Premartensitic Transition in Ni$_{2+x}$Mn$_{1-x}$Ga Heusler Alloys

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The temperature dependencies of the resistivity and magnetization of a series of Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.09$) alloys were investigated. Along with the anomalies associated with ferromagnetic and martensitic transitions, well-defined anomalies were observed at the temperature of premartensitic transformation. The premartensitic phase existing in a temperature range 200 – 260 K in the stoichiometric Ni$_2$MnGa is progressively suppressed by the martensitic phase with increasing Ni content and vanishes in Ni$_{2.09}$Mn$_{0.91}$Ga composition.

In Ni$_2$MnGa, like in many other Heusler alloys containing manganese, the indirect exchange interaction between magnetic ions results in ferromagnetism which is usually described in terms of the local magnetic moment at the Mn site. For the stoichiometric Ni$_2$MnGa a structural transition of the martensitic type from the parent cubic to a complex tetragonally based structure occurs at $T_M = 202$ K while ferromagnetic ordering sets at $T_C = 376$ K. The martensitic transition temperature $T_M$ was found to be sensitive to the composition, and values of $T_M$ between 175 and 450 K have been reported. A specific feature of the Ni-Mn-Ga system is that in alloys with a high $T_M (> 270$ K) a number of intermartensite transformations can be induced by an external stress, whereas in most alloys with lower $T_M$ the martensitic transition is preceded by a weakly first order premartensitic phase transition.

The inelastic neutron scattering experiments performed on stoichiometric Ni$_2$MnGa showed the existence of a soft [\(\xi(0)\)TA$_2$] phonon mode in a wide temperature interval, which is common to martensitic alloys having bcc structure. An important observation in these measurements was that the TA$_2$ phonon branch at a wave vector of $\xi_0 \approx 0.33$ incompletely condenses at the premartensitic transition $T_P \approx 260$ K, well above the martensitic transition $T_M = 220$ K. On cooling from $T_P$ to $T_M$ the frequency of the soft mode increases. This would suggest that the soft mode formation is associated with the premartensitic phase transformation rather than with the martensitic one. By transmission electron microscopy observation it was established that the premartensitic phase consists in a micromodulated "tweed" structure without macroscopic tetragonal distortions so that the parent cubic symmetry is preserved. The modulation of the premartensitic phase was found to correspond to the wave vector $\xi_0 \approx 0.33$.

It is necessary to stress that although no premartensitic transition was found in compositions with high $T_M$, the precursor phenomenon (softening of the [\(\xi(0)\)TA$_2$] phonon branch at the wave vector $\xi_0 \approx 0.33$) has been clearly observed by inelastic neutron scattering. Except for the partial condensation of the TA$_2$ phonon branch observed by Zheludev et al., the only essential difference between the inelastic neutron scattering results performed on three samples of different stoichiometry is that the width in $\xi$ where softening occurs becomes broader as $T_M$ increases.

At the present the reason why the premartensitic transition is observed only in the alloys with $T_M \leq 260$ K seems to be unclear. There is strong evidence that the magneto-elastic interaction plays a crucial role in the formation of the premartensitic phase. Also, the theoretical investigation predicts that the premartensitic transition is observed only in the case of large values of the magneto-elastic coupling parameter. From the results of magnetic and transport measurements of several near-stoichiometric Ni$_{2-x}$Mn$_{1+x}$Ga samples it can be concluded that the premartensitic transition is less sensitive to the change of composition than the martensitic one. This gives ground to suggest that a deviation from the stoichiometry can lead to the disappearance of the premartensitic transition in some critical composition.

The importance of the conduction electron density in stabilizing the Heusler structure was noted a long ago and, in particular, it was suggested that the structure is stabilized because the Fermi surface touches the Brillouin zone boundary. From this point of view a partial substitution of Mn for Ni in Ni$_{2+x}$Mn$_{1-x}$Ga alloys resulting in an increase of the conduction electron density should increase the martensitic transition temperature. This makes it possible to determine the compositional dependencies of $T_M$ and $T_P$. For this purpose we have studied temperature dependencies of electrical resistivity and magnetization in Ni$_{2-x}$Mn$_{1+x}$Ga alloys in which Mn is partially substituted for Ni in the range of $x = 0 - 0.09$.

The polycrystalline Ni$_{2+x}$Mn$_{1-x}$Ga ingots were prepared by a conventional arc-melting method in Ar atmosphere. The ingots were homogenized in vacuum at 1100 K for 9 days and slowly cooled to room temperature. Room temperature X-ray diffraction showed single-phase cubic structure of the alloys. The samples for the resistivity and magnetization measurements were spark cut from the ingots and were of 0.6 $\times$ 1 $\times$ 6 mm$^3$ dimensions. The electrical
resistivity was measured in a temperature range 100 – 450 K by ac four-terminal method. Magnetic measurements were done by a SQUID magnetometer.

The temperature dependencies of resistivity $\rho$ measured at cooling in Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.09$) samples are shown in Fig. 1. Except for the Ni$_{2.09}$Mn$_{0.91}$Ga composition, the $\rho(T)$ dependencies in the other samples exhibit three well-defined anomalies at temperatures corresponding to the ferromagnetic ($T_C$), premartensitic ($T_P$) and martensitic ($T_M$) transitions. With deviation from the stoichiometry the change in a slope of the resistivity curve related to the ferromagnetic transition shifts to lower temperatures, and the jump-like behavior of $\rho$ related to the martensitic transformation shifts to higher temperatures. This decrease of $T_C$ and increase of $T_M$ with increasing Ni content is in good agreement with $\rho(T)$ measured at cooling in Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.04$) samples. It is also interesting to compare the behavior of the resistivity at $T_M$ and $T_P$ measured at heating and cooling for Ni$_{2.04}$Mn$_{0.96}$Ga and Ni$_{2.08}$Mn$_{0.92}$Ga (Fig. 3). In the case of Ni$_{2.04}$Mn$_{0.96}$Ga, the resistivity shows a significant temperature hysteresis at $T_M$ whereas the temperature hysteresis at $T_P$ is small, which is in agreement with published results. In the Ni$_{2.08}$Mn$_{0.92}$Ga sample the two-step-like anomaly observed at cooling completely disappears upon warming up and the resistivity smoothly decreases down to the extreme value. Moreover, the hysteretic feature seen in the upper part gradually narrows and vanishes in the down part. This testifies that the observed two-step-like behavior of the resistivity is not a peculiar feature of the martensitic transition in the $x = 0.06 - 0.08$ samples but is the outcome of simultaneously occurring premartensitic and martensitic transitions.

The anomaly of resistivity corresponding to $T_P$ had been completely taken up by the martensitic phase for the highest Ni composition in the series, Ni$_{2.09}$Mn$_{0.91}$Ga, and resistivity shows only two anomalies corresponding to the ferromagnetic and martensitic phase transitions (Fig. 1). In our opinion, these findings are consistent with the absence of the premartensitic transition in Ni-Mn-Ga alloys with a high $T_M$ temperature.

The temperature dependencies of magnetization $M$ measured in a 100 Oe magnetic field also showed clear anomalies at $T_P$ in the $x = 0 - 0.04$ samples. However, such anomalies were not observed, neither upon cooling nor upon heating, in the $x = 0.06 - 0.08$ samples. Actually, the absence of them upon warming up agrees with the corresponding resistivity data. Since in the $x = 0.06 - 0.08$ samples the martensitic and premartensitic transitions are merged, the related to $T_P$ anomalies of $M$ are not observed upon cooling probably because they are masked by the drastic decrease of $M$ occurring upon the martensitic transformation. An example of $M(T)$ dependence for the compositions with separated $T_P$ and $T_M$ is shown in Fig. 4. $M(T)$ revealed a pronounced dip in magnetization of the sample at $T_P$. The drastic decrease in magnetization at $\approx 227$ K, shown in the inset of Fig. 4, is common for transformations from ferromagnetic martensite to ferromagnetic austenite in Ni-Mn-Ga alloys and will be not discussed here. The temperature of the premartensitic transition $T_P$ is equal to 262 K, which is in excellent agreement with the corresponding resistivity data. Instead of a smooth diminution of the magnetization at $T_M$, the premartensitic transition is attended by a complicated behavior of the magnetization. The rapid decrease of magnetization in the temperature interval from 268 to 262 K can be a consequence of the freezing of the atomic displacements related to the soft $\frac{1}{4}[110]$ phonon mode. In this case the appearance of modulations of the cubic phase results in an increase of magnetic anisotropy which explains the drop of magnetization. The upturn in magnetization at temperatures below $T_P = 262$ K is due presumably to the ordering of the premartensitic phase. This suggestion is consistent with the evolution of the Bragg peak at $q = (\frac{1}{4} + 0)$ (Ref. 9) and the results of ultrasonic measurements, which clearly demonstrated that the premartensitic phase becomes fully developed and ordered at temperatures below $T_P$.

The martensitic transformation in Ni$_{2+x}$Mn$_{1-x}$Ga alloys is believed to occur due to the contact between the Fermi surface and a Brillouin zone boundary. In this sense the compositional dependence of $T_M$ in Ni$_{2+x}$Mn$_{1-x}$Ga can be understood as resulting from a change of the Fermi energy due to the increase in the conduction electrons concentration upon substitution of Mn for Ni. On other hand, it has been suggested that the origin of the premartensitic transition lies in specific nesting features of the multiply connected Fermi surface. The effect of uniaxial stress on the anomalous phonon branch in Ni$_2$MnGa results in the shifting of the phonon anomaly and the premartensitic transition temperature $T_P$ to higher $q$-values and temperatures. External stress can actually change the geometry.
of the Fermi surface and modifies the nesting vector. The fact that $T_P$ does not depend on $x$ in Ni$_{2+x}$Mn$_{1-x}$Ga alloys means presumably that the increase in the conduction electrons concentration does not affect significantly this particular part of the Fermi surface.

Summarizing our speculation about the compositional dependence of the martensitic and premartensitic phase transitions, we argue that the premartensitic phase is suppressed by the martensitic phase with deviation from the stoichiometry in Ni$_{2+x}$Mn$_{1-x}$Ga alloys. The premartensitic transition couples with the martensitic transition in the range of $x$ from 0.06 to 0.08 and completely vanishes at 264 K in the critical composition $x = 0.09$ of Ni$_{2+x}$Mn$_{1-x}$Ga alloys. However, we do not rule out the possibility that the premartensitic transition gives rise to an intermartensitic transition in alloys with higher Ni content. Actually, such a possibility has been mentioned in 17, where the authors analyze data collected from the literature for a broad range of Ni-Mn-Ga compositions. From this point of view it is also worth mentioning that in a simpler classification the experimentally observed modulations of the martensitic phase in Ni-Mn-Ga alloys correlate with the temperature of martensitic transition $T_M$ as follows: 5-layered martensite is observed in alloys with $T_M < 270$ K, whereas alloys with $T_M > 270$ K exhibit 7- or 10-layered martensitic structures. This characteristic martensitic transition temperature $T_M = 270$ K where the modulation of the martensitic phase changes from 5 to 7 (or 10) layers accords well with the critical temperature $T_P = 264$ K at which the premartensitic phase vanishes.

Very recently [3] a phenomenological theory of structural and magnetic phase transitions in Ni$_{2+x}$Mn$_{1-x}$Ga alloys which takes into account strain, crystal lattice modulation, magnetic order parameter and interaction between these subsystems has been developed. It has been shown that the addition of an order parameter $\psi$ accounting for the crystal lattice modulation of the premartensitic phase to the general expression of the free energy [3] leads to an intermartensitic transition. On the compositional phase diagram this transition results from an extension of the line of the premartensitic transition into martensitic phase. The results of numerical calculations indicate that the premartensitic transition temperature as a function of concentration in Ni$_{2+x}$Mn$_{1-x}$Ga alloys intersects the line of the martensitic phase transition at $x \sim 0.11$. This agrees fairly well with the experimental value $x = 0.09$.

In conclusion, the most novel and significant findings of our experiments are that the premartensitic phase is progressively suppressed by the martensitic phase until it completely vanishes in the critical composition Ni$_{2.09}$Mn$_{0.91}$Ga at 264 K. If the suggested features of the Fermi surface indeed are responsible for $T_M$ and $T_P$, this means that the increase in the conduction electrons density does not modify the nesting vector and affects mainly the Fermi energy.

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FIG. 1. Temperature dependencies of electrical resistivity in Ni$_{2+x}$Mn$_{1-x}$Ga (x = 0 – 0.09).

FIG. 2. Temperatures of ferromagnetic ($T_C$), premartensitic ($T_P$) and martensitic ($T_M$) phase transitions as a function of Ni content in the Ni$_{2+x}$Mn$_{1-x}$Ga alloys.

FIG. 3. Features of $\rho(T)$ at martensitic and premartensitic transitions in Ni$_{2.04}$Mn$_{0.96}$Ga and Ni$_{2.08}$Mn$_{0.92}$Ga upon cooling and heating.

FIG. 4. Temperature dependence of magnetization $M$ in Ni$_{2.02}$Mn$_{0.98}$Ga in the vicinity of the premartensitic transition. The inset shows $M(T)$ in the entire temperature interval.
1 - \( \text{Ni}_2\text{MnGa} \)
2 - \( \text{Ni}_{2.02}\text{Mn}_{0.98}\text{Ga} \)
3 - \( \text{Ni}_{2.04}\text{Mn}_{0.96}\text{Ga} \)
4 - \( \text{Ni}_{2.06}\text{Mn}_{0.94}\text{Ga} \)
5 - \( \text{Ni}_{2.09}\text{Mn}_{0.91}\text{Ga} \)

\( \rho \), relative units

T, K
The graph shows the variation of temperature $T$, in Kelvin (K), with Ni content. The different markers and lines represent:
- $T_M$ (triangles)
- $T_P$ (inverted triangles)
- $T_C$ (circles)

The temperature $T$ decreases as the Ni content increases, with $T_M$ decreasing the most, followed by $T_P$, and $T_C$ increasing slightly with increasing Ni content.
1 - \( \text{Ni}_{2.04}\text{Mn}_{0.96}\text{Ga} \)

2 - \( \text{Ni}_{2.08}\text{Mn}_{0.92}\text{Ga} \)
Ni$_{2.02}$Mn$_{0.98}$Ga
cooling down
100 Oe