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journal or publication title	International Journal of Applied Electromagnetics and Mechanics
volume	12
page range	41-48
URL	<a href="http://hdl.handle.net/10232/00000217">http://hdl.handle.net/10232/00000217</a>

# Ni Excess and Electronic Structures of Multi-Functional Ni<sub>2.17</sub>Mn<sub>0.83</sub>Ga

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## Abstract

The electronic structures of Ni<sub>2.17</sub>Mn<sub>0.83</sub>Ga predict that the tetragonal, the orthorhombic and the monoclinic structure can be a martensitic phase and the monoclinic structure is the most stable. The stabilization of the monoclinic structure mainly comes from the difference of the kinetic energy. Then, the Ni excess plays an important role in the stabilization of the crystal structure. The Ni excess atoms make the tetragonal and orthorhombic structures unstable and the monoclinic structure stable. It is also found that the Ni excess atoms prefer the Mn sites and the magnetic moments in the monoclinic structure are smaller than those in the other structures.

## 1. Introduction

The Heusler alloy  $\text{Ni}_2\text{MnGa}$  is ferromagnetic and takes place a phase transition from a tetragonal to a cubic structure with increasing temperature. The alloys  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  have the shape memory property, which comes from a martensitic transformation. Wedel et al [2] reported that  $\text{Ni}_{2.16}\text{Mn}_{0.84}\text{Ga}$  takes places a cubic-to-tetragonal transformation. On the other hand, Inoue et al [3] observed the coexistent state of an orthorhombic and a monoclinic structure as the martensitic structure of  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  of  $x=0.18$  and  $0.19$  and  $\text{Ni}_2\text{Pd}_{0.16}\text{Mn}_{0.84}\text{Ga}$ . The two structural and magnetic transition temperatures approach with increasing Ni composition and merge at the range of  $x=0.18 - 2.0$  of  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  [1,4]. These interesting results suggest that external magnetic fields and temperatures can control the shapes of the materials. That is, the alloys are expected as multi-functional materials for device applications.

Under these experimental results, the electronic structures of  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  were calculated and showed that the peak of the local Ni DOS (density-of-state) near the Fermi level plays an important role for the structural transition [5]. That is, the redistribution of Ni d-electrons is strongly related with the transformation between the tetragonal and the cubic structure. In this paper, the electronic structures of  $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$  are calculated to investigate the influence of the replacement of Mn with Ni atoms.

## 2. Crystal structure and method of calculation

The total energy and the density of states (DOS) are compared for the cubic, the tetragonal (tet.-), the orthorhombic (orth.-) and the monoclinic (mono.-) structure. Among the four crystal structures, the mono.-structure has the lowest symmetry and the other structures have also the mono.-symmetry. The other structures are treated as the mono.-structure with a different angle of  $\theta$  in Fig.1. The value of the angle  $\theta$  is  $71.565$  degrees for the cubic structure. If the surface of this paper is assumed to be parallel to a  $zx$ -plane, Mn and Ga atoms sit on the  $y=0$  and  $1/2$  planes and Ni atoms on the  $y=1/4$  and  $3/4$  planes. The unit cell has twelve Ni, six Mn and six Ga. The  $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$  is treated as an ordered alloy where a sixth of Mn atoms in the stoichiometric  $\text{Ni}_2\text{MnGa}$  are replaced with Ni atoms. The Ni excess atoms can occupy the Mn or Ga sites. We consider three cases for the site of the Ni excess atoms: the three cases are described by the abbreviations of Ni(Mn), Ni(Ga1) and Ni(Ga2) and the Ni excess by Ni(e). Fig.1 shows the case that the Ni(e) atoms occupy the Ga2 sites and the Ga atoms move to the Mn sites. The case of  $\theta = 99.301$  degrees was observed in  $\text{Ni}_2\text{Pd}_{0.16}\text{Mn}_{0.84}\text{Ga}$ [3].

We calculated the total energy as a function of the lattice constants and determined the theoretical value of the lattice constant. The value  $0.40635$  nm correspond to the lattice constant  $0.38139$  nm of the tetragonal structure which is in good agreement of the

experimental value 0.38394 nm [2]. The volumes of the four structures are assumed to be equal to the volume of the cubic structure.

Band calculations were carried out self consistently by the LMTO-ASA method. The exchange correlation potential was treated within the framework of the local-spin-density (LSD) approximation.

### 3. Total energy and stable crystal structure

The total energies per formula unit for  $\text{Ni}_{2.17}\text{Mn}_{0.84}\text{Ga}$  were calculated for the four crystal structures and three types of the Ni(e) position. In the each structure, the total energy of the case Ni(Mn) is lowest among the three cases. The differences of the total energy between the cubic structure and the other ones were also estimated. The values per formula unit of the difference are +3.8, -1.4 and -98.5 mRyd for the tet.-, the orth.- and the mono.-structure, respectively. This result suggests that the martensitic structures may be the orth.- and/or the mono.-structure but not the tetragonal one. The magnitude of the difference for the mono.-structure is very large compared with the values of the other structures. This corresponds to the results of Inoue et al[3] that the martensitic structure is in the coexistent state of a mono.- and the orth.-structures as that of  $\text{Ni}_2\text{Pd}_{0.16}\text{Mn}_{0.84}\text{Ga}$  and the mass fraction of the monoclinic structure is about 0.9.

The above results were obtained by using the experimental value of the ratio of the lattice constant and the total energy of the tet.-structure is higher than that of the cubic structure. Then, we calculated the  $c/a$  ratio dependence of the total energy, for the case that the c-axis of the tet.-structures is selected to be the b-axis of the mono.-structure. That is shown in Fig.2. The minimum value is near the  $c/a=1.05$ , while the experimental value is 1.205[2]. It is impressive that the curve is almost flat near the minimum value and the energy decreases rapidly with decreasing the ratio  $c/a$ . The features suggest that the tetragonal structure is metastable.

## 4. Density of state

### 4.1 Total density of state

Now, we study the difference of the total energy on the basis of the DOS (density of states) of the four crystal structures. The total DOS for the case Ni(Mn) are compared for the cubic and the mono.-structure in Fig.3. The high peaks of the DOS of the cubic structure spread in the mono.-structure. The large change shows that the up and down spin states contribute to stabilize the mono.-structure. The band energies are integrated and the difference ( $E$ ) between the cubic and the mono.-structure is shown in the lower figure of Fig.3. The values are positive at the Fermi level for both spin states.

The DOS of the tet.- and orth.- structures are compared with that of the cubic structure in

Fig.4. The peaks of DOS are splitted owing to the lowering of the symmetry of the crystal structure. As seen in the down spin state, the DOS of the cubic structure is situated in the lower energy range. Therefore, the integrated energy of the cubic structure is lower than those of the tet.- and orth.- structures. The  $E$  of the tet.-structure is also shown in Fig.4, which is similar to that of the orth.-structure. The magnitude of the  $E$  of the mono.-structure is larger than the others because the change of the DOS is large.

#### 4.2 Local density of state

To study the above feature in more detail, we pay attention to the local DOS of the. In the case Ni(Mn), the local DOS for the cubic structure is shown in Fig.5 for the d-states of Ni, Mn and Ni(e) atoms. The DOS of the Ni(e) is similar to that of Mn rather than the Ni at the normal sites because the Ni(e) atom has the eight Ni first-neighbours as the Mn atom. These local DOS change in the mono.-structure as compared in Fig.5. The large valley of the Ni(e) and Mn disappears and the occupied states generally move to the states with the lower energy. Thus, the band energy largely contributes to the stabilization of the mono.-structure.

The DOS of the cases of Ni(Ga1) and Ni(Ga2) are compared with that of the case Ni(Mn) in Fig.6. The DOS shapes of the cubic structure are preserved in the two cases. The Ni(e) in all the cases has the eight Ni atoms as the second and the third neighbours but the first neighbours is the two Ga atoms in the case Ni(Mn) and the two Mn atoms in the cases of Ni(Ga1) and Ni(Ga2). The local circumstances of the case Ni(Mn) is different from the others. The difference is one of the causes which brings the large difference in the band structures. Thus, the case of the Ni(Mn) has the lowest energy among the three cases.

Then, we turn our attention to the tet.- and orth.-structures. The degeneracy of the band energy in the cubic structure is raised owing to the lowering of the symmetry in the tet.- and orth.-structures. However, the change of the Ni(e) DOS is small and the DOS preserve the shape of the cubic structure as shown in Fig.7. In the down spin bands, the DOS of the cubic structure is situated in the lower energy range. The  $E$  of the Ni(e) in the orth.-structure is also shown in Fig.7, which is similar to that of the tet.-structure. The value of  $E$  at the Fermi level is very small for the up spin states but is negative for the down spin states. Thus, the tet.- and orth.-structures become unstable. These features are reflected in Fig.4.

### 5. Contributions to total energy

We described that the total energies of the mono.- and orth.-structure are lower than that of the cubic structure but the orth.-structure is higher. On the other hand, the integrated band energy shows that the energy of the ortho.-structure is higher than that of the cubic structure. Here, the contributions to the total energy are studied. The contributions of the kinetic, potential and exchange energy are shown by the symbols of  $E_k$ ,  $E_v$  and  $E_x$  in Fig.8. Their

values are for the case Ni(Mn) and their standards are the values of the cubic structure. The contribution  $E_x$  is positive, that is, the magnitude of the exchange energies of the three structures are smaller than that of the cubic structure. This corresponds to the magnitude of the magnetic moment. The Mn moment (about  $2.94 \mu_B$ ) in the mono.-structure is smaller than that (about  $3.25 \mu_B$ ) in the cubic, tet.- and orth.-structures. The contribution  $E_k$  is very large for the mono.-structure, compared with the other structures and stabilizes the mono.-structure. This suggests that the shapes of the Brillouin zone largely affect the total energy.

## 6. Conclusion

The total energies of  $Ni_{2.17}Mn_{0.83}Ga$  suggest that the mono.-, the orth.- and the tet.-structure can become the martensitic structure and the tet.-structure may be metastable among these structures. The kinetic energy largely contributes to the stabilization of the mono.-structure and the cubic, tet.- and orth.-structure are very competitive. The Ni excess atoms prefer the Mn sites than the Ga sites. The Ni excess plays an important role for the stability of the crystal structure, that is, the Ni excess atoms make the tet.- and orth.-structures unstable and the monoclinic structure stable.

The magnetic moment on the Mn in the mono.-structure is about  $0.3 \mu_B$  smaller than that in the other structures.

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## Figure captions

Fig.1. The unit cell of  $\text{Ni}_{2.17}\text{Mn}_{0.83}\text{Ga}$  in the monoclinic structure equivalent to the cubic structure. The y-axis is assumed to be vertical to the surface of this paper. The Ni excess atoms are replaced with the Ga2 atoms and the Ga atoms move to the Mn sites. The Mn (solid circle) and Ga (solid square) atoms are in the  $y=0$  and  $1/2$  planes and the Ni (open circle) atoms in  $y=1/4$  and  $3/4$  planes.

Fig.2. The  $c/a$  dependence of the total energy for the tetragonal structure. The three cases of the Ni excess are distinguished: Ni at Mn sites, Ni at Ga1 sites and Ni at Ga2 sites.

Fig.3. The total DOS for the cubic and monoclinic structures in the case of the Ni excess at Mn sites. The difference of the integrated band energy between the cubic and the monoclinic structure are also shown. The vertical line shows the Fermi level of the cubic structure.

Fig.4. The total DOS of the down spin states for the cubic, orthorhombic and tetragonal structures in the case of the Ni excess at Mn sites. The difference of the integrated band energy between the cubic and the monoclinic structure are also shown. The vertical line shows the Fermi level of the cubic structure.

Fig.5. The local DOS of the up spin d-states for the cubic and monoclinic structures in the case of the Ni excess at Mn sites. The vertical line shows the Fermi level of the cubic structure.

Fig.6. The Ni excess DOS of the up spin d-states in the monoclinic structure for the three cases of the Ni excess position: Mn and two Ga sites. The vertical line shows the Fermi level.

Fig.7. The Ni excess DOS of the down spin d-states in the cubic, tetragonal and orthorhombic structure. The differences of the integrated band energy between the cubic and the other structure are also shown for the orthorhombic structure. The vertical line shows the Fermi level.

Fig.8. The contributions to the total energy  $E_{\text{tot}}$  for the monoclinic, orthorhombic and tetragonal structures. The standards of the values are the values for the cubic structure. The kinetic, potential and exchange energies are described by the symbols  $E_k$ ,  $E_v$  and  $E_x$ .