomic Wigner-Seitz radii 1.286, 1.323, 1.302, 1.302 and 1.402Å, respectively, for Ni, Mn, Fe, Co and Ga atoms were chosen.

Results and discussion

First we calculated the lattice parameter, volume of unit cell, bulk modulus, total and partial magnetic moment obtained from both USPP-GGA and PAW-GGA approximation in Ni_2XGa(X = Mn, Fe, Co) alloy systems, as listed in table 1. We also compared with experimental values and results from other published calculations [20-25]. The relaxed processes include both atomic positions and unit cell volumes. In order to simulate a real system, all the relaxed results should meet the following requirement: (1) the proper external pressure should be in the range of very small values, around to zero (-3 to 3 kB); (2) the total atomic forces and each atomic force must be less than 0.02eV/Å. After the structural optimizations, the bulk modulus was calculated in each phase. For that, we created few deformations of the volume within the range -3% and 3% of the equilibrium volume V_0 and the results were fitted by the Birch-Munaghan equation [26,27]. Clementi et al. [28] have calculated the atomic radius of each atom. The radii of Mn, Fe and Co are respectively 1.61Å, 1.56Å and 1.52Å. We can observe the same decreasing tendency of the lattice parameter from table 2, as well as the unit cell volume. We can conclude that the size effect of the X element is important for the martensitic structural change of these three systems. The decrease of total magnetic moment, namely gradually weakened ferromagnetism mainly depends on the 3d state electronic status of the X atom. The difference between Ni_2MnGa and Ni_2FeGa is close to 0.8 μ_B whereas the difference between Ni_2FeGa and Ni_2CoGa is close to 1.6 μ_B. Therefore, the effect of the X element is not just limited to structures, but also extends to magnetic properties. The theoretical results are in very good agreement with the experimental data and other calculation results [20-25].

Ni_2XGa	Method used	a [Å]	V_0 [Å^3]	B [GPa]	μ^{tot} [μ_B]	μ^{Ni} [μ_B]	μ^{X} [μ_B]	μ^{Ga} [μ_B]
Ni_2MnGa	USPP-GGA	5.805	195.640	151.2	4.20	0.35	3.52	-0.06
	PAW-GGA	5.784	193.456	157.9	4.00	0.35	3.32	-0.06
	From reference	5.823[20]	197.432[21]	156.0 [24]	4.17[24]	0.36[25]	3.43[25]	-0.04[25]
Ni_2 Fe Ga	USPP-GGA	5.752	190.291	164.3	3.41	0.28	2.91	-0.04
	PAW-GGA	5.740	189.086	168.0	3.23	0.26	2.76	-0.04
	From reference	5.741[21]	189.169[21]	...	3.04[23]	...	...	...
Ni_2Co Ga	USPP-GGA	5.6987	185.063	170.8	1.80	0.14	1.58	-0.02
	PAW-GGA	5.6890	184.125	194.5	1.66	0.14	1.42	-0.02
	From reference	5.405[24]	...	...	1.78[24]	0.16[24]	1.55[24]	-0.02[24]

Table 1: The optimized lattice parameter (a), volume of unit cell (V_0), bulk modulus (B), total and partial magnetic moment obtained from both USPP-GGA and PAW-GGA approximation in Ni_2XGa (Fm-3m, cubic phase) obtained in this work. Experimental values and results of other calculations [20-25] are also listed for comparison.

Using the optimized structure parameters obtained from USPP-GGA approximation, keeping the volume of unit cell as a constant, we calculated the variation of the total energies, partial and total magnetic moments with the tetragonal distortion of three ferromagnetic shape memory alloys Ni_2XGa(X = Mn, Fe, Co) at absolute zero temperature (T = 0 K). Our assumption for this work is that, although the calculations are made at zero temperature, the different structures should appear at least as metastable minima.

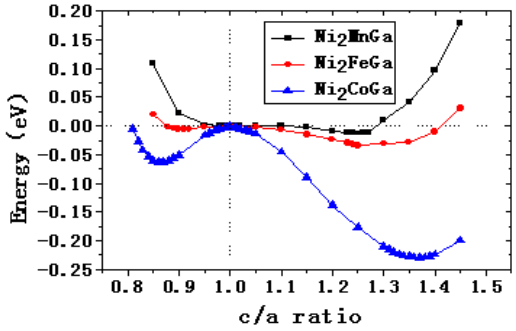

Fig 1 Relative variation of the total energy as a function of the tetragonal distortion in three different alloy systems: Ni_2MnGa (black line), Ni_2FeGa (red line), Ni_2CoGa (blue line). Zero energy corresponds to the energy of the $L2_1$ structure in each case using USPP approximation.

The total energy as a function of the tetragonal c/a ratio of the three alloy systems is shown in figure 1. Each alloy has two local energy minima, within the c/a ratio range from 0.80 to 1.45. For the stoichiometric Ni_2MnGa, Ni_2FeGa and Ni_2CoGa compounds, the first local minimum is c/a = 1, 0.91 and 0.86 respectively and the second local minimum is c/a = 1.25, 1.25 and 1.37 respectively. The point c/a = 1 corresponds to the structure of the parent austenite phase, space group Fm-3m, (#225); c/a = 1.25 corresponds to a kind of martensite. According to the results of A. T. Zayak and P. Entel et al. [29], a non-modulated martensite of Ni_2MnGa with c/a ratio ≈ 1.2 is the most stable phase at the extremely low temperature, which is consistent with our calculation results in this case. It means that at the absolute zero temperature, the c/a = 1.25 tetragonal non-modulated martensite phase has been predicted. With the gradual increase of temperature, the metastable 5M, 3M, $L2_1$ structure will appear one after another.

In the Ni_2FeGa and Ni_2CoGa compounds, we can find a local maximum at c/a = 1 (whereas c/a = 1 is a minimum of energy in the Ni_2MnGa compound). Due to the different structure stability (c/a < 1, c/a = 1 and c/a > 1) of the Ni_2XGa (X = Mn, Fe, Co), when the temperature increases, the transition sequence will be different. Moreover, it is known that there is a strong competition between intermetallic compound and a disordered FCC second γ phase precipitation in the experiments. Thus it is difficult to form pure Ni-Fe-Ga intermetallic compounds in as-cast alloys, except using the melt-spinning technique [30]. The Ni_2CoGa alloy has the deepest energy minima, so the martensitic phase of this alloy is the most stable one. However, this deepest energy difference between austenite and martensite also means that this alloy is the most difficult one to obtain a good shape memory effect. Such difference can be attributed to two aspects: one is the atomic size of the X atoms, and the other one is their chemical potentials.

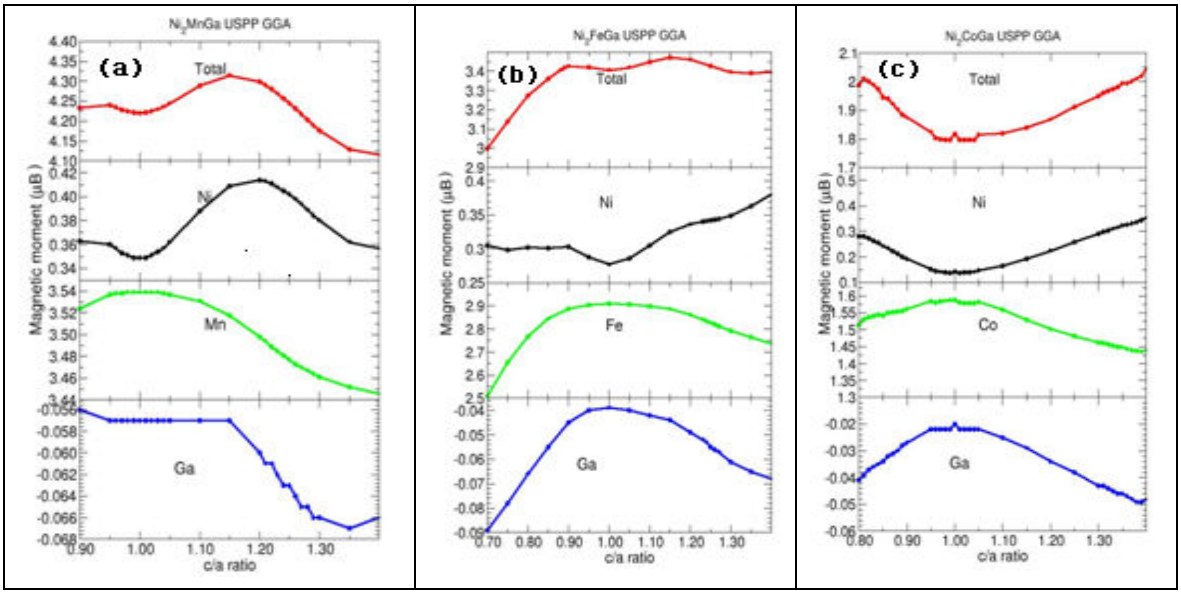

Fig. 2 Evolution of the total and partial magnetic moments with the c/a ratio in Ni_2XGa: (a) X = Mn; (b) X = Fe; (c) X = Co

The calculated total magnetic moment and contributions associated with individual atoms in Ni_2XGa, as a function of the c/a ratio are shown in figure 2. It can be seen that the principal contribution to the total magnetic moment is mainly given by X = Mn, Fe, Co. Since the magnetic moment of Ga atom is very small, we ignored the contribution of Ga to the total variation of magnetic moment. The shape of the total magnetic moment curve is given by Ni atom except for Ni_2FeGa, because there are two Ni atoms contributing to the total magnetic moment change. With X= Mn, as shown in fig 2 (a), the evolution of Ni moment is wavelike and follows the variation of total magnetic moment, whereas Mn moment uniformly decreases after the maximum point at c/a=1. In Ni_2FeGa, shown in figure 2 (b), the shape of Ni moment curve is parabolic with only one single minimum, differing from the case of Ni_2MnGa. So the variation tendency of total magnetic moment for Ni_2FeGa is determined by strong combined effects of Ni and Fe atomic magnetic moments. The situation for Ni_2CoGa differs from the first two types, as shown in fig 2 (c). The variation of total magnetic moment is similar to the Ni moment, but the curve is parabolic, not wavelike.

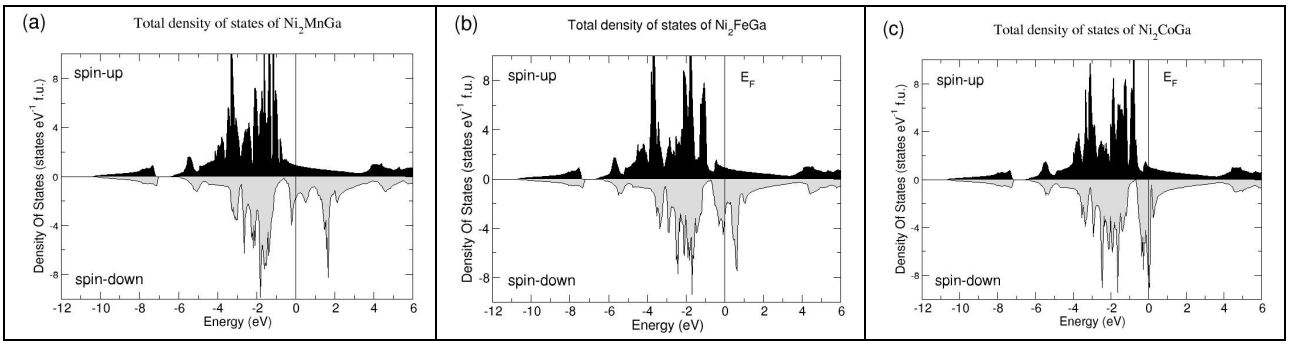

Fig. 3 Calculated spin-resolved total density of states for (a) Ni_2MnGa, (b) Ni_2FeGa, and (c) Ni_2CoGa

In order to investigate the change of magnetic properties, it is necessary to calculate the spin-resolved total density of states, see e.g. [31, 32]. These spin resolved densities have further been calculated in the cubic Ni_2XGa compounds (X = Mn, Fe, Co), as shown in figure 3. For the three stoichiometric alloys, we can clearly see that the spin-up and spin-down components from -10 eV to -2 eV in total density of states are quite similar. From Ni_2MnGa to Ni_2CoGa, the spin-down electron density of states at Fermi level are increasing gradually, therefore, Ni_2MnGa has the largest total magnetic moment, whereas it is smallest in Ni_2CoGa. We also calculated the partial density of states, and came to the conclusion that such variation is due to the contribution of 3d states of X (X = Mn, Fe, Co). In Ni_2MnGa compound, we cannot see any peak in the up spin part close to the Fermi level but 3 peaks in the down spin part (-0.2, 0.8 and 1.8 eV). The Fermi level is localized in the valley of the down spin density of states. The presence of the local minimum of the spin down density of states shows a stability of the compound.

Conclusion

We have investigated the energy stability of three compounds Ni_2XGa (X = Mn, Fe, Co) and the effect of the substitution on the properties. The substitution of the Mn by the Fe and Co changes the phase stability because the c/a value corresponds to a change of the minimum energy. The shape of the total magnetic moment curve with the c/a ratio variation is normally given by the Ni atom, but not for Ni_2FeGa. In the latter case the shape is given by the combined effect of the Fe and Ni atom. The study of the total density of state shows a degradation of magnetism in Ni_2FeGa and Ni_2CoGa compounds as compared to Ni_2MnGa. The bonding between the Ni atoms in the Ni_2MnGa is modified in the Ni_2FeGa and Ni_2CoGa compounds and the bonding between Ni and X atoms appears. The computational results show a destabilization of the cubic structure if Fe or Co substitutes Mn atom. This effect might influence the different phases and phase transitions in the ferromagnetic shape memory alloys.

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