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Adiabatic Temperature Changes at Structural and Magnetic Phase Transitions in $Ni_{45}Mn_{43}CoSn_{11}$ at High Magnetic Fields

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The adiabatic temperature change (ΔT_{ad}) in $Ni_{45}Mn_{43}CoSn_{11}$ has been measured by a direct method in magnetic field changes up to 14 T. Large reversible magnetocaloric effects resulting in ΔT_{ad} of about $= -11$ and 5 K have been observed for magnetic field changes of 14 T at the magnetostructural ($T_A \sim 260$ K) and magnetic transitions ($T_C \sim 320$ K), respectively. The impact of the thermomagnetic history on ΔT_{ad} at high magnetic fields has been reported. The significant observed changes in the relaxation time of ΔT_{ad}, depending on the type of the phase transitions, magnetization, and demagnetization cycle are discussed.

Index Terms— **Adiabatic temperature changes, Heusler alloys, kinetic effects, magnetostructural transition (MST).**

I. Introduction

THE magnetocaloric effect (MCE) refers to the phenomenon in which magnetic materials change their temperature in response to a change in magnetic field. In some Heusler alloys, the effects originate from temperature-induced martensitic transitions between two crystal phases with significantly different magnetic structures (magnetostructural phase transition) [1]–[5]. In some cases, the magnetostructural transitions (MSTs) are associated with large adiabatic temperature changes (ΔT_{ad}), and therefore with large cooling effects compared to that resulting from magnetic subsystem only (i.e., with no structural change). Such MST is characterized by the large changes in magnetization related properties such as magnetoresistance, Hall effects, exchange bias, and magneto-optics [5]–[12].

Most Ni–Mn-based magnetocaloric materials have been studied using indirect methods, i.e., such as determining the isothermal entropy changes and the adiabatic temperature change through $M(H)$ magnetization isotherms and heat capacity measurements. However, direct measurements of ΔT_{ad} are able to provide straightforward information concerning the factors affecting ΔT_{ad} [13]. One of the methods (the so-called "extraction" method) for direct measurements of ΔT_{ad} is described in [14]. Using quasi-static high magnetic fields for this kind of measurement makes this method reliable and attractive for studying time-dependent phenomena. The most promising working materials for magnetic refrigerators are those that show the first-order MSTs near room temperature. However, it is known that magnetic hysteresis (a characteristic property of a first-order transition) and time-dependent effects can have a significant impact on the values of MCE parameters. Thus, the study of the kinetic effects of the MSTs in the Heusler alloys can have a significant impact on the search for new magnetic refrigeration materials [15]. Previous studies indicate that the MCE at the MST obtained during the first magnetization cycle are usually larger than those of subsequent cycles, i.e., the process is irreversible [16], [17]. The search for magnetocaloric materials with reversible (or nearly reversible) MCE can be considered as a step forward in the development of energy efficient magnetic cooling technologies.

In previous studies, we have discussed the application of hydrostatic pressure to tune the MST temperature to room temperature and increase the MCEs in $Ni_{45}Mn_{43}CoSn_{11}$ [18]. Here, we present a study of the kinetics of the MST in $Ni_{45}Mn_{43}CoSn_{11}$ in magnetic fields up to 14 T using extraction method (a direct method). The extraction method provides the opportunity to apply uniform magnetic fields in a larger volume with longer exposure times, and with variable rates of field change.

II. Materials and Methods

A 3 g polycrystalline ingot of $Ni_{45}Mn_{43}CoSn_{11}$ was prepared by arc melting in a high-purity argon atmosphere using 4N purity elements (Ni: 99.9%, Mn, Sn: 99.9999%, and Co: 99.99%). The details of the sample preparation have been published in [18]. To determine the phase purity and crystal structures, the X-ray diffraction (XRD) measurements were carried out on a powdered sample using Cu-Kα radiation. Thermomagnetic curves $M(H, T)$ have been acquired using a quantum design superconducting quantum interference device

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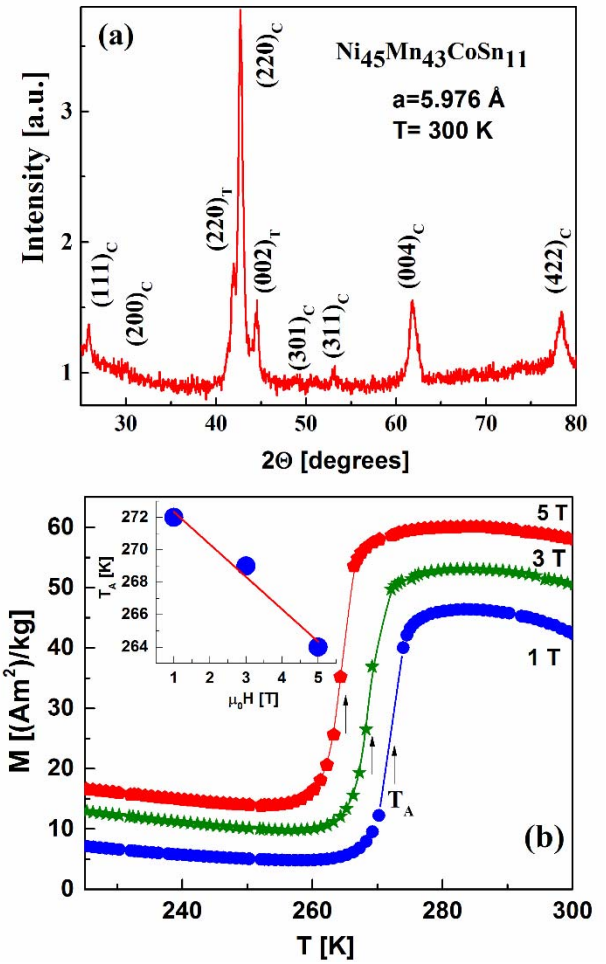

Fig. 1. (a) Room-temperature XRD of $Ni_{45}Mn_{43}CoSn_{11}$ Heusler alloy. The indices "T" and "C" are used to indicate the martensitic tetragonal and austenitic cubic phases, respectively. (b) $M(T)$ curves obtained at magnetic fields up to 5 T. The phase transitions temperatures (T_A) from low magnetization martensitic to ferromagnetic austenitic phases are indicated by the arrows.

magnetometer in a temperature interval of 5–400 K. The direct measurements of the adiabatic temperature change have been performed using the sample extraction technique based on a bitter-type magnet in fields up to 14 T and a temperature range of 4.2–350 K, implemented by Y. Koshkid'ko and J. Cwik at the International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland (for details of this setup see [17]).

III. Results and Discussion

The room-temperature XRD pattern of $Ni_{45}Mn_{43}CoSn_{11}$ is shown in Fig. 1(a). It shows that the sample is in mixed martensitic and austenitic phases. The austenitic and martensitic phases were found to be $L2_1$ cubic and tetragonal structures, respectively. The cubic structure dominates at room temperature, as the peaks from the martensitic phase were of low intensity, about 18% of that of the austenitic phase. The obtained structures and lattice parameters are similar to those previously reported [12]. The magnetization data $M(T)$ for $Ni_{45}Mn_{43}CoSn_{11}$ measured while heating the sample in different applied magnetic fields are shown in Fig. 1(b). The field-induced metamagnetic behavior was experimentally

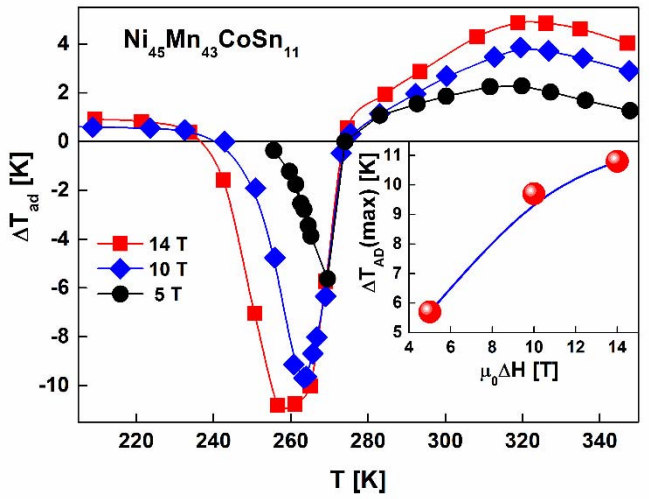

Fig. 2. Adiabatic temperature change (ΔT_{ad}) of $Ni_{45}Mn_{43}CoSn_{11}$ as a function of temperature for different $\mu_0 \Delta H$ values obtained during the first heating. Inset: maximum ΔT_{ad} at MST at different magnetic fields.

confirmed in $M(H)$ measurements (not shown). The thermomagnetization curves shift to the lower temperature with increasing applied magnetic field. The shift of the MST temperature (T_A) from a low magnetization martensitic to a ferromagnetic austenitic phase by about -2 K/T was detected for this sample [see the inset of Fig. 1(b)]. The temperature of the phase transition from a low magnetization martensitic to a ferromagnetic austenitic phase (T_A) was determined by the maximum of the derivative of magnetization with respect to temperature during the heating cycle. Such a large magnetization change associated with the field-induced martensitic transition indicates the likelihood of a large MCE.

Fig. 2 shows the temperature dependences of the adiabatic temperature changes measured in the magnetic fields up to 14 T. Negative and positive adiabatic temperature changes characteristic for the antiferromagnetic–ferromagnetic and ferromagnetic–paramagnetic phase transitions, respectively, have been observed. This behavior is consistent with the magnetic ordering determined from magnetization measurements [see Fig. 1(b)]. The maximum value of ΔT_{ad} (about -11 K) was observed near the MST from a low magnetization state (antiferromagnetic or paramagnetic) to a ferromagnetic austenitic phase for a field change of 14 T. A direct MCE of about 5 K was observed near the Curie temperature (T_C) for a field change of 14 T, and this value was found to increase with increasing magnetic field. The inset of Fig. 2 shows the maximum ΔT_{ad} at different magnetic fields at MST and suggests a saturation in the magnitude of ΔT_{ad} with increasing magnetic field change, which is typical for MSTs in strong magnetic fields. A partial kinetic arrest related to the delay in the formation of the martensite phase causes to have a positive MCE in the lower temperature region (i.e., below ~235 K) [19].

The adiabatic temperature changes as a function of temperature for a field change of 14 T during two cycles of magnetization with continuous heating and cooling are shown in Fig. 3. Here, it is shown that this effect is nearly reversible in terms of the temperature (see second cycle). The main reason for this behavior is the completion of the MST from

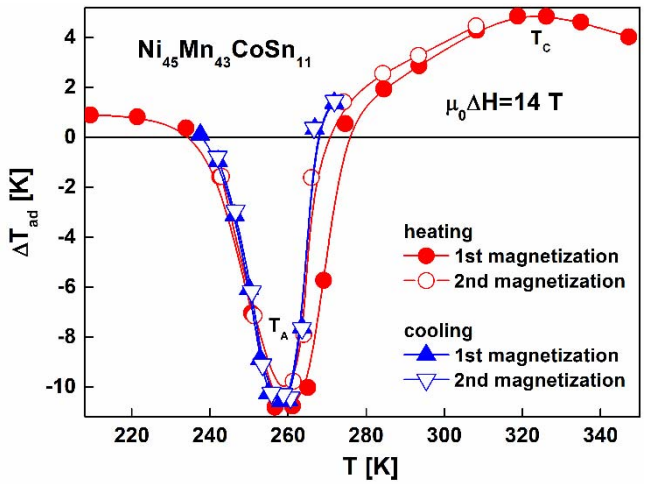

Fig. 3. Adiabatic temperature change of $Ni_{45}Mn_{43}CoSn_{11}$ as a function of temperature (T) for $\mu_0 \Delta H = 14$ T during two heating and cooling cycles.

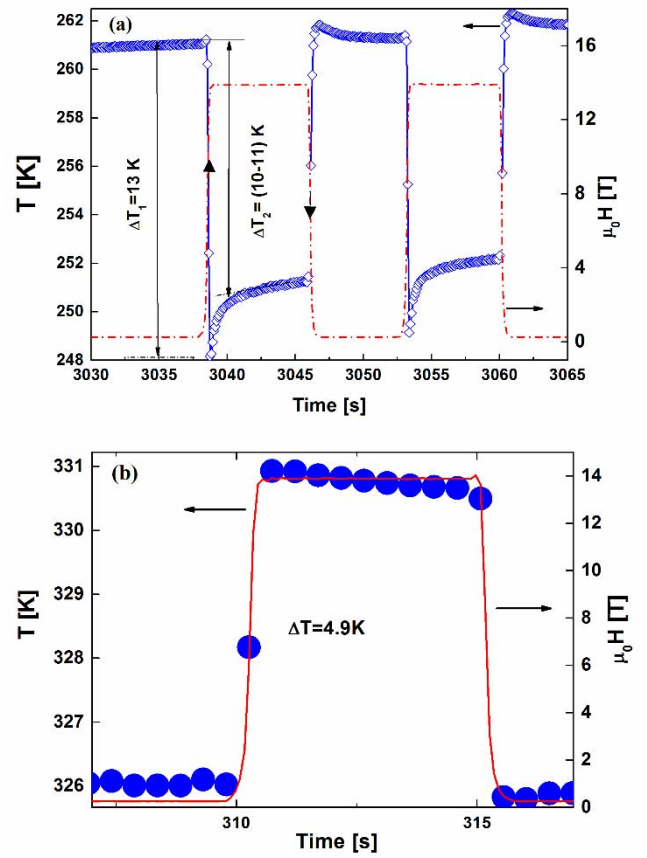

Fig. 4. (a) Adiabatic temperature change of $Ni_{45}Mn_{43}CoSn_{11}$ for the first and second applications of magnetic field in the temperature region near the MST. ΔT_1 is the initial value of the adiabatic temperature change, and ΔT_2 is the value of the adiabatic temperature change after relaxation. (b) ΔT_{ad} of $Ni_{45}Mn_{43}CoSn_{11}$ near the Curie temperature.

weakly magnetic martensite state to the ferromagnetic-like austenite phase (Fig. 1).

Fig. 4(a) shows the adiabatic temperature change in the temperature region near the MST for the first and second applications of the magnetic field. A time delay in ΔT_{ad} was observed with respect to changes in the magnetic field [see Fig. 4(a)]. When the magnetic field is switched ON, a sharp change in temperature occurs, which is caused by the adiabatic magnetization of the sample. The relaxations of the sample temperature were observed, and the relaxation time is different when the magnetic field is switched ON and OFF. However, the relaxation is much slower in the vicinity of T_C [see Fig. 4(b)]. Therefore, the process observed at the MST cannot be related to the heat exchange between the sample and the environment, and is therefore an intrinsic feature of the MST. It is well-known from ferromagnetic resonance investigations that the spin–lattice and spin–electron relaxation in ferromagnetic metals occurs on a nanosecond timescale, 9 orders of magnitude faster than that observed in our case. In addition, this long relaxation time cannot be connected with magnetic aftereffect [20] when there is a delay between the increase of magnetic field and magnetization.

Initially, at 260 K [Fig. 4(a)], the sample is in a mixed martensitic–austenitic state. By applying a magnetic field, and the induced MCE, the temperature decreases sharply to 248 K, leading to a non-equilibrium martensitic state with an embedded (frozen) austenitic phase. Afterwards, a part of austenitic phase slowly transforms to martensite and, as a result, the temperature slowly increases up to 251 K and approaches equilibrium. When the magnetic field is switched OFF, the MCE causes the temperature to increase to 261 K, which is higher than the initial temperature, a clear indication of a non-equilibrium state. Since this state is very close to the austenitic phase (Fig. 1), the relaxation time decreases. Thus, it can be concluded that these slow relaxation processes are connected with phase transformations which do not strictly follow the changes in magnetic field. The relaxation of the adiabatic temperature changes cannot be observed in the pulsed magnetic fields with short time pulses. Therefore, the observed values of ΔT_{ad} using pulsed magnetic fields near MSTs may differ significantly from those measured in quasi-static magnetic fields [2], [21]. The largest value of ΔT_{ad} was observed in the first magnetic field application. Therefore, ΔT_{ad} after relaxation should be considered as the accurate one.

IV. Conclusion

We used a direct method to study the adiabatic temperature change (ΔT_{ad}) of $Ni_{45}Mn_{43}CoSn_{11}$ in magnetic field changes up to 14 T. For the first field application, ΔT_{ad} reaches -13 K with the initial temperature close to the MST. Because of relaxation processes after cycling, this temperature does not exceed -11 K for subsequent field cycles. The relaxation processes last several seconds when the field is switched ON and OFF, and the relaxation time is smaller in the latter case. It is shown that the relaxation process may be related to martensite–austenite phase transformations when the sample heating and cooling is due to an MCE. Therefore, even for the very narrow temperature hysteresis of the MST in $Ni_{45}Mn_{43}CoSn_{11}$, complete irreversibility can be achieved only in a static magnetic field. Thus, the correct value of ΔT_{ad} cannot be determined by measurements in the pulsed magnetic fields. Hence, a detailed investigation of the relaxation time as a function of temperature, magnetic field amplitude, and composition can only be done accurately using a direct method.

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