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Ab initio study of properties of Co- and Cu- doped Ni-Mn-Ga alloys

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Abstract

The influence of Co and Cu doping on Ni-Mn-Ga alloy is investigated using the first-principles exact muffin-tin orbital method in combination with the coherent-potential approximation. The energy difference between the austenite (A) and the nonmodulated (NM) martensite $\Delta E_{\text{A-NM}}$ depends linearly on the Cu concentration and distribution, with a minimum for all Cu at Mn sites and a maximum for all Cu at Ga sites. For alloys simultaneously doped by Co in Ni sublattice and Cu in Mn or Ga sublattice, the effects of the individual dopants on $\Delta E_{\text{A-NM}}$ and $(c/a)_{\text{NM}}$ and are almost independent. The alloy with composition $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$ exhibits decreased equilibrium $(c/a)_{\text{NM}}$ and increased $\Delta E_{\text{A-NM}}$ in comparison with $Ni_{50}Mn_{25}Ga_{25}$, which is in agreement with the previous experimental results.

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1. Introduction

The Ni_2MnGa Heusler alloy has attracted a lot of interest because it exhibits interesting magnetomechanical effects such as a giant magnetic-field-induced strain (MFIS). This phenomenon is a consequence of the coupling

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between the magnetic microstructure and martensite twin microstructure combined with the high mobility of twin boundaries [1]. The MFIS occurs in martensite, i.e. below martensitic transformation, which takes place at T_M = 202 K for stoichiometric Ni_2MnGa, whereas austenite with cubic ordered $L2_1$ structure is stable above T_M. The Curie temperature T_C is about 376 K [2]. Controlling T_M and T_C is important task for the practical exploitation of the interesting properties of material. It can be achieved, for example, by using off-stoichiometric composition or doping with an additional element [3].

Several kinds of martensites have been observed in the Ni-Mn-Ga system. The modulated phases with ratio $c/a < 1$ exhibit MFIS up to 10% [4]. Giant MFIS has never been reported for the nonmodulated (NM) martensite with a purely tetragonal lattice and $(c/a)_{NM} \approx 1.17 – 1.23$ [5]. However, a MFIS of 12% has recently been reported in the NM phase for a structure with reduced $(c/a)_{NM}$ = 1.147, achieved by simultaneous doping by 4 at. % of Cu and Co with the resulting alloy composition $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$ [6]. Doping also increased transformation temperatures of this alloy above room temperature, T_M = 330 K and T_C = 393 K.

Previous experimental investigations of Ni-Mn-Ga doping showed that T_M increases for the Co- and Cu-doped alloys deficient in Mn or Ga [7,8], whereas it decreases if Co or Cu replaces Ni atoms [3,9]. With the help of *ab initio* simulations the site preference has been clarified: Co exhibits tendency to occupy the Ni sublattice and Cu atoms always occupy the sublattice of the host elements in deficiency [10]. The energy difference between the austenite and the nonmodulated martensite $\Delta E_{A\text{-}NM}$ has been also obtained from *ab initio* calculations. It correlates well with the experimentally determined T_M: a larger difference in total energies corresponds to a higher T_M [11].

In our previous theoretical work, we analyzed the development of calculated total energies along the tetragonal deformation path to obtain the equilibrium $(c/a)_{NM}$ and $\Delta E_{A\text{-}NM}$ [11]. The Cu doping in Ga sublattice results in a strong increase of $\Delta E_{A\text{-}NM}$, but just a small change of equilibrium $(c/a)_{NM}$. On the other hand, if Cu goes to Mn sublattice, the increase of $\Delta E_{A\text{-}NM}$ is much smaller but a noticeable decrease of $(c/a)_{NM}$ is seen. Both quantities $\Delta E_{A\text{-}NM}$ and $(c/a)_{NM}$ strongly decrease with increasing concentration of Co at Ni sites. Further, we have found that doping effects can be well estimated using a linear superposition of the effects of individual dopants for alloys doped simultaneously by Co in Ni site and Cu in Ga site (general formula $Ni_{50-x}Co_xMn_{25}Ga_{25-z}Cu_z$).

In this article, we extend the previous investigation of the simultaneous Co and Cu doping in Ni-Mn-Ga alloys. We especially focus on the Cu doping in Mn sublattice and we also show that the Cu distribution between Ga and Mn sublattices can be used for further fine tuning of properties. In the end we calculate and discuss the properties of alloy $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$, which showed the most interesting behavior in the previous experiments [6].

2. Computational method

The first-principles calculations were carried out using the exact muffin-tin orbital (EMTO) method in combination with the full charge density (FCD) technique [13], which is suitable to accurately describe the total energy with respect to anisotropic lattice distortions such as tetragonal deformation. The chemical disorder caused by doping elements was included by using the coherent-potential approximation (CPA) [14,15]. The exchange correlation was described using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [16]. We used the same setting for calculations as in our previous work [11].

For alloys with different Cu and Co doping concentrations described by general formula $Ni_{50-x}Co_xMn_{25-y}Ga_{25-z}Cu_{y+z}$, we calculated a series of total energies as a function of c/a in the range between c/a = 0.9 and 1.4 at a constant volume, which describes the tetragonal deformation of austenite phase with $L2_1$ structure (c/a = 1). Calculated total energies are related to the energy of cubic structure for the given composition.

3. Results

For alloys with general formula $Ni_{50-x}Co_xMn_{25-y}Ga_{25}Cu_y$ where Cu atoms replace Mn atoms, we have found that the effects of Cu and Co additions are almost independent from each other, i.e. that the effects of combined doping can be estimated as the linear superposition of the effects of single element dopings. This is similar to the previously studied case of simultaneous doping with Cu replacing Ga atoms [12]. Figure 1(a) shows the total energy as a function of tetragonal ratio c/a for the alloy with constant concentration 5% of Co in Ni sublattice and different concentration z of Cu in Mn sublattice. The decrease of $\Delta E_{A\text{-}NM}$, which arises from doping by 5% of Co, is partially

compensated by Cu doping. However, even 7.5% Cu is not sufficient to compensate $\Delta E_{\text{A-NM}}$ up to the value obtained for stoichiometric Ni_2MnGa alloy, because the effect of Cu doping in Mn sites is weaker than in the case when Cu is in Ga sites (see Fig 2(a) in Ref [12]). On the other hand, the equilibrium $(c/a)_{\text{NM}}$ slightly decreases with increasing Cu concentration in Mn sites. Also alloys with constant 5% Cu concentration exhibit the same linear superposition of doping effects (Fig. 1(b)). Here, the $(c/a)_{\text{NM}}$ is slightly decreased and $\Delta E_{\text{A-NM}}$ is increased due to the presence of Cu in Mn site, however further increasing Co concentration in Ni sublattice decreases both quantities.

The effect of Cu distribution between Ga and Mn sublattices can be used for finer tuning of $(c/a)_{\text{NM}}$ and $\Delta E_{\text{A-NM}}$. In alloys without any Co both quantities linearly increase with increasing Cu concentration in Ga sites and decreasing Cu concentration in Mn sites (Fig. 2(a)). The influence of Cu on $\Delta E_{\text{A-NM}}$ is relatively strong, because there is a large difference between $\Delta E_{\text{A-NM}}$ for $Ni_{50}Mn_{20}Ga_{25}Cu_5$ and $Ni_{50}Mn_{25}Ga_{20}Cu_5$ alloys (0.405 mRy/atom, 1 Ry = 13.606 eV = $2.170 \cdot 10^{-18}$ J). Similar linear increasing of $\Delta E_{\text{A-NM}}$ can be seen also for alloys with Co present in Ni sublattice (Fig. 2(b)). However, this effect is much weaker than in the case of no Co doping, because 5% of Co in Ni site causes that $\Delta E_{\text{A-NM}}$ for both types of Cu doping will be closer to each other. The difference between $\Delta E_{\text{A-NM}}$ for $Ni_{45}Co_5Mn_{20}Ga_{25}Cu_5$ and $Ni_{45}Co_5Mn_{25}Ga_{20}Cu_5$ alloys is 0.162 mRy/atom only. The influence of Cu distribution on $(c/a)_{\text{NM}}$ is smaller than on $\Delta E_{\text{A-NM}}$, but still distinguishable. However, it also further decreases with increasing Co concentration. The difference between $(c/a)_{\text{NM}}$ for alloys with no Co doping is 0.038, whereas if 5% of Co is present in Ni sublattice, these difference is 0.017 only.

To compare our results with experiment we calculated also total energies along the tetragonal deformation path for experimentally prepared alloy with composition $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$. Experimental measurements shows reduction of $(c/a)_{\text{NM}}$ and increased transformation temperature T_M. The latter should correspond to larger energy difference $\Delta E_{\text{A-NM}}$. As can be seen from Fig. 3 our results corresponds qualitatively to experimental findings: $(c/a)_{\text{NM}}$ exhibit the same ≈4% decrease as in experiment (from 1.256 for stoichiometric Ni_2MnGa to $(c/a)_{\text{NM}}$ = 1.208, compare with vertical lines in Fig. 3) and $\Delta E_{\text{A-NM}}$ is increased from 0.379 mRy/atom to 0.420 mRy/atom.

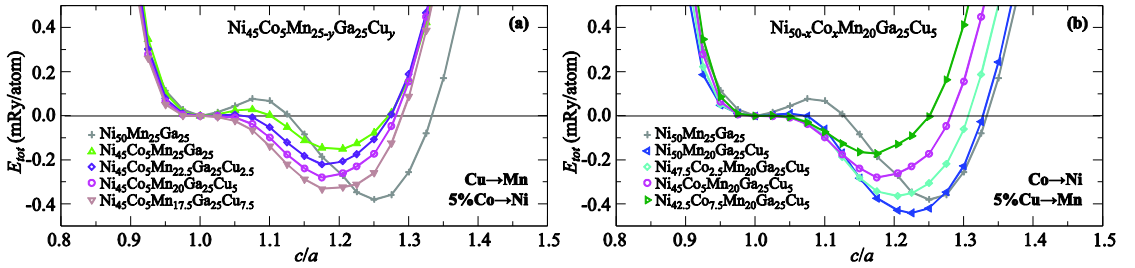

Fig. 1. Total energy as a function of the tetragonal ratio c/a for doped alloys with different concentrations y of Cu in the Mn sublattice and constant concentration 5% of Co in the Ni sublattice (a), and different concentration x of Co in the Ni sublattice and constant concentration 5% of Cu in the Mn sublattice (b).

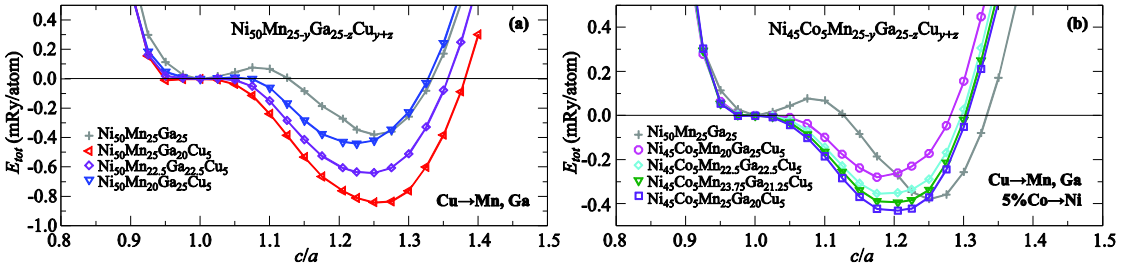

Fig. 2. Total energy as a function of the tetragonal ratio c/a for alloys with different distributions of Cu in the Mn and Ga sublattice with no Co doping (a), and with 5% of Co in the Ni sublattice (b).

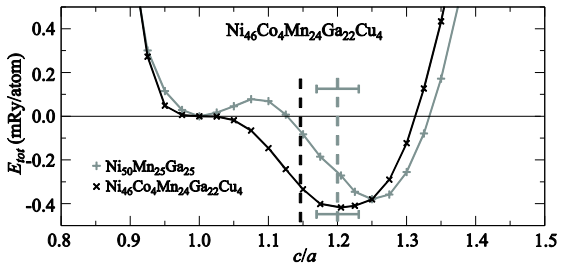

Fig. 3. Calculated total energy as a function of the tetragonal ratio c/a for experimentally prepared alloy with composition $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$. Total energy of $Ni_{50}Mn_{25}Ga_{25}$ alloy is also shown for comparison. Vertical dashed lines correspond to experimental values of c/a. For $Ni_{50}Mn_{25}Ga_{25}$ alloy the horizontal error bar indicates the range of experimental c/a values [5].

4. Conclusions

The Co and Cu doping of Ni-Mn-Ga Heusler alloys has been studied using the EMTO-CPA first-principles method. We have found the same independent effects of the individual dopants on $\Delta E_{\text{A-NM}}$ and $(c/a)_{\text{NM}}$ for alloys simultaneously doped by Co in Ni sublattice and Cu in Mn sublattice, which was already observed for the case where Cu was used instead of Ga. For alloys where Cu is distributed between Mn and Ga sublattices the $\Delta E_{\text{A-NM}}$ increases linearly with increasing Cu concentration in Ga site and decreasing concentration in Mn site. The effect of Cu distribution on $(c/a)_{\text{NM}}$ is small but clearly distinguishable. Our theoretical results are in a good agreement with experimental findings for alloy with composition $Ni_{46}Co_4Mn_{24}Ga_{22}Cu_4$.

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