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Ternary Diagrams of Ni-Mn-Ga from First Principles

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Abstract. The composition dependences of the magnetic and elastic properties of Ni-Mn-Ga Heusler alloys are investigated by using *ab initio* calculations. The off-stoichiometric compositions are realized by the coherent-potential approximation. Two types of off-stoichiometric approaches are proposed. Through a series of researches, the equilibrium lattice constants, bulk modulus, magnetic moments, formation energies of Ni-Mn-Ga alloys are obtained and mapped onto ternary diagrams.

Introduction

Among the Mn-based alloys, Ni-Mn-Ga Heusler systems have received significant attention regarding their magnetic shape memory properties for compositions close to stoichiometry and their magnetocaloric properties at off-stoichiometric compositions [1, 2, 3, 4]. The unique properties of Ni-Mn-Ga alloys resulting from the coupling between the magnetic and structural phase transitions. In general, Ni-Mn-Ga alloys exhibit remarkable richness of physical properties, varying significantly with their chemical composition. The ability to obtain different compositional phase diagrams involving desired physical properties is a major challenge for improving Heusler-based technology [4]. Large efforts are made experimentally to find optimal compositions with better properties. On the one hand, compositional phase diagrams can be obtained experimentally by using composition spreads that allow for controlled simultaneous synthesis and characterization of large arrays of samples. On the other hand, compositional diagrams can be obtained theoretically by means of density functional theory (DFT) and Monte-Carlo approaches[4, 5]. At present, computational approaches on the level of DFT have been quite successful in describing electronic, structural, and magnetic properties of Heusler alloys.

In this study, we calculate magnetic and structural properties in a series of Heusler alloys using *ab initio* calculations and then analyze the distribution of these properties onto ternary diagrams.

Computational details

In order to calculate the electronic structure of Ni-Mn-Ga alloys, we used the spin-polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) package [6]. By constructing the exchange-correlation potential, we took the generalized gradient approximation (GGA) in the formulation of Perdew, Burke and Ernzerhof (PBE). The equilibrium energy calculations were carried out for austenitic $L2_1$ structure (space group $Fm3m$). The chemical disorder was treated by the coherent potential approximation (CPA). The maximum number of CPA iterations and the CPA tolerance were set to 20 and 0.01 mRy, respectively. The self-consistent calculations were carried out using a regular **k**-mesh grid of 57^3 with 4495 **k** points. All calculations were converged to 0.01 mRy of the total energy.

In this study, we considered 37 compositions, where there are three stoichiometric compositions (Ni_2MnGa, Mn_2NiGa, and Ga_2MnNi). Besides, 14 compositions have Ni excess and 10 compositions have Mn(Ga) excess, respectively. We note, the excess of an atom means that its concentration is more than 50 %. To create off-stoichiometric compositions, we used two approaches. In the first one, for

all compositions we fixed Ni, Mn, and Ga atoms at $8c$, $4a$, and $4b$ Wyckoff positions, respectively. In the second one, for Ga-excess compositions we fixed Ga, Mn, and Ni at $8c$, $4a$, and $4b$ positions, respectively. We would like to point out that in this work we did not to consider the third type of off-stoichiometric approach, where for the Mn-excess compositions Mn atoms fix $8c$ position. In this regard we should do addition calculations for the cubic lattice with space group of F-$43m$.

Due to the fact that Mn excess atoms located at the Ni sites or Ga sites can interact antiferromagnetically (AFM) with Mn atoms at regular Mn sublatice, it is necessary to consider a different initial spin configuration. Therefore, we took into account three spin configurations refereed as FM (spins of Mn located at the Ni, Mn, and Ga sites are parallel) and two ferrimagnetic FIM-1 (spins of Mn located at the Mn and Ga sites are parallel while the spin of Mn at the Ni site is reversed) and FIM-2 (spins of Mn located at the Mn and Ni sites are parallel while the spin of Mn at the Ga site is reversed).

Results of *ab initio* calculations

The distributions of the equilibrium lattice parameter mapped onto the ternary diagram of Ni-Mn-Ga are presented in Fig. 1. Calculations were carried out for two types of off-stoichiometric approach. Here we denote these approaches as No.1 and No. 2 in accordance with our discussion in the previous section. As can be seen in Fig. 1 that in general, the both distributions of the lattice parameter have similar trend. Namely, the largest lattice parameter (6.5 Å) is observed in the left corner of the diagram, which corresponds to the Ga-excess compositions. In contrast, a decrease in the lattice parameter is found with increasing Mn and Ni concentrations. It is obvious that areas with minimal lattice parameter ($\approx$ 5.7 Å) correspond to the Mn- and Ni-excess compositions (See the top and right corners of the diagrams).

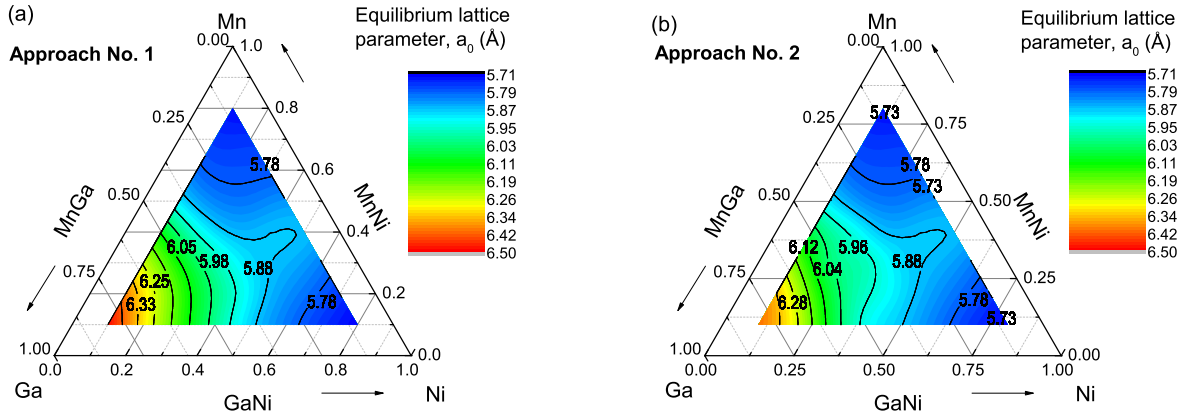

Fig. 1: The distribution of the equilibrium lattice parameter mapped onto the ternary diagram of Ni-Mn-Ga. Results are obtained for the (a) first and (b) second type of off-stoichiometric approach.

Fig. 2 illustrates the distribution of the bulk modulus mapped onto the ternary Ni-Mn-Ga diagram obtained for both off-stoichiometric approaches. Our calculations have shown that the lowest bulk modulus ($\approx$ 62 GPa) is found for the Ga-excess compositions, whereas the mean value ($\approx$ 170 GPa) corresponds to the Ni-excess compositions, and, finally, the highest bulk modulus (265 GPa) can be observed for the Mn-excess compositions. It should be noted that the bulk modulus was calculated by using the standard thermodynamic equation coupling a bulk modulus with a derivative of energy with respect to volume. Moreover, the theoretical value of bulk modulus for the stoichiometric Ni_2MnGa is closed to 152 GPa, while the experimental value is 148 GPa [1]. We can see a good agreement between our results and experimental data.

The distributions of the total magnetic moment mapped onto the ternary diagram of Ni-Mn-Ga are shown in Fig. 3. We can see from Fig. 3 that the highest magnetic moment is found for composi-

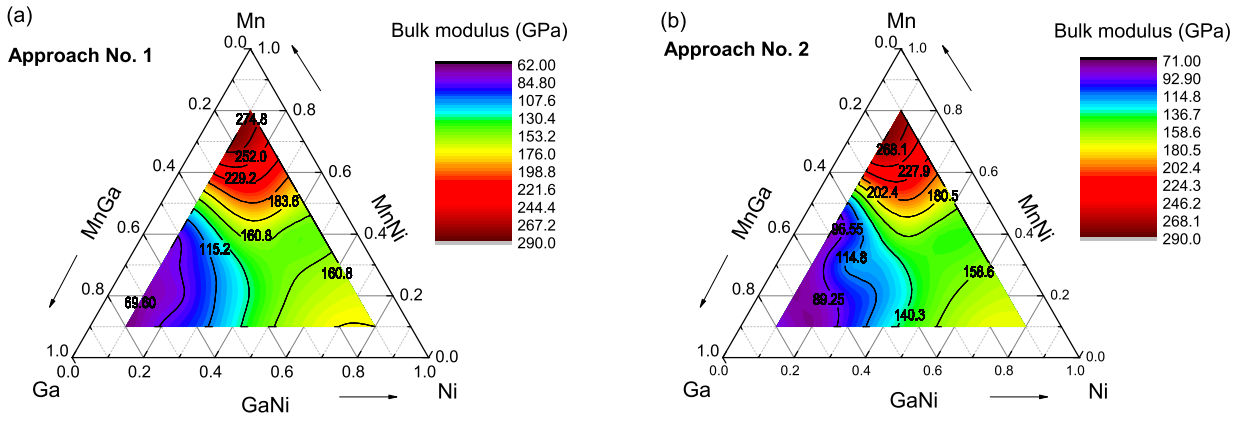

Fig. 2: The distribution of the bulk modulus mapped onto the ternary diagram of Ni-Mn-Ga. Results are obtained for the (a) first and (b) second type of off-stoichiometric approach.

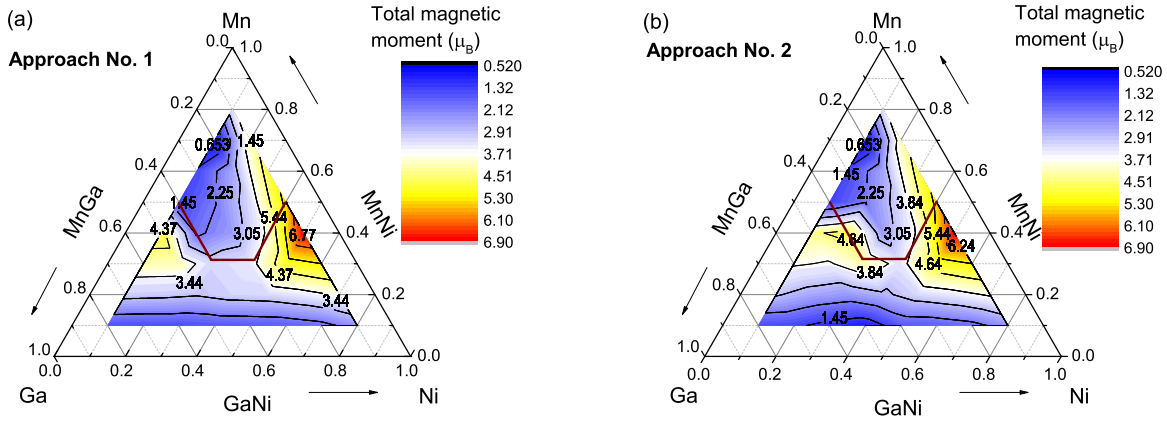

Fig. 3: The distribution of the total magnetic moment mapped onto the ternary Ni-Mn-Ga diagram. Results are obtained for the (a) first and (b) second approaches. Here, the solid line separates the regions between the FM (a bottom part) and FIM-1 (a top part) stable configurations in austenite.

tions with the average Mn and Ni concentrations. On the other hand, the smallest magnetic moment appears in the Mn- and Ga-excess compositions. Furthermore, we found that the FIM-1 (FM) order is favors for compositions located in the top (middle and bottom) part of the diagram, respectively. Moreover, the FIM-1 and FM (see the bottom part of diagram) phases have approximately the same magnetization. This is due to the fact that the latter phase involves the Ga-excess compositions. As the result, the magnetization of FM phase is reduced due to the negligible magnetic moment of Ga.

In order to determine stable compositions in austenitic phase, we calculated the formation energy using following equation

$$\Delta E_{mix} = E_{tot} - \left(xE^{\mathrm{Ni}} + yE^{\mathrm{Mn}} + zE^{\mathrm{Ga}}\right). \quad (1)$$

Where, E_{tot} is the total energy, x, y, z are the Ni, Mn, and Ga concentrations, respectively. $E^{\mathrm{Ni(Mn,Ga)}}$ is the energy of a pure element. $\Delta E_{mix} < 0$ indicates on a phase stability.

Fig. 4 shows the distributions of the formation energy mapped onto the ternary Ni-Mn-Ga diagram. Evidently, the most stable compounds are found for the Mn- and Ni-excess compositions. We can see that the in the case of off-stoichiometric approach No. 1 the unstable Ga-excess compositions take up of ≈ 30 % of the whole diagram (See, Fig. 4(a)). In contrast, in the case of second approach (No. 2) we can observe a decrease in the area of unstable Ga-excess compositions (See, Fig. 4(b)). Besides, it shifts to the left corner of the ternary diagram containing the Ga-excess compositions.

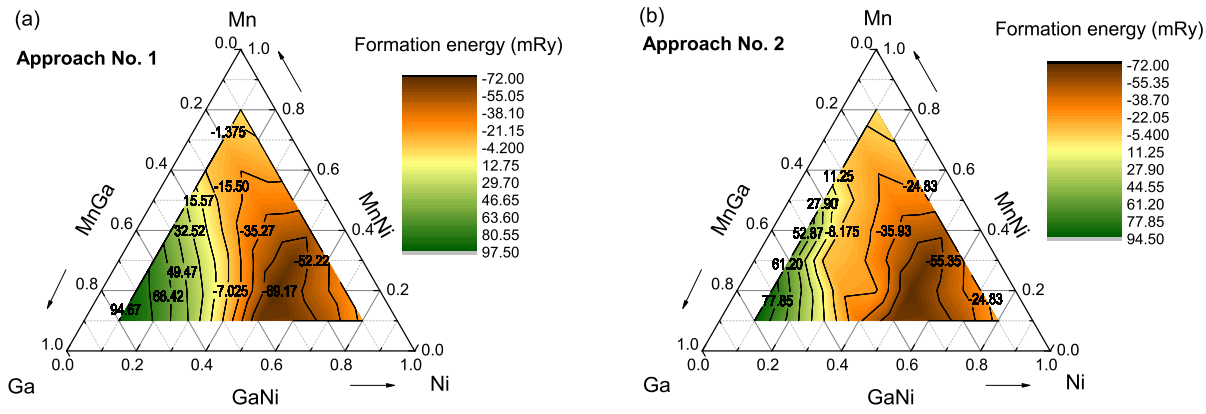

Fig. 4: The distribution of the formation energy mapped onto the ternary diagram of Ni-Mn-Ga. Results are obtained for the (a) first and (b) second type of off-stoichiometric approach.

Summary

A systematic study of the magnetic and structural properties of Ni-Mn-Ga alloys has been performed by means of first-principles calculations. The equilibrium lattice parameter, total magnetic moment, bulk modulus, and formation energy were mapped onto the ternary diagram of Ni-Mn-Ga alloys. Our calculations have shown that the largest lattice parameter, the smallest magnetic moment and bulk modulus were found for the Ga-excess compositions, while the smallest lattice parameter and the mean value of the bulk modulus were observed for the Ni-excess compositions. Besides, the Mn-excess compositions characterize by the largest bulk modulus and a small lattice parameter and magnetic moment. The highest magnetic moment is found for compositions with average Mn and Ni concentrations. Finally, the compositions with a significant Ga excess are unstable in austenite.

Acknowledgments

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