Electron Concentration and Structural Transformation of Ni$_2$MnGa-Based Shape Memory Alloys

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In shape memory Ni$_2$MnGa based alloys, the structural transition temperature ($T_t$) increases with increasing valence electron concentration per atom ($e/a$). That is, when Ni or Mn atoms in Ni$_2$MnGa are replaced with a fourth element (X atom), the $T_t$ increases with increasing atomic number of the X atom. To examine the experimental results, the electronic structures of these alloys were calculated for the cubic and monoclinic structures. The difference of total energies between the two structures was also calculated as a function of $e/a$. It was found that the features of $T_t$ ($e/a$) are similar to those of $\Delta E$ ($e/a$). Their features are different in the lower and higher ranges than the boundary $e/a = 7.625$. The two features are characterized by two cases: a case that X atoms occupies Ni sites and the other case that X atoms occupy Mn sites. The characteristics mainly come from the difference of the density of states of X atoms at Ni and Mn sites.

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1. Introduction

The Heusler alloys Ni$_2$Mn$_{1-x}$Ga$_x$ are ferromagnetic and have the shape memory property. The stoichiometric Ni$_2$MnGa ($x = 0$) transforms from a cubic (high temperature phase) to a tetragonal structure (low temperature phase).$^1$ However, Ni$_{2.14}$Mn$_{0.86}$Ga ($x = 0.18$ and 0.19) and Ni$_2$(Pd$_{0.12}$Mn$_{0.88}$)Ga transform from a cubic (high temperature phase) to a coexistent state of an orthorhombic and a monoclinic structure (low temperature phase).$^2$ The structural transition temperatures ($T_t$) and the Curie point ($T_c$) approach with increasing the Ni concentration and merge at the range of $x = 0.18$–0.2 of Ni$_{2.3}$Mn$_{0.7}$Ga.$^3$ Under these experimental results, it is reported by Ishida et al. that the tetragonal and orthorhombic structures may be metastable and the monoclinic structure is the most stable among these structures for Ni$_{2.17}$Mn$_{0.83}$Ga and Ni$_2$(Pd$_{0.17}$Mn$_{0.83}$)Ga.$^4$ This suggests that the coexistence states of the monoclinic and orthorhombic structures may appear at low temperature. The coexistent state corresponds to one observed by Inoue et al.$^5$

The valence electron concentration per atom ($e/a$) is an influential factor for the structural transition temperature. The relationship between $T_t$ and $e/a$ was examined for ternary alloys Ni–Mn–Ga and pseudo ternary alloys Ni–Mn–Ga–X. In ternary alloys Ni–Mn–Ga, the observed transition temperature $T_t$ is 202 K for Ni$_2$Mn$_{0.8}$Ga ($e/a = 7.5$), 340 K for Ni$_2$Mn$_{0.82}$Ga ($e/a = 7.635$) and 350 K for Ni$_2$Mn$_{0.81}$Ga ($e/a = 7.6425$).$^1,2,5$ The variation of $T_t$ ($e/a$) observed by Chernenko et al. and Tsuchiya et al. were represented by three straight lines with different slopes in the range of $e/a = 7.50$–7.80.$^6,7$ On the other hand, in pseudo ternary alloys Ni–Mn–Ga–X with Co or Fe additions, the relationship $T_t$ ($e/a$) seems to be also represented by a polygonal line at the boundary of $e/a \approx 7.625$.$^8$ That is, $T_t$ ($e/a$) varies from 220 K to 317 K at the range of $e/a = 7.57$–7.63 for Ni$_{2.20–0.2}$Fe$_{0.80}$Ga, from 301 to 313 K at the range of $e/a = 7.5975–7.6125$ for Ni$_{2.16–0.4}$Co$_{0.84}$Ga and from 342 to 518 K at the range of $e/a = 7.64$–7.69 for Ni$_{2.16}$Mn$_{0.84}$–Co$_{0.16}$Ga.$^8$ The relation between $T_t$ and $e/a$ is represented by some curves. These interesting results suggest that $T_t$ can be controlled by the concentration of the added element. In this paper, the electronic structures are calculated for pseudo ternary alloys Ni–Mn–Ga–X and ternary alloys Ni–Mn–Ga to investigate the relationship between $T_t$ and $e/a$.

2. Crystal Structure and Method of Calculation

It was suggested that the tetragonal and orthorhombic structures may be metastable and the monoclinic structure is the most stable among four structures for Ni$_2$Mn$_{0.83}$Ga, as described in the previous section. In this paper, we pay attention to the cubic and monoclinic structures. The monoclinic structure has the lowest symmetry among four structures and the other structures also have the monoclinic symmetry. We treated the cubic structure as the monoclinic one with a unique angle of $\beta$ shown in Fig. 1 to calculate under the same condition. The $\beta$ angle of the monoclinic structure, which is equivalent to the cubic structure, is 71.56 degrees and one of the real monoclinic structure 98.46 degrees.$^4$ If the surface of this paper is assumed to be paralleled to a zx-plane, Mn and Ga atoms site on the $y = 0$ (or 1) and 1/2 planes and Ni atoms on the $y = 1/4$ and 3/4 planes in Fig. 1. Each of nickel, manganese and gallium in Ni$_2$MnGa has the four different atomic sites. For example, the four Mn atoms are distinguished by the symbols of Mn(1), Mn(2), Mn(3) and Mn(4) of which the sites are 1a, 1f, 2m and 2n sites in the unit cell with the P2/m symmetry of the tenth space group. The sites are the 1c, 1b, 2m and 2n sites for the Ni atoms and the 2j, 2l, 4o and 4e sites for Ga atoms. The twenty-four atoms in the unit cell are shown in Fig. 1. This unit cell corresponds to the observed monoclinic structure having the shuffling of 6 layers of (220).
Electron Concentration and Transformation of Ni₂MnGa-Based Alloys

3. Results and Discussion

3.1 Density of states

3.1.1 Density of states in the sys-M2

We examine the local density of states (DOS) of the sys-N1 and the sys-M2 for the two structures, in order to examine the effect of substituting Ni(1) atoms or Mn(2) atoms for the X atoms. Then, we pay attention to the DOS of d-states of the X atom, because they are most different in the two systems. The X atom is strongly affected by the surrounding atoms, which are eight Ni atoms in the sys-M2 and four Ni atoms and four Ga atoms in the sys-N1. First of all, we pay attention to the local DOS of the X atom (X-DOS) in the sys-N1 and the sys-M2 for the two structures, in order to examine the effect of substituting Ni(1) atoms or Mn(2) atoms for the X atoms.

The alloy where a sixth of Mn atoms in stoichiometric Ni₂MnGa are replaced with Ni atoms is described as Ni₂₋₁₇Mn₀.₈₃Ga in the previous papers. In this paper, the alloy is described as Ni₂(Ni₁₋₆Mn₅/₆)Ga where the excess Ni atoms at the Mn(1) sites are described in parentheses with the Mn atoms. Here, we consider two cases where Ni or Mn atoms in Ni₂₋₁₇Mn₀.₈₃Ga are replaced with the X atoms. That is, X atoms are replaced with Ni atoms at the Ni(1) sites or Mn atoms at the Mn(2) sites. The former alloys are described as sys-N1 and the latter alloys as sys-M2 in this paper. The alloys in the sys-N1 and the sys-M2 are described as (Ni₅/₆X₁/₆)₂(Ni₁₋₆Mn₅/₆)Ga and Ni₂(Ni₁₋₆Mn₄/₆X₁/₆)Ga respectively. The environments of the constituent atoms are largely different in the cubic structure and the monoclinic structure.

When transition elements are chosen as the X atoms, (Ni₅/₆X₁/₆)₂(Ni₁₋₆Mn₅/₆)Ga (sys-Ns1) is in the range of e/a = 7.5–7.625 and Ni₂(Ni₁₋₆Mn₄/₆X₁/₆)Ga (sys-M2) in the range of e/a = 7.625–7.8. The range of e/a for the sys-N1 and the sys-M2 correspond to the range of e/a = 7.50–7.80 of Tsuchiya et al. When we cannot choose a real element as the X atom for the special value of e/a, we adopt an artificial atom. The artificial atom is described like Z27.5 where the number of 27.5 means the atomic number and the number of electrons. When we estimate the value of e/a, the numbers of valence electrons of Z27.5 and Z28.5 are assumed to be 9.5 and 10.5, respectively.

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.

The alloy where a sixth of Mn atoms in stoichiometric Ni₂MnGa are replaced with Ni atoms is described as Ni₂₋₁₇Mn₀.₈₃Ga in the previous papers. In this paper, the alloy is described as Ni₂(Ni₁₋₆Mn₅/₆)Ga where the excess Ni atoms at the Mn(1) sites are described in parentheses with the Mn atoms. Here, we consider two cases where Ni or Mn atoms in Ni₂₋₁₇Mn₀.₈₃Ga are replaced with the X atoms. That is, X atoms are replaced with Ni atoms at the Ni(1) sites or Mn atoms at the Mn(2) sites. The former alloys are described as sys-N1 and the latter alloys as sys-M2 in this paper. The alloys in the sys-N1 and the sys-M2 are described as (Ni₅/₆X₁/₆)₂(Ni₁₋₆Mn₅/₆)Ga and Ni₂(Ni₁₋₆Mn₄/₆X₁/₆)Ga respectively. The environments of the constituent atoms are largely different in the cubic structure and the monoclinic structure.

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3.1.2 Density of states in the sys-N1

As described above, the circumstances of the X atom in the sys-N1 are different from those in the sys-M2. It is expected that the X-DOS is different between the two systems.

The X-DOS in the sys-N1 is compared for the cubic structure and the monoclinic structure in Fig. 3. In the cubic structure, the X-DOS of the sys-N1 has peaks in the large valley of the X-DOS in the sys-M2. In the monoclinic structure, the DOS of the sys-N1 roughly preserves the shape of the cubic structure, compared with the case of the sys-M2. Therefore, the moldering of the DOS peaks with transforming from the cubic structure to the monoclinic structure is smaller in the sys-N1 than in the sys-M2. It is guessed that the energies difference (ΔE) between the two structures is smaller in the sys-N1 than the sys-M2.

Next, we examine the change of the DOS against e/a. In the cubic and the monoclinic structures, although the changes due to the difference of the X atom are seen in the majority spin as shown Figs. 3(a) and (c), the changes are extremely small, compared with those in the sys-M2 (in Figs. 2(a) and (c)). In the minority spin, the X-DOS shown in Figs. 3(b) and (d) is more occupied with increasing the atomic number. Therefore, the change of the X-DOS due to the difference of the X atom are seen in the majority structure, and the monoclinic structure in Fig. 3. In the cubic structure, the X-DOS of the sys-N1 has peaks in the large valley of the X-DOS in the sys-M2. It is expected that the energies difference (ΔE) of the total energies between the cubic and the monoclinic structures is smaller in the sys-N1 than the sys-M2.

The magnetic moment per atom for the cubic structure decreases like a straight line for the sys-N1 and like a sigmoid line for the sys-M2 with increasing e/a as shown in Fig. 4. The magnetic moment per atom of the cubic is 2.87 μB for X=Fe (e/a = 7.667), 1.57 μB for X=Co (e/a = 7.708) of the sys-M2 and 1.21 μB for X=Co (e/a = 7.542) of the sys-N1. The magnetic moment of Co for the sys-M2 is about 23 percent greater than Co in the sys-N1. This is due to the difference of the DOS of shapes of DOS curve between the sys-M2 and the sys-N1. The magnetic moment of Fe for the sys-M2 is about 30 percents greater than magnetic moment of bcc Fe.

3.3 Total energy and valence electron concentration

The difference (ΔE) of the total energies between the cubic and the monoclinic structures were calculated as a function of the valence electron concentration per atom (e/a). The total energies of (Ni5/6X1/6)2(Ni1/6Mn5/6Ga) (sys-N1) were calculated for X=Co, Z27.5 and Ni and those of Ni5/Ni1/6Mn5/6X1/6Ga (sys-M2) for X=Mn, Fe, Co, Z27.5, Ni and Z28.5. Their values per unit cell are plotted by tri-angles for the sys-N1 in Fig. 5 and by circles for the sys-M2. The e/a range of the former is e/a = 7.542–7.625 and one of the latter e/a = 7.625–7.77. The case of X=Ni in the sys-N1 is equivalent to the case of X=Mn in the sys-M2 which corresponds to e/a = 7.625. The curve consists of a straight line and a parabolic line with a boundary of e/a = 7.625. The
Electron Concentration and Transformation of Ni$_2$MnGa-Based Alloys

The electron concentration and transformation of Ni$_2$MnGa-based alloys are studied in this section. The figures illustrate the local density of states (DOS) for X atoms in the system (a) and (b) for the cubic structure and (c) and (d) for the monoclinic structure. The upper and lower panels show the majority and minority spin DOS, respectively. The Fermi level is indicated by the vertical line.

Fig. 3 Local DOS of X atoms in the sys-N1. Three curves distinguish for the case of X=Co, Z27.5 and Ni in (Ni$_{5/6}$X$_{1/6}$)$_2$(Ni$_{1/6}$Mn$_{5/6}$)Ga, respectively. The DOS (a) and (b) of the cubic structure are shown in the left-hand side and those (c) and (d) of the monoclinic structure in the right-hand side. The upper (a) and (c) and the lower (b) and (d) are of the majority and the minority spin. The vertical line shows the Fermi level.

Fig. 4 Magnetic moment per atom of the X atom against the valence electron concentration ($e/a$) in the cubic structure. The open circles and the open triangles show the sys-M2 and the sys-N1, respectively. A open square shows the magnetic moment of the Mn atom in Ni$_2$MnGa.

The difference $\Delta E$ increases linearly with increasing $e/a$ in the range of the sys-N1. On the other hand, $\Delta E$ changes like a parabola with a top at X=Co, with increasing $e/a$ in the range of the sys-M2. That is, the variation of $\Delta E$ is steeper for the sys-M2 than for the sys-N1.

Now, we examine relation between the difference $\Delta E$ and change of the X-DOS. As seen in Fig. 2 and Fig. 3, the X-DOS of the sys-N1 (X atoms at the Ni sites) and the sys-M2 (X atoms at the Mn sites) are fairly different in the cubic structure. When the cubic structure transforms to the monoclinic one, the change of the X-DOS is larger in the sys-M2 than in the sys-N1. Therefore, the structural transformation brings larger differences $\Delta E$ for the sys-M2, compared with
those of the sys-N1. Furthermore, we noticed that change of the X-DOS due to the difference of the X atom is larger for the sys-M2 than the sys-N1. These features correspond to the linear change and the parabolic change of the $\Delta E (e/\alpha)$, respectively. Thus, the differences $\Delta E$ are reflected on the differences of the DOS curves due to different structures and different X atoms. The variation $\Delta E (e/\alpha)$ is compared with the structural transition temperature $T_t (e/\alpha)$ in followings.

The Helmholtz free energy $F$ is expressed as

$$F = U - T S,$$

where $U$ is the internal energy, $T$ is a temperature and $S$ is the entropy. The differences of $F$, $U$ and $S$ between the cubic and monoclinic structures satisfy the equation

$$\Delta F = \Delta U - T_t \Delta S = 0$$

at the transition temperature $T_t$. Therefore, $T_t$ can be estimated by $\Delta U/\Delta S$. However, we cannot calculate $\Delta S$ and the total energy does not include the temperature effects on the electronic structures and the lattice vibration energy. As generally speaking, it is very difficult to calculate $T_t$ as well as the Curie temperature from the electronic structure. When we assume daringly $\Delta U = \Delta E$ and use the observed values of $T_t$, we can estimate very roughly the $\Delta S$. For example, the values of $\Delta S$ for $e/\alpha = 7.5$–$7.77$ are $\Delta S = 2.0$–$0.3$ $\text{J/gK}$, which decrease with increasing $e/\alpha$. These values should be evaluated seriously because of the reasons described above.

In the followings, we compare $T_t$ and $\Delta E$. The heavy broken line in Fig. 5 corresponds to a line connecting three points of ternary alloys Ni–Mn–Ga: Ni$_2$(Mn)Ga ($e/\alpha = 7.5$), Ni$_2$(Ni$_{1/6}$Mn$_{5/6}$)Ga ($e/\alpha = 7.625$) and Ni$_2$(Ni$_{5/6}$Mn$_{1/6}$)Ga ($e/\alpha = 7.75$). To examine the correspondence between $\Delta E$ and $T_t$, they are compared for the ternary alloys Ni–Mn–Ga and the pseudo ternary alloys Ni–Mn–Ga–X in Fig. 6. To the left axis and those of $\Delta E$ to the right axis. In the Fig. 6, the curves of $\Delta E$ are shown by the solid or open marks of the $T_t (e/\alpha)$. In Fig. (a), the solid diamonds and cross and large square of ternary alloys Ni–Mn–Ga, Ni$_2$(Ni$_{1/6}$Mn$_{5/6}$)Ga and Ni$_2$(Ni$_{5/6}$Mn$_{1/6}$)Ga are plotted by diamonds and cross, which were observed by Tsuchiya et al. and Inoue et al., respectively. These values distribute along the heavy broken line in Fig. 5. The $T_t$ values of the pseudo ternary alloys Ni–Mn–Ga–X are also plotted in Figs. (b) and (c). In the lower range $e/\alpha < 7.625$, their values distribute along the heavy line of $\Delta E (e/\alpha)$ obtained for the sys-N1. That is, the heavy line of the sys-N1 corresponds to the data plotted by the solid squares for $(e/\alpha, T_t) = (7.6125, 313 \text{ K})$, $(7.605, 311 \text{ K})$ and $(7.5975, 301 \text{ K})$ of Ni$_{12.16-\alpha}$Co$_\alpha$Mn$_{0.84}$Ga and the solid triangles for $(e/\alpha, T_t) = (7.57, 220 \text{ K})$, $(7.59, 266 \text{ K})$, $(7.61, 292 \text{ K})$ and $(7.63, 317 \text{ K})$ of Ni$_{12.20}$Fe$_\alpha$Mn$_{0.80}$Ga. Next, we pay attention to the data plotted in the higher range $e/\alpha > 7.625$ which are shown in Fig. 6(c) by the solid circles for $(e/\alpha, T_t) = (7.64, 342 \text{ K})$, $(7.67, 429 \text{ K})$, $(7.69, 518 \text{ K})$ in Ni$_{12.16}$Mn$_{0.84}$Co$_\alpha$Ga. They are along the heavy curve for the sys-M2. The correspondence between $\Delta E (e/\alpha)$ and $T_t (e/\alpha)$ described above suggests that the X atoms prefer the Ni sites for the range $e/\alpha < 7.625$ and the Mn sites for the range $e/\alpha > 7.625$, when the constituent atoms of Ni$_2$MnGa are substituted for the X atoms. The value $e/\alpha = 7.625$ seems to be the critical point for the structural transition temperature.

4. Conclusion

The electronic structures of $(\text{Ni}_{5/6}X_{1/6})\text{(Ni}_{1/3}\text{Mn}_{5/3})\text{Ga}$ (sys-N1) and Ni$_2$(Ni$_{1/6}$Mn$_{5/6}$X$_{1/6}$)Ga (sys-M2) were calculated for the cubic structure and the monoclinic one to examine the electron concentration dependence of the structural transition temperature $T_t (e/\alpha)$. The difference of the total energies between the cubic structure and the monoclinic one is also calculated as a function of the concentration $\Delta E (e/\alpha)$. 
It was found that the features of $T_t (e/a)$ and $\Delta E (e/a)$ are similar each other. That is, there is a good correspondence between $T_t (e/a)$ and $\Delta E (e/a)$. Their curves consist of two parts with a boundary of $e/a = 7.625 \ (Ni_2(Ni_{1/6}Mn_{5/6})Ga)$. In the range $e/a < 7.625 \ (sys-N1)$, they increase linearly with increasing $e/a$ and in the range $e/a > 7.625 \ (sys-M2)$, they vary along a heavy line. Paying attention to the X atom which replaces the Mn or Ni atom in $Ni_2(Ni_{1/6}Mn_{5/6})Ga$, we can guess the variation of $\Delta E (e/a)$ from the local DOS of the X atom and the occupancy. The X atom occupies the Ni site in the range $e/a < 7.625 \ (sys-N1)$ and the Mn site in the range $e/a > 7.625$. The change of the local DOS is larger for the X atom at the Mn site than the X atom at the Ni site, when the crystal structure changes between the cubic structure the monoclinic one. The changes reflect on the features of $\Delta E (e/a)$. Thus, the site of the X atom is an important factor in considering the structural transition temperature.

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