Incommensurate structures of intermediate phase and martensite phase in Ni$_2$MnGa

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Abstract. Neutron diffraction measurements using single crystal and powder synchrotron X-ray diffraction measurements revealed that an intermediate (I-) phase and a martensite (M-) phase in Ni$_2$MnGa have incommensurate modulated structures. The modulation vectors of the I- and M-phases are nearly equal to $q = 0.341 <220>^*$ at 210 K and $q = 0.427 <220>^*$ at 100 K, respectively. Moreover, displacements of Ni, Mn and Ga atoms in both the I- and M-phase are expressed by sinusoidal waves with the same phase and almost the same amplitudes.

1. Introduction
A Heusler-type intermetallic compound of Ni$_2$MnGa is known to transform from a L$_2_1$-type parent phase (P-phase) to an intermediate phase (I-phase) at about 250 K [1, 2] and then to a martensite phase (M-phase) at about 200 K [3]. The first report on the crystal structure of the M-phase was made by Webster et al. [3]. They suggested a pseudo-tetragonal structure with $c/a < 1$ for the M-phase. After that, frequently mentioned 5-layered or 10-layered modulated structure (5M or 10M) for the M-phase was reported by Martynov et al. [4] and by Pons et al. [5]. On the other hand, a 7-layered or 14-layered modulated structure (7M or 14M) for the M-phase was reported by Brown et al. [6]. Moreover, an incommensurate modulated structure for the M-phase was suggested by Zheludev et al. using neutron diffraction [7] and by Righi et al. using powder X-ray diffraction [8]. Concerning the structure of the I-phase, a 3-layered or 6-layered modulated structure (3M or 6M) was reported by Zheludev et al. [7] and by Brown et al. [6]. An incommensurate structure for the I-phase was suggested by Tsuchiya et al. using an electron diffraction pattern [9].
Despite the many investigations described above, the crystal structures of the I-phase and the M-phase have not been clarified yet. In this study, therefore, we investigated the crystal structure of the I-phase and M-phase by combining neutron and synchrotron X-ray diffraction measurements.

2. Experimental procedure
For neutron diffraction experiments, a single crystal of Ni$_2$MnGa was grown by a floating zone method and was heat-treated at 1173 K for 24 h for homogenization and then at 923 K for 24 h to obtain a highly ordered L2$_1$-type structure. A specimen with a dimension of $5.0 \times 1.9 \times 1.9$ mm$^3$ and all edges parallel to $<001>_{\text{P}}$ was cut from the single crystal. Neutron diffraction measurements were made with a triangular spectrometer (TAS-1) using a non-polarized neutron beam at the 2G beam-line of JRR-3 at Japan Atomic Energy Agency (JAEA). A wavelength of 0.236 nm was selected for the neutron experiments. Horizontal collimation used was of open - 40° - sample - 40° - 80°. A pyrolytic graphite filter was used to attenuate higher-order harmonic contamination. Measurements were made at 245 K, 210 K, 200 K and 100 K by sweeping the scattering vector $q = [h-2-h0]_{\text{P}}$ in the range of $-0.1 \leq h \leq 2.1$.

For synchrotron diffraction measurements, the ingot of homogenized Ni$_2$MnGa was crushed into a powder specimen and it was subjected to ordering and annealing heat-treatment at 923 K for 3 h to eliminate the residual strain. Synchrotron X-ray diffraction measurements of powder specimens were made with a Debye-Scherrer-type imaging plate camera using a wavelength of 0.0500 nm at the BL02B2 beam-line at Japan Synchrotron Radiation Research Institute (SPring-8). Measurements were made during a successive cooling process at 280 K, 220 K, 190 K, 160 K, 130 K and 90 K.

3. Results
Figure 1(a) and (b) shows neutron diffraction profiles of the I-phase in Ni$_2$MnGa, which were obtained at 245 K and 210 K, respectively. In Figure 1(a) two satellite reflections are seen at the incommensurate positions of $h = 0.341$ and 1.659 between the fundamental reflections of $h = 0$ and 2. When the specimen was cooled to 210 K the satellite reflection positions remained almost constant but their intensities increased as shown in Figure 1(b). Figure 1(c) and (d) show profiles of the M-phase and were obtained at 200 K and 100 K, respectively. In Figure 1(c), four satellite reflections are seen at incommensurate positions of $h = 0.425$, 0.854, 1.146 and 1.575 between the fundamental reflections. When the specimen was cooled to 100 K (in Figure 1(d)) the satellite reflections moved slightly towards $h = 0.427$, 0.861, 1.139 and 1.573 while their intensities increased slightly. These results suggest that the I- and M-phases have incommensurate structures and the satellite intensities of the I- and M-phase are dependent on temperature, and also suggest that satellite position of the M-phase...
Figure 2  Powder synchrotron X-ray diffraction profiles of Ni$_2$MnGa at (a) 280 K, (b) 220 K and (c) 90 K. Observed and calculated intensities are indicated with open red circles and the solid black line, respectively. Short lines and the solid line below the diffraction profiles indicate peak positions of each phase (black, blue, red and green indicate P, I, M and MnO) and the difference between observed and calculated intensities.

depend on temperature but that of the I-phase is independent of temperature.

To obtain atom positions for the two phases, powder synchrotron measurements were carried out. Results are shown in Figure 2. At 280 K (Figure 2(a)) the profile is indexed by typical L2$_1$-type peaks of the P-phase and a small amount MnO impurity. The appearance of MnO is due to oxidation of the powder specimen during the heat-treatment. When the specimen is cooled to 220 K (Figure 2(b)), new peaks of the I-phase appear with those of the P-phase and of MnO. At temperatures of 190 K or lower peaks of the P-phase completely disappear and new peaks of the M-phase appear with those of the I-phase and of MnO. A typical example at 90 K is shown in Figure 2(c). The coexistence of the M- and I-phases at 90 K is due to the so-called size effect of the martensitic transformation temperature.

4. Discussion

In order to investigate atom positions, we carry out the Rietveld analysis using the results of powder synchrotron X-ray diffraction measurements. For the Rietveld analysis, we introduce hypothetical commensurate structures for the I- and M-phases although they have incommensurate structures as described above. That is, in neutron diffraction experiments satellite positions of the I-phase are close to $h = 13/38$ and $63/38$. Therefore, we introduce a 76-layered structure with a space group of $P2_1/m$ for the I-phase. Similarly, the satellite positions of the M-phase are close to $3/7$, $6/7$, $8/7$ and $11/7$. Therefore, we introduce a 14-layered structure with a space group of $P2_1/m$ for the M-phase. In addition, we assume that all atoms move only within the basal plane corresponding to $(1 1 0)_P$ along the $[1 1 0]_P$ direction in association with the martensitic transformations. This behaviour is also seen in the movement of atoms in copper based shape memory alloys [10, 11]. We fixed the monoclinic angle $\beta$ of the I- and M-phase to 90.0° and 90.2° considering the results of TEM observations [5].

Using these hypothetical structures and assumptions we performed Rietveld analyses using RITAN-2000 [12] and results are shown in Figure 2 with the diffraction profiles described above. Diffraction profiles were completely fitted by the L2$_1$-type P-phase for Figure 2(a) by assuming the
coexistence of the I- and P-phases for (b) and by assuming the coexistence of the M- and I-phases for (c). These results mean that the hypothetical structures of the I- and M-phases which were introduced from the results of neutron diffraction using a bulk single crystal are consistent with actual crystal structures of the I- and M-phases in the powder specimen. Incidentally, the amount of MnO impurity was less than 0.5 mass%.

Considering the Ni, Mn and Ga atom positions obtained by Rietveld analyses we determined the atom displacements $\Delta x$ from the position of the parent phase. The displacement $\Delta x$ of Ni, Mn, Ga atoms can be fitted by the following sinusoidal curve

$$\Delta x(n) = A_i \sin(2\pi \times 13n / 76)$$

for the I-phase. Here $n$ stands for the layer number of the basal plane. Also they can be fitted by a sinusoidal curve of

$$\Delta x(n) = A_m \sin(2\pi \times 3n / 14)$$

for the M-phase. Modulation amplitudes of Ni, Mn and Ga atoms in the I-phase, $A_i$, are almost 0.03 at 220 K and those in the M-phase, $A_m$, are almost 0.06 at 90 K. The modulation amplitude of each atom for the I-phase, $A_i$, increased from 0.03 to 0.04 as the temperature was decreased from 220 K to 90 K. It should be noted that the modulation amplitude of the I-phase is smaller than that of the M-phase even at the same temperature. This result corresponds to the difference in satellite intensity of neutron diffraction between the I- and M-phase.

5. Conclusions

Both the intermediate and the martensite phases of Ni$_2$MnGa have incommensurate modulated structures. The modulation vectors of the I- and M-phases are nearly equal to $q = 13/76 <1 1 0>^*$ and $q = 3/14 <1 1 0>^*$, respectively. Moreover, displacements of Ni, Mn and Ga atoms in both the I- and M-phase are expressed by sinusoidal waves with the same phase and almost the same amplitudes. The results obtained by neutron diffraction and synchrotron x-ray diffraction are consistent.

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7. References

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