Magnetic Properties of the Ferromagnetic Shape Memory Alloys Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ in Magnetic Fields

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Abstract: Thermal strain, permeability, and magnetization measurements of the ferromagnetic shape memory alloys Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ ($x = 2.0, 2.5, 2.7$) were performed. For $x = 2.7$, in which the martensite transition and the ferromagnetic transition occur at the same temperature, the martensite transition starting temperature $T_{Ms}$ shift in magnetic fields around a zero magnetic field was estimated to be $dT_{Ms}/dB = 1.1 \pm 0.2$ K/T, thus indicating that magnetic fields influences martensite transition. We discussed the itinerant electron magnetism of $x = 2.0$ and 2.5. As for $x = 2.5$, the $M^4$ vs. $B/M$ plot crosses the origin of the coordinate axis at the Curie temperature, and the plot indicates a good linear relation
behavior around the Curie temperature. The result is in agreement with the theory by Takahashi, concerning itinerant electron ferromagnets.

**Keywords:** shape memory alloys; thermal strain; magnetization; magnetic properties; magnetic field; itinerant electron ferromagnet

1. Introduction

Ferromagnetic shape memory alloys have been extensively studied as potential candidates for smart materials. Among these alloys, Ni$_2$MnGa is the most familiar alloy [1]. It has a cubic $L_2_1$ Heusler structure (space group $Fm\bar{3}m$) with the lattice parameter \(a = 5.825\) Å at room temperature, and it orders ferromagnetically at the Curie temperature \(T_C \approx 365\) K [2,3]. Upon cooling from room temperature, a martensite transition occurs at the martensite transition temperature \(T_M \approx 200\) K. Below \(T_M\), a superstructure forms because of lattice modulation [4,5]. For Ni-Mn-Ga Heusler alloys, the \(T_M\) can vary from 200 to 330 K by nonstoichiometrically changing the concentration of composite elements.

Several studies on Ni-Mn-Ga alloys address the martensite transition and the correlation between magnetism and crystallographic structures [6–18]. Ma et al. [7] studied the crystallography of Ni$_{50+x}$Mn$_{25}$Ga$_{25-x}$ alloys (2 ≤ \(x\) ≤ 11) by powder X-ray diffraction and optical microspectroscopy. In the martensite phase, typical microstructures were observed for \(x < 7\). The martensite variants exhibit configurations typical of self-accommodation arrangements. The TEM image of Ni$_{54}$Mn$_{25}$Ga$_{21}$ indicates that the typical width of a variant is about 1 \(\mu\)m.

Umetsu et al. [19] made a phase diagram of Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ alloys (−25 ≤ \(x\) ≤ 6). The martensite transition temperature \(T_M\) and the ferromagnetic transition temperature (Curie temperature) \(T_C\) cross over at around \(x = 2.5\). The martensite transition temperature of Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ is higher than that of the stoichiometric composition. This property is very useful from the viewpoint of developing commercial applications.

The interaction between magnetism and crystallographic rearrangements was discussed in references [1,8,17,18]. Murray et al. [18] studied polycrystalline Ni-Mn-Ga alloys. The magnetization step at \(T_M\) is also observed. This is a reflection of the magnetic anisotropy in the tetragonal martensite phase. In the martensite phase, a strong magnetic anisotropy exists. Under these circumstances, the magnetization that reflects the percentage of magnetic moments parallel to the magnetic field is smaller than that of the austenite phase, where the magnetic anisotropy is not strong in the weak magnetic field. Therefore, the magnetization step is observed at \(T_M\).

NMR experiments indicate Mn-Mn indirect exchange via the faults in Mn-Ga layers interchange, which are caused by excessive amounts of Ga [13]. This result indicates that the exchange interaction between Mn-Mn magnetic moments is sensitive to lattice transformation: during such a transformation, the magnetism changes from that of a soft magnet in the austenite phase to that of a hard magnet in the martensite phase; this is due to higher magnetic anisotropy. Dai et al. [20] reported this softening of the lattice; they did so by measuring the elastic constants of a Ni$_{0.50}$Mn$_{0.28}$Ga$_{0.216}$ single crystal using the ultrasonic continuous-wave method. \(C_{11}\), \(C_{33}\), \(C_{66}\) and \(C_{44}\) modes were investigated; every mode
indicated an abrupt softening around $T_M$. This lattice softening appears to be affected by the abrupt expansion just above $T_M$ when cooling from the austenite phase.

Takahashi proposed a spin fluctuation theory of itinerant electron magnetism [21,22]. The induced magnetization $M$ is written as the formula of

$$\left(\frac{M}{M_s}\right)^4 = 1.20 \times 10^6 \frac{T_c}{T_A} \frac{H}{M} \quad (1)$$

where $M_s = N_0 g \mu_B^2 P_S$ is the spontaneous magnetization in the ground state; $N_0$ is the molecular number; $P_S = \mu S$, where $g$ is the $g$-factor and $S$ is a spin; $T_A$ is the spin fluctuation parameter. Nishihara et al. [23] measured the magnetization of Ni and Ni$_2$MnGa. Good linearity is observed in the $M^4$ vs. $H/M$ plot at the Curie temperature for Ni. This result indicates that the critical index $\delta$ (defined as $H \propto M^{\delta}$) is 5.0.

In this study, we focused on the physical effects of magnetic fields. By using polycrystalline samples, it was possible for us to provide information concerning the easy axis of magnetization in a martensite structure; we made temperature-dependent strain measurements under constant magnetic fields. In this paper, permeability, thermal strain, and magnetization measurements were performed for polycrystalline Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ ($x = 2.5, 2.7$) in magnetic fields ($B$). Thermal strain and magnetization results of Ni$_{52}$Mn$_{25}$Ga$_{23}$ ($x = 2.0$) were used for discussing the magnetic field dependence of the martensite transition temperature and magnetization [24]. The results of thermal strain in a magnetic field and magnetic-field-induced strain yield information about the twin boundary motion in the fields. The experimental results were compared with those of other Ni-Mn-Ga single crystalline or polycrystalline alloys, and correlations between magnetism and martensite transition were found. Itinerant magnetism is also discussed, based upon the results of the magnetic field dependence of the magnetization and compared with the predictions of Takahashi’s theory [21,22].

The martensite transition temperature $T_M$ and reverse martensite phase transition $T_R$ are used when these are quoted from the references. To define these temperatures clearly, we used $T_M$ and $T_R$ as the martensite transition starting temperature $T_{Ms}$ and the reverse martensite temperature finishing temperature $T_{Rf}$ in our research results.

2. Experimental Procedures

The Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ ($x = 2.5, 2.7$) alloys were prepared by arc melting 99.99% pure Ni, 99.99% pure Mn, and 99.9999% pure Ga in an argon atmosphere. To obtain homogenized samples, the reaction products were sealed in double-evacuated silica tubes, and then annealed at 1123 K for 3 days and quenched in cold water. The obtained samples were polycrystalline. From X-ray powder diffraction, the monoclinic 6M phase martensite structure and the $D0_{22}$ tetragonal structure were mixed at 298 K. The size of the sample was 2.0 mm $\times$ 2.0 mm $\times$ 4.0 mm.

The measurements in this study were performed at atmospheric pressure ($P = 0.10$ MPa). Thermal strain measurements were performed using strain gauges (Kyowa Dengyo Co., Ltd., Chofu, Japan). The electrical resistivity of the strain gauges was measured by the four-probe method. The strain gauge was fixed parallel to the longitudinal axis of the sample.

Thermal strain measurements were performed using a 10 T helium-free cryo-cooled superconducting magnet at the High Field Laboratory for Superconducting Materials, Institute for Materials Research,
Tohoku University. The magnetic field was applied along the sample’s longitudinal axis. The thermal strain is denoted by the reference strain at 360 K.

Magnetization measurements in a steady field at 5K and temperature dependence of the magnetization at 0.10 T were performed using a SQUID magnetometer installed at Ryukoku University. As for $x = 2.7$, the high temperature magnetization between 320 K and 370 K were performed using a home-made magnetometer within a weak AC fields (with the frequency $f = 73$ Hz and the maximum field $B_{\text{max}} = 0.0050$ T, which has a compensating high homogeneity magnetic field. AC fields were applied along the sample’s longitudinal axis.), using an AC wave generator WF 1945B (NF Co., Ltd., Yokohama, Japan) and an audio amp PM17 (Marantz Co. Ltd., Kawasaki, Japan). The magnet was the same magnet with the thermal strain measurements. Pulsed magnetization measurements were performed using a Bitter-type water-cooled pulsed magnet (inner bore: 26 mm; total length: 200 mm) in a pulsed magnetic field at Ryukoku University. The magnetic field was applied along the sample’s longitudinal axis. The values of magnetization were corrected using the values of spontaneous magnetization for 99.99% pure Ni. The magnetic permeability measurements were performed in AC fields, which is as same as the AC magnetometer. Thermal experiments were carried out by means of DSC, using a rate of 10 K/min.

3. Results and Discussion

3.1. Magnetic Properties of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ ($x = 2.5$)

Figure 1a shows the temperature dependence of permeability. When heating from 300 K, permeability increases gradually. As shown in Figure 1a, permeability increases above 343 K and suddenly decreases around 350 K. When cooling from a high temperature, permeability shows a sudden increase at 355 K and decreases below 342 K. The sudden changes in permeability indicate that the ferromagnetic transition occurs around 350 K. The temperature dependence of permeability for Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ is similar to that of Ni$_{52}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{23}$’s, which shows a transition of a ferromagnetic–martensite (Ferro–M) phase to a ferromagnetic–austenite (Ferro–A) phase [25]. The step above 343 K (heating process) and below 342 K (cooling process) reflects stronger magnetic anisotropy in the tetragonal martensite phase, compared with that in the cubic austenite phase [8,18,24].

Polycrystalline Ni$_{49.5}$Mn$_{28.5}$Ga$_{22}$, Ni$_{50}$Mn$_{28}$Ga$_{22}$, and Ni$_{52}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{23}$ alloys also indicate the magnetization (or permeability) step at $T_M$ [9,18,26] below the field of 10 mT. Figure 1b indicates the temperature dependence of the differential of permeability $d\mu/dT$. The martensite transition starting temperature $T_{Ms}$ and reverse martensite finishing temperature $T_{Rf}$, which correspond to the characteristic temperature of martensite transition for thermal strain shown in Figure 2, are indicated by arrows.

Figure 2 shows the linear thermal strain of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. $B$ means magnetic field and the unit is T (tesla). $B$ is equal to $\mu_0 H$, where $\mu_0$ is the absolute permeability of a vacuum; the unit of $H$ is A/m. At zero magnetic fields, the memory strain was observed, as polycrystalline Ni$_{53.6}$Mn$_{27.1}$Ga$_{19.3}$ [10]. When heating from 300 K, a slight strain was observed, first at zero magnetic fields. Above 342 K, a sharp strain is observed. The results of previous studies [6,7] suggest that this is because of the reverse martensite transition $T_{Rf} = 347$ K, which is denoted by an arrow. When cooling from 360 K, a sudden
decrease is observed at 341 K. The martensite transition starting temperature $T_{Ms}$ is 341 K, defined as the midpoint temperature of the transition. The permeability at the Ferro–M phase is very low compared with that of the Ferro–A phase. The results of permeability and linear strain measurements indicate that the region above $T_{Ms}$ is a Ferro–A phase and that below $T_{Ms}$ is a Ferro–M phase. The permeability measurement results indicate that the ferromagnetic transition from the paramagnetic–austenite (Para–A) phase to the Ferro–A phase occurs around $T_C = 350$ K (see Figure 1a). At zero magnetic fields, and in magnetic fields, there is no visible anomaly around $T_C$. When cooling from 360 K, the thermal strain also shows a peak at 336 K. This may be attributed to the intermingling of the $L2_1$ austenite lattices and the $6M$ martensite lattices at the martensite transition. A sequential phenomenon is observed in single crystalline Ni$_{2.19}$Mn$_{0.81}$Ga [20]. The thermal strain shows an anomaly around $T_1 = 323$ K and $T_2 = 313$ K. The reason of this anomaly is open question at the present time. The contraction at $T_{Ms}$ under zero field is about $0.8 \times 10^{-3}$ (0.08%). As for other Heusler alloys, Ni$_{52}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{23}$ and Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga, the contraction occurs at the martensite temperature [26]. The strain at $T_M$ of polycrystalline Ni$_{52}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{23}$ was estimated as 0.14% contraction. This value is larger than that of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. After zero field measurements of the linear strain, measurements in magnetic fields from 3 T to 10 T were performed. The strains at $T_{Ms}$ under the magnetic field were estimated as 0.08% contraction, which is the same as that at zero magnetic field (0.08%).

**Figure 1.** (a) Temperature dependence of the magnetic permeability $\mu$ of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ in AC fields with $f = 73$ Hz and $B_{max} = 0.0050$ T. The origin of the vertical axis is the reference point when the sample is empty in the pickup coil of the magnetic permeability measurement system; (b) the $d\mu/dT$ vs. $T$. $T_{Ms}$ and $T_{Rf}$, which correspond to the characteristic temperature of martensite transition for thermal strain shown in Figure 2, are indicated by arrows.
Figure 1. Cont.

Figure 2. Temperature dependence of the linear thermal strain of Ni\textsubscript{52.5}Mn\textsubscript{24.5}Ga\textsubscript{23} in static magnetic fields.
Figure 3 shows the magnetic-field-induced strain at 300 K (Ferro–M phase) in a static magnetic field. When increasing the magnetic field from zero field, a sudden contraction occurs up to 1 T. Above 1 T, a gradual contraction is observed. When decreasing the magnetic field from 10 T, a modicum of strain occurs. Below 1 T, a sudden strain is observed. The magnetic-field-induced strain at 10 T is $-50$ ppm or $-0.005\%$.

The reasons that magnetic-field-induced strain is smaller than the strain at $T_M$, in the linear strain measurements, were elucidated in references [18,24,27].

On heating from the martensite phase, an abrupt increase occurred in the field-induced strain around $T_M$. They suggest that this is caused by lattice softening near $T_M$. As for the thermal strain of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$, shown in Figure 2, peaks appear for both $T_{Ms}$ and $T_{Rf}$ in zero field and all values of the magnetic field. The peak at $T_{Rf}$, which is associated with heating, is larger than the one at $T_{Ms}$, which is associated with cooling. These peaks indicate that the lattice expands abruptly. The ultrasonic continuous-wave measurements by Dai et al. [20] indicated abrupt softening around $T_{M}$. This lattice softening appears to be affected by the abrupt expansion just above $T_{M}$ or $T_{R}$, when cooling or heating from or to the austenite phase, respectively.

**Figure 3.** Magnetostriction of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ at 300 K in a static magnetic field of up to 10 T.

![Graph showing magnetostriction](image)

Figure 4 shows the magnetic phase diagram of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. With increasing field, $T_{Ms}$ and $T_{Rf}$ gradually increase. The shifts in $T_{Ms}$ and $T_{Rf}$ around zero magnetic field are estimated as $dT_{Ms}/dB = 0.9 \pm 0.2$ K/T and $dT_{Rf}/dB = 0.8 \pm 0.2$ K/T, which is larger than those of the Ni$_{52}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{23}$ alloy’s $(dT_{Ms}/dB = 0.5$ K/T) [26]. In Section 3.2, we will discuss the shifts in $T_{Ms}$ and $T_{Rf}$ under magnetic fields.
Figure 4. Magnetic phase diagram of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. Filled triangles indicate the martensite transition start temperature $T_{Ms}$. Filled circles indicate the reverse martensite finishing temperature $T_{Rf}$.

![Magnetic phase diagram of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$](image)

Figure 5a shows the magnetization curves of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ at 5 K in a static magnetic field measured by a SQUID magnetometer. The unit of magnetization $M$ is Am$^2$/kg in the SI unit system or emu/g in the CGS unit system (both have identical numerical values). The saturation magnetization was 79.6 Am$^2$/kg. The spontaneous magnetization was 77.7 Am$^2$/kg (which was derived from the Arrott plot) as shown in Figure 5b. This spontaneous magnetization value is equal to a magnetic moment of 3.35 $\mu_B$/f.u. This absolute value corresponds to 3.75 $\mu_B$/Mn. The Mn magnetic moment of 3.75 $\mu_B$ is comparable to the magnetic moment of Mn on the B site, which is approximately 3.58 $\mu_B$/Mn (as obtained from the powder neutron scattering experiments performed by Ahuja et al. [28]). Detailed expressions about the magnetic moments of Ni$_{50+x}$Mn$_{27-x}$Ga$_{23}$ alloys ($-25 \leq x \leq 6$) were described by Umetsu et al. [19].

Figure 5c shows the temperature dependence of magnetization at 0.10 T. During the heating process, a decrease in magnetization occurred between 350 and 360 K, which corresponds to the magnetic transition, as shown in Figure 1a. Notably, this abrupt decrease in the $M$-$T$ curve at $T_{Ms}$ is different from that of usual ferromagnets. The assumed reason is that martensite transition occurs just below the Curie temperature $T_C$ for Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. For $x = 5$, the $M$-$T$ curve shows a gradual decrease at $T_{Ms}$ during the heating process. At this composition, the magnetic transition occurs in the martensite phase.

Figure 6a shows the magnetization curves of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ in a pulsed magnetic field up to 2.2 T. The $M$-$B$ curves were measured from low temperatures. The hysteresis of the $M$-$B$ curve is considerably small. The magnetocaloric effects in other magnetic materials were also reported; for example, Levitin et al. [29] reported for Gd$_5$Ga$_3$O$_{12}$. They performed magnetization measurements at an initial temperature of 4.2 K, where the magnetic contribution to heat capacity is comparable to that of the lattice heat capacity. In our experiment, the temperature change of the sample due to the magnetocaloric effect is considered to be within 1 K. This is because these experiments were performed around room temperature, where the lattice heat capacity is much larger than the heating
or cooling power of the magnetocaloric effect. Moreover, $M$-$B$ curves in Figure 6a show rather small hysteresis, which indicates that the magnetizations have been measured under a static temperature condition.

Figure 5. (a) Magnetization of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ in a static magnetic field; (b) Arrott plot of magnetization at 5 K; (c) temperature dependence of magnetization at 0.10 T.
Figure 6. (a) Magnetization of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$ in a pulsed magnetic field up to 2.2 T; (b) Arrott plot of the magnetization of Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. Dotted straight lines are extrapolated lines; (c) $M^4$ vs. $B/M$ plot for Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$. Dotted straight lines are extrapolated lines.
The $M$-$B$ curves show ferromagnetic behavior below 350 K. Clearly, the field dependence of magnetization at the Ferro–A phase above $T_{Rf} = 347$ K is different from that of the Ferro–M phase around $T_R$. At the Ferro–M phase, magnetization increases with magnetic fields. On the other hand, at the Ferro–A phase between 334 and 356 K, a sudden increase in magnetization occurs between 0 and 0.1 T.

Figure 6b shows the Arrott plot of Ni$_{52.5}$Mn$_{24.4}$Ga$_{23}$. This plot was also used for estimating the spontaneous magnetization to discuss the $dT_M/dB$ by means of the Clausius-Clapeyron relation. The spontaneous magnetization in Ni$_{52.5}$Mn$_{24.4}$Ga$_{23}$ at 338 K, just below $T_R$ is $39.1 \text{ Am}^2/\text{kg}$, which was obtained by the Arrott plot in Figure 6b. When using this value as the $M_s$, the magnetocrystalline anisotropy energy in the martensite phase of Ni$_{52.5}$Mn$_{24.4}$Ga$_{23}$ is $M_sB_s/2 = K_0 = 1.7 \times 10^5 \text{ J/m}^3$, which is on the same order as that in the martensite phase of Ni$_2$MnGa. These magnetic properties were also shown for Ni$_{51.9}$Mn$_{23.2}$Ga$_{24.9}$ [11], Ni$_{49.5}$Mn$_{25.4}$Ga$_{25.1}$ [12], and Ni$_{54}$Mn$_{21}$Ga$_{25}$ [13].

At large $B/M$ values, the $M^2$ vs. $B/M$ plot seems to show a linear relation. However, around $T_C$, the $M^2$ vs. $B/M$ plot strays out from a linear relation at low $B/M$ values. Therefore, we made an attempt of other plot.

Figure 6c shows the $M^4$ vs. $B/M$ plots. The $M^4$ vs. $B/M$ plot indicates a good linear relation around the Curie temperature $T_C = 350$ K. The critical index $\delta$ for $M^\delta$ vs. $B$ is 5.0. The result is in agreement with the theory by Takahashi for weak itinerant electron ferromagnets [21,22].

The $M^{3.6}$ vs. $B/M$ plot for Ni$_{52}$Mn$_{25}$Ga$_{23}$ is shown in Figure 7. The magnetic properties were reported in our former research [24]. This plot indicates a good linear relation around the Curie temperature $T_C = 356$ K. The critical index $\delta$ is 4.6. Nishihara et al. [23] investigated the magnetic field dependence of the magnetization of Ni$_3$MnGa around $T_C = 363$ K. The critical index $\delta$ is 4.77. As for Takahashi theory’s formula as shown in Equation (1), the critical index $\delta$ is 5.0. Therefore, we analyze of the characteristic temperature $T_A$ for Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$.

From the magnetic moment 3.75 $\mu_B$/Mn obtained from our magnetization measurement and the gradient of $M^4$ vs. $B/M$ in Figure 6c, we calculated the characteristic temperature $T_A$ as $1.06 \times 10^4$ K. This value is comparable to the value of Co$_2$CrGa ($1.0 \times 10^4$ K) [30] and Ni ($1.76 \times 10^4$ K) [21]. These results reflect the nature of itinerant magnetism for Ni$_{52.5}$Mn$_{24.5}$Ga$_{23}$.

Figure 7. $M^{3.6}$ vs. $B/M$ plot for Ni$_{52}$Mn$_{25}$Ga$_{23}$. Dotted straight lines are extrapolated lines.
3.2. Magnetic Properties of Ni\textsubscript{52.7}Mn\textsubscript{24.3}Ga\textsubscript{23} (x = 2.7)

\(\text{Ni}_{52.7}\text{Mn}_{24.3}\text{Ga}_{23}\) is an alloy in which the martensite transition and ferromagnetic transition occurred at the same temperature [19]. Figure 8 shows the temperature dependence of the linear thermal strain of \(\text{Ni}_{52.7}\text{Mn}_{24.3}\text{Ga}_{23}\) in static magnetic fields, parallel to the longitudinal direction of the sample. With increasing field, \(T_{Ms}\) and \(T_{Rf}\) gradually increased. The shifts in \(T_{Ms}\) and \(T_{Rf}\) around zero magnetic field are estimated as \(dT_{Ms}/dB\) and \(dT_{Rf}/dB\) as 1.1 ± 0.2 K/T. Thermal strain results indicate that, with cooling from austenite phase, the elongation occurred at \(T_{Ms}\). The same phenomenon was observed in the \(\text{Ni}_{12.19}\text{Mn}_{0.81}\text{Ga}\) and \(\text{Ni}_{12.20}\text{Mn}_{0.80}\text{Ga}\) polycrystalline samples. It should be noted that these alloys also show the martensitic and ferromagnetic transitions at the same temperature [31]. For the temperature dependence of the linear thermal strain of \(\text{Ni}_{52.7}\text{Mn}_{24.3}\text{Ga}_{23}\) perpendicular to the longitudinal direction, contraction occurred at \(T_{Ms}\) with cooling from austenite phase. As for the lattice parameters of \(\text{Ni}_{52.7}\text{Mn}_{24.3}\text{Ga}_{23}\), martensite phase \(c\)-axis parameter is 11% larger than austenite phase \(a\)-axis parameter, and, martensite phase \(a\)-axis parameter is 6% smaller than austenite phase \(a\)-axis parameter [19]. Therefore, it is conceivable that the difference of these linear strains parallel or perpendicular to the longitudinal direction of the sample is that the sample is oriented to some extent.

**Figure 8.** Temperature dependence of the linear thermal strain of \(\text{Ni}_{52.7}\text{Mn}_{24.3}\text{Ga}_{23}\) in static magnetic fields, parallel to the longitudinal direction of the sample.
Figure 9a shows the magnetization process of Ni$_{52.7}$Mn$_{24.3}$Ga$_{23}$. The experiments were performed in steady fields. This is because that this alloy shows the martensite transition and ferromagnetic transition at the same temperature. Then the latent heat is not small at $T_C$. In order to avoid heating or cooling due to the ferromagnetic and martensite transition, we measured in steady fields and isothermal processes. The magnetization suddenly changes at $T_C = 356$ K. The spontaneous magnetization change $\Delta M$ is 28 Am$^2$/kg. The $M^4$ vs. $B/M$ plot is shown in Figure 9b. This plot did not indicate a linear relation around the Curie temperature. Takahashi’s theory can be applied to isotropic ferromagnet. Below $x = 2.5$, $T_C$ is higher than $T_M$ and a ferromagnetic transition occurs in the austenite phase. Between $T_M$ and $T_C$, the magnetic property is isotropic ferromagnet. On the contrary, $x = 2.7$ transfers from the martensite ferromagnet to the austenite paramagnet. In the martensite phase, magnetic anisotropy is larger than that in the austenite phase. Therefore, it is supposed that Takahashi’s theory cannot be applied to $x = 2.7$.

**Figure 9.** (a) Magnetization of Ni$_{52.7}$Mn$_{24.3}$Ga$_{23}$ in a static field; (b) $M^4$ vs. $B/M$ plot for Ni$_{52.7}$Mn$_{24.3}$Ga$_{23}$.
3.3. The Magnetic Field Dependence of the Martensite Transition Temperature

Now we discuss about the field dependence of the martensite transition temperature.

The martensite transition temperature change (d\(T\)) induced by magnetic field change (dB) is approximately given by the Clausius-Clapeyron relation [8,32,33]:

\[
\frac{dB}{dT} = \frac{\Delta S}{\Delta M} \text{[T/K]}
\]

where, \(\Delta S\) and \(\Delta M\) are the differences in entropy and magnetization between austenite and martensite phase. The entropy change \(\Delta S\) was calculated by DSC result.

For Ni\(_{52}\)Mn\(_{25}\)Ga\(_{23}\), the entropy change \(\Delta S\) due to the martensite transition is 20 J/kg-K. The magnetization change \(\Delta M = 11\) Am\(^2\)/kg, therefore \(\Delta S/\Delta M = 1.8\) T/K, and \(dT_M/dB = 0.55\) K/T. The experimental result of \(dT_M/dB\) is 0.43 ± 0.1 K/T [24].

For Ni\(_{52.5}\)Mn\(_{24.5}\)Ga\(_{23}\), the entropy change \(\Delta S\) is 22 J/kg-K. Magnetization change \(\Delta M = 17\) Am\(^2\)/kg, therefore \(\Delta S/\Delta M = 1.3\) T/K, and \(dT_M/dB = 0.77\) K/T. The experimental result of \(dT_M/dB\) is 0.9 ± 0.2 K/T (this work).

For Ni\(_{52.7}\)Mn\(_{24.5}\)Ga\(_{23}\), the entropy change \(\Delta S\) is 26 J/kg-K. Magnetization change \(\Delta M = 34\) Am\(^2\)/kg, therefore \(\Delta S/\Delta M = 0.76\) T/K, and \(dT_M/dB = 1.3\) K/T. The experimental result of \(dT_M/dB\) is 1.1 ± 0.2 K/T (this work). The \(dT_M/dB\)'s are approximately as same as that of the calculated values.

Khovailo et al. [34,35] discussed the correlation between the shifts in \(T_M\) for Ni\(_{2+x}\)Mn\(_{1-x}\)Ga (0 ≤ \(x\) ≤ 0.19) using theoretical calculations according to Clausius-Clapeyron formalism. The experimental values of this shift for Ni\(_{2+x}\)Mn\(_{1-x}\)Ga (0 ≤ \(x\) ≤ 0.19) are in good agreement with the theoretical calculation results. In general, in a magnetic field, the Gibbs free energy is lowered by the Zeeman energy \(\Delta MB\), which enhances the motive force of the martensite phase transition. Thus the \(T_M\)'s of the ferromagnetic Heusler alloys are considered to have shifted in accordance with magnetic fields because high magnetic fields are favorable for ferromagnetic martensite phases.

The relationship between magnetism and \(T_M\) in magnetic fields is discussed for other Ni\(_2\)MnGa-type Heusler alloys. Table 1 shows the spontaneous magnetizations and \(dT_M/dB\) values of Ni\(_{2+x}\)Mn\(_{1-x}\)Ga, Ni\(_{52}\)Mn\(_{12.5}\)Fe\(_{12.5}\)Ga\(_{23}\), Ni\(_{2}\)Mn\(_{0.75}\)Cu\(_{0.25}\)Ga, Ni\(_{2}\)MnGa\(_{0.88}\)Cu\(_{0.12}\), and Ni\(_{52}\)Mn\(_{25}\)Ga\(_{23}\). As for Ni\(_{2+x}\)Mn\(_{1-x}\)Ga alloys, shifts in the \(T_M\) of the magnetic fields were observed by magnetization measurements [2,34,36,37]. The \(T_M\) and \(T_C\) of Ni\(_{2}\)MnGa (\(x = 0\)) are 200 and 360 K, respectively. The region above \(T_M\) is the Ferro–A phase. A sample where \(x = 0\) for Ni\(_{2+x}\)Mn\(_{1-x}\)Ga showed a phase transition from the Ferro–A to the Ferro–M phases at \(T_M\). A sample where \(x = 0.19\) showed ferromagnetic transition and martensite transition at \(T_M\). When \(x = 0\), the shift in \(T_M\) was estimated as \(dT_M/dB = 0.2\) K/T [20] and where \(x = 0.19\), \(dT_M/dB = 0.8\) K/T [37]. The shift in \(T_M\) where \(x = 0.19\) was higher than that for \(x = 0\). The last four alloys in Table 1 show re-entrant magnetic transition. In these alloys, ferromagnetic transition occurs at the martensite transition. Below \(T_M\), the paramagnetic martensite phase (Para–M) appears. On the other hand, above \(T_M\), the austenite ferromagnetic phase (Ferro–A) appears. The ground states of these alloys are the ferromagnetic martensite phase at low temperature. Therefore, re-entrant magnetism appears. In a magnetic field, the ferromagnetic phase is more stable than the paramagnetic phase is. Therefore, \(T_M\) decreases with increasing magnetic fields while the ferromagnetic phase area
increases; the sign of $dT_M/dB$ is negative. In these alloys, the values of $dT_M/dB$ are large. This means that strong magneto-structural coupling was revealed through magnetic properties and phase transitions.

**Table 1.** Spontaneous magnetization and $dT_M/dB$ in Heusler Ni$_2$MnGa type magnetic shape memory alloys. $M_M$ and $M_A$ indicate the spontaneous magnetizations in the martensite phase and austenite phases, respectively. Ferro and Para indicate the ferromagnetic and the paramagnetic phases, respectively. $T_C^M$ indicates the Curie temperature in the martensite phase, and $T_C^A$ indicates the Curie temperature in the austenite phase. The * symbols in this table (eg. *1) indicate the references as shown in Remarks column.

| Sample           | $M_M$      | $M_A$      | $dT_M/dB$ (K/T) | Remarks   |
|------------------|------------|------------|----------------|-----------|
| Ni$_2$MnGa       | 90 Am$^2$/kg at 180 K (*1) Ferro | 80 Am$^2$/kg at 220 K (*1) Ferro | 0.20 (*2) | *1 [2]; |
| Ni$_{25}$Mn$_{0.1}$Ga | 2.0 (a.u.) at 300 K Ferro | 0 (a.u.) at 350 K Para | 0.80 ± 0.5 | [34] |
| Ni$_2$Mn$_{12}$Fe$_{12}$Ga$_3$ | 63.1 Am$^2$/kg at 250 K Ferro | 52.7 Am$^2$/kg at 300 K Ferro | 0.5 | [26] |
| Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga | 42.4 Am$^2$/kg at 300 K Ferro | 0 Am$^2$/kg at 307 K Para | 1.2 | [26] |
| Ni$_2$MnGa$_{0.88}$Cu$_{0.12}$ | 37.3 Am$^2$/kg at 330 K Ferro | 0 Am$^2$/kg at 340 K Para | 1.3 | [38] |
| Ni$_{32}$Mn$_{25}$Ga$_{23}$ | 42 Am$^2$/kg at 333 K Ferro | 34 Am$^2$/kg at 335 K Ferro | 0.43 ± 0.1 | [24] |
| Ni$_{25}$Mn$_{24.5}$Ga$_{23}$ | 39 Am$^2$/kg at 338 K Ferro | 22 Am$^2$/kg at 343 K Ferro | 0.9 ± 0.2 | this work |
| Ni$_{27.5}$Mn$_{24.2}$Ga$_{23}$ | 34 Am$^2$/kg at 352 K Ferro | 0 Am$^2$/kg at 356 K Para | 1.1 ± 0.2 | this work |
| Ni$_{45}$Co$_2$Mn$_{36}$In$_{13.3}$ | 0 Am$^2$/kg at 270 K Para | 70 Am$^2$/kg at 320 K Ferro | −4.3 | [33] |
| Ni$_{41}$Co$_{2}$Mn$_{31}$Ga$_{19}$ | 20 Am$^2$/kg at $T_C^M$ ≤ $T$ ≤ $T_M$ Para or weak Ferro | 59.2 Am$^2$/kg at $T_M$ ≤ $T$ ≤ $T_C^A$ Ferro | −2.95 | [39] |
| Ni$_{41}$Co$_{2}$Mn$_{32}$Ga$_{18}$ | 4.0 Am$^2$/kg at $T_C^M$ ≤ $T$ ≤ $T_M$ Para or weak Ferro | 53.3 Am$^2$/kg at $T_M$ ≤ $T$ ≤ $T_C^A$ Ferro | −2.8 | [39] |
| Ni$_{41}$Co$_{2}$Mn$_{31.5}$Ga$_{18.5}$ | $T_C^M$ ≤ $T$ = 316 K ≤ $T_M$ Para or weak Ferro | 79 Am$^2$/kg at $T_M$ ≤ $T$ = 388 K ≤ $T_C^A$ Ferro | −4.2 | [40] |

3.4. **Magneto-Structural Coupling of Ni$_2$MnGa-type Heusler Alloys**

Finally, we comment on the $x$–$T$ phase diagram of Ni$_2$MnGa-type Heusler alloys. As for the $x$–$T$ phase diagram of Ni$_{50+x}$Mn$_{17-x}$Ga$_{23}$ alloys ($−25 ≤ x ≤ 6$), the $T_M$ increases with increasing $x$. In contrast, the $T_C$ decreases with decreasing $x$. Kataoka et al. [41] explained the phase diagram of Ni$_2$Mn$_{1-x}$Cu$_x$Ga (0 ≤ $x$ ≤ 0.40) alloys. They conceived of the Landau-type phenomenological free energy as a function of martensitic distortion and magnetization. Their analysis showed that the bi-quadratic coupling term of martensitic distortion and magnetization, together with a higher order term, play an important role in the interplay between the martensite and ferromagnetic phases. Their calculation was based on the phenomenological free energy, shown as:

$$F_{tot} = F_{ela} + F_{mag} + F_{mag-ela}$$  (2)

where, $F_{tot}$ is the total free energy; $F_{ela}$, the free energy of the elastic strain $e_{ij}$; $F_{mag}$, the free energy of the magnetic system (including the magnetic exchange energy and the magnetocrystalline anisotropy energy) and $F_{mag-ela}$, the energy of the interaction between the distortion and the magnetization. The calculated $x$–$T$ phase diagram of Ni$_2$Mn$_{1-x}$Cu$_x$Ga agrees well with the phase diagram, which was
obtained from the experimental results. In addition, using the martensitic distortion coefficient $e_3$, they suggested that the bi-quadratic term, $e_3^2 M^2$, in $F_{\text{mag-ela}}$, affects large magneto-structural coupling. $(e_3 = (2e_{zz} - e_{xx} - e_{yy})/\sqrt{6}$, where, $e_{xx}$, $e_{yy}$ and $e_{zz}$ are strains along $x$, $y$, and $z$ axis, respectively). Thus, strong magneto-structural coupling was shown to have an important role in the magnetic properties and phase transitions of ferromagnetic shape memory alloys. Large magnetocrystalline anisotropy influences magneto-elastic coupling $F_{\text{mag-ela}}$ by means of the bi-quadratic term, $e_3^2 M^2$. In Ni$_{50-x}$Co$_x$Mn$_{31.5}$Ga$_{18.5}$ $(0 \leq x \leq 9)$, magnetization $M$ increases with the magnetic field between 338 K and 388 K [40]. The thermal hysteresis of the thermal strain also decreases at high magnetic fields. Other Heusler compounds, such as Ni$_{50-x}$Mn$_{12.5}$Fe$_{12.5}$Ga$_{25-x}$, show an $x$-$T$ phase diagram similar to that of Ni$_2$Mn$_{1-x}$Cu$_x$Ga [26]. The magnetic field-induced strain in single crystals, or magnetostriiction in polycrystals, of Ni$_2$MnGa, Ni-Co-Mn-Ga, and Ni-Co-Mn-In alloys also suggest a strong magneto-structural coupling. The $x$-$T$ phase diagram of Ni$_{50-x}$Mn$_{27-x}$Ga$_{23}$ alloys ($-25 \leq x \leq 6$) also shows the same characters as that of Ni$_2$Mn$_{1-x}$Cu$_x$Ga $(0 \leq x \leq 0.40)$ alloys [19]. The $x$-$T$ phase diagram of Ni$_{50-x}$Mn$_{27-x}$Ga$_{23}$ indicates a strong magneto-structural coupling for Ni$_{50-x}$Mn$_{27-x}$Ga$_{23}$ alloys.

To apply this theory to our present work, further theoretical consideration is needed to apply this theory for analyzing the relationship between the martensite variant structure and the magnetic field, which is reflected by the Zeeman term, and Jahn-Teller effect, which is applied to the ferrites and perovskite compounds [42,43].

4. Conclusions

Thermal strain, permeability, and magnetization measurements were performed on the Heusler alloys Ni$_{52.3}$Mn$_{24.5}$Ga$_{23}$ ($x = 2.5$) and Ni$_{52.7}$Mn$_{24.3}$Ga$_{23}$ ($x = 2.7$).

1. Thermal strain: When cooling from the austenite phase, a steep decrease in the thermal strain was obtained because of the martensite transition. $T_M$ and $T_K$ increased gradually with increasing magnetic fields. For $x = 2.5$, the shift in $T_M$ in the magnetic field was estimated as $dT_M/dB = 0.9 \pm 0.2$ K/T. For $x = 2.7$, the shift in $T_M$ in the magnetic field was estimated as $dT_M/dB = 1.1 \pm 0.2$ K/T.

2. The $dT_M/dB$ values determined from the thermal strain results are approximately as same as the values calculated by the Clausius-Clapeyron relation.

3. For $x = 2.5$, at the Curie temperature, the $M^4$ vs. $B/M$ plot crossed the origin of the coordinate axis, and the $M^4$ vs. $B/M$ plot indicates a good linear relation around the Curie temperature $T_C = 350$ K. The result is in agreement with the theory by Takahashi for weak itinerant electron ferromagnets. From the magnetic moment and the gradient of $M^4$ vs. $B/M$, we calculated the spin fluctuation parameter $T_\lambda$ as $1.06 \times 10^4$ K, which is comparable to the value of Ni $(1.76 \times 10^4$ K).

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Author Contributions

Takuo Sakon designed, directed, carried out the experiments and wrote the paper, Kohei Otsuka carried out the DSC measurements, Junpei Matsubayashi carried out the permeability and magnetization measurements by means of helium-free magnet, Yuushi Watanabe carried out the thermal expansion and magnetostriction measurements, Hironori Nishihara carried out the magnetization measurements by means of SQUID magnetometer, Kenta Sasaki carried out the thermal expansion and magnetostriction measurements, Satoshi Yamashita, Rie Y. Umetsu, and Takeshi Kanomata made and homogenized the samples. Hiroyuki Nojiri supported this experimental project at IMR, Tohoku University, Takeshi Kanomata also advised about the scientific meanings of this study and edited the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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