Research of Magnetocaloric Effect For Ni-Mn-In-Co Heusler Alloys by the Direct Methods in Magnetic Fields Up to 14 T

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This paper is devoted to the study of magnetocaloric effect (MCE) in Ni-Mn-In-Co Heusler alloys by direct methods in high magnetic fields. Ni-Mn-In-Co Heusler alloys demonstrate the inverse MCE in the magnetostructural transition area. The adiabatic temperature change value (ΔT_{ad}) is determined by direct extraction method in magnetic fields up to 10 T. It is shown that the value of ΔT_{ad} increases with decrease in the difference between the temperature of magnetostructural transition and the Curie point temperatures of the compounds. The amount of isothermal heat emission (sorption) for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ alloy is determined as a result of magnetization in magnetic field up to 10 T in the magnetostructural transition area. The obtained results are discussed from the viewpoint of magnetic and lattice subsystems influences on the total entropy change (ΔS_t).

Index Terms—**Direct method, Heusler alloy, high magnetic field, magnetocaloric effect (MCE).**

I. INTRODUCTION

MAGNETOCALORIC effect (MCE) is an (ΔT_{ad}) adiabatic temperature change or (and) an (ΔS) isothermal entropy change of a magnet under the magnetic field action. Nowadays the direct study of the MCE attracts much attention. It is suggested that this effect will create a basement of the new magnetic refrigeration technology, which will be more energy efficient and environmentally friendly. Ni-Mn-X (X = Ga, In, Sn, Sb) Heusler alloys attract public attention as a promising magnetic coolant at room temperature since they demonstrate the magnetostructural transition and giant MCE near room temperature [1]. In addition, Heusler alloys are interesting for their technological parameters: relatively low cost in comparison with rare earth materials, the absence of toxic elements and high strength [1], [2]. One of the most attractive is the family of Ni-Mn-In-Co Heusler alloys, which demonstrate the giant inverse MCE. For example, in $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ it is observed $\Delta T_{\mathrm{ad}} = -8$ K in the magnetic field of 1.95 T [3].

In the most of works MCE in Heusler alloys are carried out by indirect methods (by calculation of ΔS isothermal entropy change from magnetization curves) [4]. However, the main parameter of the refrigerator is the temperature span created by it, the reliable measurement of ΔT_{ad} adiabatic temperature change is very important. The most reliable ΔT_{ad} values can be obtained by direct methods only. Earlier it was shown in [5], that it is possible to observe saturation of the ΔT_{ad} value in rather high magnetic fields in Ni-Mn-In-Co alloy. In particular, for $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ sample, it was shown that saturation in the ΔT_{ad} value occurs in magnetic field about 6 T [6], [7]. As a rule, the researches of the MCE for individual compositions are carried out in high magnetic fields. The ΔT_{ad} study for a Ni-Mn-In samples series with different magnetostructural transition temperatures was performed in [8]. It was shown that the ΔT_{ad} value increases with decreasing difference between the temperatures of magnetostructural transition and the Curie point in high magnetic fields. The similar studies for Heusler alloys Ni-Mn-In-Co did not conduct previously.

Therefore, the purpose of the present paper is a systematic study of the MCE values of the Ni-Mn-In-Co Heusler alloys with different magnetostructural transition temperatures by direct and indirect methods in high magnetic fields. The objects of study are $Ni_{43}Mn_{(50-y)}In_yCo_7$ at $12.1 < y < 12.45$, the chemical composition of them varies with $y = 0.1..0.15$ step.

II. EXPERIMENTS

A. Samples

The chemical composition of $Ni_{43}Mn_{(50-y)}In_yCo_7$ family samples was selected based on the previous studies results [9]. Our estimates show that samples with $12.1 < y < 12.45$ have a magnetostructural transition near the room temperature. The samples of the $Ni_{43}Mn_{37.8}In_{12.2}Co_7$, $Ni_{43}Mn_{37.7}In_{12.3}Co_7$, and $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ compositions were synthesized by the argon arc-melting method. The remelting was done by four times with a preliminary turnround of the ingot for obtaining a better homogeneity. The ingots were subjected to annealing at 1023 K temperature for 50 h after melting. Mass loss amounted to 0.1% of the total mass after melting and annealing. Chemical composition control of the samples was carried out using EDX analysis.

By the neutron diffraction methods, it was shown that all of investigated alloys have a cubic structure $L2_1$

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or mixture of $L2_1$ and $B2$ above the magnetostructural transition temperature. The samples have a mixture of two $5M$ and $7M$ modulated monoclinic structures below the transition temperature [10], [11].

B. Methods of Experiment

The differential scanning calorimetry (DSC) measurements were carried out using DSC 204 F1 NETZSCH device (with 10 K/min speed at heating and cooling) in temperature range from 175 to 375 K. Total entropy change (ΔS_t) as a result of magnetostructural transition in zero magnetic field was estimated from endothermic peaks of DSC curves using

$$\Delta S_t = \int_{T_S}^{T_F} (T)^{-1} \cdot \frac{d(Q - Q_{\text{baseline}})}{dT} dT \qquad (1)$$

where $d(Q - Q_{\text{baseline}})/dT$ is the heat flow change as a temperature function which corrected by the baseline Q_{baselime}, T_S and T_F are the initial and final temperatures of the magnetostructural transition in the heating process, respectively. The magnetization measurements were carried out in an automatic mode with the specified experimental protocol of the VersaLab "Quantum Design" device in the 100–400 K temperature and the 0.005–3 T magnetic field ranges. The ΔS_{isoter} isothermal entropy change was calculated based on data of the temperature dependences of the magnetization (measured for a given field), with the help of the Maxwell relation

$$\Delta S_{i\text{soter}}(T, \Delta H) = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH. \qquad (2)$$

It should be noted that formally the Maxwell relation is not applicable for the first-order phase transitions, as it leads to an uncertainty of derivative of magnetization on temperature at the discontinuity point. However, the magnetization jump is not observed in vicinity of the magnetostructural transition in this case. It allows carrying out such estimates.

The extraction method was used for the direct measurements of ΔT_{ad} adiabatic temperature change in magnetic fields up to 14 T in the 4.2–350 K temperature range. This method was implemented on the basis of Bitter coil magnet and the experimental device created by Dr. Koshkid'ko and Dr. Cwik [8], [12] in the International Laboratory of high magnetic fields and low temperatures (Wroclaw, Poland).

In addition, the determination of q [J/kg] isothermal heat emission (sorption) of alloys were carried out by given experimental device (for more details, see [8], [14]). For this purpose, the sample is placed in good thermal contact with the massive copper block. The hot end of the differential thermocouple places in the copper block close to the sample. In turn of the "copper block + sample" system is installed in the heat-insulated sample holder. Magnetic field up to 14 T is created by the Bitter coil magnet. After achievement of a preset magnetic field value the "copper block + sample" system was quickly entered into the maximum magnetic field area by means of the linear actuator. The sample is magnetized, and the rapid input of the sample allows achieving of almost adiabatic conditions. As a result of the MCE manifestation, the heat is transferred (taken away) to the copper block. Therefore, it leads to a change of the copper block temperature (dT_M), which is fixed by an installed thermocouple. The Hall sensor located in the sample holder allows measuring of the magnetic field. Then, q isothermal heat emission (sorption) is calculated by

$$\frac{dQ}{m} \cong \left(\frac{M}{m}\right) \cdot C \cdot dT_M, \quad M \gg m \qquad (3)$$

where M is the copper block mass, C is the specific heat of the block, m is the sample mass, and dT_M is the temperature change of the copper block due to MCE of the sample. The ratio of the masses of the copper block and the sample is more than 10:1.

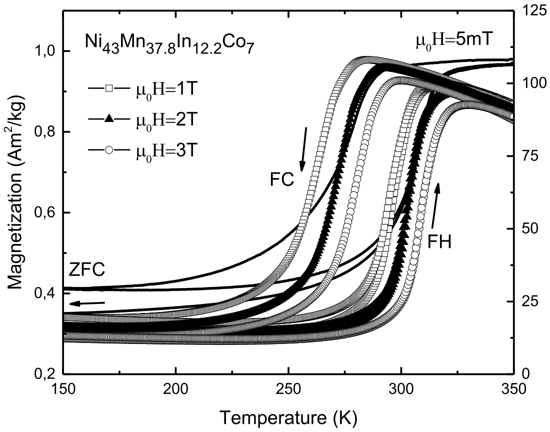

Fig. 1. Temperature dependences of the magnetization for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ Heusler alloy at various magnetic fields.

III. RESULTS AND DISCUSSION

A. Magnetic Measurements

The dependences of $M(T)$ measured in 5 mT, 1, 2, and 3 T magnetic fields for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ sample are presented in Fig. 1.

As can be seen from the $M(T)$ dependence at $\mu_0 H = 5$ mT (Fig. 1), when the temperature is lowering, the magnetization of the $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ sample decreases sharply and increases when the temperature is growing. The meta-magnetostructural phase transition takes place as a result. The nature of this transition is usually treated as transition from ferromagnetic cubic austenitic phase to a low-symmetry martensitic phase with weak magnetization, which is in spin-glass state [10]. Therefore, there is a connection between the structural transition and abrupt drop of the magnetic properties simultaneously, which determines the large MCE magnitude and its negative sign. All the samples studied in this paper (not shown) have qualitatively similar temperature dependences of magnetization. The characteristic temperatures of the first-order phase transition for all the samples were determined by linear extrapolation of $M(T)$ dependences (see Table I).

As can be seen from the $M(T)$ curve (Fig. 1), magnetic field increase leads to a shift of the hysteresis of the first-order phase transition to lower temperature, while the temperature hysteresis width increases from 30 K at $\mu_0 H = 5$ mT to

TABLE I

CHARACTERISTIC TEMPERATURE, HYSTERESIS WIDTH OF FIRST-ORDER PHASE TRANSITION, $\Delta S_{\mathrm{isoter}}$, ΔS_t, ΔT_{ad}, AND CURIE TEMPERATURE

№	Sample	A_s/A_f at 5mT, K	M_s/M_f at 5mT, K	hysteresis width, 5mT/3T, K	ΔS_{isoter} (μ_0H=3 T), J/(kg·K)	ΔS_t (DSC), J/(kg·K)	ΔT_{ad} ,K /T$_{\max}$, K	T_c, K
1	$Ni_{43}Mn_{37.8}In_{12.2}Co_7$	283/316	288/247	30/34	10,06	17,85	-3/267	427
2	$Ni_{43}Mn_{37.7}In_{12.3}Co_7$	274/304	272/236	34/37	9,6	12,8	-2,7/256	427
3	$Ni_{43}Mn_{37.65}In_{12.35}Co_7$	258/287	248/222	40/50	9,96	10,65	-2,5/250	427

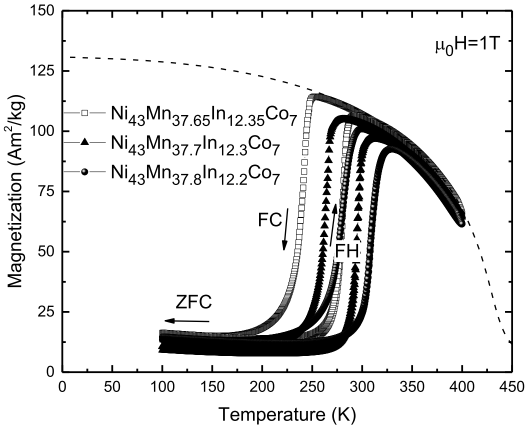

Fig. 2. Temperature dependences of the magnetization for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$, $Ni_{43}Mn_{37.7}In_{12.3}Co_7$, and $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ Heusler alloys at $\mu_0 H = 1$ T magnetic field. The dashed line is calculate curve of the temperature dependence of the magnetization at $\mu_0 H = 1$ T for the sample without a magnetostructural transition (austenite).

34 K at $\mu_0 H = 3$ T. Such behavior is observed for all the studied Heusler alloys (see Table I). This broadening of the temperature hysteresis can finally lead to elimination of the transition at sufficiently high magnetic fields in some compositions of Ni-Mn-In Heusler alloys [15].

The characteristic temperatures dependence of the first-order phase transition in the $Ni_{43}Mn_{(50-y)}In_yCo_7$ ($12.1 < y < 12.45$) Heusler alloys can be traced from the $M(T)$ curves measured at $\mu_0 H = 1$ T (see Fig. 2).

As can be seen from Fig. 2, Mn percentage increase leads to an increase in the first-order phase transition temperature. Therefore, it is possible to control the characteristic temperatures of the transition by replacing In by Mn. At the same time, the $T_c = 427$ K Curie temperature (determined on the basis of the DSC results) remains the same for all studied samples of Heusler alloys. A similar tendency remains for all the studied magnetic field values (is not shown).

In addition, it follows from the graph (Fig. 2) that a sample with lower phase transition temperatures has a larger hysteresis loop width. Here, the wider hysteresis is associated with the growing influence of the entropy change in the magnetic subsystem and an increase of the transition shift in a magnetic field [15]. In Fig. 2, the dashed line is calculate curve of the temperature dependence of the magnetization at $\mu_0 H = 1$ T for the sample without a magnetostructural transition (austenite). The calculated curve was constructed by using the approach proposed in [16]. This dashed curve represents magnetization values at $\mu_0 H = 1$ T for austenite with different manganese content.

B. MCE in Isothermal Condition (Indirect Method)

The total entropy change (ΔS_t) as a result of the magnetostructural transition in a zero magnetic field is estimated from the endothermic peaks of the curves of the heat flow DSC (1). The isothermal entropy change ($\Delta S_{\mathrm{isoter}}$) due to the first-order phase transition is determined on the basis of the Maxwell relation (2) and the temperature curves of the magnetization. The results are shown in Table I. From the data presented in Table I, it is seen that as the temperature of the phase transition decreases and the ΔS_t values decrease. At the same time, the $\Delta S_{\mathrm{isoter}}$ value does not demonstrate this dependence. The highest value of $\Delta S_{\mathrm{isoter}}$ and ΔS_t is observed in the $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ sample: $\Delta S_{\mathrm{isoter}} = 10.1$ J/(kg · K) and $\Delta S_t = 17.85$ J/(kg · K). This alloy has the smallest temperature distance between the magnetostructural transition and the Curie temperatures. Earlier, a similar dependence for Ni-Mn-In-Co alloys was demonstrated in [8], [9], and [15].

In the magnetostructural transition area, there is a competition of contributions from the magnetic and lattice subsystems [15], [17]. In the case of comparing the $\Delta S_{\mathrm{isoter}}$ and ΔS_t values, it is clear that the $\Delta S_{\mathrm{isoter}}$ is less than the ΔS_t. The reason of it may be the temperature transition shift in magnetic field that is not sufficient to complete the first-order transition in external field 3 T.

C. MCE in Adiabatic Condition (Direct Method)

The ΔS_t increases with decreasing difference between the magnetostructural transition and the Curie point temperatures as was shown in [8], [9], and [15] for various compositions of Ni-Mn-In-based Heusler alloys. The maximal ΔS_t values were found for the samples in which the magnetostructural transition is observed near the Curie temperature T_c. In contrast, the ΔT_{ad} values obtained from direct measurements does not show this trend [8], [9], [21], [22]. This behavior of ΔT_{ad} can be explained by the fact that the magnetic fields used in [7], [12], [18], and [19] were not high enough to complete the magnetostructural transition. In [8], a similar tendency (ΔT_{ad} increases with a decrease of the temperature difference of the magnetostructural transition and T_c) was observed in magnetic field up to 14 T for Ni-Mn-In. Such systematic study for Ni-Mn-In-Co alloys have not been carried out previously.

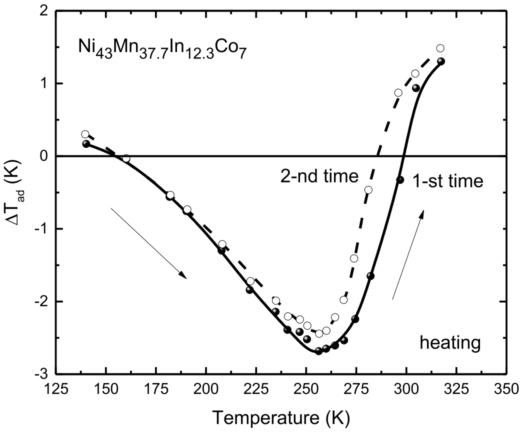

Fig. 3. Temperature dependence of the ΔT_{ad} magnetocaloric effect for $Ni_{43}Mn_{37.7}In_{12.3}Co_7$ Heusler alloy at $\mu_0 H = 10$ T magnetic field, measured by the direct method.

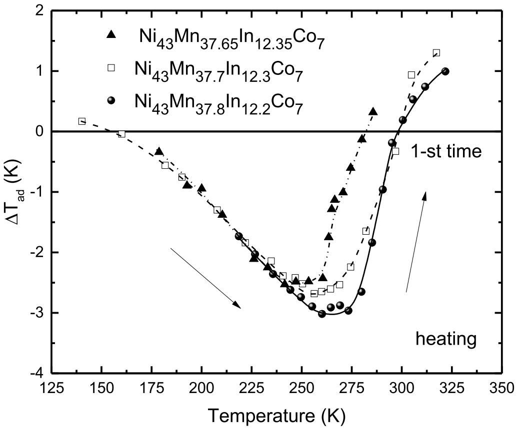

Fig. 4. Temperature dependences of the ΔT_{ad} magnetocaloric effect for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$, $Ni_{43}Mn_{37.7}In_{12.3}Co_7$, and $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ Heusler alloys at $\mu_0 H = 10$ T magnetic field, measured by the direct method.

Earlier our group showed [6], [7] that ΔT_{ad} measured by a direct method in high magnetic fields for $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ has a saturation effect approximately at $\mu_0 H = 6$ T. This alloy from article was created in the same series of samples. Therefore, for studying of limiting MCE values ΔT_{ad} researches were carried out in magnetic fields up to 10 T. This value of the magnetic field considerably exceeds the saturation fields of the ΔT_{ad} value for studied alloys.

To study the MCE in adiabatic conditions by direct method in high magnetic fields the device described above was used. Direct MCE measurements in adiabatic conditions were carried out on $Ni_{43}Mn_{37.8}In_{12.2}Co_7$, $Ni_{43}Mn_{37.7}In_{12.3}Co_7$, and $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ Heusler samples. In the Fig. 3, the temperature dependences of the inverse MCE of $Ni_{43}Mn_{37.7}In_{12.3}Co_7$ sample at magnetic field up to 10 T and for the first and second turns on the field is presented. The solid line corresponds to the "first" turn on of the magnetic field, and the dashed line corresponds to the "second" one. As can be seen from the graph, the MCE values for the second turn on are less than for the first, i.e., there is an irreversible ΔT_{ad}. Irreversible ΔT_{ad} is observed for all investigated alloys (not shown).

The maximum MCE value is equal to $\Delta T_{\mathrm{ad}} = -2.7$ K at $T = 256$ K and $\mu_0 H = 10$ T for $Ni_{43}Mn_{37.7}In_{12.3}Co_7$ sample in the first-order phase transition area. The MCE sign varies depending on which subsystems (lattice, magnetic [15]) prevail at a given temperature. With the predominance of the lattice subsystem influence, the MCE sign is negative, because there is a transition from a low-symmetric martensitic phase (a mixture of two $5M$ and $7M$ monoclinic structures) to a highly symmetric austenite (cubic $L2_1$), i.e., $\Delta S > 0$. At a distance from the magnetostructural transition, the contribution from the structural transition to the MCE decreases and the magnetic subsystem contribution prevails. At low temperatures, there is a slight decrease in magnetization with increasing temperature (Fig. 2), which leads to a direct ΔT_{ad} at a temperature below 150 K (Fig. 3). In addition, direct MCE is observed above 300 K. In this case, the direct MCE is connected with a paraprocess around the T_c. Working temperature range of the used device does not allow to measure MCE directly in Curie point temperature area.

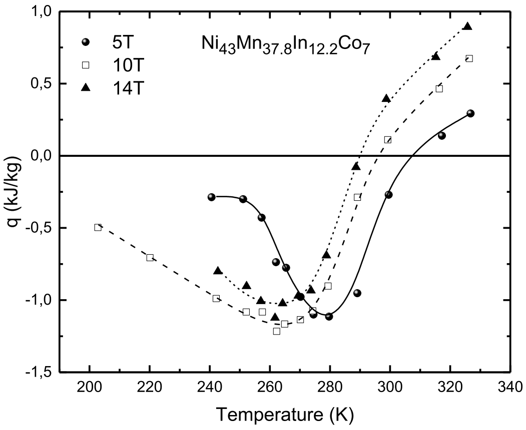

Fig. 5. Temperature dependences of the q isothermal heat emission (sorbtion) of the $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ Heusler alloy at different 5, 10, and 14 T (circle, square, and triangle elements, respectively) magnetic fields.

The graph (Fig. 4) demonstrates the temperature dependences of the MCE for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$, $Ni_{43}Mn_{37.7}In_{12.3}Co_7$, $Ni_{43}Mn_{37.65}In_{12.35}Co_7$ Heusler alloys at $\mu_0 H = 10$ T magnetic field, measured by the direct method. For studied Heusler alloys the maximum of the temperature dependences of ΔT_{ad} shifts to higher temperatures due to the characteristic temperatures change of the first-order phase transition at a constant Ni, Co value with an Mn content increase and In content decrease (Fig. 4). In this case, the ΔT_{ad} value increases. It is explained by rapprochement of first-order phase transition characteristic and Curie point temperatures (the $T_c = 427$ K) in these alloys (see Table I).

The temperature dependence of the isothermal heat emission (sorption) of materials at different 5, 10, and 14 T (Fig. 5) magnetic fields has been constructed for the $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ alloy.

It is seen from Fig. 5, the temperature of the q maximum for the alloy at $\mu_0 H = 5$ T differs from the maximum temperatures at $\mu_0 H = 10$ and 14 T. The q maximum shifts to lower temperatures at the magnetic field increase. It is connected with the shift of the magnetostructural transition temperature to the low temperatures region at increasing magnetic field. In [6] and [7] it was shown, that q reaches saturation at $\mu_0 H = 8$ T for the $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ sample. Therefore, a further increase in the applied magnetic field up to 10 T leads to a slight change in q, while the maximum is observed. The isothermal heat emission (sorption) of the alloy decreases slightly at $\mu_0 H = 14$ T. It can be explained by the fact that, at high fields the magnetic subsystem of the alloy has a higher degree of ordering and its contribution produce the positive influence to the MCE diminishing the overall inverse MCE.

IV. CONCLUSION

The series of the $Ni_{43}Mn_{(50-y)}In_yCo_7$ ($12.1 < y < 12.45$) Heusler alloys was synthesized. The increase of the characteristic temperatures of the magnetostructural transition was observed with increasing of manganese content (or decreasing of indium content) in the synthesized alloys. The MCE study was conducted by the direct method in magnetic field up to 10 T. It was shown that the ΔT_{ad} values increase with a growing of the magnetostructural transition temperatures of the compounds, as well as the ΔS_t values. The q values were determined for $Ni_{43}Mn_{37.8}In_{12.2}Co_7$ at different magnetic fields, $q = -1.2$ kJ/kg at $\mu_0 H = 10$ T.

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