Chelyabinsk Physical and Mathematical Journal. 2020. Vol. 5, iss. 2. P. 186–193.

DOI: 10.24411/2500-0101-2020-15205

MAGNETOCALORIC EFFECT IN $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ RIBBON HEUSLER ALLOY IN CYCLIC MAGNETIC FIELDS

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Magnetocaloric properties in ribbon sample of $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ Heusler alloy are studied by a direct method in cyclic magnetic fields. A strong anisotropy in the magnetocaloric effect is observed in weak magnetic fields, obtaining a large value of MCE when the field is applied parallel to the ribbon plane. The field dependence of the MCE anisotropy is studied and its decrease is clearly revealed in moderate fields. It was found that in cyclic magnetic fields, the MCE value near the magnetostructural phase transition depends on the rate of temperature scanning: a higher rate of the temperature sweep results in greater value of the MCE.

Keywords: *magnetocaloric effect, cyclic magnetic field, Heusler alloy, ribbon, anisotropy.*

1. Introduction

The interest in the study of materials with the magnetocaloric effect (MCE) is due to the possibility of using them in prospective solid-state magnetic refrigeration technologies. The search for materials with necessary magnetocaloric properties is actually in progress by many research groups in the world [1; 2]. In recent years, much attention is paid to the study of materials with coupled first-order magnetostructural phase transitions (FOMPT). In this case, the total change of entropy is equal to $\Delta S = \Delta S_{\mathrm{s}} + \Delta S_{\mathrm{m}}$ where ΔS_{s} is the entropy change due to the structural transition and ΔS_{m} is the magnetic entropy change. This can give rise to a giant MCE in these materials. For instance, a giant MCE was observed in Ni-Mn-In-(Co) alloy, where the adiabatic temperature change is more than 6 K for $\mu_0 \Delta H = 1.9$ T [2]. But this and similar studies are performed under conditions that significantly differ from those that will be in magnetic refrigerators. In real refrigerators the magnetic material will be subjected to an alternating magnetic field. To improve the efficiency of magnetic cooling, it is needed to use alternating magnetic fields of a high frequency. The frequencies of thermomagnetic cycles, in turn, are limited by the rate of the heat transfer in the material [3]. To increase the rate of the heat transfer, therefore, it is necessary to increase the surface area of the working body, which can be done by making it in the form of a battery of thin plates.

The study was supported by a grant of the Russian Science Foundation, project no. 18-12-00415. Research was carried out using the equipment available at the Analytical Center for collective use of the Dagestan Federal Research Centre, Russian Academy of Sciences.

However, strong anisotropy effects of MCE can occur in thin samples of alloys produced by different technologies, for example by rapid cooling in the form of melt spun ribbons. The effect of thermomagnetic relaxation processes on the magnetocaloric properties of magnetic materials in alternating magnetic fields can also occur. Particularly, these effects can be strong in the vicinity of the FOMPT. All these peculiarities should be taken into account in designing the prototypes of magnetic refrigerators.

Heusler alloys Ni-Mn-X (X = Ga, In, Sn, Sb) are promising materials for their use in magnetic refrigerators. First, in these alloys, large values of MCE at FOMPT are observed [4–7]. Second, there is an established technology for producing high quality ribbons (thickness is 10–20 microns) of these alloys, with rather high values of MCE [8–11].

2. Results and Discussion

The aim of this paper is to study the anisotropy and time dependence of MCE in ribbon samples of a Heusler alloy in alternative magnetic fields of low frequencies. The use of a direct method is necessary for the correct estimation of the MCE value at MSPT, since the use of indirect methods around first-order transitions can give untrue, often overestimated values. For example, the giant MCE reported in [12–14] was not further confirmed by direct measurements [15]. In addition, at present, except for the direct method proposed by authors, there are no other methods to measure the MCE in alternating magnetic fields [16]. The frequency of the cycles of the magnetic field used in our experiments is less than 1 Hz, which is, of course, much lower than the operating frequency of the prototypes of magnetic refrigerators, but such studies can indicate trends in the behavior of the magnetocaloric effect at higher frequencies.

In the present work, the MCE is studied in melt-spun ribbon of Ni-Mn-Sn Heusler alloys by direct technique, in a low (up to 4 kOe) and a moderate (18 kOe) magnetic field by the modulation method [16]. The frequency of the alternating magnetic field in the experiment was 0.3 Hz. The alternating magnetic field was applied to the sample during the experiment. This method has been already tested on many material samples, including Gd, manganites and Heusler alloys [16–19]. The specific heat was measured by an ac-calorimetery technique. Samples with $1 \times 3 \times 0.015$ mm^3 dimensions were cut from ribbons obtained by rapid quenching from the melt. Ribbons have a textured microcrystalline structure, with elongated column grains perpendicularly oriented to the ribbon plane [9].

According to the magnetization data (Fig. 1a) Curie point occurs at 311 K. FOMPT begins at $M_S = 256$ K, and ends at $M_f = 252$ K. Corresponding temperatures in the austenite phase are $A_S = 275$ K, and $A_f = 278$ K, respectively. With further cooling, the $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ undergoes a phase transition from low to high magnetization state in the martensite phase. The application of a 20 kOe magnetic field shifts the temperature of FOMPT to lower temperatures, and the temperature ferromagnetic-paramagnetic transition to a higher one.

Fig. 1b shows the temperature dependence of the specific heat for $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ in a zero magnetic field and in the magnetic field of 18 kOe. High-temperature specific heat anomaly displays a maximum at $T = 312.5$ K, corresponding to the ferromagnetic-paramagnetic phase transition, which takes place in the austenite phase. At temperatures of 250 K in cooling run and 273.5 K in heating one, a second anomaly in the specific heat corresponding to the FOMPT is observed. The width of the hysteresis is about 16 K.

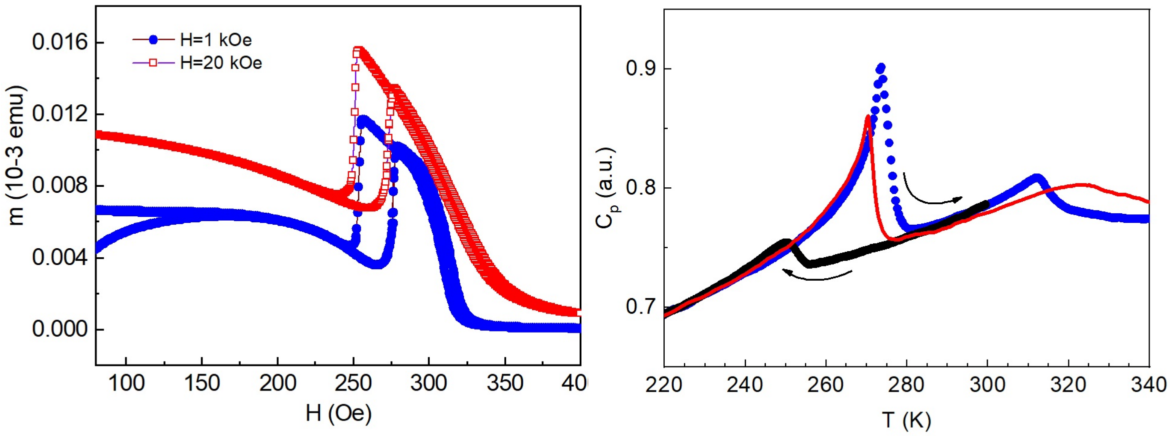

Fig. 1. a) Magnetization M(T) of $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ in heating and cooling runs in magnetic fields of 1 and 20 kOe; b) Specific heat of $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ at heating and cooling (zero-field) and in a magnetic field (18 kOe) in heating run (red line)

To study the anisotropy of the MCE, measurements were performed in two geometries: 1 — the ribbon plane being perpendicular to the magnetic field, and 2 — the ribbon plane being parallel to the magnetic field. All other conditions were identical and the same differential thermocouple was used in both experiments. Figure 2 shows the temperature dependence of the adiabatic temperature change ΔT_{ad} in $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ when H is applied parallel to the ribbon plane. There are a direct MCE due to the PM-FM phase transition, and inverse MCE at FOMPT. Thermal hysteresis is observed in the magnetostructural transition region. The maximum value of the direct effect is equal to $\Delta T_{ad} = 0.6$ K. An abrupt change in sign of the MCE is observed at magnetostructural phase transition, being the value of the inverse effect much smaller than the corresponding to the direct one, either in heating and cooling runs. At a further cooling of the martensite phase, again a direct magnetocaloric effect is observed, with a maximum at $T = 240$ K. This effect is due to the transition to the ferromagnetic state in the martensite phase.

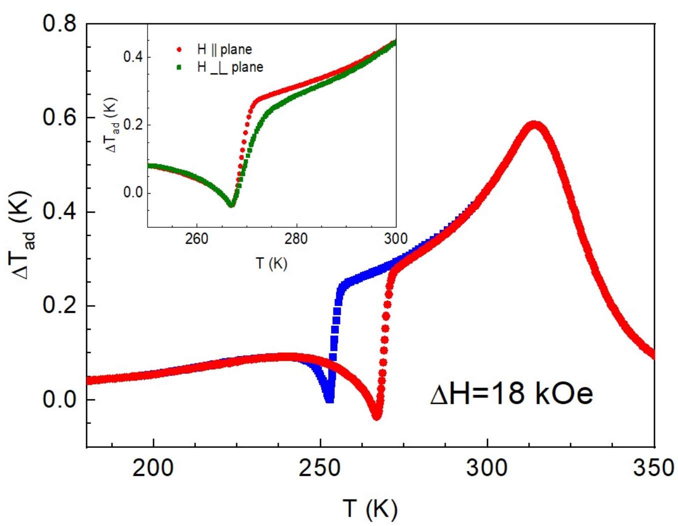

Fig. 2. MCE in $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ in heating and cooling runs at magnetic field change of 18 kOe. Inset — anisotropy of MCE

It is known that usually thin magnetic films exhibit anisotropy associated with the shape of the sample: the magnetization along the plane of the sample is much higher than in the perpendicular direction of magnetization due to the shape anisotropy [20], and with a field increasing the anisotropy decreases. It would be reasonable to expect that the same effect is inherent to MCE. Indeed, the anisotropy of the MCE is observed in the studied sample, but in a field of 18 kOe, this effect is very weak (see inset in Fig. 2, shown for the heating run only). Stronger anisotropy of MCE appears in weak fields (Fig. 3), and the anisotropy is observed in the whole temperature range in which the MCE occurs. The MCE value is larger when the magnetic field is applied along the plane of the sample. In addition, in weak applied fields a more significant difference between the values of MCE at FOMPT in heating and cooling runs is observed.

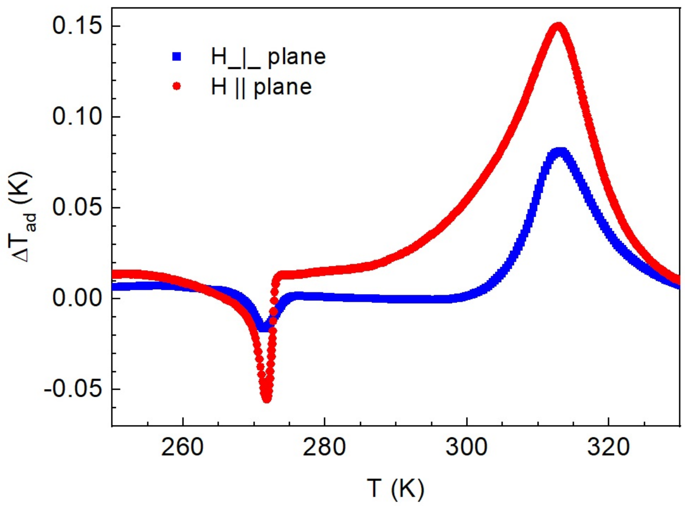

Fig. 3. Anisotropy of MCE in $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ at magnetic field changes of 3 kOe applied perpendicular and parallel to the ribbon plane

In view of the possible use of Heusler alloys in magnetic refrigerators the study of the temporal dependence of the magnetocaloric effect is a very interest issue. In Fig. 4 the temperature dependences of the MCE in the heating run at three different heating rates are shown. In the FM-PM magnetic phase transition region, it is seen that the MCE value the same at all modes. Nevertheless, there is a strong dependence of the MCE on the heating rate around the FOMPT. At a sample heating rate of 3.6 K/min, the inverse MCE value is equal to $\Delta T_{ad} = \breve{}0.17$ K, and the inverse and direct effects are nearly equals in modulus. At 2.2 K/min rate of temperature scan, the maximum value of the effect is equal to $\Delta T_{ad} = \breve{}0.07$ K, and at 0.6 K/min the effect is only $\Delta T_{ad} = \breve{}0.027$ K. The longer time the sample is in the transition area, the MCE is smaller. In addition, the temperature of the maximum of MCE is shifted to higher temperatures with the rate of temperature scan. This may be partly due to the fact that the lock-in amplifier that is used to measure the differential thermocouple signal has no time to instantly adjust to the maximum useful signal, as a consequence that in this region there is a strong phase change between the variation of the sample temperature and the applied magnetic field. But the increase of the MCE with rate of temperature scan is not explained by the instrumental effect. In this case, the measured signal should be less because the lock-in amplifier does not have time to tune the true value of MCE. Further confirmation of the truth of these results is the measurement of the MCE at the same conditions around the FM-PM transition, where a time dependence of MCE is not observed.

The observed behavior significantly differs from published reports of time dependence of MCE [21–24]. In general, these results are related to the so-called magnetic field first application effect, when a large MCE near the MSPT originates. The first application of a magnetic field results in an irreversible phase transition. With further magnetic field on/off cycling the MCE decreases and becomes similar to the normal time-independent MCE. The irreversible character of the magnetic field-induced martensitic transformation makes a sensitive contribution of the structural subsystem to ΔT_{ad} to be only appreciated during the first application of the magnetic field. Thereafter, the behavior of ΔT_{ad} is essentially determined by the magnetic subsystem only. Combination of these factors results in the observed behavior of the adiabatic temperature change during subsequent actions of the magnetic field, i. e., becomes reversible and typical of conventional MCE. In contrast to these findings [21–24], in our experiment we did not study the effect of the first run, as the alternating magnetic field is applied to the sample during all the experiment (as it would be in real magnetic refrigerators), and during the experiment there are thousands of field on/off cycles. Since the contribution of the structural subsystems only appears at the first field application, but the MCE value continues to decrease, we are actually observing some relaxation processes in the subsystem. It is appropriate to compare these times (tens of seconds) with relaxation times in FeRh [25], where the magnetization changes slightly over time more than 10^3 s.

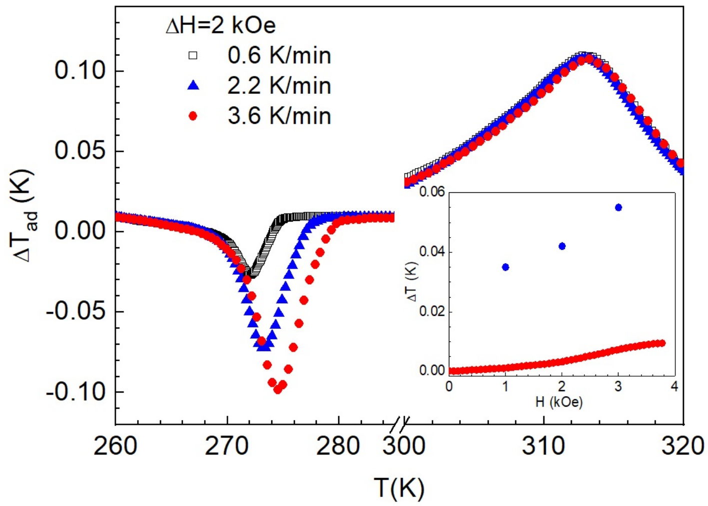

Fig. 4. MCE in $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ at different rates of temperature sweep. Inset — field dependence of MCE at 272 K

The reason for the unusual behavior of the MCE, in the studied Heusler alloy, can be its independence of either the external magnetic field long-time relaxation processes, and/or relaxation processes that take place under the influence of an alternating magnetic field. Effect of alternating magnetic fields on the magnetostructural phase transitions is little studied, and further researches are needed. Perhaps the long-time relaxation processes are characteristic to all materials, although in bulk materials the characteristic relaxation times can be of tens of hours, and in thin films and ribbons, as we have seen, these times are tens of seconds. It was recently found, that continuously application of cyclic magnetic filed within the temperature hysteresis loop in $Ni_{47}Mn_{40}Sn_{12.5}Cu_{0.5}$ Heusler alloy results in «inverse MCE — direct MCE» crossover due to irreversible martencite-austenite transition [26]. The observed in weak fields in the $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ Heusler alloy cannot be explained in a similar way, since the applied weak magnetic fields cannot cause magnetostructural phase transitions. Therefore, the observed phenomenon of the dependence of the MCE on the temperature sweeping rate can be due to relaxation processes.

3. Conclusion

In conclusion, the study of relaxation processes may provide the key to understanding the difference of MCE in the heating and cooling runs observed in Heusler alloys [24]. This difference may be due to various relaxation processes in these protocols, even if the same rate of the temperature is scanned. Thus, research of magnetocaloric properties of materials in the real conditions, in which they will be used in actual magnetic refrigerators, need to discuss about the prospects of the practical use of these materials in magnetic refrigeration technology. The results of this work show that the relaxation processes and anisotropy effects of MCE need to be taken into account at the design of magnetic refrigerators to get the highest cooling power efficiency of the machine.

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Accepted article received 10.05.2020
Corrections received 25.05.2020

Челябинский физико-математический журнал. 2020. Т. 5, вып. 2. С. 186–193.

УДК 537.622 DOI: 10.24411/2500-0101-2020-15205

МАГНИТОКАЛОРИЧЕСКИЙ ЭФФЕКТ В ЛЕНТОЧНОМ ОБРАЗЦЕ СПЛАВА ГЕЙСЛЕРА $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ В ЦИКЛИЧЕСКИХ МАГНИТНЫХ ПОЛЯХ

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Исследованы магнитокалорические свойства ленточного образца сплава Гейслера $Ni_{50.3}Mn_{36.5}Sn_{13.2}$ прямым методом в циклических магнитных полях. В слабых магнитных полях наблюдается сильная анизотропия магнитокалорического эффекта: магнитокалорический эффект в образце больше в случае приложения магнитного поля параллельно плоскости ленты. С ростом магнитного поля наблюдается уменьшение анизотропии эффекта. Обнаружено, что в циклических магнитных полях значение магнитокалорического эффекта вблизи магнитоструктурного фазового перехода зависит от скорости изменения температуры образца: чем выше скорость развёртки температуры, тем выше значение магнитокалорического эффекта.

Ключевые слова: *магнитокалорический эффект, циклическое магнитное поле, сплав Гейслера, лента, анизотропия.*

Поступила в редакцию 10.05.2020
После переработки 25.05.2020

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Работа поддержана грантом РНФ, проект № 18-12-00415. Исследование проведено с использованием оборудования Аналитического центра коллективного пользования Дагестанского федерального исследовательского центра РАН.