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MAGNETISM

Magnetocaloric Effect and Magnetostriction in a $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler Alloy in AC Magnetic Fields

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Abstract—The magnetocaloric effect (MCE) and the magnetostriction in the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy have been measured in ac magnetic fields to 8 T. It is shown that the contributions of the magnetic and structural subsystems to MCE have opposite signs; in this case, the contribution of the magnetic subsystem is dominant. The anomalous temperature dependence of the magnetostriction during the magnetostructural phase transition (PT) is explained by competition of the processes of growing austenite phase nuclei and the striction processes in them.

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1. INTRODUCTION

The MEC-based technology of magnetic cooling is considered as an alternative to the traditional cooling technology used at the present time. However, no effective and commercially-proven cooling machines acting on the basis of MEC have been designed yet, although dozen prototypes of such coolers were proposed [1, 2]. The main reason is the absence of materials with the required value of MEC in a magnetic field allowable for practice. Because of this, the main researcher groups in the world are searching for materials with parameters suitable for manufacturing magnetic coolers. It was shown experimentally that the entropy change only due to ordering of magnetic moments in external magnetic field is insufficient to design effective refrigerators. Because of this, in recent times, intense studies have been directed at searching for materials in which the change in magnetic state is accompanied by a change in the lattice structure and volume [3].

There are many materials promising for use as a working substance in the technology of magnetic cooling: for example, Heusler alloys, in which MCE are high and observed near room temperatures [4]. The Ni–Mn–In Heusler alloys also attract attention due to the fact that they demonstrate an interesting combination of magnetic and structural PTs [5–7]. A specific feature of MCE in substances with magnetostructural PTs is the simultaneous change in the magnetic entropy and lattice entropy under the action of a magnetic field, which leads to "giant" adiabatic change in temperature [8–15].

In this work, we have studied the magnetocaloric properties, the thermal expansion, and the magnetostriction of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy near the magnetostructural and magnetic PT in cyclic magnetic fields up to 8 T. The measurements of MCE and the magnetostriction in ac magnetic fields make it possible to determine the signs of contributions of various subsystems searching for most promising magnetocaloric materials with the given properties.

2. EXPERIMENTAL

The magnetocaloric properties in ac magnetic fields were studied using a modulation method. That is, an ac low-frequency magnetic field acts on the material under study and induces temperature oscillation in it. A phase-sensitive nanovoltmeter measures an alternating signal from a thermocouple cemented to a sample. An ac magnetic field is generated by an electromagnet and a power unit with external control. A controlling ac voltage is fed to the power unit from an SR830 phase-sensitive nanovoltmeter [16, 17]. The cyclic action of magnetic field on the sample was carried out using a linear actuator that placed the sample in the field and removed it from the field at a given frequency.

The thermal expansion and the magnetostriction were measured by the tensometric method [18]. The magnetostriction in ac field was measured as follows. A constant current is passed through a tensometric bridge. And the sample with a cemented strain gauge is subjected to the action of the ac magnetic field. The

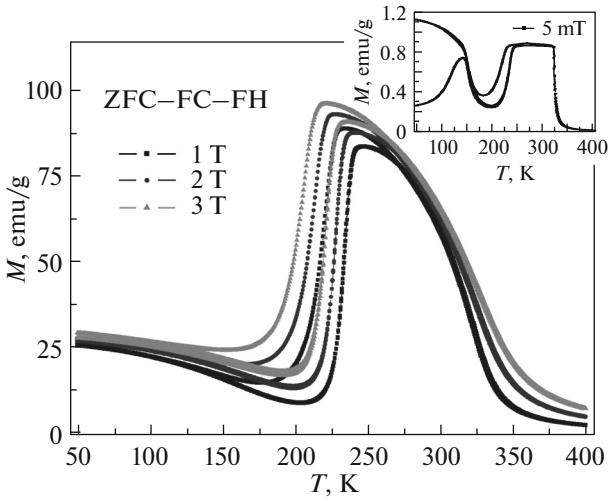

Fig. 1. Temperature dependences of the magnetization of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy measured in strong (1, 2, 3 T) and weak (5 mT; the inset) magnetic fields obtaining by the ZFC–FC–FH protocol.

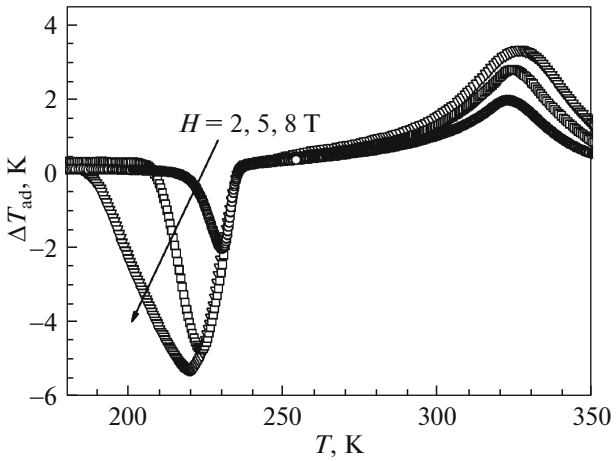

Fig. 2. Temperature dependences of MCE of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy measured on heating in strong magnetic fields.

ac signal forms at the output of the tensometric bridge as a result of a change in the sample size with a change in the field. This signal is measured by a synchronous detector. Thus, the character of changing the lattice parameters is studied at the same conditions, at which MCE is measured. A similar method of the study was used when studying the properties of rare-earth intermetallic compounds in [19]. The experimental studies of $\Delta T_{ad}(T)$, $\Delta l/l(T)$, and $\varepsilon(T)$ were performed in the temperature range 77–350 K on heating in magnetic fields up to 8 T. Owing to the high rate of varying magnetic field, we were able to comply with adiabatic conditions during the measurements, which was confirmed during measuring the field dependence of MCE in Gd in the vicinity of the Curie temperature in the presence of a heat-exchange gas and without it [17].

3. RESULTS AND DISCUSSION

The thermomagnetic measurements of $M(T)$ on heating after zero field cooling (ZFC), field cooling (FC), and field heating (FH) were carried in the temperature range 50–400 K in magnetic fields to 3 T by vibrational magnetometry (VSM, Versalab, QD). The heating and cooling rates were 5 K/min. Figure 1 shows the results of these measurements as the temperature dependences of the magnetization measured in ZFC, FC, and FH regimes.

Figure 2 shows the temperature dependences of MCE of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ alloy measured on heating in high cyclic magnetic fields with amplitudes of 2, 5, and 8 T. As is seen from Fig. 2, an inverse MCE is observed near the magnetostructural PT, and the MCE value increases with field and shifts to lower temperatures. The temperature range in which the inverse MCE is observed is limited from above by the martensite–austenite transition temperature and is not dependent on field. The existence of such boundaries is a result of the existence of the regions of irreversibility of the first-order PT induced by magnetic field. The more detailed explanation of the nature of this phenomenon is given [9]. To determine the sign of the contribution of the structural subsystem to MCE, we measured the thermal expansion (Fig. 3) and the magnetostriction (Fig. 4) in the same conditions at which MCE was measured.

As is seen in Fig. 3, as temperature decreases, dependence $\Delta l/l_0 = f(T)$ has an anomaly as the change in the sign of the thermal expansion coefficient (the insert) near the martensitic transformation and this anomaly shifts to lower temperatures as magnetic field increases. The latter is a result of the fulfillment of the Clausis–Clapeyron equation, according to which switching on magnetic field leads to a decrease in the characteristic temperatures of the magnetostructural PT: $\Delta T = -(\Delta M/\Delta S)H$, where ΔM is the change in the magnetization and ΔS is the entropy change.

The total entropy change ΔS_{tot} during magnetostructural PTs is the algebraic sum of the structural ΔS_{str} and the magnetic ΔS_m contributions: $\Delta S_{tot} = \Delta S_{str} + \Delta S_m$. The problem of the sign of the structural contribution to ΔS_{tot} was considered in [20], where it was shown that the contribution sign can be determined using a dimensionless parameter

$$\xi = \alpha\beta T_k,$$

where α is the thermal expansion coefficient, β is the coefficient relating the intensity of the exchange interactions with the distance between magnetoactive atoms. In the case when the exchange interactions are

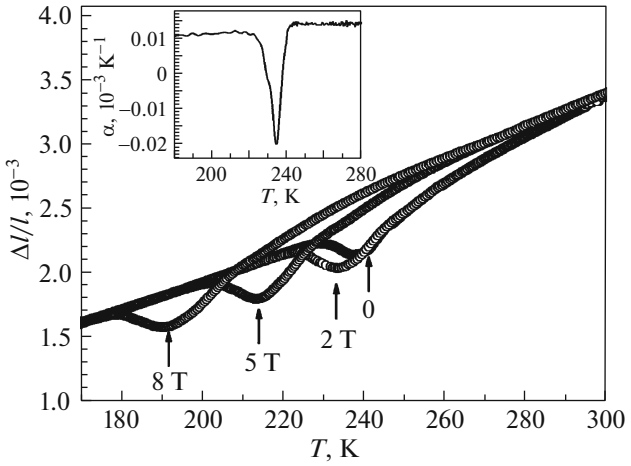

Fig. 3. Temperature dependences of the thermal expansion of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy measured on heating without field and in fields of 2, 5, and 8 T (the inset shows the thermal expansion coefficient).

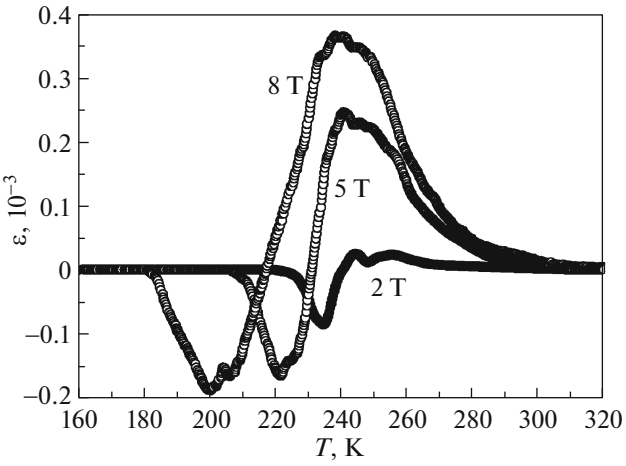

Fig. 4. Temperature dependences of the magnetostriction of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy measured on heating in strong magnetic fields.

weakened with an increase in the distance between atoms $\beta < 0$, and conversely.

If $\xi < 0$, contributions ΔS_{str} and ΔS_m are added in the opposite case, they are subtracted. Taking into account that in our case $\alpha < 0$ and $\beta < 0$ (when switching on magnetic field, the decrease in the distance between atoms (lattice compression) is accompanied by an increase in the magnetization), it can be said that the MCE observed in a Ni–Mn–In alloy is the difference of the inverse magnetic and the direct structural contributions.

The estimations performed using the experimental data presented in Figs. 2 and 3 and empiric dependence $\Delta V = f(\Delta S)$ presented in [21] show that the contribution of the structural subsystem in MCE observed experimentally is insignificant. According to our data, as temperature decreases near the martensitic transformations, the sample expands, and the change $\Delta l/l_0$ at the austenite–martensite transition width is almost 0.26×10^{-3}; in this case, the magnetic field causes a lattice compression, a decrease in the structural entropy and, as a result, a sample heating in adiabatic conditions. Using approximate relationship $\Delta V/V_0 \approx 3\Delta l/l_0$ and the experimental data on $\Delta l/l_0$, we obtain $\Delta V/V_0 = -0.078\%$. Based on dependence $\Delta V = f(\Delta S)$ [21] and the above value of $\Delta V/V_0$, we can state that the contribution of the structural subsystem is not higher than 1 J/(kg K), respectively, while the total entropy change calculated by formula $\Delta S_m = -\Delta T_{ad} C_P(H)/T$ is −5.51 J/(kg K). To calculate ΔS, we used the data on the heat capacity of the sample with close composition [22].

Figure 4 shows the temperature dependences of the magnetostriction in various fields. The curves were obtained by the measurement of the magnetostriction in a cyclic field, but they can be also obtained as the difference between the thermal expansion curve in a given field and the thermal expansion curve in a zero field. From the data of Fig. 4, we can say that, as the sample is heated from the low-temperature martensite phase near the magnetostructural PT, a negative magnetostriction, first, is observed, it decreases to some value ε_{max} and, then, begins to increase. At the sample temperature T_0, the magnetostriction changes its sign and, then, increases to ε_{max} at the end temperature of the martensite–austenite PT. Further heating leads to a decrease in the magnetostriction to zero in the Curie point.

Such complex temperature dependence of the magnetostriction in strong magnetic fields has a simple physical explanation. First, ferromagnetic austenite nuclei form in the martensite slightly magnetic phase under action of a strong magnetic field and their magnetization leads to a compression of the sample crystal lattice. On reaching ε_{min}, the austenite (less dense) phase nuclei start to actively grow (increase in the size), which leads to a lattice expansion. At temperature T_0, the processes of growing the nuclei and their magnetostriction compression during the magnetization are equalized and, further, the process of growing austenite nuclei prevails, and the magnetostriction achieves value ε_{max} as PT ends. In the high-temperature austenite phase, the lattice structure is no longer changed, and the magnetostriction was only related to a change in the magnetization (classical case $\varepsilon \sim M_S^2$).

Figure 5 shows, for comparison, the magnetostriction curves obtained by direct measurement in a cyclic field and the curves obtained by an indirect method from the temperature dependences of the thermal expansion (as the difference of thermal expansion

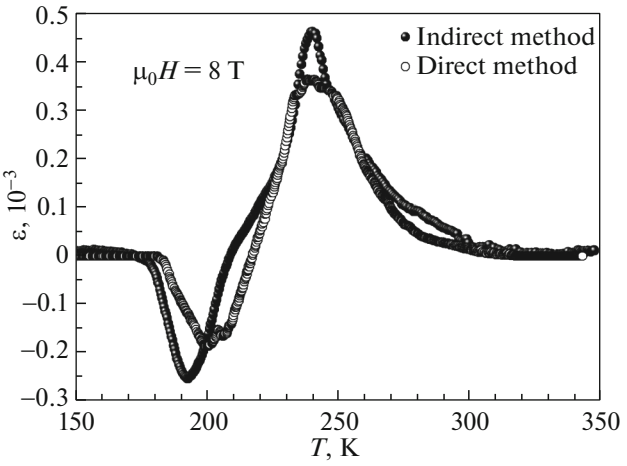

Fig. 5. Temperature dependences of the magnetostriction of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy obtained by the indirect method using formula $(\Delta l/l)_H - (\Delta l/l)_0$ and measured by the direct modulation method.

curve measured in a zero field and that measured in a given magnetic field). It is clearly seen that the magnetization curves are similar, which confirms the reliability of the data on the magnetostriction measured in alternating magnetic fields.

4. CONCLUSIONS

Thus, we have studied the magnetocaloric effect and the magnetostriction of the $Ni_{49.3}Mn_{40.4}In_{10.3}$ Heusler alloy in alternating magnetic fields to 8 T. It was shown that the observed MCE was mainly related to changes in the magnetic subsystem. The model explaining the observed anomalous temperature dependence of the magnetostriction during the magnetostructural phase transition has been proposed.

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