PHASE TRANSITIONS AND THERMOPHYSICAL PROPERTIES OF $Ni_{50.2}Mn_{39.8}In_{10}$ GEISSLER ALLOY

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The results of measurements of heat conduction (K), heat capacity (C_P), electrical resistance (ρ) and data of differentially scanning calorimetry (DSC) of $Ni_{50.2}Mn_{39.8}In_{10}$ Geissler alloy in T=25 – 350 K interval are given. The anomalies evidencing on the phase transitions of I and II orders with T_C=321 K, M_S=296 K are observed on curves of DSC and $C_P(T)$. The strong increase of heat conduction at transition martensite – austenite ΔK=3.2 Vt/m*K caused by the increase of electron contribution because of the electron mobility increase at transition in high-symmetry phase, is revealed. The lattice heat conduction changes insignificantly at the transition that shows on the insensibility of phonons to structural disorder.

Keywords: Geissler alloys, heat conduction, heat capacity, phase transitions, electrical resistance.

INTRODUCTION

The physical properties of functional materials on the base, of which the innovation technologies can be formed, are always in the focus of attention of researchers. Ni-Mn-In Geissler alloys are also related to such type materials, in which magnetic structural phase transitions (MSPT) and big values of magnetocalloric effect (MCE) are observed, that presents the definite applied interest for technology of magnetic cooling. Meanwhile, Geissler alloys can be used as model objects for the study of interference mechanism of electron, phonon and magnetic subsystems of magnetic alloys. The alloys of Ni-Mn-In series attract one’s attention also by the fact that in them the interesting combination of magnetic and structural phase transitions [1,2] is observed, and that the insignificant changes in relation of components lead to drastic changes of their physical properties that shows the extreme sensibility of the properties to elemental composition change [3].

The possibility of practical use of such materials in innovative technologies, in particular, in technology of magnetic cooling as the working substance is the important factor stimulating the experimental and theoretical investigations of materials with MSPT and phenomena connected with them. The efficiency of refrigerating machine work based on MSC directly depends on heat removal velocity and working refrigerator substance, i.e. from alloy heat conduction. This shows on necessity of investigation of heat conduction of refrigerating machine working substance. Note, the heat conduction measurement is the reliable and checked method of definition of acting scattering mechanisms of solid state heat carriers, but this is the fundamental problem of solid state physics.

The magnetic, electric and magnetocalloric properties of different compositions of Ni-Mn-In system, investigated by us, have investigated enough. The researchers pay significantly less time to study of heat-conducting properties of Ni-Mn-In alloys, in spite of the fact that heat conduction is the important technical parameter of solid state.

We know the several works where their heat conduction is investigated [4 – 10]. Thus, in work [4] dedicated to the study of heat conduction and thermal e.m.f. of $Ni_{50}Mn_{34}In_{16}$ alloy, the $\rho(T)$. (T) strong anomalies near magnetic and structural phase transitions, which are explained by the changes in the alloy electron subsystem taking under consideration the scattering of heat carriers on boundaries of twinning, are revealed. The heat conduction anomalies of Ni-Mn-Ga alloy observed near phase transitions the authors [10] are connected with changes in alloy phonon subsystem. The strong increase of heat conduction of Ni-Mn-Sn [7] and Ni-Mn-In [9] alloys observed at transition martensite – austenite authors explain by the influence of heat conduction electron component. As it is seen from above mentioned, the necessary investigations for making things clear in behavior of Geissler alloy heat conduction near phase transition temperatures are needed.

The given work is dedicated to investigation of heat conduction of $Ni_{50.2}Ni_{39.8}In_{10}$ alloy in wide temperature interval from 25K up to 350K. The electric resistance and heat capacity, necessary for interpretation of obtained results are measured parallel. The data of differentially scanning calorimetry (DSC) are used for the study of phase results.

THE SAMPLE AND EXPERIMENT TECHNIQUE

The investigated sample is obtained by the method of arc-heated melting in argon atmosphere and it presents itself the rectangular plate by sizes 8.9x3.3x0.89 mm^3. The homogenizing is carried out at T= 900 ^{o}C during 48 hours in vacuum. The measurement of electric resistance is carried out by four-contact method and the measurement of the heat capacity is carried out by method of a.c. - calorimetry. The low-temperature measurements of heat conduction are carried out in cryostat of closed type CFSG-310. The temperature regulation in heat conduction measurement process, are carried out automatic mode on the program developed in laboratory. At heat conduction measurement the sample is put in radiation shield for the decrease of heat loss on radiation. The sample average temperature approximately corresponds to shield one. In measurement process the vacuum in the system is supported not more than 10^{-4} mm. Hg. The cuprum-constantan and chromel-constantan thermocouples are used as the temperature gauges. In the figure for $K(T)$ the data only for T >25 K, where one can measure the temperature, are given, because of the fact that the thermocouples don't have the necessary sensibility for detail measurement of temperature gradient at helium temperatures. The temperature drop on the sample is from $\Delta T \approx 3 \div 4$ K in interval of low temperatures and up to 5÷6 K in the interval of high ones. The error at measurement of heat conduction isn't more than 5%.

RESULTS AND DISCUSSION

The results of carried investigations are given in fig.1 – 4. At decrease of the temperature in austenite paramagnetic (PM) phase at $T_C \approx 321$ K the magnetic phase transition PM – FM, which strongly goes to magnetic structural phase transition ferromagnetic (FM) (austenite) – anti-ferromagnetic (martensite) at M_S=296 K takes place (Fig.1).

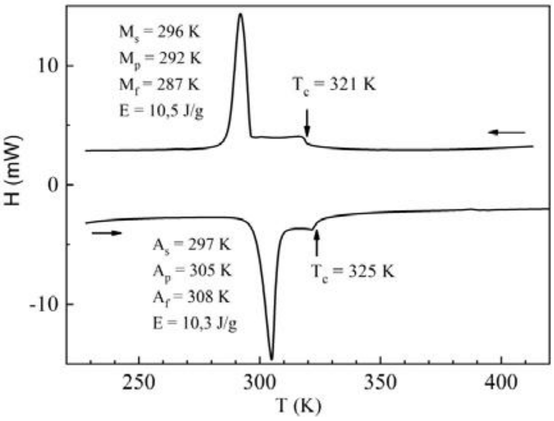

Fig.1. Data of DSC analysis in the mode of heating and cooling.

It is necessary to note that the question on magnetic state of martensite in Ni-Mn-In alloy is the debatable one [11-13].

The closeness of magnetic and structural phase transitions (T_C=321 K, M_S=296 K) supposes that in the given temperature interval the system is in structurally heterogeneous state (co-existence of martensite and austenite). The hysteresis observable in Fig.1 shows on magnetic structural nature of phase transition of I order. The strong peaks caused by latent heat of phase transition and temperature hysteresis ΔT = 13 K character for phase transitions of I order are also visible in the Fig. 1. The insignificant anomalies near magnetic phase transition and difference in T_C values in the heating and cooling modes attract one's attention that is probably connected with phase heterogeneity. The results of heat capacity measurements given in Fig.2, are the illustration of above mentioned. It is seen that at T decrease in austenite phase λ-formed maximum character for phase transitions of II order, is observed. At further T decrease the strong increase C_P, relating to phase transitions of I order is observed. The difference in value ΔC_P at heating and cooling presents the most interest: peak ΔC_P at cooling increases multiply the peak ΔC_P at heating that is probably connected with influence of latent heat of phase transition relating to structural transitions [14]. The further trend of $\Delta C_P(T)$ has the general form for solid state.

Before the discussion of results of heat conduction measurements, let's pay attention on the dependence of electric resistance on temperature which we measure, for estimation of electron component of heat conduction (Fig.3). As it is seen from the figure, the electric resistance in paramagnetic austenite phase slowly decreases with the temperature decrease, having the small anomaly near magnetic phase transition paramagnetic-ferromagnetic. The discontinuous increase of electric resistance more than in two times in very narrow temperature interval takes place near MSPT high-symmetry austenite (ferromagnetic) – low-symmetry tetragonal martensite (anti-ferromagnetic), that shows on high quality of the sample.

For analysis of $\rho(T)$ behavior we usually use the following expression:

$$\rho(T) = \frac{m^*}{e^2 \tau n},$$

where m^* is electron effective mass, τ is relaxation time, n is electron concentration.

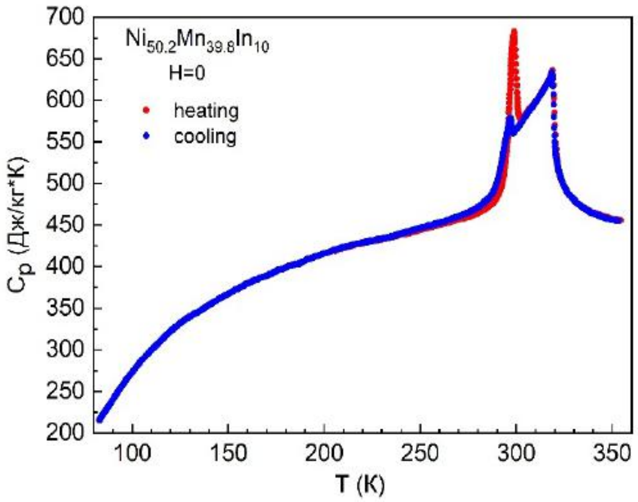

Fig.2. C_P(T) diagram in heating and cooling modes.

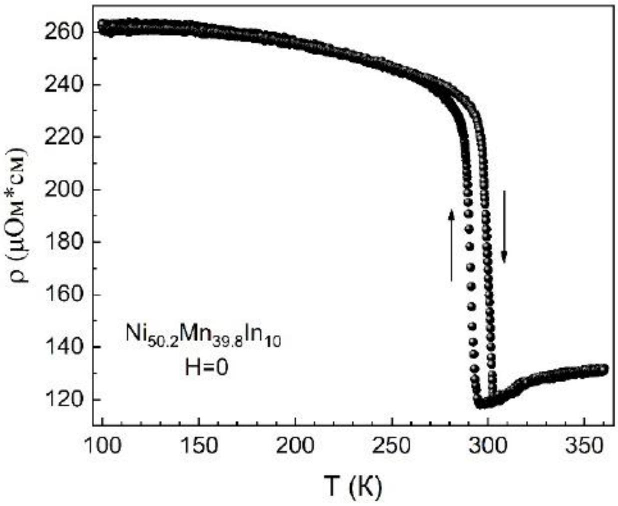

Fig.3. Temperature dependence of electric resistance.

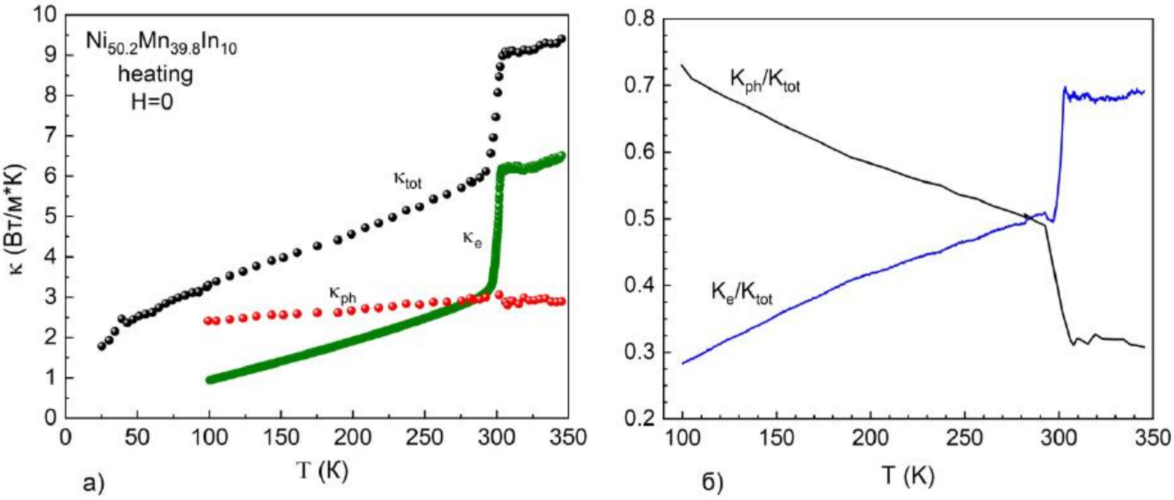

Fig.4. a) Temperature dependence of general (K_{tot}), electron (K_e) and phonon (K_{ph}) components of heat conduction; b) temperature dependence of the relative parts of electron and phonon components of heat conduction.

ρ increase, as it is seen from the expression for $\rho(T)$, can be the sequence of both the decrease of current carrier concentration and the increase of the electron scattering velocity τ_e^{-1} at transition in less symmetrical phase. The results of normal Hall coefficient investigation shows [9] that R_0 weakly changes at transition martensite – austenite that shows on the non-participation of n change to observable anomaly trend of $\rho(T)$. Therefore, the increase of electric resistance at transition in martensite phase is connected with the decrease of electron mobility at sample transition in strongly distorted tetragonal martensite phase as a result of increase of electron collision frequency τ_e^{-1} on structural defects.

Let's discuss the results of heat conduction measurements which are given in Fig.4.

In general case the heat conduction of magnetic materials can be presented as the sum of three summands:

$$K_{tot} = K_e + K_{ph} + K_m,$$

where K_e, K_{ph} and K_m are electron, phonon and magnetic components of heat conduction, correspondingly. As usual, the magnetic component is ignored because of its relative smallness [15]. That's why one can consider that both conduction electrons and phonons can be reliable for observable trend $K_{tot}(T)$. Generally, K_e dominates in metals, K_{ph} dominates in dielectrics, but K_e and K_{ph} are values of one order in multi-component alloys [16]. It is necessary to note the two peculiarities in the behavior of measured value $K_{tot}(T)$. This is absence of low-temperature maximum, character for crystalline solid states and discontinuous increase near phase transition martensite – austenite. Considering the last anomaly, we can say the following. It is obvious that it can be connected with both increase of electron component and changes in phonon subsystem. For dividing of K_e and K_{ph} we use Wiedemann-Franz law $K_e=L\sigma T$, where L is Lorenz number, σ is electric conduction which is equal to $1/\rho$. However L is value depending on temperature, which is equal to L_0 – 2.44*10^8 Vt^2/K^2 only in interval elastic electron collisions when relaxation times by energies and impulses are equal between each other, i.e. when one can introduces the unique relaxation time. $L= L_0$ in low temperature interval when electrons scatter on impurities and at high $T>\Theta$ (Θ is Debye temperature) when elastic electron-phonon interactions dominate. $L=f(T)$ in temperature intermediate region. However, the assumption for strong deluted metallic alloys is confirmed that the elastic electron-defect interactions (defects in the given case are: impurities, structural heterogeneities and boundaries) and use of Wiedemann-Franz law $K_e=L_0\sigma T$ in order to mark out K_e, is approved. Generally, the existing practices of K_e estimation for alloys takes under consideration this assumption [5, 7, 8, 10, 17], though the question about rightness of Wiedemann –Franz law in direct region of the transition requires more detail investigation.

The experimental curve $K_{tot}(T)$, electron component, estimated from $K_e=L_0\sigma T$ and phonon contribution K_{ph}, obtained as their difference $K_{ph}=K_{tot}-K_e$ are given in Fig.4.

The data graphic analysis given in Fig.4 shows that the difference $K_{tot}(aust.)$ – $K_{tot}(mart.)$ approximately coincides with data $K_e(aust.)$ – $K_e(mart.)$ and ≈ 3.2 $Vt/m*K$ and from this point of view whole increase of heat conduction is connected with electron component at MSPT.

K_{ph} weak dependence on temperature and the absence of strong anomalies near phase transitions evidence on insensibility of phonon scattering to structural defects appearing at austenite-martensite transition. The relation of contributions of electrons and phonons in general heat conductions strongly changes on the dependence on temperature (Fig.4b). As it is seen from the figure, at low temperatures the phonon contribution dominates under electron ones. The opposite case takes place when temperature is higher than transition ones.

Analysis of reference on heat conduction of Geissler alloys unambiguously indicates the presence of an anomaly near the MSPT temperature in the form of strong increase of heat conduction. However, there are different interpretations of this phenomenon. In one case, this anomaly is associated with an increase in the phonon contribution [10], in another case is connected with an increase in the electron contribution at phase transition [7, 9], in the third case [5] it is assumed that both electron and phonon subsystems simultaneously take part in this process.

The differences in the technology of sample obtaining are the one of the possible reasons for the observable discrepancies. In one case it is the well-known method of electric arc melting [7, 9], in the other case it is the method of mechanical alloying [18]. The samples obtained by different methods may have different microstructure and different response to external influence.

CONCLUSION

Based on the measurements of heat conduction, heat capacity, magnetization and electric resistance of $Ni_{50.2}Ni_{39.8}In_{10}$ sample, the following conclusions can be done. Magnetic and magneto-structural phase transitions with closely located transition temperatures (TC=321 K, MS=296 K) are observed in this composition. The heat capacity jump ΔC_P at heating near MSPT significantly exceeds the value of the jump at cooling, which is a consequence of the influence of the latent heat of the phase transition.

Anomalous increase of electrical resistance at the transition austenite - martensite is caused by the decrease in the mobility of conduction electrons. The strong increase of heat conduction at the martensite-austenite transition, achieving 50 %, is caused by the increase in the contribution of the electronic component. The weak temperature dependence of phonon heat conduction shows on the insensibility of phonons to structural disorder.

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