Martensitic transformation and magnetotransport properties of Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy

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Abstract. The structure, electrical and magnetic properties of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy, in which the temperature of the martensitic transformation is close to room temperature and practically coincides with the Curie temperature of austenite, have been investigated. The martensitic transformation in the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy proceeds with the formation of modulated martensite type 14M. It has been established that the spontaneous transformation from martensite to austenite is accompanied by a decrease in the specific resistance of 45%. In the martensitic transformation induced by a magnetic field of 18 kOe, a negative magnetoresistance is observed, reaching \(\sim 15\)%.

1. Introduction

Ferromagnetic Heusler alloys with martensitic transformation represent a special class of materials in which there is a magnetically controlled shape memory effect, giant magnetostriiction, magnetoresistance, magnetocaloric effect and other properties and effects [1-6]. Heusler alloys based on Ni – Mn – X ternary systems (X = In, Sn, Sb) can be distinguished into a separate group of materials [1]. When the temperature in the Ni-Mn-X alloys of stoichiometric composition changes, only the magnetic phase transition from the ferromagnetic to the paramagnetic state is observed, for example in the alloy Ni\textsubscript{50}Mn\textsubscript{25}In\textsubscript{25} (Ni\textsubscript{2}MnIn) [7]. However, in Ni-Mn-In alloys of non-stoichiometric compositions with changes in temperature or element concentration, a more complex sequence of phase transformations is observed, which includes not only magnetic, but also structural (martensitic) phase transitions [2, 8]. As a result of the magnetostructural transition in non-stoichiometric Ni-Mn-In Heusler alloys, a significant change in magnetization is observed under the influence of temperature or magnetic field [5, 9, 10]. This change in magnetization is responsible for such material properties as magnetoresistance, shape memory effect, Hall effect, reverse magnetocaloric effect [11–16].

The study of the features of martensitic and magnetic transitions of Ni-Mn-In Heusler alloys is of interest to clarify the effect of structural transformations and magnetic ordering on functional characteristics and physical properties. Further studies are important for understanding the role of various factors affecting the behavior of Heusler alloys of similar chemical composition with an optimal microstructure under external influences, as well as from the point of view of their applicability in relatively simple and high-tech areas of modern technology.

This paper presents the results of studies of the structure and properties of the three-component ferromagnetic alloy Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11}, in which the martensitic transformation temperature is close to room temperature and practically coincides with the Curie temperature of austenite [8].
2. Experimental details
The Ni$_{47}$Mn$_{42}$In$_{11}$ alloy was melted by the method of arc melting in an argon atmosphere. The ingot was subjected to homogenizing annealing in vacuum in a sealed quartz ampoule at 1123 K for 24 h, followed by air cooling.

Structural studies were performed on a Neophot-30 optical microscope on thin sections after etching. The electron-microscopy studies were carried out using a JEM-200CX transmission electron microscope and a Quanta-200 scanning electron microscope with a local electron probe microanalysis. Magnetic measurements were performed using a pulsed vibration-coil magnetometer in magnetic fields with a strength of up to 350 kOe, the electrical resistivity was measured by a four-contact method in a magnetic field with a strength of up to 18 kOe in the temperature range from 80 to 400 K. Investigations of the structure and magnetic properties were carried out at the Collective Use Center "Experimental Center of Nanotechnologies and Promising Materials" of Institute of Metal Physics of Ural Branch of RAS.

![Graph](image)

**Figure 1.** Temperature dependences of the amplitude magnetic susceptibility $\chi_{ac}$ for Ni$_{47}$Mn$_{42}$In$_{11}$ alloy measured upon heating and cooling. The variation in the magnetic susceptibility of alloys in the low temperature region are shown in insets.

3. Results and discussion
Figure 1 shows the temperature dependences of the amplitude magnetic susceptibility $\chi_{ac}(T)$, measured upon cooling and heating for the Ni$_{47}$Mn$_{42}$In$_{11}$ alloy. When the alloy was cooled from 350 K, an abrupt increase in the magnetic susceptibility is observed in the dependence of $\chi_{ac}(T)$ corresponding to the Curie temperature of austenite $T_{CA} \approx 310$ K. With further cooling at the $T_M$ temperature, martensitic transformation occurs, accompanied by an abrupt decrease in the value of $\chi_{ac}$ and by existence of a temperature hysteresis that is characteristic of the first-order phase transitions. Then the anomaly, which is associated with a change in the magnetic state of martensite, is observed in lower temperature region at critical temperature $T_{CM}$ in the $\chi_{ac}(T)$ dependence (insets in figure 1). It should be noted that the Curie temperature of austenite in the Ni$_{47}$Mn$_{42}$In$_{11}$ alloy is close to the temperature of the martensite point: $T_{CA} \approx T_M$. Thus, the magnetic transition practically coincides with the structural transformation; in fact, a magnetostructural transition is observed in this alloy.
Thus, we can conventionally single out four regions in temperature dependences of amplitude magnetic susceptibility of studied Heusler alloy: 1) the temperature region with $T > T_{CA}$, which corresponds to the paramagnetic austenite phase; 2) the range with $T_{M} < T \leq T_{CA}$, which corresponds to the ferromagnetic state of the austenite phase; 3) temperature range $T_{CM} < T < T_{M}$, in which alloy are situated in the martensite state with zero spontaneous magnetization; and 4) temperature range with, where the ferromagnetic martensite phase occurs.

At high temperatures the investigated alloy has cubic crystal lattice ordered by the type of $L_2^1$ phase [16]. Upon cooling, a martensitic transformation and transformations of the crystal lattices occur [17].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Microstructure of Ni$_{47}$Mn$_{42}$In$_{11}$ after annealing.}
\end{figure}
After annealing at 1123 K for 24 h and subsequent cooling to room temperature, the structure of the alloy is polycrystalline. At room temperature, in the structure of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy, along with the high-temperature phase L\textsubscript{2\textsubscript{1}}, martensite crystals are well revealed (figure 2). They are arranged in a certain way, forming packet-like joints (see figure 2, a). Inside individual packets, fine martensitic plates with plane interfaces are arranged in parallel to one other. The scanning electron microscopy study of the fine structure of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy showed that the martensitic crystals thickness was changed from 300 nm to 2.0-2.7 \(\mu\text{m}\). Inside one grain in adjacent packets, the crystals were often arranged at an angle of \(\sim 60\) or 120 degrees. The structure also contains growing crystals with pointed ends (see figure 2, b).

The electron microscopy study of the fine structure showed that martensite crystals in the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy have an internal lamellar structure that resembles twins [17]. It was found that the deformation during the martensitic transformation in the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy occurs by slip of the (110)-type planes in direction \([\text{110}]\). Periodically arranged lamellar structure was stacking faults. Stacking faults have a fairly high density and form by slip of the (110)-type planes in the direction \([\text{110}]\) with respect to one other by a small part of the L\textsubscript{2\textsubscript{1}} lattice period, so that every seventh plane remains in its place. The appearance of extra reflections in the electron diffraction patterns in the martensitic structure in distances of 1/7 distance between the main structural reflections characterizes the long-period martensite 14M phases (see Figure 2, c). The martensite phase formed during the transformation was ordered [18]. The martensite crystals, reaching the grain boundary, induce additional stresses and thus favors the growth of crystals in the neighboring grain. Since the temperature of the martensitic transformation in the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy is close to room temperature, a reversible nature of the martensite transformation was experimentally observed: the appearance and disappearance of martensitic crystals under the electron beam, thereby moving the coherent phase boundaries of the martensite crystals. Thus, during cooling in the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy, a martensitic transformation of the L\textsubscript{2\textsubscript{1}}\textarrow{14M} type was observed with the formation of the modulated structure of the long-period martensite.

Figure 3. Field dependences of the magnetization of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy measured at temperatures of 78, 200, and 280 K.

Figure 3 shows the field magnetization dependences \(M(H)\) of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy, measured at three characteristic temperatures: \(T = 78\) K \((T < T_{\text{CM}})\), \(T = 200\) K \((T_{\text{CM}} < T < T_{M})\) and \(T = 280\) K \((T \approx T_{M} < T_{CA})\). At \(T = 78\) K \((T < T_{CM})\) in the martensitic state, the magnetization curve of the Ni\textsubscript{47}Mn\textsubscript{42}In\textsubscript{11} alloy shows abrupt increase in magnetization in weak magnetic fields \(H < 10\) kOe, which is conditioned by
the occurrence of spontaneous magnetization $M_{SM}$ in the martensite state. With a further increase in the magnetic field strength up to 250–300 kOe, a weak reversible linear increase in the magnetization is observed in $M(H)$ curve, probably due to the existence of a paraprocess. In a magnetic field above 300 kOe, the magnetization starts to increase more abruptly with an increase in the magnetic field strength, and the magnetic hysteresis is observed. The magnetic field induced transformation apparently starts in magnetic fields above 300 kOe. However, the magnetic field strength is insufficient for the structural transformation at $T = 78$ K. At higher temperatures $T = 200$ K ($T_{CM} < T < T_M$) and $T = 280$ K ($T = T_M < T_{CA}$) spontaneous magnetization in the martensite state is absent in magnetization curves of the Ni$_{47}$Mn$_{42}$In$_{11}$ alloy. An abrupt increase in magnetization is observed in critical field $H_{cm}$, which is caused by the structural transformation of martensite into austenite conditioned by the induced magnetic field. We defined critical field $H_{cr}$ as the magnetic field in which an abrupt increase in magnetization is observed in magnetization curves with an increase in the magnetic field strength (see figure 3). The structural phase transition is accompanied by hysteresis, which is characteristic of first-order phase transitions. At a temperature $T = 200$ K, the magnetization curve does not reach magnetic saturation. This fact indicates incompleteness of the sample into the austenite state. At a temperature $T = 280$ K, the magnetization curve almost reaches magnetic saturation. In this case, the sample completely transforms into the austenite state and we can determine spontaneous magnetization of austenite $M_{SA}$ in the austenite state induced by the magnetic field by approximation to zero magnetic field as it is shown in figure 3. The martensitic phase has low $M_{SM}$ magnetization values, which may be due to the fact that Mn atoms are in the paramagnetic state at $T_{CM} < T < T_M$ or the existence of mixed antiferro- and ferromagnetic exchange interactions between Mn magnetic moments in the martensite, which lead to complex noncollinear magnetic structure at $T < T_{CM}$ [8].

The temperature dependences of the electrical resistivity $\rho(T)$ of the Ni$_{47}$Mn$_{42}$In$_{11}$ alloy, measured during heating and cooling (figure 4), were determined. In the process of alloy heating from 80 K to the reverse martensitic transformation temperature $T_M \approx 325$ K, the dependence $\rho(T)$ has a nonmetallic character. With growing temperature, a small decrease from 2.65 to 2.3 $\mu$Ohm-m in electrical resistivity is observed. With the further heating, electrical resistivity drops from 2.4 to 1.2 $\mu$Ohm-m in the neighborhood of the $T_M$ temperature. It has a relation to the change in the alloy structure from martensite at $T < T_M$ to austenite at $T > T_M$. Further heating to temperature above $T_M$ leads to the increase in the electrical resistivity with growing temperature; i.e., the dependence $\rho(T)$ has a normal metallic character. Like the martensitic transformation, the dependence $\rho(T)$ is characterized by the existence of a temperature hysteresis. The maximum relative change in electrical resistivity $\Delta\rho/\rho$ in the process of spontaneous martensitic transformation is $45\%$. Thus, the change in the crystal lattice type of martensitic transformation is accompanied with a significant change in the resistance. The nonmetallic nature of the dependence $\rho(T)$ at $T < T_M$ may be conditioned by the fact that some regions with austenite structure characterized by lower values of the electrical resistivity begins to be formed in the alloy already at temperatures considerably lower than $T_M$.

Figure 5 shows the temperature dependence of the magnetoresistance of the investigated alloy in a magnetic field of 18 kOe ($\rho(H = 18$ kOe) - $\rho(H = 0))/\rho(H = 0)$. A drastic increase in the magnetoresistance is observed in a narrow temperature range in the vicinity of the $T_M$ temperature, where the martensitic transformation induced by the magnetic field occurs [19]. The maximum absolute value of the magnetoresistance is $\approx 15\%$ and it proves to be considerably lower than the change in resistance in the process of the spontaneous martensitic transformation which is $\approx 45\%$ (see figure 4). The low values of the magnetoresistance in a magnetic field of 18 kOe are conditioned by the fact that the magnetic field strength value of 18 kOe is not sufficient for the entire specimen to transform to the austenite state, since the martensitic transformation induced by the magnetic field occurs within a wide magnetic field range which reaches 200 kOe [8].
Figure 4. Temperature dependence of the resistivity of Ni$_{47}$Mn$_{42}$In$_{11}$ alloy.

Figure 5. Temperature dependence of the magnetoresistance of Ni$_{47}$Mn$_{42}$In$_{11}$ alloy in a magnetic field of 18 kOe.

4. Conclusion
The structure, electrical and magnetic properties of the three-component ferromagnetic alloy Ni$_{47}$Mn$_{42}$In$_{11}$ were investigated. When cooled in the Ni$_{47}$Mn$_{42}$In$_{11}$ alloy, a martensitic transformation is observed with the formation of the modulated structure of the long-period martensite (L2$_1$→14M). The magnetic properties of the high-temperature ferromagnetic austenitic and low-temperature martensitic phases are determined in a wide temperature range. It has been established that the spontaneous magnetization of the alloy in the martensitic state is less than the spontaneous
magnetization in the austenitic state induced by a magnetic field. It is shown that the relative change in electrical resistance during the spontaneous martensitic transformation is 45%. It was found that negative magnetoresistance is observed near the temperatures of the martensitic transformation and the magnetic transition $T_{CM} \approx T_{CA} \approx 325$ K.

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