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Measurement-Protocol Dependence of the Magnetocaloric Effect in Ni-Co-Mn-Sb Heusler Alloys

C. Salazar-Mejía,1,* V. Kumar,2 C. Felser,2 Y. Skourski,1 J. Wosnitza,1,3 and A.K. Nayak4

1 Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany
2 Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany
3 Institut für Festkörper- und Materialphysik, TU Dresden, 01062 Dresden, Germany
4 School of Physical Sciences, National Institute of Science Education and Research, HBNI, Jatni-752050, India

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Ni-Co-Mn-Sb-based Heusler shape-memory alloys that undergo a martensitic-structural transition around room temperature are well known for exhibiting large magnetic entropy change and elastocaloric effect. Here, we report the observation of a large adiabatic temperature change of $-11$ K in a Ni-Co-Mn-Sb system by using direct adiabatic temperature-change measurements in pulsed magnetic fields. We show that a large magnetic cooling can be achieved in a wide temperature range spanning from 120 to 270 K by purposefully varying the chemical composition. The temperature- and field-dependent irreversibility of the effect is analyzed through a detailed experimental study of the protocol-dependent magnetocaloric effect. The present study is an important contribution towards the understanding of irreversible magnetocaloric effects in materials with magnetostructural transition.

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I. INTRODUCTION

It has been proposed that solid-state-based magnetic cooling has enough potential to replace the conventional gas-based cooling technique [1–3]. However, most of the magnetic materials showing a large magnetocaloric effect (MCE) contain rare-earth elements [2,4]. In recent years, it has been found that some of the transition-metal-based Heusler shape-memory materials exhibit a large MCE comparable to that of the rare-earth-based systems [5–7]. However, thermal hysteresis is a critical issue for the performance of cooling devices based on the magnetocaloric effect [8–11]. Specifically, in the case of Heusler alloys that undergo a first-order magnetostructural transition, thermal hysteresis, intrinsic of the transition, not only lead to irreversible effects, but to magnetocaloric properties that strongly depend on the measurement protocol at which they are obtained, for instance, whereas the initial temperature is approached on cooling or on heating [12–14]. As a consequence, the temperature-dependent adiabatic temperature change ($\Delta T_{ad}$) and isothermal entropy change ($\Delta S_{iso}$) of Heusler alloys exhibit, likewise, thermal hysteresis and are protocol dependent [11,13,15–19]. This is commonly overlooked in the literature, especially when calculating the magnetocaloric properties from indirect measurements. However, hysteresis should always be taken into consideration in order to properly characterize a magnetocaloric material, such as reported for FeRh [20], La-Fe-Si [14,21,22], Ni-Mn-Ga [21], and Ni-(Co)-Mn-In [12,17], among others. The recently proposed approach that considers the hysteresis on Heusler alloys as a desirable property to be exploited in multicaloric cooling cycles [23], also supports the necessity to properly characterize the magnetocaloric effect in first-order materials.

Among the Heusler shape-memory materials, Ni-Co-Mn-Sb-based alloys have been widely studied. It has been shown that members of this family exhibit, among other phenomena, elastocaloric [24], magnetocaloric [25,26], and shape-memory [26,27] effects at room temperature. Ni-Co-Mn-Sb alloys have further been shown to display exchange bias [28] and kinetic arrest [29]. In general, the Ni$_{50-x}$Co$_x$Mn$_{38}$Sb$_{12}$ alloys (with $x = 5$, 6, and 7) undergo at $T_M$ a first-order martensitic transition from a high-temperature ferromagnetic austenite to a low-temperature martensitic phase, which exhibits lower magnetic moment. Thus, the ferromagnetic transition at $T_C$ appears above $T_M$. The increase of Co content shifts the martensitic transition toward lower temperatures while increasing slightly the ferromagnetic transition temperature [27,30]. The broadness of the transition also increases with Co content. Although a large MCE, specifically, a large magnetic entropy change determined from indirect measurements,
has been reported for the Ni-Co-Mn-Sb system, direct measurements of the adiabatic temperature change have not been reported. In this work, we report the adiabatic temperature change, $\Delta T_{ad}(T)$, of the Heusler alloys $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{38}\text{Sb}_{12}$ with $x = 5, 6$, and $7$, through direct measurements in pulsed magnetic fields up to 20 T. In order to properly characterize MCE materials, high fields (above 2 T) are often needed to completely induce the transition and, in that way, avoid entering in a minor cycle or in a mixed state. Additionally, measurements under high magnetic fields give information such as on the maximum $\Delta T_{ad}$ value at the transition, as the maximum temperature range where these values can be achieved, the field dependence of the transition temperatures, and the temperature region where the effect is reversible. The latter point, i.e., the irreversibility of the effect, is analyzed. Furthermore, a detailed experimental study of the protocol-dependent MCE of $\text{Ni}_{45}\text{Co}_5\text{Mn}_{38}\text{Sb}_{12}$ is presented. $\Delta T_{ad}$ for this alloy is characterized following different measurement protocols and a large difference between $\Delta T_{ad}$ recorded using cooling protocol and those recorded using heating protocol is reported.

II. EXPERIMENT

Polycrystalline ingots of $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{38}\text{Sb}_{12}$, $x = 5, 6$, and $7$, are prepared following Ref. [30]. Magnetization measurements are carried out in a physical property measurement system (Quantum Design). Direct measurements of $\Delta T_{ad}$ are performed in a home-built experimental setup in pulsed magnetic fields at the Dresden High Magnetic Field Laboratory (HLD). Short pulse durations (20–50 ms) not only allow for adiabatic conditions, making it possible to measure $\Delta T_{ad}$ without heat losses, but also probes the thermal kinetics of materials on a time scale matching the one suitable for applications, i.e., 1–100 Hz [31]. Additionally, the high fields available allow, in this case, the martensitic transition to be induced over a wide temperature range.

III. RESULTS AND DISCUSSION

Temperature-dependent magnetization curves $M(T)$ for the three different Co concentrations are presented in Fig. 1. $M(T)$ data are recorded on cooling and subsequent heating for applied magnetic fields of 0.01, 2, 6, and 14 T. $\text{Ni}_{45}\text{Co}_5\text{Mn}_{38}\text{Sb}_{12}$ [Fig. 1(a)], undergoes a martensitic transition at $T_M = 252.5$ K from a high-temperature ferromagnetic austenite to a low-temperature ferrimagnetic martensitic phase, which exhibits a lower magnetic moment. A thermal hysteresis of around 11 K is intrinsic to the first-order magnetostructural transition and the reverse transition takes place upon heating around $T_d = 264$ K. The Curie temperature is $T_C = 344$ K. With increasing Co content, $T_C$ slightly increases, for instance, for $x = 6 T_C \approx 350$ K. Concomitantly, the martensitic transition is shifted toward lower temperatures, as previously reported [27,30]. Specifically, for $x = 6$ and $x = 7$, the martensitic transition takes place upon cooling at around 212 K [Fig. 1(b)] and 179 K [Fig. 1(c)], respectively. At the same time, the transition broadens as Co increases, while the hysteresis of the transition remains almost constant.

Magnetic field stabilizes the higher-moment magnetic phase, in this case the austenite. Therefore, the martensitic transition shifts toward lower temperature with field, as shown for all samples in Fig. 1 and specifically in the inset, where the field dependence of $T_M$ is plotted. The sensitivity of the transition to the magnetic field is quantified by $dT_M/dH$, which is $-1.7$, $-2.2$, and $-3.2$ K/T for $x = 5, 6$, and $7$, respectively. This is a rather weak field dependence compared with other Heusler alloys [19,32]. It is worth mentioning that the martensite-to-austenite transition in these materials can be induced by large magnetic fields even at low temperatures [33].

The adiabatic temperature change $\Delta T_{ad}(T)$ is measured for all samples close to the martensitic transition. The results are presented in Fig. 2. Magnetic field pulses of 6 and 20 T are applied. Thereby, the sample is always heated up to the austenitic phase and cooled down to the

![Fig. 1. Temperature-dependent magnetization curves](image-url)
no MCE is recorded. This shows that the MCE effect is highly irreversible in these alloys and depends strongly on the measurement history, as previously reported [6,27]. This irreversibility in the MCE in combination with large shape-memory effects [27], makes these materials potential candidates to be used in a multicaloric cooling cycle (based on magnetocaloric and elastocaloric effects), where thermal hysteresis is exploited [23].

We have previously reported on a large relative length change of up to 1% on the alloys with $x = 5$ and $x = 6$ due to the magnetic-field-induced martensitic transition. Specifically, for the $x = 5$ alloy, a one-way magnetic shape-memory effect is found at $T_i = 258, 260$, and 262 K. The initial application of the magnetic field induces the martensite transition that leads to an expansion of the sample. Upon subsequent field sweeps, the length of the sample stays almost constant indicating that the material remains in the austenitic phase [27]. As shown in Fig. 2, at these temperatures, the $x = 5$ alloy also shows large irreversibility. For example, at $T_i = 260$ K, the sample cools down by 7 K in the up sweep, but warms up by only 3.1 K in the down sweep, indicating that almost half of the sample stays in the austenitic phase. Simultaneous measurements of the magnetostriction and the adiabatic temperature change could shed more light into the correlation between length and temperature change in these alloys.

$\text{Ni}_{45}\text{Co}_{5}\text{Mn}_{38}\text{Sb}_{12}$ shows a large difference in the MCE for field pulses of 6 and 20 T, as 6 T is not sufficient to induce the transition in the investigated temperature range, while 20 T is, as discussed later. The alloys with $x = 6$ and 7 show a higher sensitivity of the transition to the field $dT_M/dH$ (see inset of Fig. 1) so that close to $T_M$ 6 T is sufficient to induce the transition.

The samples exhibit broad $\Delta T_{ad}(T)$ plateaus for the 20-T pulses that extend approximately in the temperature range from 245 to 260 K for $x = 5$, 190 to 225 K for $x = 6$, and 130 to 180 K for $x = 7$. The latter alloy has a broader transition leading to a MCE that extends over a large temperature range. Furthermore, the $\Delta T_{ad}$ values found in these alloys are among the largest found so far under high magnetic fields [6,34–37].

In general, the magnetocaloric effect decreases as $x$ increases, as shown in Fig. 2. This is related to the fact that $|T_C - T_M|$ increases with Co substitution (Fig. 1) and, due to the contradictory role of the magnetic and structural contributions to the magnetocaloric effect in metamagnetic Ni$_2$Mn-based Heusler alloys, the MCE also decreases [38,39].

We choose the $x = 5$ sample to study the measurement-protocol dependence of the MCE. Prior to the $\Delta T_{ad}$ characterization, isothermal magnetization curves $M(H)$ are measured. These measurements allow estimation of the MCE expected at different temperatures, although dynamic effects due to the field-sweep rates and differences between

![FIG. 2. Adiabatic temperature change of Ni$_{45}$Co$_{5}$Mn$_{38}$Sb$_{12}$ (black), Ni$_{44}$Co$_{6}$Mn$_{38}$Sb$_{12}$ (green), and Ni$_{43}$Co$_{7}$Mn$_{38}$Sb$_{12}$ (blue) near the martensitic transformations, obtained for magnetic field pulses of 6 (circles) and 20 T (squares). Closed symbols indicate $\mu_{ad}$ values obtained for field up and open symbols for down sweeps. The inset shows the recorded time-dependent data of $\Delta T_{ad}$ at the initial temperature $T_i = 220$ K for $x = 6$, together with the time-dependent magnetic field.](Image)
isothermal and adiabatic measurements cannot be ruled out. Figure 3 shows $M(H)$ at 250, 254, and 259 K, recorded up to 14 T in static fields for different measurement protocols: (i) $T_i$ reached on discontinuous cooling, (ii) $T_i$ reached on discontinuous heating, and (iii) $T_i$ reached on continuous heating. In the first two protocols, the sample is always heated up to the austenitic phase and cooled down to the martensitic phase (or vice versa) before reaching the initial temperature $T_i$. In the case of continuous heating, $T_i$ is just approached heating directly from the previously measured temperature. The transition region of the 0.01-T $M(T)$ curve is shown in the inset of Fig. 3(d), where additionally, the austenitic start and finish temperature $T_A^S = 260$ K and $T_A^F = 265$ K and the martensitic start and finish temperature $T_M^S = 253$ K and $T_M^F = 251$ K are indicated. These temperatures characterize the martensitic transition. At 250 K ($T < T_A^S$), both curves, measured on cooling and on heating, are almost the same [Fig. 3(a)], as the sample is mainly in the martensitic state for both cases before applying field. The small difference between the curves arises from the fact that the thermal hysteresis loop is not completely closed at this temperature and some little amount of austenitic state could still be present when $T_i$ is reached on cooling. The transition from martensite to austenite is induced by around 6.5 T. Under field removal, the sample transformed back to the martensitic phase at around 2.5 T. Indeed, a field of 9 T is sufficient to complete the field-induced martensitic transition.

For the second case [see Fig. 3(b)], 254 K is reached on (i) cooling from 350 K, (ii) on heating from 100 K, and (iii) on heating directly after measuring $M(H)$ at 250 K (continuous heating). 254 K lies below the austenitic start temperature $T < T_A^S$ and just between $T_M^C$ and $T_M^S$, the martensitic finish and start temperatures, respectively. Therefore, there is a small difference between the measurements performed on cooling and heating. In case (i), the sample is in a mixture of austenitic and martensitic phases before the measurement, while in case (ii) the sample starts from a pure martensitic phase. In case (iii), discontinuous heating, the results differ slightly from case (ii) as some austenitic phase (with higher magnetic moment) is retained in the sample from the previous measurement at 250 K.

Figure 3(c) shows the results for the $M(H)$ curves recorded at 259 K under the same conditions explained above. This temperature is just below $T_A^S$ and the difference between the measurements performed using the discontinuous heating and continuous heating protocols is notable. In the case of continuous heating, some austenitic phase is already present in the sample before applying field as a result of the previous $M(H)$ measurement at 254 K. Therefore, the induced transition takes place at lower critical field. When the temperature is reached on cooling, the sample is in the austenitic ferromagnetic state, as 259 K lies above $T_M^S = 253$ K, so no induced transition is observed when applying the field, as shown in the inset of Fig. 3(e).

In a next step, we characterize $\Delta T_{ad}(T)$ of Ni$_{45}$Co$_5$Mn$_{38}$Sb$_{12}$ following discontinuous heating and discontinuous cooling protocols as well as a continuous heating protocol. $\Delta T_{ad}(T)$ is determined under applied fields of 2, 6, and 20 T and the results are presented in Fig. 4.

The first thing to notice is that there is a big difference on the $\Delta T_{ad}(T)$ obtained using the heating protocol and those measured using the cooling protocol. The curves are shifted in temperature, as expected. This temperature difference between the curves follows the thermal hysteresis observed in the $M(T)$ curves. In a general picture, the martensitic transition can be induced by magnetic field. Specifically, the sample transforms from the martensitic to the austenitic phase, as field stabilizes the higher-moment phase. Consequently, on cooling, the induced transition could only take place below $T_M^S$ (where some martensitic phase starts being present in the sample) and, on heating, the transition can be induced up to a temperature $T_M^S$ (inset of Fig. 4). As $T_M^S < T_M^C$, both $\Delta T_{ad}(T)$ curves, recorded using cooling and heating protocols, extend over different
instance, for the cooling protocol, the maximum difference strongly for the heating and cooling protocols. For ally, there is a large difference in the maximum 6 K for field changes of 6 and 20 T, respectively. Additionally, Ni45Co5Mn38Sb12 exhibits the largest MCE for 6 T also continuous heating data are recorded (squares). Inset: schematic of the adiabatic cooling in the case of using the heating (continuous blue arrow) or cooling (discontinuous green arrow) protocol. See text for details.

FIG. 4. Adiabatic temperature change of Ni_{45}Co_{5}Mn_{38}Sb_{12} around the martensitic transformation, obtained under magnetic field pulses of 2, 6, and 20 T following discontinuous heating (circles) and discontinuous cooling (triangles). For a field change of 6 T also continuous heating data are recorded (squares). Inset: schematic of the adiabatic cooling in the case of using the heating (continuous blue line) in comparison to the MCE measured using cooling.

From $M(H)$ presented in Fig. 3, one can see that 2 T is not sufficient to complete the martensitic transition. Consequently, the MCE on heating is small. When measuring using the cooling protocol, the MCE is negligible.

A field change of 6 T only induces the transition in a narrow temperature range (Fig. 3). The maximum $\Delta T_{ad}$ differs strongly for the heating and cooling protocols. For instance, for the cooling protocol, the maximum $\Delta T_{ad}$ is $-2.8$ K reached at 254 K, while for the heating protocol, $\Delta T_{ad}$ is up to 2.5 times larger with $-7$ K at 260 K.

Furthermore, measurements for $\mu_0 H = 6$ T following the continuous heating protocol are performed. As found earlier, the results obtained in this way depend on the temperature steps at which the measurements are taken, i.e., each $\Delta T_{ad}$ depends on the previous one [12], therefore, results obtained this way have to be considered carefully. The $\Delta T_{ad}$ values obtained using this method are lower than the ones obtained under discontinuous heating as the previous field application induces partially, or completely, the transition to the austenitic phase and some of the austenite is retained after field removal [27,29]. This arrested austenite (not present in the case of discontinuous heating) does not contribute to the cooling MCE.

For field pulses of 20 T, the adiabatic temperature change has a maximum $\Delta T_{ad} = -11.3$ K, as the field is large enough to induce the transition in the measurement temperature range (see Fig. 3). It is important to notice that for the 20-T pulses the MCE is almost reversible (see, for instance, the data for up and down sweeps in Fig. 2). Even a field change of 10 T is sufficient to induce and complete the transition, as seen in Fig. 3. Thus, this large $\Delta T_{ad}$ would also be achieved with smaller fields of 10 T.

IV. CONCLUSIONS

To summarize, we investigate the magnetocaloric effect of the Heusler alloys Ni_{45}Co_{5}Mn_{38}Sb_{12}, Ni_{44}Co_{6}Mn_{38}Sb_{12}, and Ni_{43}Co_{7}Mn_{38}Sb_{12} for magnetic field changes of 2, 6, and 20 T. For a field change of 20 T, Ni_{44}Co_{5}Mn_{38}Sb_{12} exhibits the largest MCE of $-11.3$ K, however, Ni_{44}Co_{6}Mn_{38}Sb_{12} exhibits the largest MCE for 6 T, $-9.5$ K. A detailed study on the measurement-protocol dependence of the MCE of Ni_{45}Co_{5}Mn_{38}Sb_{12} is performed. A large difference between $\Delta T_{ad}$ recorded using the cooling protocol and those recorded using the heating protocol is found. The reversibility and reproducibility of the magnetocaloric effect strongly depends on the thermal hysteresis and the sensitivity to the field of the martensitic transition. The magnetocaloric effect also depends on the measuring protocol. Our results show that the thermal hysteresis of the first-order transition should always be considered when investigating the MCE in Heusler alloys.

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