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# Equilibrium phase diagram of $Ni_2MnGa$ under [0 0 1] compressive stress

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The stress-temperature equilibrium phase diagram of $Ni_2MnGa$ has been constructed by using a single crystal. We confirmed the existence of the triple point at which the intermediate phase, the martensite phase and the X-phase coexist. In addition, we found that the transformation from the parent phase to the intermediate phase proceeds via the X-phase even in the absence of external stress.
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Martensitic transformation in $Ni_2MnGa$ has attracted much attention, partly because a large magnetic field-induced strain (MFIS) appears in the martensite phase [1–4] and partly because the transformation is of interest in studying the interrelation between crystal structure and magnetism [5,6]. Thus, many studies have been undertaken in this system, and it is now widely accepted that stoichiometric $Ni_2MnGa$ transforms from an $L2_1$-type parent phase (P-phase) to an intermediate phase (I-phase) at about 250 K [7,8], then further transforms to a martensite phase (M-phase) at about 200 K on cooling [5,7,8].

In addition to these phases, we recently found that a new phase, the X-phase, is induced from the P- and I-phases by applying a compressive stress in the $[0\,0\,1]_P$ direction [9]. The existence of the X-phase has subsequently been confirmed by Karaman et al. [10] by similar experiments. They also reported that the reversible MFIS can be realized by using the magnetic field-induced $X \leftrightarrow I$ transformation and its reverse. Thus, the X-phase is important from both the fundamental point of view and from an applied point of view, in applications such as actuators. In our previous study [9], we constructed a phase diagram by using the transformation start stress and transformation start temperature. However, these values are not equilibrium ones, and we need the equilibrium phase diagram if we are to undertake a thermodynamic analysis. In the present study, therefore, we construct the stress–temperature equilibrium phase diagram of the $Ni_2MnGa$ under a compressive stress applied in the $[0\,0\,1]_P$ direction.

A single crystal of $Ni_2MnGa$ was grown by a floating zone method, and was homogenized at 1123 K for 86.4 ks. A specimen of $4 \times 2 \times 13\ mm^3$, with the longest edge parallel to the $[0\,0\,1]_P$ direction, was cut out from the single crystal, then heat-treated at 923 K for 86.4 ks to obtain a highly ordered $L2_1$-type structure. The surface of the specimen was electropolished in an electrolyte composed of 95% $CH_3COOH$ and 5% $HClO_4$. The martensitic transformation temperatures, $M_s$ and $A_f$, of the present specimen were obtained by magnetic susceptibility measurements to be 199 and 206 K, respectively. Thus, the equilibrium temperature between the I-phase and the M-phase was 202.5 K ($T_{0,I \leftrightarrow M} = (M_s + A_f)/2$).

Compressive tests were made using an Instron-type mechanical testing machine with a constant strain rate of $5 \times 10^{-5}\ s^{-1}$. The stress was measured by using a load-cell and the strain was measured by attaching a strain gage for the $P \leftrightarrow X$ and $I \leftrightarrow X$ transformations, and by calibrating the movement of the cross-head for the $X \leftrightarrow M$ and $I \leftrightarrow M$ transformations. Magnetic susceptibility under some compressive stresses was measured by applying a low magnetic field of $400\ A\ m^{-1}$ in the $[0\,0\,1]_P$ direction.

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Figure 1 shows the stress-temperature equilibrium phase diagram of $Ni_2MnGa$ determined by the present study. The symbols P, I, X and M stand for the corresponding phases. In the following, we show how the phase boundaries in Figure 1 are determined, starting from the high temperature region to the lower temperature region.

First of all, we show the equilibrium stress between the P- and X-phases. For the compressive test, we use a strain gage that is sensitive to small changes in strain. A typical stress–strain curve obtained at 260 K is shown in Figure 2a, where the initial state is the P-phase. The curve has an obvious bend point due to the $P \rightarrow X$ transformation, indicated by the arrow. Since there is no hysteresis between the mechanical loading and unloading processes, the stress $\sigma_{0,P\leftrightarrow X}$ indicated by the arrow corresponds to the equilibrium stress between the P- and X-phases. The absence of the hysteresis, furthermore, suggests that $P \leftrightarrow X$ is possibly a second-order transformation. The values of $\sigma_{0,P\leftrightarrow X}$ thus obtained in the temperature range of $258\ K \leqslant T \leqslant 266\ K$ are shown in Figure 1 by solid circles. Below 258 K, the equilibrium stress $\sigma_{0,P\leftrightarrow X}$ cannot be detected even by attaching the strain gage because the bend point on the stress–strain curve is obscure in the small stress region. Therefore, we determined the phase boundary of the $P \leftrightarrow X$ transformation in this region by magnetic susceptibility measurements, which are described later.

The X-phase induced from the P-phase described above transforms to the M-phase by further increasing the compressive stress. That is, successive $P \rightarrow X \rightarrow M$ transformation occurs. Since the strain gage peels off during the $X \rightarrow M$ transformation, we measured the stress–strain curves by calibrating the movement of the cross-head. A typical stress–strain curve obtained at 260 K is shown in Figure 2b, where the initial state is the P-phase. In the curve, the bend point due to the $P \rightarrow X$ transformation described above is not clear, only the stage due to the $X \rightarrow M$ transformation appearing

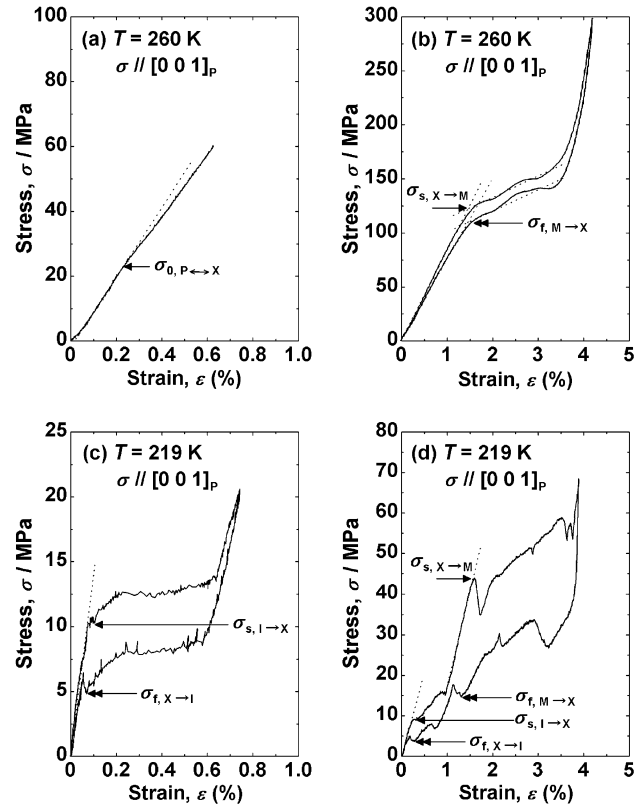


**Figure 2.** Stress–strain curves of $Ni_2MnGa$ obtained by applying compressive stress in the $[0\,0\,1]_P$ direction. The set temperature of (a) and (b) was 260 K, while that of (c) and (d) was 219 K. The strains in (a) and (c) were obtained by attaching a strain gage, while those in (b) and (d) were obtained by calibrating the movement of the cross-head.

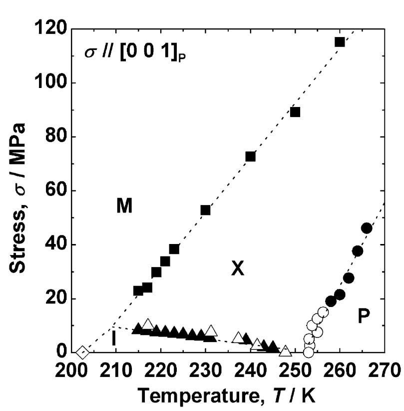


**Figure 1.** Stress-temperature equilibrium phase diagram of stoichiometric $Ni_2MnGa$ under a compressive stress applied in the $[0\,0\,1]_P$ direction. Solid circles, solid triangles and solid squares indicate the equilibrium stresses of the $P \leftrightarrow X$, $I \leftrightarrow X$ and $X \leftrightarrow M$ transformations, respectively, obtained by compressive tests. Open circles, open triangles and an open diamond indicate the equilibrium temperatures of the $P \leftrightarrow X$, $I \leftrightarrow X$ and $I \leftrightarrow M$ transformations, respectively, obtained by magnetic susceptibility measurements.

clearly. This stage starts at $\sigma_{0,P\leftrightarrow X}$, as indicated by an arrow in the mechanical loading process. The unloading process also has only one stage due to the $M \rightarrow X$ transformation, and this stage finishes at $\sigma_{f,P\rightarrow X}$, as indicated by a double arrow. We define the equilibrium stress between the X- and M-phases, $\sigma_{0,X\leftrightarrow M}$, as the average of $\sigma_{s,X\rightarrow M}$ and $\sigma_{f,M\rightarrow X}$. Similar measurements were done at 250 K and the values of $\sigma_{0,X\leftrightarrow M}$ are shown in Figure 1 as solid squares.

In order to determine the equilibrium stress between the I- and X-phases, we made a compressive test by attaching a strain gage. A typical stress–strain curve obtained at 219 K is shown in Figure 2c, where the initial state is the I-phase. The curve has one stage due to the $I \rightarrow X$ transformation, starting at $\sigma_{s,I\rightarrow X}$, as indicated by an arrow in the mechanical loading process. In the unloading process, the curve also has one stage due to the $X \rightarrow I$ transformation, finishing at $\sigma_{f,X\rightarrow I}$, as indicated by a double arrow. Taking the average of $\sigma_{s,I\rightarrow X}$ and $\sigma_{f,X\rightarrow I}$, we define the equilibrium stress between the I- and X-phases, $\sigma_{0,I\leftrightarrow X}$. The values of $\sigma_{0,I\leftrightarrow X}$ thus obtained in the temperature range of $215\ K \leqslant T \leqslant 245\ K$ are shown in Figure 1 as solid triangles.

The X-phase induced from the I-phase described above transforms into the M-phase. That is, successive $I \rightarrow X \rightarrow M$ transformation occurs [9]. Since the strain gage peels off in the high strain region, we measured the stress–strain curves by calibrating the movement of the cross-head. A typical stress–strain curve at 219 K

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