Influence of intermartensitic transitions on transport properties of Ni_{2,16}Mn_{0.84}Ga alloy

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Magnetic, transport, and x-ray diffraction measurements of ferromagnetic shape memory alloy Ni_{2,16}Mn_{0.84}Ga revealed that this alloy undergoes an intermartensitic transition upon cooling, whereas no such a transition is observed upon subsequent heating. The difference in the modulation of the martensite forming upon cooling from the high-temperature austenitic state [5-layered (5M) martensite], and the martensite forming upon the intermartensitic transition [7-layered (7M) martensite] strongly affects the magnetic and transport properties of the alloy and results in a large thermal hysteresis of the resistivity $\rho$ and magnetization $M$. The intermartensitic transition has an especially marked influence on the transport properties, as is evident from a large difference in the resistivity of the 5M and 7M martensite, $(\rho_{5M} - \rho_{7M})/\rho_{5M} \approx 15\%$, which is larger than the jump of resistivity at the martensitic transition from the cubic austenitic phase to the monoclinic 5M martensitic phase. We assume that this significant difference in $\rho$ between the martensitic phases is accounted for by nesting features of the Fermi surface. It is also suggested that the nesting hypothesis can explain the uncommon behavior of the resistivity at the martensitic transition, observed in stoichiometric and near-stoichiometric Ni-Mn-Ga alloys.

I. INTRODUCTION

Intermetallic compounds undergoing thermoelastic martensitic transformation when in the ferromagnetic state (ferromagnetic shape memory alloys) have attracted considerable interest (see, for a recent review, Ref. [3]). This is due to the fact that they exhibit large magnetic-field-induced strains which can be obtained either by re-orientation of martensitic variants, or by shifting the martensitic transition temperature. In addition to this effect of practical significance, the ferromagnetic-field-induced strains which can be obtained either by re-orientation of martensitic variants, or by shifting the martensitic transition temperature. In particular, some of these alloys exhibit several phase transitions between different crystallographic modifications of martensite, induced by a change of composition, temperature or stress, or by the combination of these parameters.

A prototype of the ferromagnetic shape memory alloys, Ni$_2$MnGa, is a representative of Mn-containing Heusler alloys. It orders ferromagnetically at Curie temperature $T_C = 376$ K. Upon cooling down to $T_m = 202$ K it undergoes a reversible thermoelastic martensitic transformation from the Heusler (L2$_1$) cubic structure to a roughly tetragonal crystal structure. Both $T_m$ and $T_C$ are sensitive to stoichiometry. For instance, a partial substitution of Mn for Ni in Ni$_{2+x}$Mn$_{1-x}$Ga alloys results in an increase in $T_m$ and a decrease of $T_C$ until they couple in a composition range $x = 0.18 \rightarrow 0.20$ (Ref. [6]).

An early neutron diffraction study of the martensitic structure of stoichiometric Ni$_2$MnGa showed that along with strong tetragonal reflections there were several additional peaks on the diffraction pattern. Based on this observation, the authors suggested that the martensitic phase has a modulated crystal structure. Further studies revealed that modulation and, therefore, the crystal structure of the martensite forming from the parent austenitic phase, depends on composition (Ref. [5] and references therein). By now, five- and seven-layered martensitic phases modulated along the (110)[110] system and a non-modulated martensitic phase have been established to exist in Ni-Mn-Ga alloys. In addition, the observation of longer-period modulations of the martensite has been reported.

The crystal structure of martensite was found to be very unstable to the application of external stresses. It turned out that the sequence of stress-induced martensite-martensite transformations depends on many factors, such as the composition of the sample, temperature of the test, and the crystallographic direction along which the stress was applied. Besides composition- or stress-induced changes in the crystal structure of martensite, some off-stoichiometric Ni-Mn-Ga alloys undergo a sequence of temperature-induced martensite-martensite phase transitions. Apart from Ni-Ti (Ref. [13] and references therein) and Ni$_{50}$Mn$_{50-x}$Al$_x$ (Ref. [10]) systems, temperature-induced intermartensitic transitions have not been observed in other shape memory alloys.

In Ni-Mn-Ga intermartensitic transitions are, as evident from calorimetric measurements, first-order phase transitions. As compared with the martensitic transformation, the intermartensitic transitions exhibit several distinctive features. They are a large, exceeding 100 K, temperature hysteresis and a considerable difference in transport properties between the martensitic phases involved in an intermartensitic transition. Transport measurements of Ni-Mn-Ga alloys undergoing intermartensitic transitions [16,17,21,22,23] have indicated that the difference in the
resistivity between martensitic phases is comparable or even larger than that observed at the martensitic transformation temperature. This seems to be unusual because martensitic transformation has a stronger influence on the physical characteristics (crystal structure, Fermi surface, magnetic properties) of the materials.

Since these features of intermartensitic transitions have not been discussed earlier we have studied and analyzed the transport properties of Ni$_{2.16}$Mn$_{0.84}$Ga undergoing an intermartensitic transition. In our study we have also used a stoichiometric Ni$_{2}$MnGa sample, prepared by the same method as Ni$_{2.16}$Mn$_{0.84}$Ga.

### II. EXPERIMENTAL

A polycrystalline ingot of Ni$_{2.16}$Mn$_{0.84}$Ga composition was prepared by arc melting high purity constituent elements in argon atmosphere. In order to get a good compositional homogeneity, the ingot was re-melted several times and annealed at 1050 K for nine days with subsequent quenching in ice water. Samples for resistivity and magnetization measurements were cut from the middle part of the ingot. Temperature dependencies of resistivity and magnetization were measured with a heating/cooling rate of 1 K/min by a standard four-probe technique and by a vibrating sample magnetometer, respectively. The crystal structure of the alloy was examined using a Philips X-Pert system in a wide temperature interval. For the powder x-ray diffraction measurements, part of the ingot was crushed into a fine powder. The powder was sealed in an evacuated quartz tube and annealed at 1050 K for five days in order to remove residual stress and improve the peak shape of diffraction patterns.

### III. EXPERIMENTAL RESULTS

The temperature dependencies of electrical resistivity of Ni$_{2.16}$Mn$_{0.84}$Ga, measured upon cooling and heating, are shown in Fig. 1. Cooling from high temperatures results in the formation of a long-range ferromagnetic ordering at $T_C = 337$ K which is accompanied by a change in the slope of the resistivity curve due to the decrease in electron-magnon scattering. The jump-like increase of the resistivity at $T_m = 340$ K corresponds to the transition from the high-temperature austenitic to a low-temperature martensitic phase.

Besides the change in the slope of the curve at $T_C = 337$ K and the jump-like increase of $\rho$ at $T_m = 309$ K, one more marked change in the slope of the cooling curve is observed at $T_I = 283$ K. Since this anomaly is observed when the sample is in the martensitic state, this means that a martensite-martensite transformation occurs in Ni$_{2.16}$Mn$_{0.84}$Ga. Based on the results of transmission electron microscopy (TEM) observation of a sample of this composition, which revealed that the crystal structure of martensite in Ni$_{2.16}$Mn$_{0.84}$Ga is characterized by a five-layered modulation (5M) at room temperature and seven-layered modulation (7M) at $T = 173$ K, we conclude that the anomaly of $\rho$ at $T_I = 283$ K corresponds to the onset of intermartensitic transition from a five- to seven-layered martensite (5M $\rightarrow$ 7M).

The transition from the high-temperature austenite to a low-temperature martensitic phase.

Subsequent heating revealed a monotonous increase of the resistivity up to the reverse martensitic transformation temperature.

Since the 5M $\rightarrow$ 7M intermartensitic transition is not completed in the studied temperature interval and because of the absence of the reverse 7M $\rightarrow$ 5M intermartensitic transition upon subsequent heating, the resistivity exhibits very large thermal hysteresis. At temperatures below the martensitic transformation, the heating curve deviates from the curve measured upon cooling, and the difference between $\rho$ measured upon cooling and heating progressively increases as the temperature is increased (inset in Fig. 1). Assuming for simplicity that at $T = 100$ K there exists only a tiny frac-
The anomaly of
from the 7M martensite to the parent phase (Fig. 1). If
up when approaching reverse martensitic transformation
during direct martensitic transformation from the par-
tic transformation measured upon cooling and heating
is quite different. Whereas
sitic transformation measured upon cooling and heating
at martensitic transformation tempera-
ture, determined from the magnetization measure-
magnetic field magnetization of the 5M martensitic phase
is lower than that of the 7M phase and the difference be-
martensite. Note that in this case the heating curve is
parallel to the cooling curve, indicating that the two-
state and the sample remains in the 5M martensitic state
upon subsequent heating.

Finally, when the sample is cooled down to \( T = 269 \) K,
the resistivity upon subsequent heating exhibits behavior,
typical of the 7M martensitic phase [Fig. 2(c)], and
\( \rho \) shows a small kink at the martensitic transformation
temperature. In a temperature interval from 283 K to
309 K, the difference in \( \rho \) between heating and cool-
ing curves is \( \approx 12\% \), indicating that approximately 80%
of the 7M martensite had been formed upon cooling to
269 K. Based on the results presented in Fig. 2 one can
conclude that the 7M martensite appears upon cooling
below \( T_I = 283 \) K and the fraction of this martensitic phase considerably exceeds that of the 5M martensitic
phase at \( T < 270 \) K.

The magnetization \( M \) of Ni\(_{2.16}\)Mn\(_{0.84}\)Ga measured in
a 0.1 T magnetic field is shown in Fig. 3. The Curie tem-
perature, determined from this measurement, is equal to
340 K (inset in Fig. 3). The anomaly at \( \approx 310 \) K, ex-
hibiting a temperature hysteresis of \( \approx 6 \) K, corresponds
to the martensitic transformation. Like the resistivity,
the magnetization of the sample shows a large thermal
hysteresis in the martensitic state. A well-defined change
in the slope of the \( M(T) \) curve measured upon cooling at
\( T = 279 \) K corresponds to the onset of the intermarten-
sitic transition to the 7M phase. This characteristic tem-
perature, determined from the magnetization measure-
ments, is slightly lower than that obtained from the re-
sistivity data. This difference can be accounted for by the
fact that \( M(T) \) and \( \rho(T) \) measurements were performed
on different samples. As is seen from Fig. 3, in the 0.1 T
magnetic field magnetization of the 5M martensitic phase
is lower than that of the 7M phase and the difference be-
tween them gradually diminishes as the temperature is
lowered.

The thermal hysteresis of \( M \) is observed only in low
the measured diffraction pattern corresponds to the 5M martensite, the powder was heated above the martensitic transformation temperature $T_m$ and the measurement was performed on the powder cooled to room temperature from the austenitic state. Preliminary analysis of the room temperature diffraction pattern of Ni$_{2.16}$Mn$_{0.84}$Ga showed that the crystal structure of the martensite formed upon cooling from the austenitic phase can be interpreted as a monoclinic one with lattice parameters $a = 0.42$ nm, $b = 0.55$ nm, $c = 2.10$ nm, and $\beta = 92^\circ$.

X-ray diffraction measurement at a lower temperature, $T = 77$ K, confirmed the occurrence of the intermartensitic transition, seen on the $\rho(T)$ and $M(T)$ curves. The crystal structure of the 7M martensitic phase was interpreted as monoclinic with lattice parameters $a = 0.426$ nm, $b = 0.543$ nm, $c = 2.954$ nm, and $\beta = 94.3^\circ$. Further cooling down to $T = 10$ K did not result in a change of the diffraction pattern observed at $T = 77$ K. The results of these measurements are shown on an enlarged scale in Fig. 5.

### IV. DISCUSSION

The results of our resistivity measurements (Fig. 1) indicate that different martensitic phases are considerably distinguished by their transport properties, namely $\rho_M$ is larger than $\rho_M$ by 15%. Generally, this difference can be caused by two factors: by changes in the scattering probability and/or by changes in the electronic structure. Since both the phases exhibit similar plate-like morphology, we suggest that the 15% difference in the resistivity of these phases cannot be accounted for by an increase in the scattering centers. Therefore, the origin of this difference has to be looked for in the Fermi surface features. Indeed, it is generally acknowledged that the formation of a long-range ordering observed in a large number of compounds is associated with the nesting properties of the Fermi surface. This is true as for the case of long-range structural ordering, as for the case of long-range magnetic ordering, such as spin- or charge-density waves. The periodicity of long-range ordering is determined by the nesting vector on the Fermi surface.

It is conceivable that the various martensitic phases forming in Ni-Mn-Ga alloys are driven by the geometry of the Fermi surface that has a nesting vector corresponding to the modulation of martensite, as was suggested in. This suggestion implies that martensitic phases with different nesting vectors have different fractions of nested Fermi surface. On the other hand, it is well known that the nesting considerably affects the transport properties of a metal due to the condensation of electrons in the nesting parts of the Fermi surface. Therefore, change in the modulation can affect the number of conduction electrons $n_{eq}$ due to the change of the Fermi surface available for conduction.

In the simple relaxation time approximation

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**FIG. 3:** Temperature dependencies of the magnetization of Ni$_{2.16}$Mn$_{0.84}$Ga measured in a 0.1 T magnetic field. The inset shows $M(T)$ over the entire temperature interval.

**FIG. 4:** X-ray diffraction pattern of the 5M martensitic phase of Ni$_{2.16}$Mn$_{0.84}$Ga forming upon cooling from the high-temperature austenitic phase.
of the conduction electrons in the nesting part of Fermi surface. Assuming that without the premartensitic transition, the premartensitic transition temperature increases or decreases, depending on composition, the martensitic transformation temperature increases or decreases, depending on substitution, whereas the $T_P$ temperature is less composition dependent. In the case of increasing...
$T_m$ this leads to the disappearance of the premartensitic transition in a critical composition and, as a result, in off-stoichiometric Ni-Mn-Ga alloys a marked jump-like behavior of $\rho$ is observed.

V. CONCLUSION

Temperature-induced intermartensitic transitions observed in certain Ni-Mn-Ga alloys give rise to an anomalously large thermal hysteresis of magnetic and transport properties, which is not observed in other compounds. This thermal hysteresis is accounted for by the coexistence of both martensitic phases in a wide temperature interval. As is evident from the resistivity measurements of $\text{Ni}_2\text{Mn}_{0.84}\text{Ga}$, the difference in $\rho$ between 5M and 7M martensite is about 15%, which is even larger than that observed upon the martensitic transformation. We have suggested that such a significant difference is accounted for by the geometry of the Fermi surface that has a different nesting vector in 5M and 7M martensitic phases. If this assumption is valid, an anisotropic behavior of $\rho$ in a Ni-Mn-Ga single crystal of the same or similar composition can be reasonably expected. Therefore, further studies of single crystalline samples are required for better understanding structural instability of various martensitic phases in Ni-Mn-Ga alloys.

In the framework of the nesting hypothesis we have also discussed the peculiar behavior of $\rho$ at the martensitic transformation temperature $T_m$ in stoichiometric $\text{Ni}_2\text{Mn}_2\text{Ga}$. We have argued that this behavior of $\rho$ is caused by the condensation of conduction electrons in the nesting part of the Fermi surface occurring upon the premartensitic transition.

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