Article

Magnetostriction of Ni$_2$Mn$_{1-x}$Cr$_x$Ga Heusler Alloys

Takuo Sakon $^{1,}$*, Naoki Fujimoto $^1$, Takeshi Kanomata $^2$ and Yoshiya Adachi $^3$

1 Department of Mechanical and System Engineering, Faculty of Science and Technology, Ryukoku University, Otsu 520-2194, Shiga, Japan; t140307@mail.ryukoku.ac.jp
2 Research Institute for Engineering and Technology, Tohoku Gakuin University, Tagajo 985-8537, Miyagi, Japan; kanomata@mail.tohoku-gakuin.ac.jp
3 Graduate School of Science and Engineering, Yamagata University, Yonezawa 992-8510, Yamagata, Japan; adachy@yz.yamagata-u.ac.jp

* Correspondence: sakon@rins.ryukoku.ac.jp; Tel.: +81-77-543-7443

Received: 12 August 2017; Accepted: 28 September 2017; Published: 1 October 2017

Abstract: Among the functionalities of magnetic Heusler alloys, magnetostriction is attracting considerable attention. The alloy Ni$_2$MnGa has a premartensite phase, which is a precursor state to the martensitic transition. Some researchers have observed magnetostriction in this alloy in the premartensite phase. We performed magnetostriction studies on the premartensite phase of related Cr-substituted Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys and measured the thermal strain, permeability, magnetisation, and magnetostriction of polycrystals. Our thermal expansion measurements show an anomaly that indicates the occurrence of lattice deformation below the premartensitic transition temperature $T_P$. Our permeability measurements also showed an anomaly at the premartensitic transition. From our magnetisation results, we obtained the magnetic-anisotropy constant $K_1$. In the martensite phase, we found that the magnetic-anisotropy constant of the $x = 0.00$ alloy is larger than that of the $x = 0.15$ alloy. At 0.24 MA/m, we obtained a magnetostriction of $-120$ ppm for the $x = 0.15$ alloy. Magnetostriction in the premartensite phase is larger than that in the austenite and martensite phases at low magnetic-field strength, thus indicating that it is related to lattice softening in the premartensite phase. The $e/a$ is proportional to the magnetostriction and $T_P$, which indicates that the electron energy, the magnetostriction, and the $T_P$ are correlative each other.

Keywords: shape-memory alloys; premartensitic transition; thermal expansion; magnetostriction

1. Introduction

1.1. Magnetostriction and Magnetic Field-Induced Strain of Ferroagnetic Shape Memory Alloys

Recently, ferromagnetic shape-memory alloys (FSMAs) have been studied extensively as candidates for highly functional magnetostriction materials for use as actuators, tremblers, and magnetic sensors. Among FSMAs, the alloy Ni$_2$MnGa is the most well-known [1]. It has a cubic $L2_1$ type Heusler structure (space group $Fm\overline{3}m$) and a ferromagnetic transition that occurs at the Curie temperature $T_C = 365$ K [2,3]. During cooling from ambient temperature, a martensitic transition occurs at the martensite transition temperature $T_M = 200$ K. Below $T_M$, a superstructure state develops as a result of lattice modulation [4,5]. Conventional magnetostriction is the distortion of crystal lattice caused by the rotation of the magnetic moment. FSMAs can induce large strain through martensitic transition or rearrangements of variants induced by external magnetic fields. This is called “twinning magnetostriction”, which was discovered by Ullakko and colleagues [1,6]. They discovered $1.5 \times 10^3$ ppm magnetostriction for a single crystal of Ni-Mn-Ga. This value is comparable to the magnetostriction of 3d/rare-earth intermetallic compounds TbFe$_2$, DyFe$_2$ [7] and Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ (terfenol-D) [8]. The reverse transition from martensite phase to parent phase in magnetic fields—which
is called magnetic-field-induced strain (MFIS)—can be observed for FSMAs. The large MFIS was mainly caused by the reorientation of variants and was highly sensitive to the temperature.

The MFIS of a single crystal of Ni$_{52}$Mn$_{23}$Ga$_{25}$ exhibited a martensitic transition at room temperature [9]. A large MFIS of $-2700$ ppm was obtained at 303 K and under atmospheric pressure. A net MFIS of 5400 ppm was induced when a 0.8 MA/m applied field was rotated from the [100] to the [001] directions of the sample. Furthermore, MFISs of $6-10 \times 10^3$ ppm have been reported in single crystals of Ni$_2$MnGa near or below room temperature [10]. Some studies have also been conducted on the influence of Fe addition into Ni-Mn-Ga alloys around room temperature [11,12]. A $5.5 \times 10^4$ ppm MFIS of single-crystal Ni$_{49.9}$Mn$_{28.3}$Ga$_{23.1}$Fe$_{1.7}$ appeared at 293 K [11]. The MFIS of Ni$_{52}$Mn$_{16}$Fe$_2$Ga$_{24}$ single-crystal was $1.15 \times 10^4$ ppm at 293 K [12]. These MFIS were observed in the martensite phase.

The magnetostriction in polycrystalline Ni$_{50}$Mn$_{23.1}$Ga$_{24.6}$ was studied, which shows a martensitic transition at the martensite starting temperature $T_{M_s} = 250$ K [13]. The number of valence electrons per atom, $e/a$, for this alloy is 7.57, which is higher than that for Ni$_2$MnGa ($e/a = 7.50$). A 540 ppm magnetostriction was observed at $T_{M_s}$.

Near $T_{M_s}$, lattice softening was observed. Therefore, the physical relation between the magnetostriction and the lattice softening around $T_{M}$ is interesting. The elastic constants of a Ni$_{50.5}$Mn$_{0.284}$Ga$_{0.216}$ single crystal were studied by using the ultrasonic continuous-wave method [14]. They investigated the $C_{11}$, $C_{33}$, $C_{66}$, and $C_{44}$ modes, and found that every mode exhibited abrupt softening around $T_M$. This lattice softening appears to be affected by the abrupt expansion that occurs just above $T_M$ when cooling from the austenite phase.

1.2. Magnetostriction in Premartensite Phase

The temperature of the martensitic transition is very sensitive to the ratio of constitutive elements for ordered compounds close to stoichiometry, Ni$_2$MnGa. Between a martensitic transition from a cubic phase (austenite) to a low symmetry phase (martensite), an intermediate phase appears. This intermediate phase is preceded by a so-called “premartensite phase”. The premartensitic transition between austenite phase and premartensite phase is weakly first-order and originates from softening of the shear elastic coefficient $C' = (C_{11} - C_{12})/2$ [15–17] corresponding to a minimum on the slowest transversal phonon branch [3,18,19]. Lattice softening is the physical reason for the large variation observed at the martensitic transformation temperature [20]. At the transition, the material exhibits some kind of anomaly in the elastic [16,21], thermal [15], electric [22], and magnetic properties [20,23]. As for Ni$_{2+x}$Mn$_{1-x}$Ga polycrystal, the resistivity demonstrates either a peak ($x = 0.00-0.04$ samples) or a two-step-like behaviour ($x = 0.06-0.08$ samples) at the premartensitic transition temperature, $T_p$ [22]. The permeability demonstrates a dip at $T_p$ [23]. Singh et al. [24] have suggested that a 3M-like incommensurate premartensite phase exists in Ni$_2$MnGa.

The feature of the premartensite phase is that magnetostriction occurs. Clear magnetostricions were observed around $T_p$ in Ni$_2$MnGa alloys. A minimum was found in both the magnetostriction and the elastic modulus at $T_p$ and at the martensitic transition temperature $T_M$ in single crystalline Ni$_2$MnGa [17,25]. Matsui et al. [26] investigated magnetostriction in polycrystalline Ni-Mn-Ga alloys and found a magnetostriction of $-190$ ppm in the premartensite phase—more than three times the amount in the austenite phase. Magnetostriction measurements were performed on polycrystalline Ni$_2$MnGa [20]. It was found that the saturation magnetostriction was negative, took on moderate values of approximately $-100$ ppm, and increased greatly in absolute value at both the premartensitic and martensitic transition temperatures, which arise from lattice softening at the transitions. In this study, we performed the measurements of the thermal strain, permeability, magnetisation, and magnetostriction of Cr-substituted Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys.

1.3. Purpose of This Study

We chose Ni$_2$Mn$_{1-x}$Cr$_x$Ga because the physical properties of Ni$_2$MnGa undergo sudden changes with heat treatment. Therefore, we studied the physical properties of doped systems that could predict
high thermal stability. The values of $T_C$ and $T_M$ for the Ni$_2$MnGa alloys change drastically when they are doped by replacing Mn with a fourth element, such as Fe, Co, Ni, or Cu [27–30]. For example, replacing Mn by Co, Ni, or Cu increases $T_M$, but the value of $T_M$ for Ni$_2$Mn$_{1-x}$Fe$_x$Ga decreases with increasing Fe concentration $x$. Several authors have shown that the number of $e/a$ is closely related to the value of $T_M$ for Ni-Mn-based FSMA’s: a large $e/a$ value indicates a high $T_M$ [31–33]. However, a larger $e/a$ corresponds to a lower $T_M$ for Ni$_2$Mn$_{1-x}$Fe$_x$Ga as mentioned above. For Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys, $e/a$ decreases with Cr concentration $x$ (7.50 for $x = 0.00$ and 7.46 for $x = 0.15$). Therefore, it would be interesting to know whether the relationship between $T_p$ or magnetostriction and $e/a$ applies to Ni$_2$Mn$_{1-x}$Cr$_x$Ga. The $e/a$ becomes smaller when Mn (3d$^5$4s$^2$) is replaced by Cr (3d$^3$4s$^2$). We are interested to investigate a correlation of magnetostriction and $e/a$ which is larger and smaller than 7.50 with a result of the magnetostriction measurements of other Ni-Mn-Ga alloys.

Now we will discuss the physical properties of Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys. As for $x \leq 0.25$, two anomalies were observed on the $\rho$-$T$ curves for each sample, corresponding to the magnetic and structural phase transitions at the Curie temperature $T_C$ and the martensitic transition temperature $T_M$ [34]. Kinks corresponding to the premartensitic transition at the critical temperature $T_p$ also appeared. A clear variation was observed below the premartensitic transition temperature $T_p$, thus indicating that lattice deformation occurs below $T_p$. The martensite-austenite phase transition was investigated for a series of $0 \leq x \leq 0.7$ Heusler alloys by using X-ray diffraction, DC magnetisation, and electrical resistivity measurements [35]. For $x < 0.20$, a ferromagnetic premartensite state appeared below $T_p$. As the Cr concentration $x$ increased, the martensitic phase transition shifted to higher temperatures, whereas the ferromagnetic transition shifted to lower temperatures. For $x < 0.5$, the martensitic transition occurred in a ferromagnetic state; however, for $x > 0.5$, the transition occurred in a paramagnetic state. Doping with Cr results in a rearrangement of the electronic structure, particularly near the Fermi level. This phenomenon is clearly shown by the resistivity data, where a systematic jump-like anomaly was observed in the vicinity of the martensite–austenite phase transition.

The purpose of this study is to investigate the magnetic properties of Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys more deeply than former studies. From the permeability and magnetization results, the magnetic-anisotropy constants in the three phases (austenite, premartensite, martensite) were obtained. The magnetostriction of the polycrystals of Ni$_2$MnGa ($x = 0.00$) and Ni$_2$Mn$_{0.85}$Cr$_{0.15}$Ga ($x = 0.15$)—both of which have austenite, premartensite, and martensite phases—were performed. We compared them with each other and with Ni$_2$Mn$_{0.75}$Cr$_{0.25}$Ga ($x = 0.25$), which also has austenite and martensite phases. The relation between the magnetic anisotropy and the magnetostriction was investigated. The relations between the $e/a$ and magnetostriction and $T_p$ were also investigated, and proportional relations were obtained.

2. Materials and Methods

We prepared polycrystalline Ni$_2$Mn$_{1-x}$Cr$_x$Ga alloys by the repeated arc-melting of appropriate quantities of the constituent elements—namely, 3N Ni, 4N Mn, 4N Cr and 6N Ga—in an argon atmosphere. The reaction products were sealed in evacuated silica tubes, heated at 1073 K for three days and at 773 K for two more days, and then quenched in water. We employed strain gauges (KFL-02-120-C1-16, size: sensor grid 0.2 mm length × 1.0 mm width, film base 2.5 mm length × 2.2 mm width. Kyowa Dengyo Co. Ltd., Yamagata, Japan) to measure the thermal strain and magnetostriction of bulk samples with sizes of 3.0 mm × 3.0 mm × 4.0 mm. The zero point of the linear thermal strain $\Delta L/L$ was set at 273.15 K, and the rate of temperature change rate was 2 K/min. For the magnetostriction measurements, we applied magnetic fields by using a water-cooled magnet. We employed two gauges, and we applied the magnetic field parallel to (strain $\lambda_//$) and, separately, perpendicular to (strain $\lambda_\perp$) the gauges. The magnetic-field change rate was 8.8 kA/(ms). We calculated the magnetostriction $\lambda$ from the equation $\lambda = 2(\lambda_// - \lambda_\perp)/3$ (see [36]). Magnetostriction measurements were also performed during cooling. We performed the permeability measurements in alternating magnetic fields with a frequency of 73 Hz and a maximum field of ±0.8 kA/m (±10 Oe), which we
verified using an magnetometer. We also employed a 3611 filter amp (NF Co. Ltd., Yokohama, Japan) and a 2000/J digital voltmeter (Keithley Co. Ltd, Salem, OR, USA). The measured temperature ranged between 150 K and 400 K. The rate of temperature change was 2 K/min, the same as we used for the linear-strain measurements. We performed the magnetisation measurements by using a pulsed-field magnet with the time constant of 6.3 ms. The absolute value was calibrated against a sample of pure Ni. The bulk samples used in other measurements were also used to compare the results with each other.

3. Results and Discussion

Figure 1 shows the temperature dependence of the linear strain $\Delta L/L$ in the (a) $x = 0.00$ alloy; (b) $x = 0.15$ alloy in zero field during cooling and heating. A jump is clearly seen between 195 K and 175 K in $x = 0.00$ alloy, and between 205 K and 195 K in $x = 0.15$ alloy, because of the martensitic transition during cooling and the reverse-martensitic transition during heating. In each alloy, approximately 1000 ppm shrinkage was observed during the martensitic transition in the cooling process. Linear strain measurements of single crystalline Ni$_2$MnGa [1] and polycrystalline Ni$_{49.6}$Mn$_{27.3}$Ga$_{23.1}$ [37] were performed. The strain values were practically the same as our result. Those results were less sensitive than our measurement. Therefore, our measurements are of higher resolution. Our result is comparable to the thermal strain observed by Albertini et al. [38] in polycrystalline Ni$_2$MnGa.

Hysteresis is clearly seen between the martensitic and reverse-martensitic transitions, thus indicating that the martensitic transition is a first-order phase transition. Identical $T_P$ values were obtained for the cooling and heating processes; the difference was at most 0.2 K. Singh et al. [24] suggested from their high-resolution X-ray spectroscopy of single-crystal Ni$_2$MnGa that a 3M-like structure develops in the premartensitic phase. Considering this X-ray spectroscopy result, the linear thermal expansion results of polycrystalline sample in this study indicate that lattice deformation occurred below $T_P$.

![Figure 1](attachment:image1.png)

**Figure 1.** Temperature dependence of the linear strain $\Delta L/L$ in the (a) $x = 0.00$ alloy; and (b) $x = 0.15$ alloy. The quantity $T_{Rs}$ is the temperature where the reverse-martensitic transition starts; $T_{Mf}$ is the temperature where the reverse-martensitic transition ends; $T_{Ms}$ is the temperature where the martensitic transition starts; and $T_{Mf}$ is the temperature where the martensitic transition ends. The dotted lines are intended to guide the eye.

Figure 2 shows the permeability $\mu$ of the (a) $x = 0.00$ alloy; and (b) $x = 0.15$ alloy during heating and cooling in zero magnetic fields. For $x = 0.00$, the anomalies or jumps appeared at the martensitic transition at approximately 195 K, the premartensitic transition at approximately 255 K (at which the temperature shows a dip, which was as same as single crystal [23]), and the ferromagnetic transition at approximately $T_C = 375$ K. When cooling from 400 K through the austenite paramagnetic phase, the value of $\mu$ increases at approximately 375 K, thus indicating a ferromagnetic transition in the austenite phase. The $\mu$ value dips slightly below 255 K and decreases strongly below 195 K. The permeability curve indicates that the magnetic anisotropy is small in the ferromagnetic
austenite and premartensite phases. By contrast, the value of the permeability decreased drastically at the martensite phase transition. This result indicates that the magnetic anisotropy is large in the martensite phase. Considering that the thermal strain (as shown in Figure 1) decreases steeply with cooling between 260 K and 240 K and that the permeability shows a dip in this temperature range, we conclude that lattice deformation occurred because of the premartensitic transition. As a result, lattice deformation increases magnetic anisotropy.

As for \( x = 0.15 \), the anomalies (jumps) are due to the martensitic transition at approximately 200 K, the martensitic transition at approximately \( T_p = 225 \) K, and the ferromagnetic transition at approximately \( T_C = 340 \) K. The \( \mu \) value dips slightly below 225 K and decreases strongly below 200 K. The magnetisation displays ferromagnetic properties at 5 K, with values of 83 Am\(^2\)/kg for the \( x = 0.15 \) alloy at 4 MA/m [35]. Therefore, the martensite phase is a ferromagnetic phase. The permeability decrease in the ferromagnetic phase below 225 K is believed to be due to magnetic anisotropy. The permeability of Ni\(_{50.9}\)Mn\(_{24.6}\)Ga\(_{24.5}\) exhibited a dip around \( T_p \), whereas Ni\(_{48.3}\)Mn\(_{24.6}\)Ga\(_{24.5}\)Co\(_{2.6}\) showed a gradual decrease below \( T_p \). Ni\(_{50.9}\)Mn\(_{24.6}\)Ga\(_{24.5}\) and Ni\(_{48.3}\)Mn\(_{24.6}\)Ga\(_{24.5}\)Co\(_{2.6}\) have the same properties at \( x = 0.00 \) and \( x = 0.15 \), respectively [39]. The hysteresis (difference in cooling and heating process) of \( \mu \) of \( x = 0.15 \) in the martensite phase is presumed to be due to the difference of the nucleation in the premartensite phase in cooling and heating process. The permeability of No. 3 (Ni\(_{51.7}\)Mn\(_{24.3}\)Ga\(_{24.0}\)) polycrystal, \( T_M = 265 \) K, \( T_R = 273 \) K, \( T_p = 285 \) K) shows clear hysteresis in the premartensite phase [40]. The difference between \( T_M \) and \( T_p \), \( \Delta T = T_p - T_M = 20 \) K. This is smaller than \( \Delta T = 63 \) K for \( x = 0.00 \) in this work. As for \( x = 0.15 \), \( \Delta T = 25 \) K. Therefore, it is supposed that the hysteresis of the permeability appears when \( \Delta T \) is small.

When the magnetic anisotropy is small, the magnetic moments are easily directed along the applied alternative magnetic fields in permeability measurements. By contrast, large magnetic anisotropies mean that the magnetic moments are less easily directed along the applied AC magnetic fields. In the ferromagnetic martensite phase (tetragonal symmetry), the magnetic anisotropy is larger than in the austenite phase (cubic symmetry), thus indicating that the permeability is small [41]. Taken together, the permeability decreased below 225 K as shown in Figure 2b and the linear-strain anomaly below \( T_p \) shown in Figure 1b imply that lattice deformation and the change of magnetic anisotropy have occurred because of the premartensitic transition. The \( T_C \) values for cooling and heating are almost the same, consistent with the linear-strain results. The \( T_p \) values found for cooling and heating are also the same. Soto et al. [42] studied Fe-doped NiMnGa (Ni\(_{52.5-x}\)Mn\(_{23}\)Ga\(_{24.5}\)Fe\(_{x}\)) alloys, finding that the premartensitic transition temperature was 186 K for the \( x = 4.4 \) alloy. No significant thermal hysteresis was detected at the premartensitic transition, and no appreciable features were observed in the calorimetric curves at the premartensitic transition. By contrast, our permeability measurements showed a small dip at the premartensitic transition, and the linear
strain and permeability exhibited clear variations for the $x = 0.15$ alloy. Uijttewaal et al. [43] state that the contributions of both magnons and phonons to the free energy of premartensite and austenite only “slightly differ” and that the existence of the premartensitic transition results from a delicate interplay between the vibrational and magnetic excitation mechanisms. We considered that the clear variation in the linear strain indicates lattice deformation and a softening of the lattice. Therefore, changes in the magnetic state are ultimately reflected in the permeability changes.

Figure 3 shows the magnetisation curve for the (a) $x = 0.00$ alloy and (b) $x = 0.15$ alloy measured during cooling process. As for $x = 0.00$, the magnetisation becomes almost saturated around 0.24 MA/m above 220 K, thus indicating that the magnetic anisotropy is small. At 200 K, which is slightly higher than $T_{Ms}$, the magnetisation increases steeply from 0 MA/m. This value is comparable to the results for the permeability at 200 K because the gradient of the magnetisation is proportional to the permeability. In the martensite phase at 150 K, the magnetisation increases gradually with increasing magnetic-field strength because of large magnetic anisotropy. The properties of magnetisation curves for $x = 0.15$ are almost the same as those for the $x = 0.00$ alloy.

![Figure 3](image-url)

**Figure 3.** The magnetisation $M$ of the (a) $x = 0.00$ alloy; and (b) $x = 0.15$ alloy. Blue: martensite phase, Green: premartensite phase, Red: austenite phase.

To determine the amount of magnetic anisotropy, we determined the magnetic-anisotropy field $H_A$ from the magnetisation results. This quantity was obtained by the peak of the twice-differentiated magnetisation curve, $d^2M/d(\mu_0H)^2$, by means of the derivation method of $H_A$ by the analysis of the magnetization of Ni$_2$MnGa by Chu et al. [44]. The magnetic-anisotropy constant $K_1$ is then provided by the equation $K_1 = \mu_0M_S^2H_A/2$ [38,44], where $M_S$ is the saturation value of the magnetisation. This approach is not the actual way to properly determine the magnetic anisotropy, and might be an approximation. Therefore, error bars are indicated in Figure 4a,b. The resulting values of $H_A$ and $K_1$ are shown in Figure 4a,b, respectively. From the saturated magnetisation $M_s$ obtained from the magnetisation curves in Figure 3 and from these values of $H_A$, we found the value of $K_1$ at 150 K in the martensite phase to be $K_1 = 4.0 \times 10^6$ erg/cm$^3$ in cgs-emu unit. This value is comparable to other results for $K_1$ [38,44]. The values of $K_1$ at 220 K in the premartensite phase and at 293 K in the austenite phase are similarly found to be $K_1 = 0.34 \times 10^6$ erg/cm$^3$ and $K_1 = 0.30 \times 10^6$ erg/cm$^3$, respectively, approximately one-tenth of the value at 150 K. Albertini [38] also suggested that the value of $K_1$ above the martensitic transition temperature is smaller than that in the martensite phase.

As for $x = 0.15$, the $H_A$ at 150 K in the martensite phase is smaller than that for the $x = 0.00$ alloy at 150 K. Above $T_{Ms}$, the $H_A$ is considerably smaller than at 150 K in the martensite phase. Conversely, the values of $H_A$ in the premartensite and austenite phases are larger than those for the $x = 0.00$ alloy. The resulting value of $K_1$ at 150 K in the martensite phase is $K_1 = 3.1 \times 10^6$ erg/cm$^3$, whereas the values at 210 K in the premartensite phase and at 293 K in the austenite phase are $K_1 = 1.0 \times 10^6$ erg/cm$^3$ and $K_1 = 0.58 \times 10^6$ erg/cm$^3$, respectively. Similar to the case for the $x = 0.00$ alloy, the permeability exhibits a small dip around $T_p$. By contrast, we found a large decrease below $T_p$ for the $x = 0.15$ alloy.
This result indicates that both the magnetic anisotropy and the value of $K_1$ in the premartensite phase for $x = 0.15$ are larger than those for $x = 0.00$.

![Figure 4](image1)

**Figure 4.** (a) The temperature dependence of the magnetic-anisotropy field $H_A$; (b) The temperature dependence of the magnetic-anisotropy energy $K_1$. The error bars were indicated.

We measured the magnetostriction by using the two-gauge method described in Section 2. Figure 5 shows the magnetostriction for the (a) $x = 0.00$ alloy; and (b) $x = 0.15$ alloy. As for $x = 0.00$, the magnetostriction saturated above 0.08 MA/m in the austenite and premartensite phases. This finding is consistent with the value of the magnetic-anisotropy field $H_A = 0.083$ MA/m at 220 K (premartensite). By contrast, at 162 K in the martensite phase, the magnetostriction increased with increasing field strength, although it showed indications of saturation at 1.27 MA/m. In other words, in order to generate a high driving force for the magnetic domains variants, highly anisotropic and highly saturated magnetisation values are needed [9]. In the austenite and premartensite phases, the magnetic anisotropy was small; therefore, the motive force acts only below 0.083 MA/m. However, in the martensite phase, the anisotropy field and the magnetic-anisotropy constant $K_1$ were large (as mentioned above, the value of $K_1$ in the martensite phase was more than 10 times larger than that in the premartensite phase). Therefore, under weak magnetic fields, the variants cannot move because of the high magnetic anisotropy. The motive force then acts until 1.27 MA/m, and large magnetostriction was observed. Regarding $x = 0.15$, a magnetostriction of $-120$ ppm was observed in the premartensite phase. In the austenite and premartensite phases, the magnetostriction saturated above 0.24 MA/m, which corresponds to the anisotropic field $H_A = 0.21$ MA/m obtained from the magnetisation curves at 210 K. The magnetostriction in the martensite phase (181 K in Figure 5b) saturated at 0.95 MA/m, which is comparable to the value of $H_A = 0.75$ MA/m at 150 K. Considering the permeability shown in Figure 2b and the magnetisation plotted in Figure 3b, we conclude that this result is due to the large magnetic anisotropy in the martensite phase.

![Figure 5](image2)

**Figure 5.** The magnetostriction $\lambda$ for the (a) $x = 0.00$ alloy; and (b) $x = 0.15$ alloy, measured during cooling. The horizontal axis shows the applied magnetic field $H$. 

---

Metals 2017, 7, 410

(a)

(b)
Figure 6 shows the temperature dependence of the magnetostriction values for the (a) \( x = 0.00 \) alloy and (b) \( x = 0.15 \) alloy. As for \( x = 0.00 \), in the austenite phase, the magnetostriction value was approximately \(-60 \) ppm at 290 K, and the absolute magnetostriction value increased slightly with cooling. In the premartensite phase, the absolute magnetostriction value increased drastically, reaching a magnetostriction value of \(-180 \) ppm at 250 K. The sudden decrease between 260 K and 240 K in Figure 6a corresponds to the temperature range in which the dip in permeability is seen (Figure 2a). Singh et al. [24] suggested that a 3M premartensite phase appears below \( T_p \); therefore, the magnetostriction is correlated with lattice deformation and magnetic anisotropy. Ultrasonic measurements indicate that the shear elastic \( C' \) coefficient, \( C' = (C_{11} - C_{12})/2 \), decreases around \( T_p \) [17], indicating that lattice softening occurred around \( T_p \). The magnetostriction at 1.27 MA/m increased drastically around the martensitic transition temperature \( T_M \). At 162 K, we observed a magnetostriction of \(-330 \) ppm. This temperature dependence of the magnetostriction has the same shape as the magnetostrain of Ni\(_2\)MnGa single crystals measured at 0.4 MA/m [25]. Figure 6a also shows the temperature dependence of the magnetostriction at 0.080 MA/m, as indicated by the triangle symbols. The value of the magnetic-anisotropy field \( H_A \) in the austenite and premartensite phases is approximately 0.083 MA/m; we also show the magnetostriction values at 0.080 MA/m near \( H_A \) in Figure 6a. A sharp peak can be observed just below the premartensitic transition temperature \( T_p \) (which was defined by the thermal strain measurement in Figure 1a). In the martensite phase, the magnetic anisotropy is larger than in the premartensite phase, thus indicating that the variants cannot move in low magnetic fields. As for \( x = 0.15 \), the temperature dependence of the saturated magnetostriction values at 0.24 MA/m is equal to the anisotropic field in the austenite and premartensite phases. The full width at half maximum (FWHM) of the peak in the premartensite phase is 20 K. By contrast, the FWHM for the \( x = 0.00 \) alloy (Figure 6a) is only 10 K, thus indicating that the anomaly (dip) in the permeability of the \( x = 0.15 \) alloy is larger than that of the \( x = 0.00 \) alloy.

In the martensite phase, the magnetostriction for the \( x = 0.15 \) alloy at 1.27 MA/m and 180 K (\(-35 \) ppm) was noticeably smaller than that of the \( x = 0.00 \) alloy at 1.27 MA/m and 163 K (\(-330 \) ppm); the temperature was approximately 35 K lower than \( T_{Ms} \). This finding suggests that the amount of magnetostriction decreased with increasing Cr concentration. We also measured the magnetostriction for an \( x = 0.25 \) alloy, which had a martensitic transition starting temperature \( T_{Ms} = 214 \) K.

![Figure 6](image_url)

**Figure 6.** Temperature dependence of the magnetostriction \( \lambda \) for the (a) \( x = 0.00 \) alloy; and (b) \( x = 0.15 \) alloy.

Figure 7 shows the temperature dependence of the magnetostriction for the \( x = 0.25 \) alloy at 1.27 MA/m, which peaks around \( T_{Ms} \). This property is the same as for the Ni\(_{52.3}\)Mn\(_{23.1}\)Ga\(_{24.6}\) and Ni\(_2\)MnGa alloys [13,26]. The magnetostriction of the \( x = 0.25 \) alloy at 1.27 MA/m in the martensite phase is between \(-30 \) ppm and \(-35 \) ppm, which is equal to that of the \( x = 0.15 \) alloy. These results confirm that the magnetostriction decreases with increasing Cr concentration. For the \( x = 0.00 \) alloy, the magnetic-anisotropy constant \( (K_1 = 4.0 \times 10^6 \text{ erg/cm}^3) \) was larger than that for the \( x = 0.15 \)
alloy \((K_1 = 3.1 \times 10^6 \text{ erg/cm}^3)\). The magnetisation value for the \(x = 0.00\) alloy was also larger than that for \(x = 0.15\). We conclude that larger magnetic anisotropy and larger magnetisation generate larger magnetostriction. However, the change in the amount of magnetostriction is considerably larger than the changes in magnetisation or magnetic anisotropy. Matsui et al. [40] measured the magnetostriction of a Si-doped Ni\(_2\)MnGa polycrystal and found that the amount of magnetostriction in the martensitic phase was considerably smaller than that of a Ni\(_2\)MnGa polycrystal. Conversely, the MFIS for an Fe-doped Ni\(_{52}\)Mn\(_{24}\)Ga\(_{24}\) single crystal is \(7.5 \times 10^3\) ppm, which is twice as large as that of a Ni\(_{52}\)Mn\(_{24}\)Ga\(_{24}\) single crystal \((3.5 \times 10^3\) ppm\) [12]. They mentioned that Fe substitution for Mn improves the temperature dependence of MFIS.

![Figure 7. Temperature dependence of the magnetostriction \(\lambda\) for the \(x = 0.25\) alloy.](image)

In order to investigate the relation between valence electron \(e/a\) and the magnetostriction value around the premartensitic transition, Figure 8 (a) demonstrates the relationship between \(e/a\) and the magnetostriction value around \(T_P\). Figure 8 (b) demonstrates the \(e/a\) dependence of the \(T_P\). Table 1 shows the valence electron \(e/a\), the premartensite temperature \(T_P\), and peak value of the magnetostriction around the \(T_P\) for each composition. Three Ni-Mn-Ga polycrystals [26,40], two Ni\(_2\)MnGa single crystals [17,26], \(x = 0.00\), and \(x = 0.15\) were used for this figure. To compare between the polycrystal and single crystal, the magnetostriction \(\lambda\) of the single crystal was calculated as \(\lambda \approx 2\lambda_{100}/3\), where \(\lambda_{100}\) is the magnetostriction parallel to the [100] axis. The magnetostriction is almost proportional to the \(e/a\). As shown in Figure 8b, the \(T_P\) is also almost proportional to the \(e/a\). It was reported earlier that \(T_P\) is proportional to the \(e/a\) [45]. From these results, it is considered that the electron energy, the magnetostriction, and the \(T_P\) are correlated each other. In doped Ni\(_2\)MnGa alloys, the \(e/a\) values change; therefore, it is considered that the itinerant electric and magnetic states also vary. As a result, the magneto-structural strain (magnetostriction or MFIS) can be changed.

**Table 1.** The valence electron \(e/a\), the premartensite temperature \(T_P\), and peak value of the magnetostriction around the \(T_P\) for each composition. PC: polycrystal; SC: single crystal.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(e/a)</th>
<th>(T_P) (K)</th>
<th>(\lambda) (ppm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(<em>{51.7})Mn(</em>{24.3})Ga(_{24})</td>
<td>7.59</td>
<td>285</td>
<td>–550</td>
<td>PC Matsui [26,40]</td>
</tr>
<tr>
<td>Ni(<em>{49.9})Mn(</em>{26.2})Ga(_{24})</td>
<td>7.54</td>
<td>259</td>
<td>–360</td>
<td>PC Matsui [26,40]</td>
</tr>
<tr>
<td>Ni(_3)MnGa</td>
<td>7.50</td>
<td>259</td>
<td>–227</td>
<td>SC Seiner [17]</td>
</tr>
<tr>
<td>Ni(_2)MnGa</td>
<td>7.50</td>
<td>258</td>
<td>–180</td>
<td>PC This work</td>
</tr>
<tr>
<td>Ni(<em>{49.2})Mn(</em>{26.5})Ga(_{24})</td>
<td>7.50</td>
<td>248</td>
<td>–182</td>
<td>SC Matsui [40]</td>
</tr>
<tr>
<td>Ni(<em>{47.9})Mn(</em>{28.0})Ga(_{24})</td>
<td>7.47</td>
<td>225</td>
<td>–180</td>
<td>PC Matsui [26,40]</td>
</tr>
<tr>
<td>Ni(<em>2)Mn(</em>{0.85})Cr(_{0.15})Ga</td>
<td>7.46</td>
<td>225</td>
<td>–120</td>
<td>PC This work</td>
</tr>
</tbody>
</table>

Further research is needed both for the kinetic physics and for the itinerant magnetism for Ni\(_2\)MnGa-related alloys. The martensitic transformation in stoichiometric Ni\(_2\)MnGa alloys is preceded...
by a weakly first-order transformation from a high-temperature cubic phase to a near-cubic, modulated, intermediate (premartensite) phase related to the presence of a soft phonon mode [46]. The appearance of this transformation has been proposed as a consequence of magneto-elastic coupling. An inelastic neutron-scattering experiment performed in an external magnetic field also indicated a strong magneto-elastic interaction at the premartensitic transition. We conclude that the large magnetostriction of the $x = 0.15$ alloy is related to lattice softening in the premartensite phase, similar to that with the $x = 0.00$ alloy. We expect that magnetostriction can be observed in the premartensite phase because of the softening caused by a perturbing magnetic field. Further studies (acoustic measurements, etc.) are needed to clarify these issues.

![Figure 8](image-url)  
**Figure 8.** (a) The valence electron $e/a$ dependence of peak value of the magnetostriction around the premartensite temperature $T_P$; (b) The valence electron $e/a$ dependence of the $T_P$. Filled circles: this work. Filled triangles: polycrystal, Matsui et al. [26,40]. Cross: single, Matsui et al. [40]. Filled square: single, Seiner et al. [17]. Dotted lines are fitting lines. The error bars in this work were indicated.

4. Conclusions

We have measured the thermal strain, permeability, magnetisation, and magnetostriction of novel magnetic Heusler Ni$_2$Mn$_{1-x}$Cr$_x$Ga polycrystals. The thermal expansion measurements show an anomaly, thus indicating that lattice deformation occurs below the premartensitic transition temperature $T_P$. The permeability measurements also show an anomaly at the premartensitic transition. From the magnetisation results, we obtained the magnetic-anisotropy constant $K_1$. In the martensite phase, we found the magnetic-anisotropy constant for the $x = 0.00$ alloy ($K_1 = 4.0 \times 10^6$ erg/cm$^3$) to be larger than that for the $x = 0.15$ alloy ($K_1 = 3.1 \times 10^6$ erg/cm$^3$). Magnetostriction in the premartensite phase is larger than that in the austenite and martensite phases at low magnetic fields, thus indicating that they are related to lattice softening in the premartensite phase. The magnetostriction and $T_P$ are proportional to the $e/a$, which indicates that the electron energy, the magnetostriction, and the $T_P$ are correlated each other.

Acknowledgments: The authors would like to express our sincere thanks to Toetsu Shishido and Kazuo Obara in Institute for Materials Research, Tohoku University, and Ryuji Kouta in Faculty of Engineering, Yamagata University for their help on the sample preparation. The authors also thank to Mitsuo Okamoto in Ryukoku University for helping to make the apparatus. This project is partly supported by the Ryukoku Extension Center (REC) at Ryukoku University.

Author Contributions: Yoshiya Adachi prepared the samples; Takuo Sakon and Takeshi Kanomata conceived and designed the experiments; Naoki Fujimoto and Takuo Sakon performed the experiments; Naoki Fujimoto and Takuo Sakon analysed the data; Takuo Sakon and Takeshi Kanomata wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.
References


© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).