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Pre-martensitic state in Ni–Mn–Ga alloys

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Abstract. The pre-martensitic anomalies observed by elastic, thermal and electron microscopy measurements in the group of Ni–Mn–Ga alloys with $M_s \lesssim 200$ K have been attributed to the formation of the intermediate phase existing in the temperature range 30–60 K above the martensitic transformation temperature. The results are discussed in terms of the soft-mode condensation in this alloy system.

1. Introduction

In recent years the pre-martensitic lattice instability has been the subject of numerous investigations (see, e.g., [1, 2]). The phonon spectrum anomalies of the high-temperature phase in Ni–Al alloys were investigated [1, 2]. The noticeable decrease in frequency ω of the phonon modes with a wavevector $\boldsymbol{q} \parallel \langle 110\rangle$ and polarization vector $\boldsymbol{e} \parallel \langle 110\rangle$ (TA_2 acoustic phonon branch) in the vicinity of the martensitic transformation temperature M_s was detected. The existence of phonon modes with an anomalously low frequency of vibrations (soft modes) is the main reason for the specific intensity distribution of the electron and x-ray diffuse scattering by corresponding crystals at $T \geqslant M_s$. This was shown for the pre-martensitic region in the intermetallic compound Ni_2MnGa [3]. A significant increase in the intensities of the x-ray diffuse maxima during cooling at $T \geqslant M_s$ was observed [3]. These maxima were situated at distances from the main reflections equal to $\tau_{110}/6$ (τ_{110} is the distance between the 110- and 200-type reflections). The same maxima were also observed in the electron diffraction patterns of the high-temperature phase of Ni–Mn–Ga alloys [4]. The very pronounced system of diffuse maxima was interpreted as evidence of the existence of the intermediate phase I in the sense of intermediate between the high-temperature parent phase P and the martensitic phase M [4]. The anomalous softening of the TA_2 phonon mode in the temperature region of the appearance of the aforementioned maxima follows from the phonon spectrum of Ni_2MnGa [5]. This softening is stronger than in Ni–Al alloys.

Thus, at this moment there is information about the appearance of the pre-martensitic state in alloys such as Ni–Al. The basic feature of this pre-martensitic state is the existence of a considerable decrease in the frequency of the thermal vibrations responsible for the consequent crystal lattice rearrangement. It has to be pointed out that according to the theory of the harmonic thermal vibrations of a crystal lattice the decrease in ω is accompanied by an increase in the vibration amplitudes of the appropriate modes. In turn, this can result in some peculiarities of the physical properties of a high-temperature phase at $T \geqslant M_s$.

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The elastic and thermal properties of the parent phase in the pre-martensitic region exhibited by Ni–Mn–Ga alloys are mainly studied in present paper. Data on the structural investigations obtained by low-temperature electron microscopy are presented. The results are discussed in the framework of the concept of soft-mode condensation.

2. Experimental procedure

Several representatives of each of the three groups of Ni–Mn–Ga alloys studied in [6] were subjected to dynamic mechanical tests in a wide temperature interval. The measurements of the dynamic mechanical response of a plate-like sample in the three-point bending configuration were made in a Perkin–Elmer DMA testing machine. Specimens with average dimensions 0.5 mm $\times$ 2 mm $\times$ 10 mm were spark machined from the initial single-crystal and/or polycrystalline ingots. The specimen was placed on two fulcra of the test unit and loaded simultaneously by sinusoidal (with a frequency f) and constant loads. The temperature dependences of the specimen bend and phase angle shift between sinusoidal stress and strain during cooling and heating of unit were registered automatically. The real part of the dynamic elastic modulus, the so-called storage modulus, was obtained by dividing the stress amplitude acting on the layer (subjected to external tension) of a plate, by the amplitude magnitude of the strain of this layer. The mechanical losses $\tan\delta$, proportional to the internal friction (IF), were measured by the angle of the phase shift. The rate of change in temperature, the level of applied stress and the frequency were controlled by a computer software package.

The alloys with $M_s \lesssim 200$ K [6] displayed anomalies in the low-frequency elastic moduli and loss tangent in the pre-martensitic temperature region. Therefore, in this work, typical experimental results for only one representative of this group of alloys are presented. Since the composition of the alloy chosen, namely Ni–24.3 at.% Mn–26.0 at.% Ga, was very close to that of the stoichiometric compound Ni_2MnGa, in the following we shall refer to this compound as Ni_2MnGa. According to [6] this alloy was a single crystal with the temperature of the forward martensitic transformation equal to 175 K and temperature hysteresis of about 15 K. Thermal measurements on Ni_2MnGa were performed by the differential scanning calorimetry and thermal expansion method. A Perkin–Elmer DSC-4 thermoanalyser as well as a more sensitive microcalorimeter were used to record the calorimetric data. The rate of change in temperature and the sample mass were varied in the ranges 2–10 K min^{-1} and 20–80 mg, respectively. A Perkin–Elmer TMA-7 dilatometer was used to measure the dilatometric data. The temperature rate was 10 K min^{-1}. The specimen was a cylinder of 3.68 mm height and 2.5 mm diameter with an axis coinciding with crystallographic direction [100]. The temperature dependences of the electrical resistance and low-field magnetic susceptibility were thoroughly measured in the pre-martensitic region by the AC four-probe and the induction methods, respectively.

Finally, a Hitachi H600 transmission electron microscope equipped with a low-temperature stage was used for structural identification. The foils with the surfaces parallel to (100) and (110) planes were prepared in a double-jet unit filled with a cooled 50:50 electrolytic mixture of nitric acid and methanol. A voltage of 10 V was used.

3. Results

The heating runs of the dynamic mechanical response measurements are presented as an example in figure 1. They were obtained after cooling during which identical curves were

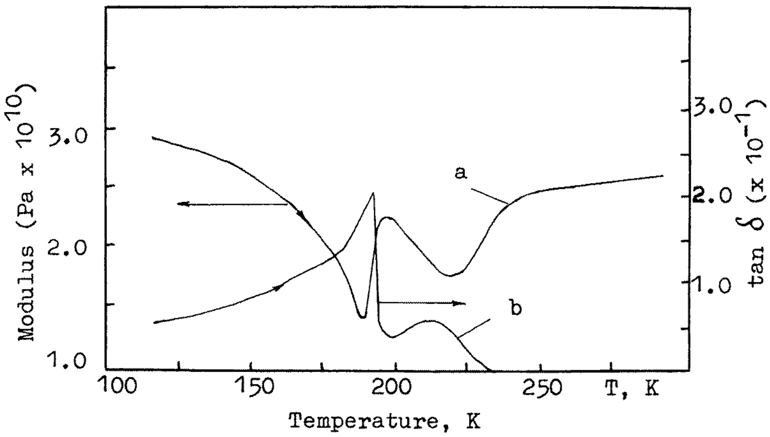

Figure 1. Evolution of modulus (*a*) and (*b*) IF of Ni_2MnGA during heating ($f = 2$ Hz; $\epsilon_0 = 10^{-4}$; $\dot{T} = 5$ K min^{-1}).

obtained. The specimen was loaded in the parent phase in such a way that the amplitude value of strain was equal to about 10^{-4}. It is obvious from figure 1 that the low-frequency elastic modulus decreases linearly from high temperatures, reflecting the increase in the lattice softening, and then exhibits, step by step, two minima of comparable height (curve a) concurrently with two corresponding maxima in the IF (curve b). The anomalies in the dynamic mechanical properties detected in the pre-martensitic region are attributed to a phase transformation into the intermediate phase which, as can be seen in figure 1, is stable over the narrow temperature interval preceding the martensitic transformation. Depending on the alloy composition this temperature interval was 30–60 K. Also similar consequences of the anomalies in the low-frequency modulus and $\tan\delta$ for the B2–R and R–B19′ martensitic transformation observed in Ti–Ni-based alloys [7]. It follows from figure 1 that the IF peak caused by the I–M transition is essentially higher than that for the P–I transformation and this was also so on increase in the load. A load increase caused an enhancement of $\tan\delta$ in the martensitic and intermediate phases. Also, it turned out that, contrary to Cu-based shape memory alloys [8], in the case of Ni_2MnGa the so-called $\dot{T}/f$ contribution to both IF peaks (where $\dot{T}$ is the rate of change in temperature) was equal to about 10% of the total peak heights.

During the mechanical response measurements the thermocouple was not in immediate thermal contact with a specimen. Therefore the linear dependences of the characteristic temperatures of both the P–I and the I–M transformations as functions of $\dot{T}$ were experimentally recorded. The equilibrium values of the temperatures of the forward and reverse transformations were found by extrapolation of the aforementioned dependences to $\dot{T} = 0$. The temperature hysteresis was determined to be equal to about 10 K and 3 K for I $\leftrightarrows$ M and P $\leftrightarrows$ I transformations, respectively.

The temperature behaviour of strain at a constant load (figure 2) shows that the strain accumulation during cooling occurs only at the I $\rightarrow$ M transformation. The symmetric minimum in the parent phase corresponds to the process of significant decrease and increase in the elastic modulus during the P $\rightarrow$ I transformation. It should be noted that the pre-martensitic minimum in the temperature curve of static strain was observed for rod-like specimens having the direction of the layer subjected to external tension in the three-point

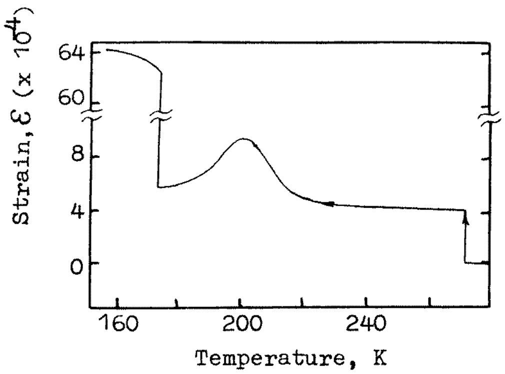

Figure 2. Strain as a function of temperature during cooling of Ni_2MnGa elastically loaded at $T = 300$ K by a stress equal to about 17.6 MPa.

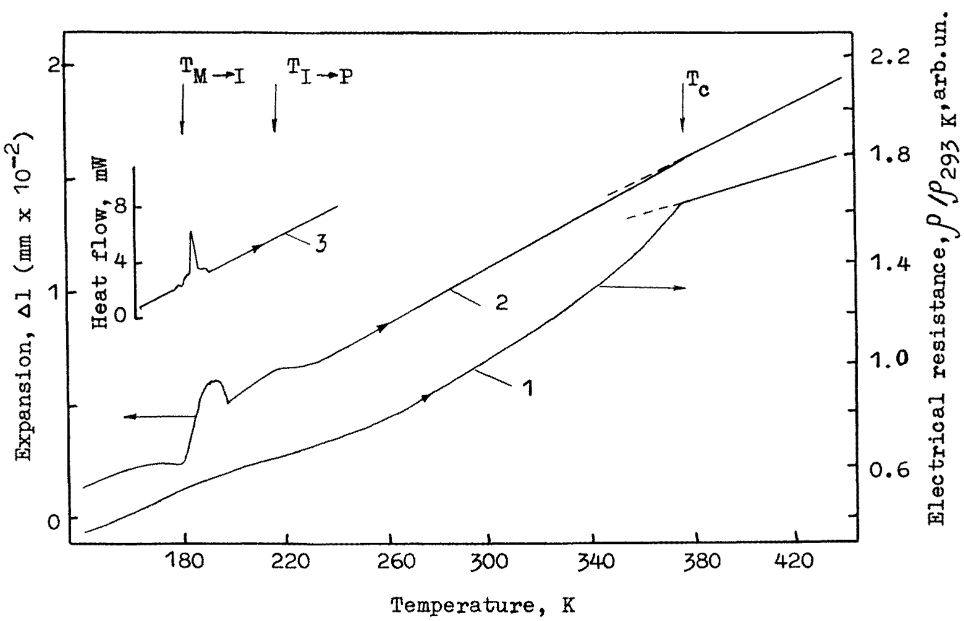

Figure 3. Temperature dependences of the electrical resistance (curve 1) and elongation (curve 2), together with the thermogram (curve 3) of Ni_2MnGa (Curie temperature T_C and temperatures of structural transformations indicated by vertical arrows).

bending test coinciding with the [100] or the [110] crystal axis.

A calorimetric run (figure 3, curve 3) as well as the temperature dependences of electrical resistance (figure 3, curve 1) and low-field magnetic susceptibility do not display any anomalies in the pre-martensitic region. The lack of an anomaly in the resistance curve at the I $\leftrightarrows$ M transformation (figure 3, curve 1) is in agreement with the previous conclusion about this type of alloy [6].

The various magnetic and structural states of Ni_2MnGa can be easily distinguished according to the dilatometric curve (figure 3, curve 2). It is seen from figure 3 that the paramagnetic-to-ferromagnetic transformation at the Curie temperature of about 370 K is accompanied not only by a step-like change in the resistance curve but also by an increase in the thermal expansion coefficient from 13.8×10^{-6} to 18.0×10^{-6} K^{-1}. The linear behaviour of elongation $\Delta 1(T)$ in the ferromagnetic parent phase is replaced by an anomalous increase in $\Delta 1(T)$ at the P $\rightarrow$ I transformation followed by the S-like curvature caused by the I $\rightarrow$ M transformation. According to the Pippard [9] relations establishing the proportionality between the thermal expansion coefficient and heat capacity, one can expect an anomalous change in the true heat capacity at the P–I transformation.

Intense streaking along $\langle 100 \rangle$-type directions was observed in the electron diffraction patterns taken at temperatures above the P $\rightarrow$ I transformation (figure 4(*a*)). During cooling in the electron microscope the streaks were replaced by the individual spots dividing the distance between the basic reflections along the $\langle 110 \rangle$-type directions into six equal parts (figure 4(*b*)). An increase in the intensity of extra spots on approaching the martensitic transformation was observed. An analysis of the electron diffraction patterns from the foils with $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ zone axes results in the conclusion that the cubic symmetry of the lattice of I still remains unchanged.

4. Discussion

It was shown [5] that the dispersion curve $\omega(\boldsymbol{q})$ of the TA_2 $[\eta\eta O]$ mode exhibits a minimum at $\eta_0 = 0.33$; in [5] the $L2_1$ notation was used. Despite the fact that ω does not reach zero [5], the possibility of soft-mode condensation as a result of the first-order transformation can be anticipated. For instance, the free surface can serve as a preferential site for new phase nucleation because the frequencies of surface phonons are always smaller than they are in the bulk [10]. In this case some lattice regions, where the atomic shifts connected with the TA_2 mode are frozen, may be considered as a new phase. The concept of soft-mode condensation can be taken as a basis for the interpretation of the experimental data presented concerning the pre-martensitic behaviour of Ni_2MnGa. In the framework of this concept the evolution of the diffuse intensity distribution during the temperature change can be explained as follows.

As a result of the existence of the TA_2 soft mode in P, dynamic regions of the lattice are formed. In these regions the atoms are displaced from their equilibrium positions in accordance with the given wave and polarization vectors of the above-mentioned vibration mode. The mean lifetime and mean dimensions of these regions increase on approaching the temperature of the P $\rightarrow$ I transformation. Therefore, the intensity of the diffuse maxima indicated by arrows in figure 4(*a*) is increasing concurrently with their width decrease. Finally, at the temperature corresponding to the P $\rightarrow$ I transformation the size and life-time of the above-mentioned regions become infinite and the system of extra reflections is formed (figure 4(*b*)).

Taking into account that ω for a soft mode decreases on approaching the temperature of the P $\rightarrow$ I transformation [5], let us consider the influence of mode softening on mean square atomic displacements. The expression $|u\boldsymbol{q}|^2 \approx kT/NM\omega^2(\boldsymbol{q})$ is valid (see, e.g., [11]), where $|u\boldsymbol{q}|^2$ is the contribution to the mean square atom displacements to account for the phonon with wavevector $\boldsymbol{q}$ and frequency ω, N is the number of atoms with mass M and k is the Boltzmann constant (in this case $\hbar\omega \ll kT$). It is obvious from the above expression that the contribution of the vibrations with $q \neq 0$ and $\omega \rightarrow 0$ will dominate. Hence, at temperatures where the minimal values of ω of the TA_2 mode occur, the amplitudes of atomic thermal vibrations will be enhanced, which results in some increase in the interatomic distances due to anharmonism. As a result a minimum-like anomaly on the dilatometric

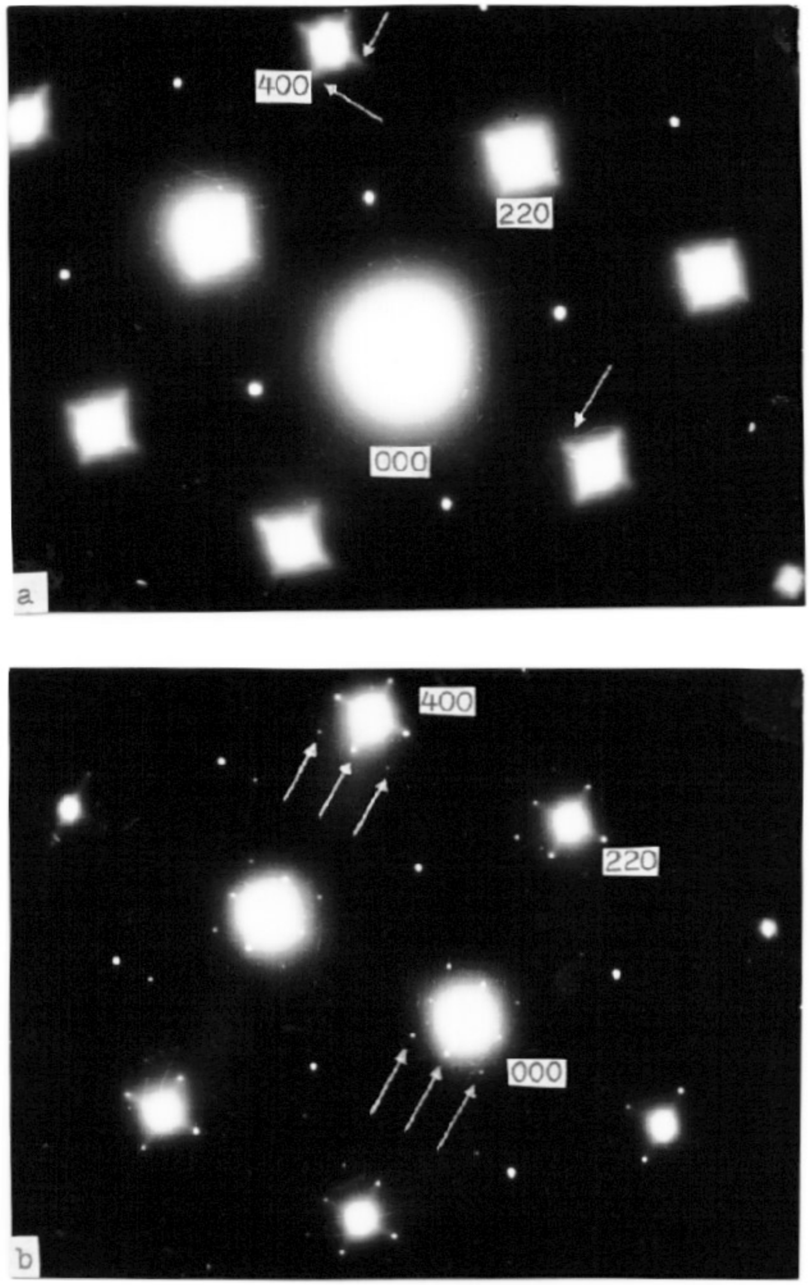

Figure 4. *In-situ* electron diffraction patterns for thin foils of Ni_2MnGa at different temperatures: (a) zone axis $[100]_P$, $T = 300$ K; (b) zone axis $[100]_P$, $T = 195$ K.

curve 2 (figure 3) corresponding to a soft-mode condensation at the P $\rightarrow$ I transformation is observed. Moreover the elastic modulus decrease during the P $\rightarrow$ I transformation (figure 1(a) and figure 2) can also be explained by the lattice parameter increase.

The temperature dependence of the IF is characterized by a maximum in the pre-martensitic region (figure 1(*b*)). An increase in $\tan\delta$ at the P–I transformation could be caused by the appearance of the new domain boundaries during formation of I with a triple lattice parameter of sixfold lattice parameter in BCC notation for the crystal structure of the initial phase. The displacements of these boundaries in the field of alternative mechanical stresses are associated with an energy dissipation, a measure of which is the IF. The origin of these 'ghost' boundaries at this moment is obscure. We failed to find them in the dark-field images observable in extra reflections of I. The lack of any anomaly related to the P–I transformation in the resistance (figure 2, curve 1) and low-field magnetic susceptibility dependences implies that this kind of boundary cannot serve as an effective hindrance for electrons and moving magnetic domain boundaries. These mobile 'ghost' boundaries causing a non-zero value of $\tan\delta$ at some stress level can serve as evidence of the first-order character of the P–I transformation, at least at a definite level of mechanical stresses. The small temperature hysteresis found in dynamic mechanical tests supports this idea. The question is open whether we address another macroscopic characteristic measured without applying stress. According to the dilatometric and calorimetric measurements we could not detect a discontinuous change in elongation or any latent heat which usually accompanies first-order transformations. The precise adiabatic measurements of the true heat capacity could actually throw some light on this problem.

5. Conclusions

We have performed investigations of the structural and physical properties of the pre-martensitic state which is realized in low-temperature Ni–Mn–Ga alloys. This state is interpreted as an intermediate phase which precedes the martensitic transformation and is a result of a condensation of the Ta_2 soft mode with $q \neq 0$. This kind of mode condensation is assumed to manifest itself through the volume increase of the lattice cell of the initial cubic high-temperature phase. The minima of the thermal expansion coefficient and elastic modulus at the P–I transformation are associated with the anomalous increase in the mean square displacements of atoms at temperatures where the TA_2 soft-mode frequency is anomalously small.

Acknowledgments

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