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Thermomagnetic and magnetocaloric properties of metamagnetic Ni-Mn-In-Co Heusler alloy in magnetic fields up to 140 kOe

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Abstract. High cooling power of magnetocaloric refrigeration can be achieved only at large amounts of heat, which can be transferred in one cycle from cold end hot end at quasi-isothermal conditions. The simple and robust experimental method of direct measuring of the transferred heat of materials with magnetocaloric effect (MCE) in thermal contact with massive copper block with definite heat capacity in quasi-isothermal regime was proposed. The vacuum calorimeter for the specific transferred heat ΔQ and adiabatic temperature change ΔT measurements of MCE materials in the fields of Bitter coil magnet up to H = 140 kOe was designed and tested on samples of $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ Heusler alloy with inverse MCE in the vicinity of meta-magneto-structural phase transition (PT). It was found, that the magnetic field H = 80 kOe produces complete PT from martensite to austenite with ΔQ = - 1600 J/kg at initial temperature 273 K.

1 Introduction

Recently, a big interest is attracted to the application of materials with a large magnetocaloric effect (MCE) at phase transition (PT) for creation of household and industrial refrigerators, operating at room temperature. High cooling power of such devices can be achieved only at high frequency of heat transfer cycles and at large amounts of heat, which can be transferred in one cycle from cold end to hot end. The maximal frequency of cycles depends on the geometry of the working body made of MCE material and the fundamental restrictions on the rate of PT in this material. The optimum configuration of working body is the plates in the honeycomb structure [1]. The rate of PT depends on the relaxation processes in the vicinity of PT. The magnetization relaxation time of Gd near the Curie point is discussed in terms of Landau-Khalatnikov equation and is experimentally estimated as $\tau \approx 50$ ms in [2]. In the present work we suggest the experimental approach for the direct measurement of transferred heat in one cycle.

A promising class of solid materials for magnetic cooling at room temperatures is that in which a first order metamagnetostructural PT is induced by the magnetic field [3,4]. In this case, so-called inverse MCE originates from a structural transition from the paramagnetic or antiferromagnetic martensite phase to the ferromagnetic austenite phase on the application of a magnetic field. Recently, much interest is attracted to Ni-Mn-In-Co alloys due to large magnetic-field-induced strains [5,6] and giant inverse MCE [7]. We created the new series of Ni-Mn-In-Co alloys with 43 at. % of Ni and 7 at. % of Co. The samples from this series were prepared by arc melting under an argon atmosphere with subsequent homogenizing annealing during 48 hours at 1173 K. Metamagnetic alloy $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ was chosen for further research. We investigate the thermomagnetic and magnetocaloric properties of this alloy in the present work only.

2 Theoretical approach

When magnetic material is subjected to a magnetic field changing by $\Delta H = H_F - H_I$ (final and initial states of the magnetic field strength) at constant pressure, two different processes may occur in a magnetic material [8]. The first is the isothermal process that occurs when the magnetic field is altered but the material remains connected to the surroundings (heat sink/heat reservoir) and, therefore, remains at constant temperature (T). The

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entropy per unit of a mass of a magnetic solid is then changed by

$$\Delta S_{\Delta H} = (S_F - S_I)_T \quad (1)$$

and $\Delta S_{\Delta H}$ is magnetic entropy change by magnetic field. The entropy change of a solid directly characterizes the specific transferred heat in one cycle of the magnetic material $\Delta Q = T \cdot \Delta S_{\Delta H}$, which indicates, how much heat can be transferred from the cold end to the hot end of the refrigerator in one ideal cycle of heat transfer.

The second is an adiabatic process that occurs when the magnetic field is modified but the material is isolated from the surroundings and, therefore, the total entropy of a solid remains constant. The temperature of a magnetic material is then changed by

$$\Delta T_{\Delta H} = (T_F - T_I)_S \quad (2)$$

and $\Delta T_{\Delta H}$ is called adiabatic temperature change.
If both the magnetization and entropy are continuous functions of the temperature and magnetic field, then the infinitesimal isobaric-isothermal entropy change can be related to the magnetization (σ), the magnetic field strength (H), and the absolute temperature (T) using one of the Maxwell relations (in integral form)

$$\Delta S_{\Delta H} = -\int_{H_I}^{H_F} \left(\frac{\partial \sigma(T,H)}{\partial T} \right)_H dH \quad (3)$$

3 Experimental approach

If a sample of magnetic material is strongly connected to the surroundings – to a massive nonmagnetic block with definite specific heat and good thermal conductivity (Fig. 1), then one can experimentally obtain the transferred heat ΔQ from the sample to the block at quasi-isothermal conditions by measuring ΔT_b – the quasi-isothermal temperature change of the block at magnetic field change

$$\Delta Q\, m = M \cdot C \cdot \Delta T_b + m \cdot c \cdot \Delta T_b \quad (4)$$

where M – the mass of the block, C – the specific heat of the block, m – the mass of the sample, c – the specific heat of the sample and. We can neglect the heat which is connected with the temperature change of the sample, if its mass is negligible compared to the mass of the block

$$\Delta Q \approx (M/m) \cdot C \cdot \Delta T_b,\ M \gg m \quad (5)$$

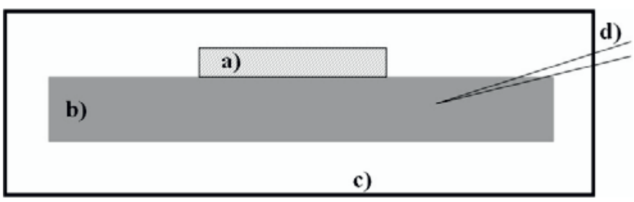

Figure 1. Scheme of direct experimental ΔQ-measurements: a) the sample with MCE, b) the massive nonmagnetic block; c) the vacuum chamber; d) the temperature sensor (diode).

4 Thermomagnetic measurements

Thermomagnetic measurements, σ(T), with zero-field-cooling (ZFC), field-cooling (FC) and field-heating (FH) routines were performed in the temperature range of 50–400 K applying in the sample plane different magnetic fields up to 30 kOe by Vibrating Sample Magnetometry (VSM, Versalab, QD). The heating and cooling rate was 5 K/min. The results of these measurements are presented in terms of the isothermal σ–H curves (Fig. 2) and the temperature dependence of the magnetization under ZFC, FC and FH protocols (Fig. 3). The temperature dependence of the entropy change was calculated from equation (3) after using the ZFC (Fig. 4). The ZFC protocol, that has been used, is described below.

The samples were heated up to 350 K (austenite ferromagnetic phase) at zero magnetic field before starting the ZFC measurements. Afterwards, they were cooling down to 50 K, where the magnetic field was applied. The Fig. 4 shows the ΔS curves for the whole experimental magnetic field range of the ZFC protocol, indicating the existence of the inverse MCE with maximum value ΔS_{ZFC} = 13 J/(kg·K) in magnetic field 30 kOe at 310 K.

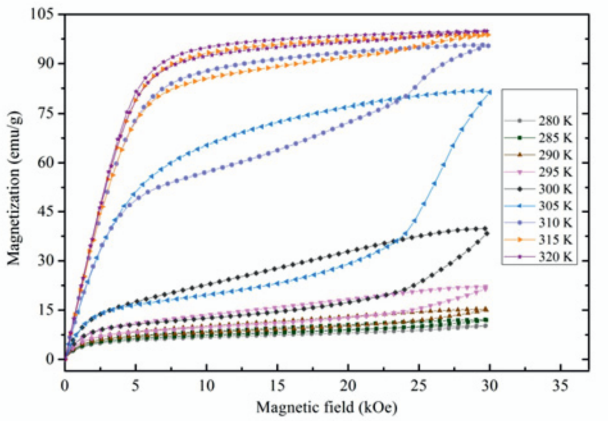

Figure 2. The isothermal magnetization curves at different temperatures, showing the magnetic-field-induced martensitic transformation.

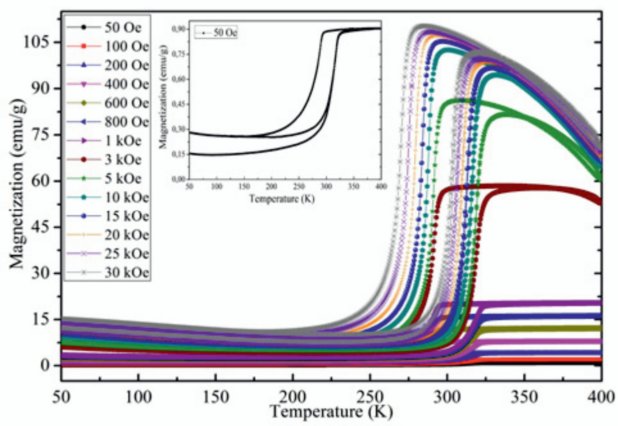

Figure 3. Thermo-magnetization curves at different fields, showing the shift of the martensitic transformation under applied magnetic field.

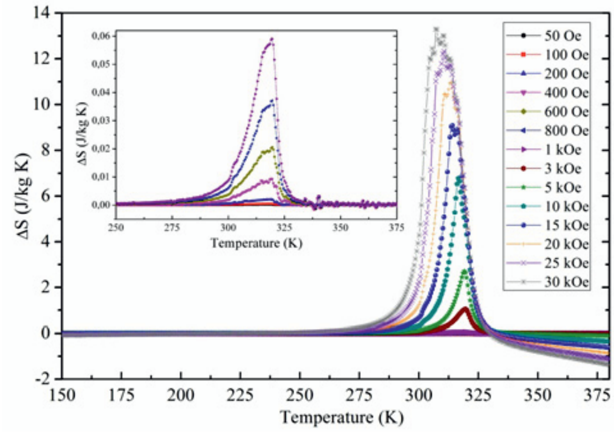

Figure 4. The calculated entropy change curves for the whole experimental magnetic field range of the ZFC protocol.

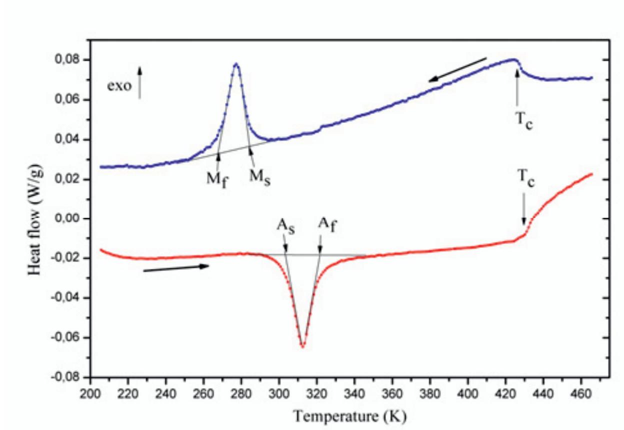

Figure 5. Differential scanning calorimetry scans. Ms, Mf and As, Af denote start and finish temperatures of the direct and reverse martensitic transformations, respectively. T_C – the Curie temperature of austenite.

5 DSC measurements

The martensitic transformation temperatures and the latent heat during the transformation were determined by differential scanning calorimetry (DSC) at heating and cooling rates of 10 K/min. As seen from Fig. 5, DSC scans of the sample demonstrate exothermic and endothermic peaks which are associated with the martensitic PT occurring in the sample. The characteristic transition temperatures M_s, M_f and A_s, A_f corresponding to start and finish temperature of direct and reverse martensitic transformation, respectively, are indicated in Fig. 5. The transition temperatures were determined as a crossing point between the extrapolation lines of the peaks and the base line. For our alloy transformation's temperatures were found to be: martensite start $M_s = 285$ K, martensite finish $M_f = 267$ K and austenite start $A_s = 304$ K, austenite finish $A_f = 321$ K. Also, the Curie temperature of austenite state is $T_C = 430$ K.

Calculated from the DSC data the heat exchanged upon direct ($L_{H\to L}$) and reverse ($L_{L\to H}$) PT are $L_{H\to L} = +3203$ J/kg and $L_{L\to H} = -4038$ J/kg. Each of these values is latent heat of direct or reverse PT and it is a maximum possible of ΔQ of this material. The average of the absolute values of $|L_{H\to L}|$ and $|L_{L\to H}|$ was taken as the change of enthalpy ΔE. In the case of thermoelastic martensitic transformation, the configuration contributions to the entropy change are absent. This allows one to estimate the total entropy change at the martensitic transformation as $\Delta S_{DSC} = \Delta E/T_0$, where $T_0 = (M_s+A_f)/2$ is the thermodynamic equilibrium temperature. For the experimentally determined $\Delta E = 3621$ J/kg and $T_0 = 303$ K, the entropy change is equal to $\Delta S_{DSC} = 12$ J/kg·K.

6 Direct ΔT-measurements

The vacuum calorimeter for placing into Bitter coil was developed. The sample was placed to vacuum chamber at adiabatic conditions. The vacuum in the chamber was achieved by forepump (down to pressure $4 \cdot 10^{-4}$ kPa). The temperature measurements were performed with the help of semiconductor light diodes (LED) under constant current (100 μA). The diode was glued on sample, the mass of diode is 3,7 mg. The change of voltage on diode occurred when the temperature of a sample is changed. The temperature sensitivity of these diodes is constant in wide region near room temperature and equals to 3,0 mV/K. Magnetic field does not affect the sensitivity of the diodes.

The protocol of experiment was as following. The vacuum calorimeter was placed into ice/water thermostat in Bitter coil and the forepump was turned on for the establishment of required vacuum. The initial temperature was set with the help of thermo-controlled system. After that, the temperature measurements were started and the magnetic field was turned on (with the rate 140 kOe/min). The magnitude of magnetic field was measured by Hall probe.

The adiabatic temperature change of the sample was measured in a direct experiment: ΔT = - 3,3 K in magnetic field 80 kOe at initial temperature 273 K (Fig. 6). Besides, the magnetic irreversibility of material was observed: the temperature change become less after some cycles of applying magnetic field.

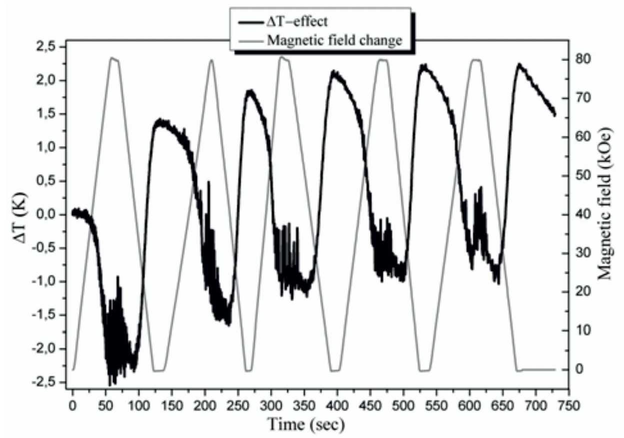

Figure 6. The time dependence of magnetic field change (gray curve) and the corresponding ΔT (black curve) of the sample at adiabatic conditions. Initial temperature is 273 K.

7 Direct ΔQ-measurements

We modified our calorimeter, following the scheme on Fig. 1, for ΔQ-measurements. The sample (m = 0,340 g) was glued (by heat-conducting glue) on the massive copper block (M = 4,523 g) and this block was wrapped in a paper, which fixed of it into a textolite framework (Fig. 7). The textolite framework was placed in a vacuum chamber. Such system ensures the specific conditions. Firstly, it decreases the heat rejection from copper block (with the sample) to its support and the environment (quasi-adiabatic conditions). Secondly, the sample remains in quasi-isothermal conditions, because its mass in 13,3 times less than the mass of the copper block and their specific heat capacities have the same order of magnitude.

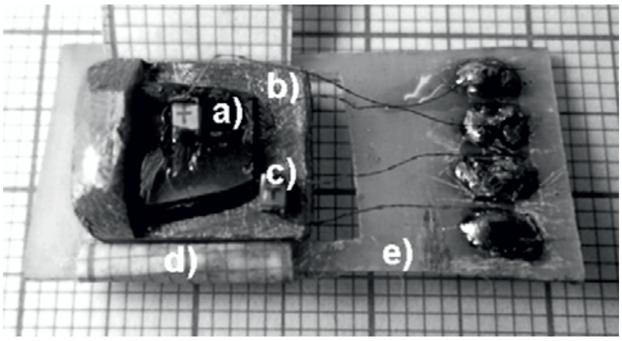

Figure 7. The appearance of the experimental setup for direct ΔQ-measurements of MCE materials: a) the sample, b) the copper block, c) the diode for temperature measuring, d) the paper, e) the textolite framework.

The time dependence of the temperature change of the copper block is presented in Fig. 8 at different magnetic fields. The initial temperature of these measurements was 273 K. The magnetic field was changed step by step: increased up to one magnitude (40 kOe) and decreased down to zero, after that increased up to more magnitude (+10 kOe) and decreased down to zero etc. The maximal magnetic field was 140 kOe.

The dependence of specific transferred heat in one cycle ΔQ on the magnetic field change at initial temperature 273 K is presented in Fig. 9. This dependence was obtained from data on Fig. 8 with applying the equation (5). It was shown, that the magnetic field of 80 kOe produces complete meta-magnito-structural PT with inverse MCE and ΔQ = -1600 J/kg. The magnetic fields higher than 80 kOe are not effective for the magnetic cooling. Thus the complete reverse martensitic transformation was observed. The maximum of absolute value was ΔQ = - 2000 J/kg at decreasing the magnetic field from 80 kOe (or more) to 35 kOe at direct martensitic transformation. This effect is connected with direct MCE in ferromagnetic austenite phase (at decreasing of magnetic field).

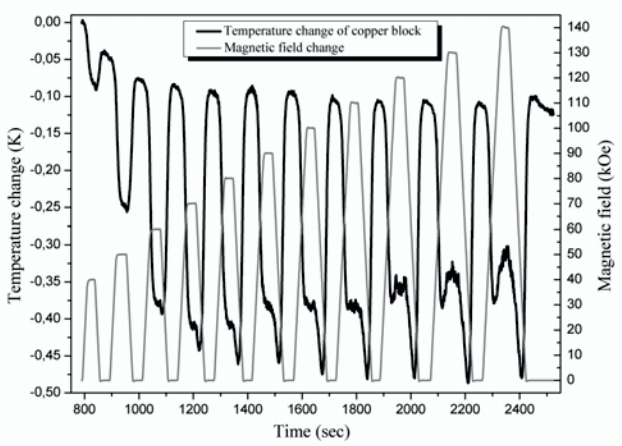

Figure 8. The time dependence of magnetic field change (gray curve) and a corresponding temperature change (black curve) of the copper block. The initial temperature is 273 K.

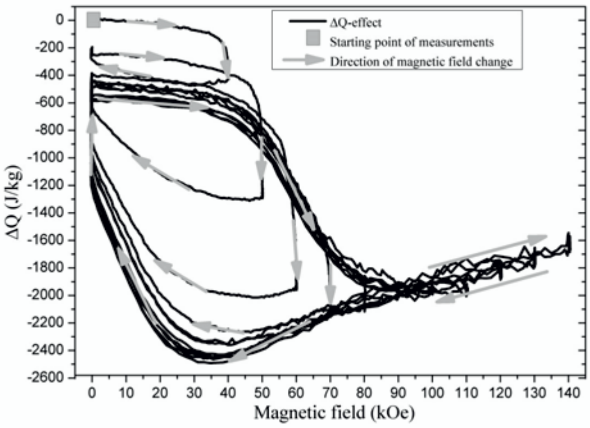

Figure 9. The dependence of ΔQ on the magnetic field (black curve). The gray arrows show the direction of the magnetic field change. Gray square shows starting point of the measurements. The initial temperature is 273 K.

8 Conclusions

The vacuum calorimeter for the specific transferred heat in one cycle ΔQ and adiabatic temperature change ΔT measurements of MCE materials in the fields of Bitter coil up to H = 140 kOe was created and tested on samples of $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ Heusler alloy with inverse MCE in the vicinity of meta-magneto-structural PT. And further the main results:

1) ΔT = -3,3 K in magnetic field 80 kOe at 273 K. The magnetic irreversibility of material was observed in these experiments.

2) The magnetic field H = 80 kOe produces complete PT from martensite to austenite with ΔQ = - 1600 J/kg at temperature of 273 K, while the magnetic fields H > 80 kOe are not effective for the magnetic cooling.

3) Our experimental data on ΔQ in quasi-isothermal process correspond to entropy change $\Delta S_{\Delta H} = \Delta Q / T =$ 5,9 J/(kg·K) (in 80 kOe). From DSC data ΔS_{DSC} = 12 J/kg·K (in zero field). It means that the magnetic field decreases the latent heat of PT. In addition we got maximal ΔS_{ZFC} = 13 J/(kg·K) (in 30 kOe at 310 K) using Maxwell relations and ZFC data.

4) The maximal specific cooling power of working body based on $Ni_{43}Mn_{37.9}In_{12.1}Co_7$ metamagnetic Heusler alloy could be estimated like $P = \Delta Q \cdot F = 16$ W/g in magnetic field H = 80 kOe, if achievable frequency have the same value F = 10 Hz like in Gd near the Curie point [2].

5) The precision of measurements in high magnetic fields is depended on mass of the sample due to long time of turning on the Bitter coil magnet (140 kOe/min).

Acknowledgments

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