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Features of the thermal conductivity and heat capacity behavior in the $Ni_{50.2}Mn_{39.8}In_{10}$ alloy near the phase transition temperatures

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Thermal conductivity (κ), heat capacity (C_P), magnetization (M) and electrical resistivity (ρ) of the $Ni_{50.2}Mn_{39.1}In_{10}$ Heusler alloy were measured in wide temperature range of $T = 25-350$ K. Anomalies were found on the $M(T)$ and $C_P(T)$ curves, indicating phase transitions of the second and first order with the Curie temperature $T_C = 322$ K and the temperature of the martensitic transition start $M_S = 296$ K. A sharp increase in thermal conductivity $\Delta\kappa = 3.2\,W/(m \cdot K)$ during the martensite−austenite transition is found, caused by the electron contribution due to the electron mobility increasing during the transition to the more symmetric phase. The lattice thermal conductivity changes insignificantly during the transition, that indicates the insensitivity of phonons to the structural disorder.

Keywords: Heusler alloys, ferromagnetic, magnetostructural phase transitions, helium temperatures, resistivity, magnetization.

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1. Introduction

Physical properties of functional materials used as basis for formation of innovation technologies are always in focus of attention of researchers. Such materials include Heusler alloys Ni-Mn-In, in which magnetostructural phase transitions (MSPT) and significant values of magnetocaloric effect (MCE) are observed, this presents a definite applied interest for the technology of magnetic cooling. Besides, Heusler alloys can be used as model objects to study mechanism of mutual effect of electronic, photon and magnetic subsystems o magnetic alloys. Alloys of family Ni-Mn-In also attract in that in them interesting combination of magnetic and structural phase transitions is observed [1,2], and in that minor changes in relation to components result in radical changes in their physical properties, this indicates extraordinary sensitivity of properties to change in element composition [3].

An essential factor, stimulating the theoretical and experimental studies of materials with MSPT and associated phenomena, is the possibility of practical application of such materials in innovation technologies, in particular, as a working fluid in the magnetic cooling technology. Operation efficiency of refrigeration machine based on MCE directly depends on rate of heat removal from the refrigerator cooling fluid, i. e. on alloy thermal conductivity. This indicates the need in study of the thermal conductivity κ of working fluid of the refrigeration machine. Note also that measurement of thermal conductivity is very reliable and proven method for determining the acting mechanisms of dissipation of heat carriers in the solid, and this is a fundamental problem of solid state physics.

Magnetic, electrical and magnetocaloric properties of different compositions of studied by us system Ni-Mn-In are studied in sufficient details. Significantly less attention if paid by researchers to study of thermal conductivity properties of Ni-Mn-In alloys in spite of that thermal conductivity is important technical parameter of solid.

We know several papers where thermal conductivity of Heusler alloys was studied [4–10]. So, in paper [4], associated with study of thermal conductivity and thermoemf of alloy $Ni_{50}Mn_{34}In_{16}$, sudden abnormalities $\kappa(T)$ are detected near magnetic and structural phase transitions, which are explained by changes in electronic subsystem of alloy considering dissipation of heat carriers at twinning boundaries. The abnormalities of thermal conductivity of Ni-Mn-Ga alloy observed near phase transitions the authors of [10] associate with changes in phonon subsystem of the alloy. Abrupt rise in thermal conductivity of alloys Ni-Mn-Sn [7], Ni-Mn-In [9], observed at transition martensite−austenite, the authors explain by the effect of electronic component of thermal conductivity. We see from above said additional studies are necessary to clarify the behaviour of thermal conductivity of Heusler alloys neat temperatures of phase transitions.

This paper relates to study of thermal conductivity of $Ni_{50.2}Ni_{39.8}In_{10}$ alloy in wide temperature range including range of helium temperatures. Simultaneously magnetization,electrical resistance and thermal capacity were measured, which are required during interpretation of the obtained results.

2. Sample and experiment procedure

Studied sample was prepared by method of electric arc melting in argon atmosphere and represented a rectangular wafer with size $8.9 \times 3.3 \times 0.89\,\text{mm}^3$. The homogenizing annealing at $T = 900^\circ\text{C}$ for 48 h in vacuum was performed. The magnetization was measured in unit Quantum Design PPMS-9T, electrical resistance — by four-contact method, thermal capacity — by AC-calorimetry. Low-temperature measurements of thermal conductivity were performed in closed type CFSG-310. Temperature adjustment and process of thermal conductivity measurement were performed in automatic mode under program developed in the laboratory. When measuring thermal conductivity the sample was loaded into radiation screen to reduce heat losses for radiation. Average temperature of sample approximately corresponded to the screen temperature. During measurements the vacuum in system at least 10^{-4} mm Hg was maintained. Copper-constantan and chromel-constantan thermocouples were used as temperature sensors. Temperature difference on sample is from $\Delta T \approx 3-4\,\text{K}$ in range of low temperatures and to $5-6\,\text{K}$ in range of high temperatures. Error during thermal conductivity measurement did not exceed 5%.

3. Results and discussion

Results of performed studies are given in Figures 1–4. When temperature decreases in austenite paramagnetic (PM) phase at $T_C \approx 322\,\text{K}$ the magnetic phase transition PM–FM occurs, which gradually transits in magnetostructural phase transition ferromagnetic (austenite) — antiferromagnetic (martensite) at temperature of martensite transformation beginning $M_S = 296\,\text{K}$ (Figure 1). Further temperature decreasing is accompanied by magnetization decreasing, and sample transit into martensite phase. The magnetic state of the martensite is characterized by zero magnetization, this can be due to occurrence of compensated antiferromagnetic ordering. Note that issue of magnetic state of the martensite in Ni-Mn-In alloy is debatable [11–13].

Proximity of magnetic and structural phase transition ($T_C = 322\,\text{K}$, $M_S = 296\,\text{K}$) supposes that in specified temperature range the system is in structural heterogeneous state (co-existence of martensite and austenite). The observed in Figure 1 hysteresis unambiguously indicates the magnetostructural nature of the phase transition of I order. The results of thermal capacity measurements shown in Figure 2 are clear illustration of the above mentioned. It is evident that upon decrease in T in austenite phase λ-like maximum is observed, it is typical for phase transitions of II order. Upon further decrease in T abrupt increase in C_P is observed, it is typical for phase transitions of I order. The

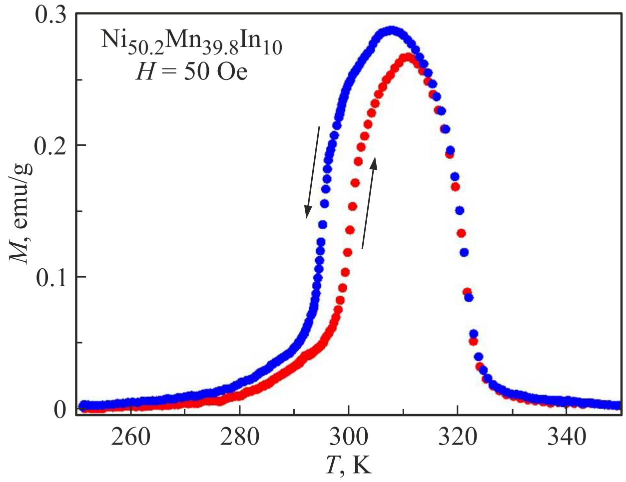

Figure 1. Magnetization vs. temperature in heating and cooling modes.

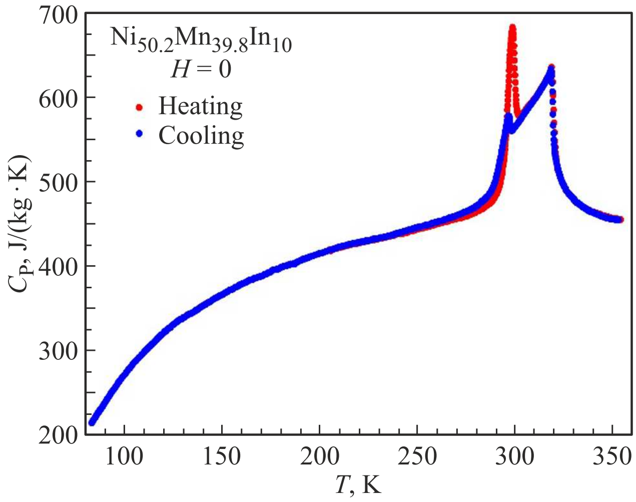

Figure 2. Dependence graph $C_P(T)$ in heating and cooling modes.

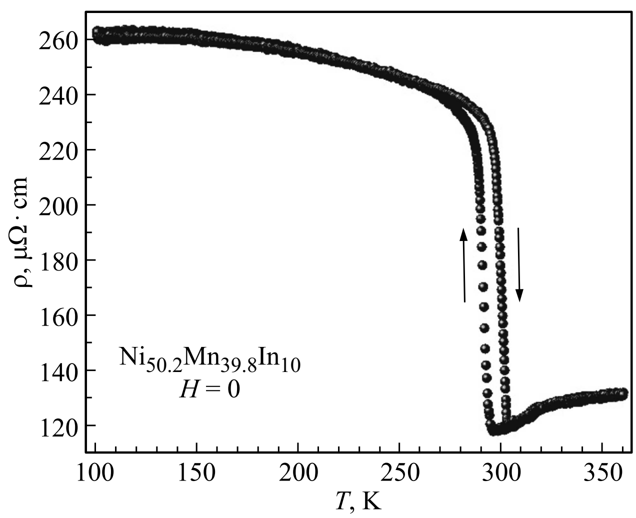

Figure 3. Electrical resistance vs. temperature.

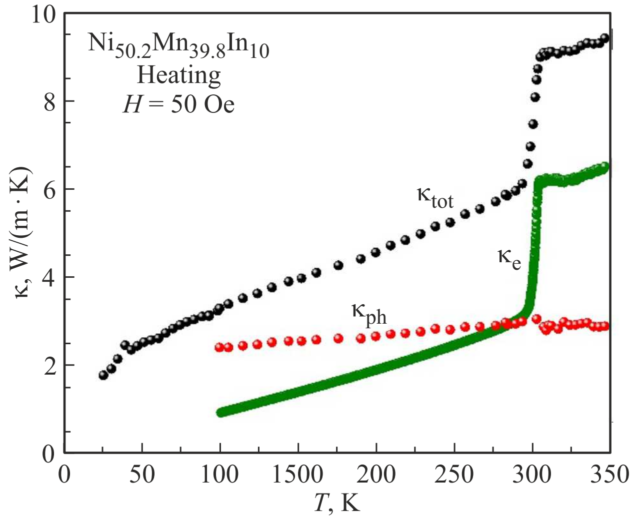

Figure 4. General (κ_{tot}), electronic (κ_{e}) and phonon (κ_{ph}) components of thermal conductivity vs. temperature (as thermocouples has no required sensitivity for accurate measurement of temperature gradient at helium temperatures, Figure shows data only for $T > 25$ K, where temperature can be measured with confidence).

great interest in this Figure relates to difference in value of ΔC_{P} during heating and cooling: peak ΔC_{P} during cooling by many times exceeds the peak ΔC_{P} during heating, this, obviously, is associated with effect of latent heat of phase transition typical of structural transitions [14]. Further graph of $C_{\text{P}}(T)$ has view typical for solids.

Before start of the discussion of measurements results of thermal conductivity let's briefly consider dependences of electrical resistance on temperature, which was measured to evaluate electron component of thermal conductivity (Figure 3). Wee see from Figure that the electrical resistance in paramagnetic austenite phase slowly decrease with temperature decreasing, demonstrating minor abnormality near the magnetic phase transition paramagnetic–ferromagnetic. Near MSPT the highly symmetric austenite (ferromagnetic) — low symmetric tetragonal martensite (antiferromagnetic) the jump-like, by more than two times, increase in electrical resistance occurs in very narrow temperature range, this can indicate high quality of sample.

For $\rho(T)$ behaviour analysis the expression is generally used:

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

where m^* — effective mass of electron, e — electron charge, τ — relaxation time, n — electron concentration.

From expression for $\rho(T)$ we see that increase in ρ can be due to both decrease in concentration of current carriers, and to increase in dissipation speed of electrons τ_e^{-1} during transition to less symmetrical phase. Results of study of Hall coefficient show [9] that it low changes during transition martensite–austenite, this indicates noninvolvement of change in n to the observed abnormal path $\rho(T)$. Therefore, the electrical resistance increasing during transition into martensite phase is associated with decrease in mobility of electrons during the sample transition into highly distorted tetragonal martensite phase as a result of increase in collision rate of electrons τ_{e}^{-1} on structural imperfections.

Let's start discussion of measurement results of thermal conductivity, see Figure 4.

Thermal conductivity of magnetic materials in the general case is a sum of three terms:

$$\kappa_{\text{tot}} = \kappa_{\text{e}} + \kappa_{\text{ph}} + \kappa_{\text{m}},$$

where κ_{e}, κ_{ph} and κ_{m} — electron, phonon and magnetic components of thermal conductivity, respectively. In general, magnetic component is neglected due to its relative low value [15]. So, we can consider that the observed $\kappa_{\text{tot}}(T)$ can be determined by both conductance electrons, and by phonons. Generally in metals κ_{e} prevail, in dielectrics — κ_{ph}, and in multicomponent alloys these values are of same order of magnitude [16]. Note two features in behaviour of measured value $\kappa_{\text{tot}}(T)$. This is absence of low-temperature maximum typical for crystal solids, and jump-like increase near the phase transition martensite-austenite. The following we can say relating the later abnormality. It is obvious that it can be associated with both increase in electronic component, and with changes in phonon subsystem. To separate κ_{e} and κ_{ph} we used Wiedemann–Franz relationship $\kappa_{\text{e}} = L\sigma T$, where L — Lorentz number. But L — depending on temperature variable equal to $L_0 = 2.44 \cdot 10^8\,\text{W}^2/\text{K}^2$ only in region of elastic electron collisions, when relaxation times by energies and pulse are equal to each other i.e. when we can introduce uniform relaxation time. In range of low temperatures when electrons dissipate on impurities, and at high $T > \Theta$ (Θ — Debye temperature), when elastic electron-phonon interactions prevail, $L = L_0$. In intermediate temperature range $L = f(T)$. But for heavily diluted metal alloys the assumption is true that in wide temperature range elastic electron-defect interactions prevail (in this case defects also include impurities, and structural imperfections, and boundaries etc.) and use of Wiedemann–Franz expression $\kappa_{\text{e}} = L_0\sigma T$ to highlight κ_{e} is justified. In any case, the existing practice of evaluation κ_e for alloys is based on such assumption [5,7,8,10,17], though issue of correctiness of Wiedemann–Franz expression in the direct transition region requires more detail study.

Figure 4 presents experimental curve $\kappa_{\text{tot}}(T)$, electronic component evaluated from relationship $\kappa_{\text{e}} = L_0\sigma T$ and phonon contribution κ_{ph} obtained as their difference $\kappa_{\text{ph}} = \kappa_{\text{tot}} - \kappa_{\text{e}}$.

Graphical analysis of data presented in Figure 4, shows that difference $\kappa_{\text{tot(aust.)}} - \kappa_{\text{tot(mart.)}}$ approximately coincides with data $\kappa_{\text{e(aust.)}} - \kappa_{\text{e(mart.)}}$ and $\sim 3.2\,\text{W}/(\text{m} \cdot \text{K})$, and as per this point of view entire increase in thermal conductivity is associated with increase in electronic component during MSPT. Low dependence of κ_{ph} on temperature and absence of abrupt abnormalities in vicinity of phase transitions indicate insensibility of phonons dissipation yo structural imperfections occurred during transition austenite–martensite.

Analysis of literature data on thermal conductivity of Heusler alloys unambiguously indicates the presence of abnormality near MSPT temperature in form of abrupt increase in thermal conductivity. But different interpretations of this phenomena exist. In one case this abnormality is associated with increase in phonon contribution [10], in another case — with increase in electronic contribution during phase transition [7, 9], in third case [5] it is supposed that both electronic and phonon subsystems simultaneously participate in this process.

One of the possible causes of observed difference can be based on technology of samples preparation. On one case this in known method of electric arc melting [7,9], in another case — method of mechanical melting [18]. The samples prepared by different methods can have different microstructure and different response to external effects.

4. Conclusion

Based on performed measurements of thermal conductivity, thermal capacity, magnetization and electrical resistance of sample $Ni_{50.2}Ni_{39.8}In_{10}$ the following conclusions can be made. In this composition the magnetic and magnetostructural phase transitions with close located transition temperatures are observed ($T_C = 322\,K$, $M_S = 296\,K$). Jump in thermal capacity ΔC_P during heating near MSPT significantly exceeds the jump during cooling, this is result of effect of latent heat of phase transition.

Abnormal increase in electrical resistance during transition austenite–martensite is due to mobility decreasing of conductance electrons. Abrupt increase in thermal conductivity during transition martensite–austenite, up to 50%, is due to increase in the electronic component contribution. Low temperature dependence of phonon thermal conductivity indicates insensitivity of phonons to structural disorder.

Conflict of interest

The authors declare that they have no conflict of interest.

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