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Electronic Structures of Ferromagnetic Shape Memory Alloys with Martensitic 14M Phase

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Ferromagnetic materials Ni_2MnGa and Ni_2FeGa have the cubic symmetry, the $L2_1$ Heusler type, at high temperature. The 14M super-cell is newly reported as the martensitic phase of these alloys. We also consider $Ni_2Mn_{1-x}Fe_xGa$. The electronic structures of these alloys are calculated to investigate the phase stability and the magnetic moments of the 14M phase against the parent phase, $L2_1$ Heusler. The total energies indicate the stability of the 14M phase. A variety of magnetic moments on Mn in the 14M phase range from $2.31\mu_B$ to $3.08\mu_B$. The magnetic moments on Fe in these materials are fairly big than that of pure iron. Especially, in the cubic structure at high temperature, the moments on Fe are estimated as big as those of $Ni_3Fe(2.88\mu_B)$. The origin of these big magnetic moments is considered as the result of Fe-Ni strong hybridization in the majority (up) spin states. The densities of states (*DOS*) reveal the big magnetic moments on Fe in these alloys.
Key words: ferromagnetic, shape memory, Ni_2MnGa, electronic structure, magnetic moment,

1. INTRODUCTION

$Ni_{2+x}Mn_{1-x}Ga$ (x=0.18~0.2) has attracted the attention of many researchers as a multifunctional alloy. The crystal structure of the martensitic phase of the alloy has been investigated in detail up to date. Ni_2MnGa is a ferromagnetic shape memory alloy and the Curie and martensitic transformation temperature are 370K and 202K respectively.[1)] Although Ni_2MnGa is basis of the multifunctional alloys, the crystal structure of Ni_2MnGa martensitic phase was not actively discussed. It was because many researchers had taken it for granted that the martensitic phase of Ni_2MnGa was the tetragonal structure. There was another granted common knowledge about magnetic moments in the Heusler alloys with Mn. The magnetic moments of those alloys are around $4.0\mu_B$ per formula unit (f.u.). However, recent experimental results overthrew the former two established common knowledge.

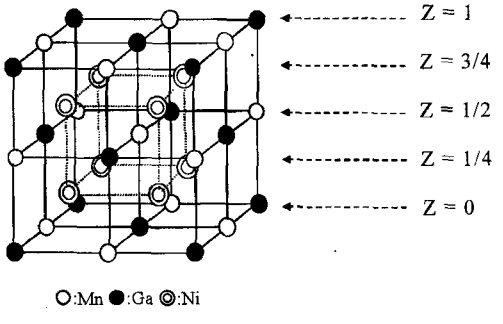

Fig.1 The cubic structure of Ni_2MnGa and Ni_2FeGa. The structure of $Ni_2Mn_{(1-x)}Fe_xGa$ at high temperature are also considered like this.

The crystal structures of the parent phase of Ni_2MnGa and Ni_2FeGa are the same $L2_1$ Heusler type shown in Fig.1. Lately, Brown et al.[2)] observed the martensitic structure of Ni_2MnGa by the high resolution neutron powder diffraction and single crystal measurements.

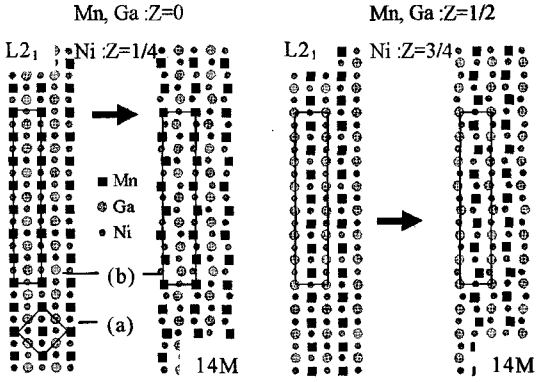

Fig.2 The image of martensitic transformation. (a) is the area of the conventional unit cell of the $L2_1$ structure and (b) is the area of the unit cell of the 14M structure as the projection on (001).

Brown et al. classified this martensitic structure as the Pnnm in the space group. We adopt their coordinates, shown in Fig.2, and take the ratio of their lattice constants into our calculation. This martensitic structure is called the 14M in accordance with Ramsdel notation. Hereafter, we describe this structure as '14M'. In this structure, the small magnetic moments on Mn are observed[2)] which moments are smaller than that of ever reported in other Huesler alloys with Mn.

In this paper, the electronic structure are calculated for Ni_2MnGa and Ni_2FeGa in the $L2_1$ Heusler and in the 14M structure. The electronic structures of Ni_2MnGa with Fe impurity, $Ni_2Mn_{(1-x)}Fe_xGa$ (x=1/7,2/7), are also done on the assumption that they have the same

structures as Ni_2MnGa have. The stability of the 14M martensitic phase, the influence of Fe impurity and the magnetic moments due to spin polarization of each atom are examined mainly.

2. CRYSTAL STRUCTURE AND CALCULATION

Two different structures, the parent phase and martensitic phase, should be taken account in the band calculation. The cubic $L2_1$ and the 14M structures have the same symmetry of Pnnm, the 58th group symmetry, in the *'INTERNATIONAL TABLES FOR CRYSTALLOGRAPHY'*.[3] Then, we handle them as the same Pnnm symmetry to treat them in the same condition as possible. The unit cells of them are shown in Fig.2 (b). In that group symmetry, each atom is classified into four atomic sites respectively. We distinguish each four atoms by the sequential number after the symbols of chemical elements, for example, Ni1, Ni2, Ni3, and Ni4.

In this paper, we also calculate the electronic structures of $Ni_2Mn_{(1-x)}Fe_xGa$ (x=1/7,2/7) except for Ni_2MnGa and Ni_2FeGa to investigate the influence of Fe element. When Mn1 is replaced with Fe, we call this Fe 'Fe1', and in this case, the ratio of Mn and Fe is six to one, $Ni_2Mn_{6/7}Fe_{1/7}Ga$. The other cases where the ratio Mn and Fe is five to two, $Ni_2Mn_{5/7}Fe_{2/7}Ga$, can be gotten by replacement of other Mn (Mn2, Mn3 or Mn4) with Fe (called as 'Fe2', 'Fe3' or 'Fe4'). Although these non-stoichiometric alloys with Fe impurity of parent phase have not the $L2_1$ symmetry, we keep on calling them '$L2_1$' to distinguish the parent phases form the martensitic phases.

Band calculations are carried out self consistently by the LMTO-ASA method.[4] The exchange correlation potential is treated within the framework of the local-spin-density (LSD) approximation.[5] To find the reasonable equilibrium lattice constants, the radii of the atomic spheres are determined in the calculations of the $L2_1$ structure. The ratio of the radii is $r_{Mn} : r_{Fe} : r_{Ni} : r_{Ga} = 1.068 : 1.044 : 1.00 : 1.082$. The radii produce the reasonable results about the lattice constant of the $L2_1$ structure as seen in Table I so we use this ratio of the radii in all the alloys calculated this time.

Table I Lattice constants. (nm)

$L2_1$	Theoretical value	Experimental Value
Ni_2FeGa	0.572	0.576 [6]
Ni_2MnGa	0.576	0.582 [2]

3. RESULTS AND DISCUSSION

3.1 Total energy and band energy

To make sure the phase stability of the 14M martensitic phase against the parent phase, the total energies are calculated for Ni_2MnGa, $Ni_2Mn_{(1-x)}Fe_xGa$ and Ni_2FeGa. The results of calculation indicate the phase stability of the 14M phase for all the materials calculated this time.

The band energies for the two structures, the $L2_1$ and 14M structure, are calculated and compared to examine the role of the constituent atoms in the stabilization of the crystal structure. They are estimated by integrating the one-electron energies (E) weighted by the density of states (DOS) over the states occupied by electrons.

$$Band\ Energy = \int^{Ef} EN(E)dE \qquad (N(E) : DOS)$$

In terms of the band energy, Ni4 and Mn4 or Ni4 and Fe4 contribute to stabilization of 14M structures. The degree of displacement of these atoms from the $L2_1$ coordinates is the largest. These pairs are nearest neighbors of each in both phases, and the interatomic distance between these two atoms in the 14M is closer than any other pairs. This result may give a hint of transformation, driving force, to the 14M phase.

3.2 Magnetic moment

The magnetic moments due to spin polarization are estimated for each atom. The calculated magnetic moments per formula unit of the alloys are shown in Table II. There are three kinds of $Ni_2Mn_{5/7}Fe_{2/7}$, according to the site occupied by Fe, as mentioned before, and each one of their magnetic moments is shown respectively. Researchers divided over the value of their moments, especially in the martensitic phase. For instance, in Ni_2MnGa Webster et al. reported 4.14 for the $L2_1$ at 0K[1], Brown et al. reported 2.4 for the $L2_1$ at 300K and 3.07 at 20K for the 14M[2] and Kikuchi et al. reported 3.81 at 4.2K for the martensitic phase[7] in the unit of μ_B/f.u..

Table II Magnetic moments per formula unit. (μ_B)

	Ni_2MnGa	$Ni_2Mn_{6/7}Fe_{1/7}Ga$	$Ni_2Mn_{5/7}Fe_{2/7}Ga$	Ni_2FeGa
$L2_1$	3.87	3.82	3.77 3.73 3.78	3.31
14M	3.26	3.18	3.14 3.26 3.31	3.16

Every moment of the 14M phases is smaller than that of the $L2_1$. All of the Ni have the moment about 0.3μ_B per atom. The main carriers of the moments are Mn and Fe. In TableIII, the moments on Mn and Fe are summarized. There are four kinds of Mn sites in the Pnnm symmetry so all of the moments are shown in TableIII. The four kinds are the same in the $L2_1$ stoichiometric alloy so one value of them is shown. The magnitudes of the moments on the four kinds of Mn show the large differences between them. This fact may have something to do with the various moments of the experimental values.

Table III Magnetic moments on Mn and Fe. (μ_B)

	Ni_2MnGa / Ni_2FeGa	$Ni_2Mn_{6/7}Fe_{1/7}Ga$	$Ni_2Mn_{5/7}Fe_{2/7}Ga$
$L2_1$	3.25 2.83	2.86 3.25 3.25 3.27	3.25 2.86 3.26 3.26 3.24 3.26 2.86 3.24 3.27 3.26 3.25 2.86
14M	3.08 2.89 2.40 2.31 2.68 2.60 2.38 2.37	2.68 2.88 2.28 2.30	3.05 2.60 2.36 2.29 3.03 2.86 2.44 2.25 3.07 2.89 2.38 2.40

The moments on Fe are underlined. Some of the Mn moments in the 14M structure are considerably smaller than their moments in the $L2_1$ structure. The moments of Fe are big, especially in the $L2_1$ structure. To understand these magnetic moments, the densities of states (DOS) are examined in the following.

3.3 Density of states

At first, we pay attention to the local *DOS* of Mn and Fe in the $L2_1$ structure. Their typical differences are seen in Fig.3 where the Mn *DOS* in Ni_2MnGa and the Fe *DOS* in Ni_2FeGa are shown. The number of d-electorns of Fe is more than that of Mn by one, so the potential around Fe is deeper than that of Mn. Therefore, the Fe *DOS* is located in lower energy range, compared with the Mn *DOS*, and the band tail (hole) of up (↑)-spin above the Fermi level is smaller for Fe than for Mn.

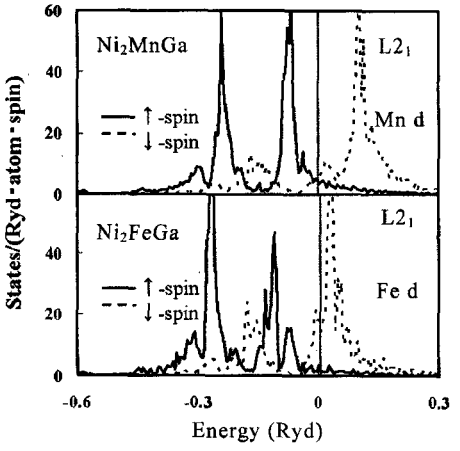

Fig.3 The local *DOS* of Mn in Ni_2MnGa (above) and Fe in Ni_2FeGa (below) of the $L2_1$ structure. The solid and dotted lines distinguish the up and down spin respectively. The vertical line shows the Fermi level.

This suggests that the number of d-electrons changes hardly in both spin states of Fe. In spite of the differences of concentration of Fe impurity, the change in the magnetic moments on Fe is very small in the $L2_1$ structure, as seen in Table Ⅲ.

The local *DOS* of Fe and Ni in Ni_2FeGa are compared in Fig.4. They have peaks at the same energy value; from this, we can guess that the d-states of Fe and Ni hybridize strongly.

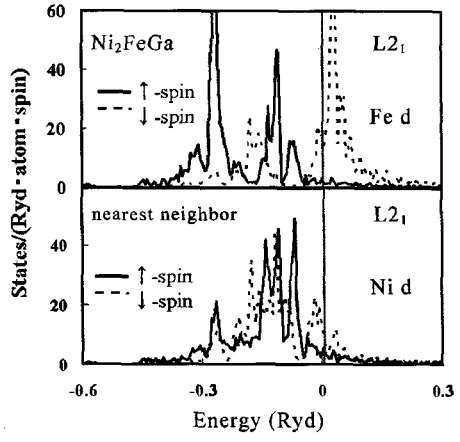

Fig.4 The local *DOS* of Fe in Ni_2FeGa (above) and its nearest neighbor Ni (below) of the $L2_1$ structure. The vertical line shows the Fermi level.

Then, comparing the *DOS* of Fe in Ni_2FeGa with that of pure iron shown in Fig.5, we notice that the peak in the low energy range is higher in Ni_2FeGa than in pure iron and the band tail (hole) of up-spin states above the Fermi level is smaller in Ni_2FeGa. Thus, the number of electrons at up-spin states of Fe surrounded by Ni increase in Ni_2FeGa, in which the magnetic moment of Fe ($2.83\mu_B$) is enhanced from the moments in pure iron ($2.2\mu_B$).

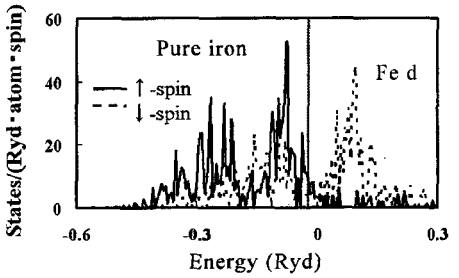

Fig.5 The local *DOS* of Fe in pure iron of the b.c.c structure. The vertical line shows the Fermi level.

These features suggest that a moment on Fe is generally enhanced when Fe is surrounded by transition elements with the more d-electrons than those of Fe. Really, Fe moments are enhanced in $Co_2Cr_{1-x}Fe_xAl$ system where the Fe is surrounded by Co (the results will be reported elsewhere).

We also show the *DOS* of Fe and Ni in Ni_3Fe in Fig.6 to examine the effect of Ni on Fe moment. In this structures (Cu_3Au-type), the number of Ni as the nearest neighbors of Fe is more than Ni_2FeGa by 4atom. The high peaks are collapsed and the d-states of Fe and Ni hybridize in lower energy range, compared with in Ni_2FeGa. The moment on Fe ($2.88\mu_B$) is enhanced.

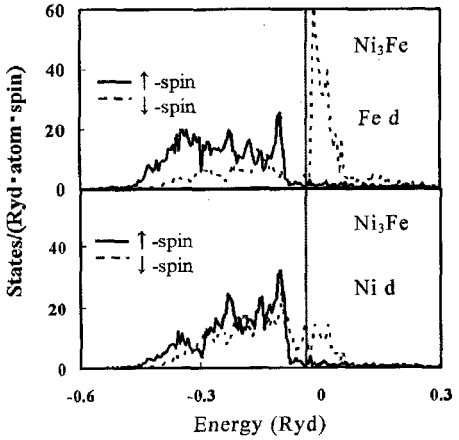

Fig.6 The local *DOS* of Fe in Ni_3Fe (above) and its nearest neighbor Ni (below) of the Cu_3Au-type structure. The vertical line shows the Fermi level.

Next, we turn our attention to the 14M structure. In Ni_2MnGa with the 14M structure, the coordinates of each atom change largely from those in the $L2_1$ structure so the environments around Mn change. The distance between the Mn and the nearest neighbors (Ni) becomes shorter in the order of Mn1, Mn2, Mn3, and Mn4. The local *DOS* of Fe and Mn in $Ni_2Mn_{1-x}Fe_xGa$ (x= 1/7,2/7) are shown in Fig.7 and Fig.8. Paying attention to the Mn *DOS*, the peaks become lower and the d-band broaden in the order of Mn1, Mn2, Mn3 and Mn4.

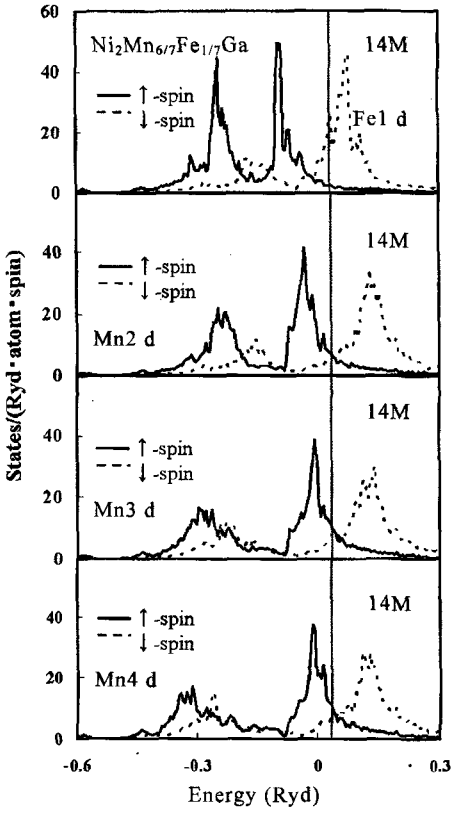

Fig.7 The local *DOS* of Fe and Mn in $Ni_2Mn_{6/7}Fe_{1/7}Ga$ of the 14M structure. The solid and dotted lines distinguish the up and down spin respectively. The vertical line shows the Fermi level.

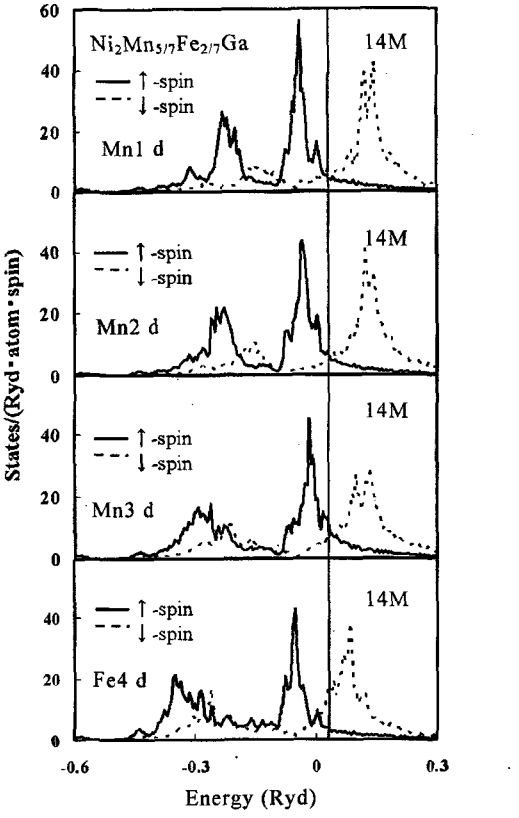

Fig.8 The local *DOS* of Fe and Mn in $Ni_2Mn_{5/7}Fe_{2/7}Ga$ of the 14M structure. The solid and dotted lines distinguish the up and down spin respectively. The vertical line shows the Fermi level.

The approaches of the neighbors strengthen hybridization, broaden the band and cause the increase of band tail (hole) of up-spin above the Fermi level. As a result, the magnetic moment on Mn changes largely in the 14M structure as shown in Table II. On the other hand, the change of the band tail of Fe is smaller as mentioned before and be seen in the *DOS* of Fe, especially Fe4 shown in Fig.8. Therefore, the change of Fe moments between in the 14M and in the $L2_1$ structure is smaller than that of Mn.

4. CONCLUSION

The electronic structures of the Ni_2MnGa and Ni_2FeGa are investigated for the $L2_1$ structure and the newly observed 14M structure. These structures are also assumed for $Ni_2Mn_{(1-x)}Fe_xGa$ (x=1/7,2/7) and calculated their electronic structures.

In view of the total energies, the phase stability of the 14M martensitic structure at low temperature is confirmed.

The magnetic moments show the varieties of the moments on Mn in the 14M structure. Some of the magnetic moments on Mn are extremely smaller than the Mn moments ever reported in other Heusler alloys. The smallest value is about $2.3\mu_B$. These small moments on Mn are caused by strong hybridization owing to the approach of the nearest neighbors.

The moments on Fe in the both structures are bigger than that in the pure iron. The big magnetic moments on Fe are brought through the hybridization with the surrounding Ni atoms. The moment on Fe is generally enhanced when Fe is surrounded by transition elements with d-electrons more than those of Fe. The impurity of Fe in $Ni_2Mn_{(1-x)}Fe_xGa$ (x=1/7,2/7) do not affect on the magnitude of the moments on Mn.

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