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# Mössbauer study on ferromagnetic shape memory alloys $Ni_2Mn_{1-x}Fe_xGa$

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ABSTRACT

The $^{57}$Fe Mössbauer effect measurements were carried out for $Ni_2Mn_{1-x}Fe_xGa$ with $0.3 \le x \le 0.7$. The spectra were described satisfactorily with one Lorentzian sextet, which was consistent with the atomic ordering of the $L2_1$ structure. The obvious change in the absolute value of the $^{57}$Fe hyperfine field ($B_{hf}$) at the martensitic transformation temperature was observed. $B_{hf}$ at 80 K was 22.3 T and independent of $x$.



## 1. Introduction

Ferromagnetic shape memory alloys have attracted much attention as a new class of actuator materials (see, for recent reviews, Refs. [1,2]). Among ferromagnetic shape memory alloys, the largest magnetic-induced strains arising from rearrangement of martensitic variants under action of a magnetic field have been observed in the most intensively studied $Ni_2MnGa$ alloy system [3].

The martensitic transformation in the stoichiometric alloy $Ni_2MnGa$ was first reported by Webster et al. [4]. $Ni_2MnGa$ has the cubic $L2_1$ Heusler structure (space group: $Fm\bar{3}m$) with the lattice parameter $a = 5.825$ Å at room temperature, and orders ferromagnetically at the Curie temperature $T_C \simeq 365$ K. In cooling process, below a martensitic transformation temperature $T_M \simeq 200$ K a superstructure is formed. This phase can be described by an orthorhombic unit cell (space group: *Pnnm*) with the lattice parameter $a = 4.2152$ Å, $b = 29.3016$ Å and $c = 5.5570$ Å at 20 K [5].

The effect of Fe-doping on transformation temperature, crystal structure and electron concentration has been studied by a number of authors, especially Kikuchi et al. [6]. They reported the magnetic and crystallographic properties of $Ni_2Mn_{1-x}Fe_xGa$ ($0 \le x \le 0.7$) alloys by replacing Mn with Fe in $Ni_2MnGa$ alloy with the $L2_1$ crystal structure. According to the results, the total magnetic moment of these alloys is almost constant, $3.81\mu_B$/f.u., for the replacement of Mn with Fe, indicating that Fe atom in $Ni_2Mn_{1-x}Fe_xGa$ ($0 \le x \le 0.7$) has a large magnetic moment compared with that of pure α-Fe. Furthermore, they reported that the Curie temperature $T_C$ of this series of samples show a broad maximum of 434 K around $x = 0.5$.

In this paper, we report the results of Mössbauer study of the ferromagnetic shape memory alloys $Ni_2Mn_{1-x}Fe_xGa$. Mössbauer spectroscopy is a useful tool to provide information about microscopic aspect in Fe-based alloys and compounds.

### 2. Experimental

The $Ni_2Mn_{1-x}Fe_xGa$ ($x = 0.3$, 0.5 and 0.7) alloys were prepared by repeated melting of appropriately composed mixtures of 99.9% pure Ni, 99.99% pure Mn, 99.95% pure Fe and 99.9999% pure Ga, in an argon arc furnace. Since the weight loss after melting was negligible, the nominal composition was accepted as being accurate. To get the homogenized samples, the reaction products were sealed in evacuated silica tubes, heated at 850 °C for 3 days and then quenched in water. X-ray diffraction spectra were taken with Cu Kα radiation on powder samples at room temperature. $^{57}$Fe Mössbauer spectroscopy measurements were carried in transmission geometry using a conventional spectrometer with a $^{57}$Co–Rh source. The measurement was performed at the fixed temperatures in the heating process from 80 to 300 K. Fitting with the obtained spectra were performed with *MossWinn 3.0* program.

## 3. Results and discussion

The $^{57}$Fe Mössbauer spectra and their fitted curves taken at several selected temperatures for $Ni_2Mn_{0.5}Fe_{0.5}Ga$ are shown in Fig. 1. They are described satisfactorily by one Lorentzian sextet revealing that the alloy is magnetically ordered with one Fe hyperfine field. This is consistent with that the atomic ordering of the $L2_1$ structure was confirmed for $Ni_2Mn_{1-x}Fe_xGa$ with $0 \le x \le 0.7$ from the appearance of the superlattice lines in X-ray diffraction spectra [6]. Partly replacing Mn with Fe in $Ni_2MnGa$, Fe atoms occupy the

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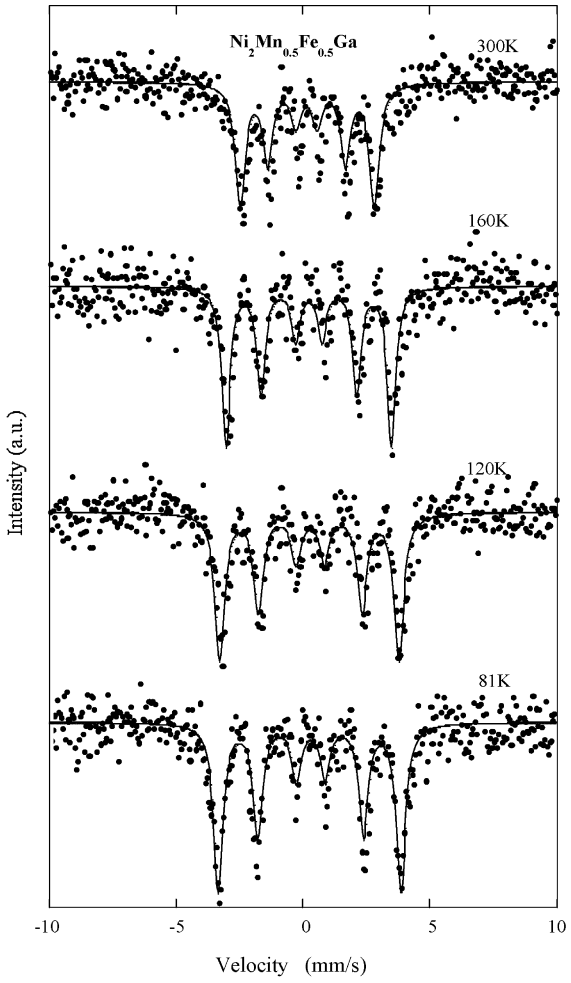


**Fig. 1.** $^{57}$Fe Mössbauer spectra and their fitted curves taken at several selected temperatures for $Ni_2Mn_{0.5}Fe_{0.5}Ga$ alloy.

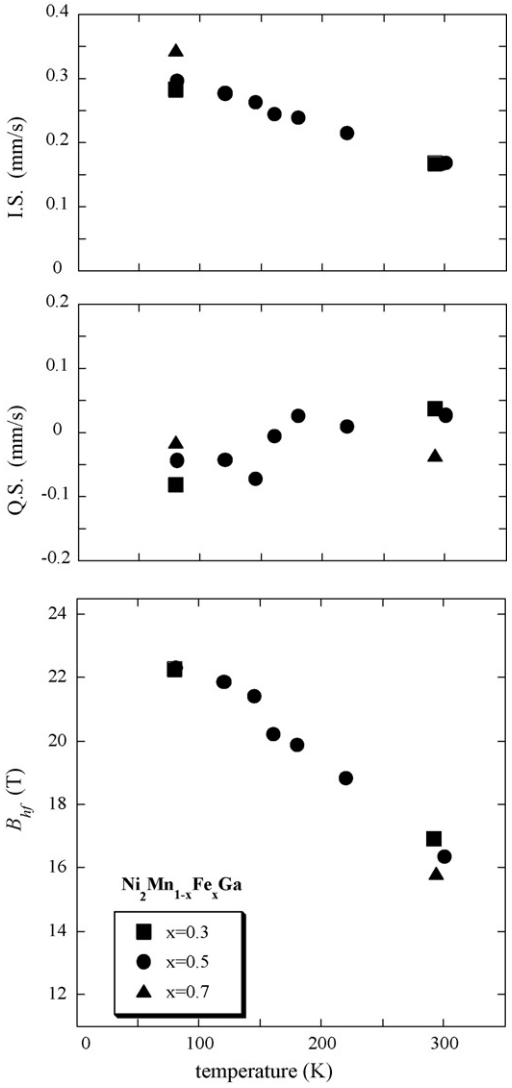


**Fig. 2.** Temperature dependences of the isomer shift (I.S.), the quadrupole splitting (Q.S.) and the $^{57}$Fe hyperfine field ($B_{hf}$) obtained by fitting for $Ni_2Mn_{1-x}Fe_xGa$ alloy.

B sites of Heusler structure preferentially. The temperature dependences of the isomer shift (I.S.), the quadrupole splitting (Q.S.) and the absolute value of the $^{57}$Fe hyperfine field ($B_{hf}$) obtained by fitting for $Ni_2Mn_{1-x}Fe_xGa$ with $x = 0.3$, 0.5 and 0.7 are shown in Fig. 2. The absolute values of Q.S. are small because of the symmetry of the crystal but a small change in Q.S. can be seen between 145 and 160 K for $x = 0.5$. We can also see an obvious change in $B_{hf}$ at the temperature. In warming process, martensitic transformation temperature was determined as 156 K by measuring the AC initial permeability [6]. Therefore, these changes are thought to correspond to a transformation between the martensitic phase and the austenitic one. The increase of the Fe hyperfine field below $T_m$ means that the Fe moment of the martensitic phase is larger than that of the austenitic one. This is consistent with the magnetization measurement, which shows that the total moment per formula unit of the martensitic phase for $Ni_2Mn_{0.5}Fe_{0.5}Ga$ is larger than that of the austenitic one [6]. The temperature dependence of magnetization for $Ni_2Mn_{0.5}Fe_{0.5}Ga$ showed an abrupt decrease of magnetization below $T_m$ at low magnetic fields because the lower symmetry of the martensitic phase enhances the magnetocrystalline anisotropy energy, but an abrupt increase of magnetization below $T_m$ was shown in cooling process at $H = 40$ kOe [6]. Fig. 3 shows the dependences of $B_{hf}$ on the Fe concentration $x$ for $Ni_2Mn_{1-x}Fe_xGa$ at room temperature and 80 K. The hyperfine field at 80 K is 23.3 T and independent of $x$. Kikuchi et al. estimated the Fe moment to be $3.0\mu_B$ and almost independent of $x$ for $Ni_2Mn_{1-x}Fe_xGa$ ($0 \le x \le 0.7$) on the basis of results of the polarized neutron scattering experiment

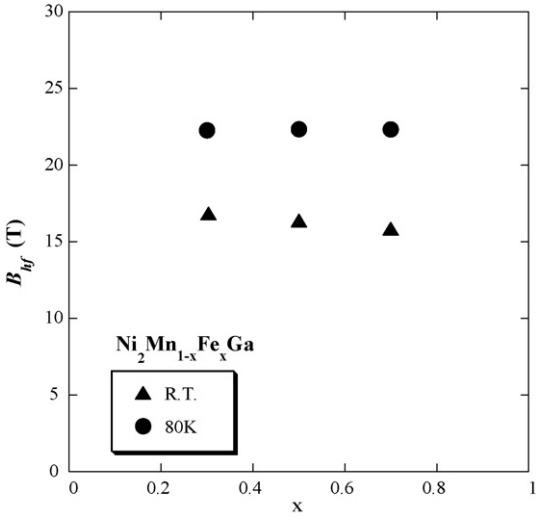


**Fig. 3.** Dependence of the $^{57}$Fe hyperfine field on the Fe concentration $x$ for $Ni_2Mn_{1-x}Fe_xGa$ at room temperature and 80 K.

for $Ni_2MnGa$ [7] and the magnetization measurements [6]. They also carried out the neutron powder diffraction measurements for $Ni_2Mn_{0.3}Fe_{0.7}Ga$ [6]. The analysis of experimental results indicates that the atoms (70% Fe, 30% Mn) of B site in $Ni_2Mn_{0.3}Fe_{0.7}Ga$ carry the moment of $3.36\mu_B$ per atom at 200 K. Recently, the band calculations for $Ni_2Mn_{5/7}Fe_{2/7}Ga$ with the $L2_1$ crystal structure were carried out self consistently by the LMTO-ASA method [8]. According to the results of calculations, the Fe atom has $2.86\mu_B$ in the case of the $L2_1$ crystal structure. In the case of the martensitic structure of 14 M, the magnetic moment of Fe atom for $Ni_2Mn_{5/7}Fe_{2/7}Ga$ is a little smaller than that in the $L2_1$ crystal structure. The magnetic moment of the Fe atom in the martensitic phase is about $2.5\mu_B$. These calculated values of the Fe moment in $Ni_2Mn_{5/7}Fe_{2/7}Ga$ are also much smaller than the Fe moment of $2.22\mu_B$ in pure α-Fe.

In a lot of kind of alloys containing Fe atoms, the hyperfine fields at Fe nuclei were found to be roughly proportional to the magnetic moments of the Fe atoms with the coupling constant of 150 kOe/$\mu_B$. The values of $B_{hf}$ at Fe nuclei for $Ni_2Mn_{1-x}Fe_xGa$ alloys in this study are much smaller compared to that expected from the coupling constant of 150 kOe/$\mu_B$. Similar phenomena were observed in $FeNi_3$ and Fe–Rh alloys [9,10]. More detailed studies of Fe moment in $Ni_2Mn_{1-x}Fe_xGa$ alloys will be necessary to understand the mechanism of the martensitic transformation.

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