Forced Magnetostrictions and Magnetizations of Ni$_{2+x}$MnGa$_{1-x}$ at Its Curie Temperature

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Abstract: Experimental investigations into the field dependence of magnetization and the relationship between magnetization and magnetostriction in Ni$_{2+x}$MnGa$_{1-x}$ (x = 0.00, 0.02, 0.04) alloy ferromagnets were performed following the self-consistent renormalization (SCR) spin fluctuation theory of itinerant ferromagnetism. In this study, we investigated the magnetization of and magnetostriction on Ni$_{2+x}$MnGa$_{1-x}$ (x = 0.02, 0.04) to check whether these relations held when the ratio of Ni to Ga and, the valence electron concentration per atom, e/a were varied. When the ratio of Ni to Ga was varied, e/a increased with increasing x. The magnetization results for x = 0.02 (e/a = 7.535) and 0.04 (e/a = 7.570) suggest that the critical index $\delta$ of $H \propto M^{\delta}$ is around 5.0 at the Curie temperature $T_C$, which is the critical temperature of the ferromagnetic–paramagnetic transition. This result confirms Takahashi’s spin fluctuation theory and the experimental results of Ni$_2$MnGa. The spontaneous magnetization $p_S$ slightly decreased with increasing x. For x = 0.00, the spin fluctuation parameter in k-space (momentum space; $T_A$) and that in energy space ($T_0$) were obtained. The relationship between $p_{\text{eff}}/p_S$ and $T_C/T_0$ can also be explained by Takahashi’s theory, where $p_{\text{eff}}$ indicates the effective magnetic moments. We created a generalized Rhodes-Wohlfarth plot of $p_{\text{eff}}/p_S$ versus $T_C/T_0$ for other ferromagnets. The plot indicates that the relationship between $p_{\text{eff}}/p_S$ and $T_0/T_C$ follows Takahashi’s theory. We also measured the magnetostriction for Ni$_{2+x}$MnGa$_{1-x}$ (x = 0.02, 0.04). As a result, at $T_C$, the plot of the magnetostriction ($\Delta L/L$) versus $M^4$ shows proportionality and crosses the origin. These magnetization and magnetostriction results were analyzed in terms of Takahashi’s SCR spin fluctuation theory. We investigated the magnetostriction at the premartensitic phase, which is the precursor state to the martensitic transition. In Ni$_2$MnGa system alloys, the maximum value of magnetostriction is almost proportional to the e/a.

Keywords: ferromagnetic Heusler alloy; magnetization; magnetostriction; itinerant electron magnetism; premartensite phase
1. Introduction

Spin fluctuation theories have advanced the attempts to elucidate the physical principles of the itinerant electron system [1–5]. According to the self-consistent renormalization (SCR) spin fluctuation theory [1], the external magnetic field \( H \) is proportional to the third power of the magnetization \( M^3 \) at the Curie temperature \( T_C \). This relation was derived by only considering the transverse modes of the thermal spin fluctuations with respect to the direction of the static and uniform magnetic moment [6,7]. Takahashi proposed SCR theory according to zero-point spin fluctuations, which assimilate both the transverse and the longitudinal components of the fluctuations [3–5,8]. An outstanding characteristic of this theory is the magnetization at \( T_C \). This theory proposed by Takahashi indicates that \( H \) is proportional to \( M^5 \) at \( T_C \).

The thermo-dynamical relationship between the magnetization \( M \) and the external magnetic field \( H \) can be expressed by the equation:

\[
H = \frac{\partial F}{\partial M} = a(T)M + b(T)M^3 + c(T)M^5 + \cdots
\]  
(1)

where \( F \) indicates the spin fluctuation free energy. This appears as Equation (2.59) in Takahashi [8].

As \( T \to T_C \), the magnetic susceptibility \( \chi(T) \) comes infinite. Therefore,

\[
\lim_{T \to T_C} a(T) = \lim_{T \to T_C} \frac{H}{M} = \lim_{T \to T_C} \frac{1}{\chi} = 0
\]  
(2)

Then, the first expansion coefficient at \( T_C \) is \( a(T_C) = 0 \).

According to the Rhodes-Wohlfarth theory [9], the third expansion coefficient \( b(T) \) in Equation (1) remains finite at \( T = T_C \). Therefore, the following formula is satisfied at \( T_C \):

\[
H = b(T_C)M^3 + c(T_C)M^5 + \cdots
\]  
(3)

Under the Takahashi theory, \( b(T) \) vanishes at \( T_C \), as shown in Equation (3.51) in Takahashi [8]. As a result, the \( M \) dependence of the magnetic fields \( H \) can be explained by the equation:

\[
H = c(T_C)M^5
\]  
(4)

In Equation (4), higher terms are ignored because their magnitudes are smaller than that of the third term. In conclusion, an \( H \propto M^5 \) relation was obtained.

\( \text{MnSi} \) [3], \( \text{CoS}_2 \) [10], \( \text{Fe}_5\text{Co}_1\ldots\text{Si} \) [11], and \( \text{Ni} \) [12] follow the relationship provided in Equation (4). The Heusler isotropic ferromagnetic alloy \( \text{Ni}_2\text{MnGa} \) also follows this relation in a cubic austenite phase [12]. For \( \text{Ni}_2\text{MnGa} \), the critical index \( \delta \) of \( H \propto M^\delta \) at \( T_C \) is \( \delta 4.70 \pm 0.5 \) [12,13].

Takahashi proposed that magnetostriction can be observed due to the itinerant spin fluctuations around \( T_C \) [8] because the magnetostriction is calculated from the spin fluctuation free energy. The relationship between the magnetostriction and the magnetization at \( T_C \) [8] in Equation (6.101) was explained using the formula

\[
\frac{\omega_b(\sigma, t_C)}{\omega_0} = K \times A(0, t_C) \times \sigma^4 \sigma_0^4
\]  
(5)

where \( t_C \) is a relative Curie temperature; \( \sigma \) and \( \sigma_0 \) are the magnetization in a magnetic field and the spontaneous magnetization, respectively; \( \omega_0 \) is the nonmagnetic volume contribution; \( \omega_b(\sigma, t_C) \) is the relative magnetic volume-striction at \( T_C \); \( K \) has a constant value in an isothermal state; and \( A(0, t_C) \) indicates the amplitude of the thermal spin fluctuations at \( T_C \). Equation (5) indicates that the magnetostriction is proportional to \( M^4 \) at \( T_C \). Kittel mentioned that the volume strain \( \Delta V/V \) is three times the value of \( \Delta L/L \) [14]. Accordingly, volume magnetostriction \( (\Delta V/V) \) discussions were applied to the results of the magnetostriction \( \Delta L/L \) in this experimental study.
For quondam research, an investigation into MnSi, which is famed for its weak itinerant magnetism, was completed [15]. The magnetostriction $\Delta L/L$ versus the square of the magnetization $M^2$ was analyzed. Around $T_C = 30$ K, the plot strayed from linearity. Takahashi proposed that around $T_C$, the magnetostriction is not proportional to the square of the magnetization. $\Delta L/L$ is proportional to $M^4$ through the origin at $T = 29$ K around $T_C$ [8]. In a previous study, we investigated the magnetostriction property of a polycrystalline Ni$_2$MnGa alloy using the self-consistent renormalization (SCR) theory of itinerant ferromagnets [13]. The magnetostriction was found to be proportional to the fourth power of magnetization. At the Curie temperature, magnetostriction crossed the point of origin. These results are in line with Takahashi’s spin fluctuation theory. In this study, we investigated Ni$_{2+x}$MnGa$_{1-x}$ ($x = 0.02, 0.04$) alloys and studied the effect of varying alloy composition (ratio of Ni and Ga atoms) on magnetostriction. We found that the valence electron concentration per atom, i.e., the ratio $e/a$, increases with increasing $x$. The $e/a$ values were 7.50, 7.535, and 7.570 for $x = 0.00, 0.02$, and 0.04, respectively. The spin fluctuation parameter in wave number space (momentum space) $T_A$ and that in energy space $T_0$ were obtained from the results of the magnetization measurement. We discuss the relation between $p_{eff}/p_S$ and $T_C/T_0$ compared with that shown in other itinerant ferromagnets by means of a generalized Rhodes-Wohlfarth plot [8]. We also investigated the $e/a$ dependences of the maximum magnetostriction around the premartensitic-austenitic transition for Ni$_2$MnGa-type alloys. Researchers have studied the correlation between magnetostriction and the valence electron concentration $e/a$, which is related to the energy of the electron system [16–18]. In our prior study, we measured the properties of Ni$_2$Mn$_{1-x}$Cr$_x$Ga [16]. In these alloys, the $e/a$ was smaller than 7.50, which is the value for Ni$_2$MnGa. In this study, we measured Ni$_{2+x}$MnGa$_{1-x}$ ($x = 0.02, 0.04$) alloys for which the $e/a$ is larger than 7.50 and investigated the $e/a$ dependence of the maximum magnetostriction in the premartensite phase.

Rizal et al. investigated the magnetic property of nanostructured Fe-Co alloys [19]. At room temperature, a strong correlation was found between the saturated magnetization and the lattice constant of the Fe-Co alloy. For Ni$_2$MnGa-type Heusler alloys, the correlations between $e/a$ and the magnetization (magnetic moment) or magnetostriction have been the subject of several investigations undertaken by varying alloy composition. Accordingly, in this article, we focused on the $e/a$ dependences of the magnetostricitions.

2. Materials and Methods

The polycrystalline samples of Ni$_{2+x}$MnGa$_{1-x}$ ($x = 0.00, 0.02, 0.04$) were prepared by arc melting the constituent elements—4N Ni, 3N Mn, and 6N Ga—several times in an Ar atmosphere. Each ingot was melted several times in order to ensure good homogeneity. The products from the arc melting process were sealed in an evacuated silica tube and solution heat-treatments were applied at 1123 K for three days. After these treatments, the sample was quenched in water. The measurement of permeability was performed in alternating current (AC) magnetic fields with a frequency of 73 Hz and a maximum field of $\pm$10 Oe. The AC magnetic fields were measured using a gaussmeter 410 (Lakeshore Cryotronix Inc., Westerville, OH, USA). The sample size chosen for the experimental investigations was $3.0 \times 3.0 \times 4.0$ mm. The magnetostriction was measured by means of a strain gauge [13]. The magnetostriction $\Delta L/L$ was measured parallel to the external magnetic field $H$—the same approach used in the experimental investigation of MnSi [15]. A helium-free superconducting magnet at the Center for Advanced High Magnetic Field Science, Osaka University, Japan was used for the magnetostriction measurements up to 5 T.

The magnetization measurements were performed using a solenoid-type pulsed-field magnet at Ryukoku University, Japan [13]. The absolute value of the magnetization was calibrated with the use of a sample of pure Ni of the same size. The same bulk sample was used in the permeability, magnetization, and magnetostriction measurements in order to compare the results. The data for magnetostriction and magnetization were the results of measurements with increasing magnetic fields beginning with a zero field.
We also used a water-cooled magnet in a steady field up to 1.6 T, which was installed in Ryukoku University, and studied the magnetostriction in order to investigate the temperature dependence of the magnetostriction around the premartensite phase.

3. Results and Discussions

3.1. Magnetic Field Dependence of the Magnetization

For the Ni$_2$MnGa alloy, martensitic transitions occurred at the temperature $T_{MS}$ of 195 K [16]. The alloy Ni$_2$MnGa also has a premartensite phase. This is a precursor (intermediate) state to the martensitic transition. In the premartensite phase, the alloy has a 3M modulated structure [20]. The austenitic–premartensitic transition occurs at the premartensitic temperature $T_P$ of 260 K. Above $T_P$, a cubic L2$_1$ type austenite phase is realized. The Curie temperature $T_C$ is 375 K, which is much higher than $T_{MS}$ and $T_P$. The ferromagnetic–paramagnetic transition at $T_C$ occurs in the cubic austenite phase, and the magnetic anisotropy constant $K_1$ in the austenite phase is 1/10 smaller than that in the martensite phase. The $K_1$ value at 150 K in the martensite phase was of the magnitude $4.0 \times 10^6$ erg/cm$^3$, and $K_1$ at 293 K in the austenite phase was $0.30 \times 10^6$ erg/cm$^3$ [16]. The magnitude of $K_1$ of Ni$_2$MnGa in the austenite phase is comparable to that of Fe. Therefore, Ni$_2$MnGa was decided to be an isotropic ferromagnet in the austenite phase. The value of $T_M$ for Ni$_{2+2x}$MnGa$_{1-x}$ increased with increasing Ni concentration $x$. The value of $T_P$ also increased with increasing $x$ for $x \leq 0.04$. Above $T_P = 265$ K for $x = 0.02$ and 275 K for $x = 0.04$, a cubic L2$_1$ type austenite phase is realized. Figure 1 plots the permeability $\mu$ for $x = 0.02$ (Figure 1a) and $x = 0.04$ (Figure 1b) during heating in a zero external magnetic field. The derivative of $\mu$ with respect to temperature, $d\mu/dT$, is also shown in Figure 1. The $T_C$ could not be defined from the $\mu$-$T$ curve because the divergence derived from Equation (2) was not found. Therefore the $T_C$ was defined as a temperature where the absolute value of the gradient of the $\mu$-$T$ curve, $d\mu/dT$, is maximum. The Curie temperatures $T_C$ were found to be 372 K and 366 K for $x = 0.02$ and 0.04, respectively, as obtained from the peaks of $d\mu/dT$ in Figure 1.

![Figure 1](image1.png)  
(a) Ni$_2$MnGa$_{1-x}$ $x = 0.02$  
![Figure 1](image2.png)  
(b) Ni$_2$MnGa$_{1-x}$ $x = 0.04$

We measured the magnetization of Ni$_{2+2x}$MnGa$_{1-x}$ around $T_C$ for the purpose of ascertaining the critical index $\delta$ of $M^{\delta-1}$ versus $H/M$. We plotted figures of $M^{\delta-1}$ versus $H/M$ for $\delta = 3.0, 4.7$, and 5.0; these are shown in Figures 2–4, respectively. The result for $\delta = 3$ is comparable to Moriya’s theory [1], that for $\delta = 5$ is comparable to Takahashi’s theory [8], and that for $\delta = 4.7$ is comparable to the former result [12]. $M^{\delta-1}$ versus $H/M$ with $\delta = 4.7$ in Figure 3 and $\delta = 5.0$ in Figure 4 show good linearity through the origin at $T_C$, denoted by the filled circles. The results suggest that for $x = 0.02$ and 0.04, the critical index $\delta$ is 4.7–5.0, which conforms to Takahashi’s theory [8] and the result found for Ni$_2$MnGa [12,13]. These relations held when the ratio of Ni to Ga and $e/a$ were varied. $H \propto M^5$ behavior was also observed for MnSi [21] and Fe [22]. Therefore, Takahashi’s theory was again shown to be acceptable for use in analyzing magnetization in terms of itinerant electron ferromagnetism in Ni$_2$MnGa system alloys.
3.2. Basic Magnetic and Itinerant Spin Fluctuation Parameters and Generalized Rhodes–Wohlfarth Plot

In this subsection, we obtain the basic and spin fluctuation parameters and discuss itinerant magnetism by means of a generalized Rhodes-Wohlfarth plot of $p_{\text{eff}}/p_S$ versus $T_C/T_0$.

The induced magnetization $M$ [8] (Equation (3.61)) is written as:

$$\left(\frac{M}{M_S}\right)^4 = 1.20 \times 10^6 \times \frac{T_C^2}{T_A^3} \times \frac{H}{M}$$

(6)
where $M_S = N_0 p_S \mu_B$ represents a spontaneous magnetization in a ground state; $N_0$ is a molecular number; $p_S = gS$, where $g$ is the Landé’s $g$-factor and $S$ is spin angular momentum; and $T_A$ is the spin fluctuation parameter in wave number space (momentum space). $T_A$ was obtained when experimental values were inserted into Equation (6), where the magnetic field $H$ is in units of kOe and the magnetization $M$ is in units of Am$^2$/kg, which is equal to emu/g.

The spontaneous magnetic moment $p_S$ ($\mu_B$) is expressed as:

$$p_S^2 = \frac{20T_0}{T_A} \times C_4 \times \left( \frac{T_C}{T_0} \right)^{\frac{4}{3}} C_4 \times 1.006089 \cdots (7)$$

where $T_0$ is the width of the spin fluctuation spectrum in the energy scale. This appears as Equation (3.61) in Takahashi [8].

From Equation (7), $T_0$ can be obtained using the formula:

$$T_0 = \frac{8147.2 \times T_C^4}{T_A \times p_S^6} \quad (8)$$

Table 1 provides the measured spontaneous magnetic moment $p_S$ and the characteristic temperatures $T_C$, calculated $T_A$, and $T_0$ for Ni$_{2+x}$MnGa$_{1-x}$. As for Ni$_2$MnGa, the measured $p_S$ of 3.93 $\mu_B$ is comparable to the theoretical band calculation result at the experimental lattice constant of the L2$_1$ cubic austenite phase, $p_S$, at 3.94 $\mu_B$ [23]. With increasing Ni fraction, the $p_S$ value decreased. This behavior appears for Ni$_{2+x}$Mn$_{1-x}$Ga [24] and Ni$_x$Fe$_{1-x}$ Invar alloys [25]. $T_0$ increased with increasing $x$. This is presumably because, in Equation (8), the right side varies with the sixth power of $p_S$, so $T_0$ varies even when $T_A$ does not change.

### Table 1. The spontaneous magnetic moment $p_S$ and the characteristic temperatures $T_C$, $T_A$, and $T_0$ for Ni$_{2+x}$MnGa$_{1-x}$.

| $x$ | $p_S$ (µB) | $T_C$ (K) | $T_A$ (K) | $T_0$ (K) |
|-----|------------|-----------|-----------|-----------|
| 0.00| 3.93       | 375       | 563       | 245       |
| 0.02| 3.79       | 372       | 566       | 288       |
| 0.04| 3.64       | 366       | 567       | 345       |

Takahashi also derived a formula [8], shown in Equation (3.47), for the relationship between $p_S$, $T_C$, $T_0$, and the effective magnetic moment $p_{eff}$ as follows:

$$\frac{p_{eff}}{p_S} \approx 1.4 \times \left( \frac{T_0}{T_C} \right)^{\frac{3}{2}} \quad (9)$$

As for Ni$_2$MnGa, $p_{eff}$ is 4.75 [24,26]. Equation (9) can be rewritten as:

$$k_m = \left( \frac{p_{eff}}{p_S} \right) \times \left( \frac{T_C}{T_0} \right)^{\frac{3}{2}} \quad (10)$$

When $k_m$ is 1.4, Equation (10) is equal to Equation (9). For Ni$_2$MnGa, a value of 1.61 for $k_m$ was obtained by substituting $p_S$, $T_C$, and $T_0$ from Table 1 and $p_{eff}$ of 4.75 into Equation (10) [26]. The values of $k_m$ for notable atoms, alloys, and compounds are Ni 1.41 [12], MnSi 1.88 [21], Ni$_2$Al 1.06 [27], Y(Co$_{0.85}$Al$_{0.15}$)$_2$ 1.08 [28], ZrZn$_2$ 0.74 [29], UCoGe 1.74 [8], and UGe$_2$ 1.61 [8]; these were calculated from the values listed in Table 2. Actinide 5f compound NpFe$_4$P$_{12}$ was also analyzed using the Takahashi theory and a $k_m$ value of 1.44 was found [30]. Table 2 provides the $k_m$ values and the magnetic moments and characteristic temperatures relating to spin fluctuation. Figure 5 is a plot of $\log(p_{eff}/p_S)$ versus $\log(T_C/T_0)$ for Ni$_2$MnGa, Ni, and notable alloys and compounds using the...
data in Table 2. The dotted line indicates the line of Equation (10) when \( k_m \) is 1.4. Figure 5 clearly shows that the relation between \( p_{\text{eff}}/p_S \) and \( T_C/T_0 \) can be explained by Equation (9). In Figure 3.3. in Takahashi [8], UGe\(_2\) had the largest value of \( T_C/T_0 \). In Figure 5 of this article, we added Ni, Ni\(_2\)MnGa, and NpFe\(_4\)P\(_{12}\). The \( T_C/T_0 \) value of Ni\(_2\)MnGa was almost the same as that of NpFe\(_4\)P\(_{12}\). The magnetic alloys and compounds that were analyzed by means of Equation (9) under the Takahashi theory were magnets with \( T_C \) values lower than room temperature. Notably, the ferromagnetic alloy Ni\(_2\)MnGa, which has a \( T_C \) higher than room temperature, can be explained by Figure 5 and Equation (6).

### Table 2. Basic magnetic parameters and \( k_m \), as obtained from Equation (10).

| Material          | \( T_C \) (K) | \( p_{\text{eff}} \) (\( \mu_B \)) | \( p_S \) (\( \mu_B \)) | \( p_{\text{eff}}/p_S \) | \( T_A \) (K) | \( T_0 \) (K) | \( T_C/T_0 \) | \( k_m \) | Reference |
|-------------------|---------------|----------------------------------|--------------------------|--------------------------|--------------|--------------|---------------|---------|-----------|
| Ni\(_2\)MnGa      | 375           | 4.75 *                           | 3.93                     | 1.21                     | 563          | 245          | 1.53          | 1.61    | This work, [26] * |
| Ni                | 623           | 3.3                              | 0.6                      | 5.5                      | 1.76 \( \times \) 10\(^4\) | 4.83 \( \times \) 10\(^3\) | 0.129         | 1.41    | [12]      |
| MnSi              | 30            | 2.2                              | 0.4                      | 5.3                      | 2.08 \( \times \) 10\(^3\) | 231          | 0.13          | 1.88    | [21]      |
| Y(Co\(_{0.85}\)Al\(_{0.15}\))\(_2\) | 41.5         | 1.3                              | 0.075                    | 17.3                     | 3.09 \( \times \) 10\(^3\) | 3.59 \( \times \) 10\(^3\) | 0.016         | 1.06    | [27]      |
| ZrZn\(_2\)        | 26            | 2.15                             | 0.138                    | 15.6                     | 0.726        | 1.41         | 0.018         | 1.08    | [28]      |
| UCoGe             | 17            | 1.44                             | 0.12                     | 12                       | 8.83 \( \times \) 10\(^3\) | 321          | 0.053         | 0.74    | [29]      |
| UGe\(_2\)         | 52.6          | 1.93                             | 0.039                    | 49.5                     | 5.92 \( \times \) 10\(^3\) | 362          | 0.0065        | 1.74    | [30]      |
| NpFe\(_4\)P\(_{12}\) | 23            | 1.55                             | 1.35                     | 1.15                     | 285          | 16.4         | 1.40          | 1.44    | [30]      |

![Figure 5](image)

The notable point from Table 2 and Figure 5 is that the \( p_{\text{eff}}/p_S \) value of Ni\(_2\)MnGa is smaller than those of other alloys and compounds. The effective moment \( p_{\text{eff}} \) was calculated from the Curie constant, \( C = N\mu_{\text{eff}}^2/3k_B = Np_{\text{eff}}^2\mu_B^2/3k_B = N\mu_B^2p_C(p_C + 2)/3k_B \). The term \( p_C \) refers to the effective moment deduced from the Curie constant \( C \). The spontaneous magnetic moment \( \mu \) is \( p_S \) (\( \mu_B \)) at 0 K. The \( p_C/p_S \) was one for local moment ferromagnetism and was larger than one for itinerant ferromagnetism. For Ni\(_2\)MnGa, \( p_{\text{eff}} \) was 4.75, as shown in Table 2; therefore, a \( p_C \) value of 3.85 was obtained from the equation \( p_{\text{eff}}^2 = p_C(p_C + 2) \). Then, the \( p_C/p_S \) value was 0.98. As a result, \( p_C/p_S \) was a little smaller than one. Webster et al. compared the magnetic moment obtained by saturation magnetization measurement, \( p_{\text{sat}} = 4.17 \) [26]. Then, \( p_{\text{sat}}/p_S \) was 0.92. In this work, the magnetization of Ni\(_2\)MnGa in the magnetic field of 5.0 T at 5 K was 4.10 \( \mu_B \)/f.u. Therefore, \( p_{\text{sat}}/p_S \) was 0.96. The Heusler compounds of CoMnSb and NiMnSb both possess the property of \( p_C/p_S < 1 \) [31]. Ott et al. proposed a simple molecular field model considering both local moments and spin-polarized itinerant electrons to explain \( p_C/p_S < 1 \) [31]. They introduced an enhanced temperature-independent
Pauli susceptibility and explained that the Curie constant decreases if the interactions between local magnetic moments and holes is antiferromagnetic. Webster mentioned that in the paramagnetic phase, only the Mn atoms carry a magnetic moment [26]. It is supposed that in the paramagnetic phase, a large moment is induced by the electrons around the Mn atom at the Mn site. Conversely, at the Ni site, the spins fluctuate at high temperature in the paramagnetic phase. Therefore, it is supposed that the magnetic moment pc at high temperature in a paramagnetic phase is smaller than the spontaneous magnetization psat and the saturation moment psat at 5 K.

3.3. Magnetization and Temperature Dependences Force Magnetostriictions

We recorded magnetostriction measurements to conduct an investigation into the magnetization dependence of forced magnetostriiction. In our earlier study, the magnetostriction of Ni2MnGa was found to be proportional to the M4 of the magnetization and clearly passed through the origin at TC [14]. In this study, we investigated Ni2+xMnGa1−x (x = 0.02, 0.04) to check whether these relations held when the ratio of Ni to Ga and e/a were varied. We plotted figures of magnetostriction ∆L/L versus M2 for δ = 2.0 and 4.0. The result for δ = 2.0 indicates a relation under Moriya’s theory [1,15], and that for δ = 4.0 indicates a relation under Takahashi’s theory [8]. Figure 6 is a plot of magnetostriction ∆L/L versus M2 for x = 0.02 (Figure 6a) and x = 0.04 (Figure 6b). The dotted lines are fitted linear plots. For the magnetostriction at TC indicated by the filled circles, the M2 linearity behavior was only observed for large magnetostriction and large magnetization area. Moreover, the dotted straight lines did not pass through the origin. These behaviors are comparable to the results for MnSi [15] and our former result for Ni2MnGa [13]. We also investigated ∆L/L versus M4 dependence, as shown in Figure 7. The plot of ∆L/L versus M4 indicates good linearity passing through the origin at TC, as indicated by the filled circles for both samples. Table 3 provides the coefficients A and k of the fitted linear plots given by the equation ∆L/L = A + kMδ for δ = 2 or 4 at TC. The standard deviations of the linear fitted lines at TC for magnetostriction ∆L/L versus M2 and ∆L/L versus M4 are shown in Figures 6 and 7, respectively, and are also listed in Table 3. The errors of the coefficient k were within ±2% for both values of δ. The proportions of the coefficient A and the magnetostriiction at 5 T (∆L/L ≃ −60 × 10−6), y0, were greater than 50% and less than 1.2% for δ = 2 and 4, respectively. This analysis indicates that the magnetostriction can be represented by the equation ∆L/L = kMδ at TC, as presented in Figure 7. As a result, the relation between magnetostriction and magnetization confirmed that the magnetostriction is proportional to the fourth power of the magnetization, as derived from Takahashi’s theory, even when the ratio of Ni to Ga and e/a were varied.

![Figure 6](image-url)
when the premartensitic transition temperature $T_e$ is $0.02$, $0.04$, and $0.04$, respectively. With increasing $x$, the magnetostriction increased; accordingly, the maximum value of the magnetostriction decreased. We assumed that if $e/a$ is increased, $T_P$ and the magnetostriction increased. Matsui et al. experimentally investigated the Ni$_2$MnGa-type alloys with $e/a > 7.50$ [17,18]. Among these alloys, Ni$_{51.7}$Mn$_{24.3}$Ga$_{24.0}$ with $T_P = 285$ K and $e/a = 7.59$ showed large magnetostriction with strain $550 \times 10^{-6}$ [17,18]. In this study, we decided to increase the concentration of Ni and decrease that of Ga because the $e/a$ values of Ni and Ga are 10 and 3, respectively, in order to increase the $e/a$ value of alloys to be above 7.50. Therefore, we prepared Ni$_{2+x}$Mn$_{1-x}$Ga$_{2}$ alloys with $x = 0.02$, producing $e/a = 7.535$, and $x = 0.04$, producing $e/a = 7.570$. Figure 8 shows the temperature dependencies of the magnetostriction at 1.6 T. The values were $250 \times 10^{-6}$ and $380 \times 10^{-6}$ for $x = 0.02$. The dotted straight lines are included as a visual guide.
and 0.04, respectively. Figure 9 shows the $e/a$ dependences of the maximum magnetostriction for Ni$_2$MnGa-type alloys. The maximum value of magnetostriction was almost proportional to the valence electron concentration per atom, $e/a$, and we also clarified the correlation between the magnetostriction and the $e/a$.

![Figure 8](image-url)

**Figure 8.** The temperature dependencies of the magnetostriction for (a) $x = 0.02$ and (b) $x = 0.04$.

The softening of the lattice around $T_P$ was investigated using ultrasonic measurements [32,33]. Seiner et al. investigated the magnetostriction around $T_P$ for a single crystal of Ni$_2$MnGa [33]. They suggested a model based on adaptive concept of premartensite, explaining the softening of $c_{44}$ and apparent $c'$ stiffening prior to the martensitic transformation and discussed the magneto-elastic coupling effect by means of these magnetostriction, and ultrasonic measurements results under magnetic fields. This consideration only involves the softening of the elastic constant. Our experimental results indicate that the $e/a$ and the magnetostriction are correlated and investigation by means of the itinerant electron magnetism is needed to better understand the fundamental origin of the magnetostriction. Future experimental and fundamental theoretical studies are needed to investigate the magneto-elastic coupling effect precisely, for example, with spectroscopy measurements for investigations of electron band structure and with itinerant electron magnetism theories.

![Figure 9](image-url)

**Figure 9.** The $e/a$ dependences of the maximum magnetostriction for Ni$_2$MnGa-type alloys. Filled triangles: polycrystal, Matsui et al. [17,18]. Cross: single crystal, Matsui et al. [17]. Filled square: single crystal, Seiner et al. [33]. The dotted line is a fitted line.
4. Conclusions

Experimental investigations of the field dependence of magnetization and the relationship between magnetization and magnetostriction for Ni$_{2+x}$MnGa$_{1-x}$ \(x = 0.00, 0.02, 0.04\) alloy ferromagnets were performed in accordance with the self-consistent renormalization (SCR) spin fluctuation theory of itinerant ferromagnetism. In this study, we investigated the magnetization of and the magnetostriction on Ni$_{2+x}$MnGa$_{1-x}$ \(x = 0.02, 0.04\) to check whether these relations held when the ratio of Ni to Ga and \(e/a\) were varied. When the ratio of Ni to Ga varied, the valence electron concentration per atom, \(e/a\), increased with increasing \(x\). The magnetization results for \(x = 0.02 (e/a = 7.535)\) and 0.04 \((e/a = 7.570)\) suggest that the critical index \(\delta\) of \(H \propto M^\delta\) is around 5.0 at the Curie temperature \(T_C\), which is the critical temperature of the ferromagnetic–paramagnetic transition. This result confirms Takahashi’s spin fluctuation theory and the experimental results obtained for Ni$_2$MnGa. The spontaneous magnetization \(p_S\) slightly decreased with increasing \(x\). For \(x = 0.00\), the obtained spin fluctuation parameter in \(k\)-space (momentum space) \(T_A\) and that in energy space \(T_0\) were 563 K and 245 K, respectively. The relationship between \(p_{eff}/p_S\) and \(T_C/T_0\) can be explained by Takahashi’s theory, where \(p_{eff}\) indicates the effective magnetic moments. We produced a generalized Rhodes-Wohlfarth plot of \(p_{eff}/p_S\) versus \(T_C/T_0\) values including those of other ferromagnets. The plot indicates that the relation between \(p_{eff}/p_S\) and \(T_0/T_C\) follows Takahashi’s theory. We also measured the magnetostriction for Ni$_{2+x}$MnGa$_{1-x}$ \(x = 0.02, 0.04\). At \(T_C\), the plot of the magnetostriction \(\Delta L/L\) versus \(M^4\) showed proportionality and crossed the origin. These magnetization and magnetostriction results were analyzed in the context of Takahashi’s SCR spin fluctuation theory. Further, we investigated the magnetostriction at the premartensite phase, which is the precursor state to the martensitic transition. In Ni$_2$MnGa system alloys, the maximum value of magnetostriction is almost proportional to \(e/a\).

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