**The effect of step-like martensitic transformation on the magnetic entropy
change of $\text{Ni}_{40.6}\text{Co}_{8.5}\text{Mn}_{40.9}\text{Sn}_{10}$ unidirectional crystal grown with the
Bridgman-Stockbarger technique**

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Abstract

We report a **step-like** martensitic transformation and its effect on magnetocaloric properties in $\text{Ni}_{40.6}\text{Co}_{8.5}\text{Mn}_{40.9}\text{Sn}_{10}$ **unidirectional crystal** grown using the Bridgman-Stockbarger technique followed by vacuum annealing at 1173 K for 72 h. This alloy undergoes successive first-order phase transitions which are attributed to the monotonic compositional variation along the crystal growth direction; the latter results in the increase of the full-width at half-maximum of the magnetic entropy change as a function of temperature (δT_{FWHM}). For a magnetic field change of 2 and 5 T, the maximum magnetic entropy change are 9.7 and 16.0 $\text{Jkg}^{-1}\text{K}^{-1}$ with an extended δT_{FWHM} of 11 and 23 K, respectively. The average hysteresis loss for a field change of 2 T is 19 Jkg^{-1} reducing the refrigerant capacity by 17%.

Keywords: **Ni-Co-Mn-Sn**; ferromagnetic shape memory alloy; **step-like martensitic transformation**; magnetic entropy change; magnetic hysteresis losses.

1. Introduction

In recent years, ferromagnetic Ni-Mn-Z (Z: group IIIA–VA elements) Heusler alloys attracted interest as a group of promising refrigeration materials due to their giant and tunable inverse magnetocaloric effect (MCE) around room temperature (RT). The latter is originated by the large positive field-induced magnetization change across the first-order martensitic transformation. Krenke et al. reported the MCE for $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$ alloys with $x=13$ and 15 [1]. Under a magnetic field change $\mu_0\Delta H$ of 5 T these authors reported a maximum magnetic entropy change ΔS_M^{peak} of $18 \text{ JK}^{-1}\text{kg}^{-1}$. The partial replacement of Ni or Mn in these Heusler alloys by Co leads to two important effects. First, the structural transition temperatures can be tuned in a wide range [2-6] and, second, the magnetization difference between martensite and austenite phases ($\Delta M_{\text{M-A}}$) increases providing more driving force to induce the structural transition at reduced magnetic fields [7, 8]. The larger $\Delta M_{\text{M-A}}$ results in larger ΔS_M^{peak} values [9]. For example, in $\text{Ni}_{50}\text{Mn}_{38}\text{Sb}_{12}$, the substitution of 5 at. % Co for Ni increases the ΔS_M^{peak} value associated to the reverse martensitic transformation from 7 to $34 \text{ JK}^{-1}\text{kg}^{-1}$ [3]. ΔS_M^{peak} of $\text{Ni}_{45}\text{Mn}_{37}\text{In}_{13}\text{Co}_5$ reaches $\sim 34 \text{ Jkg}^{-1}\text{K}^{-1}$ [4] which is nearly 4 times larger than $8.0 \text{ Jkg}^{-1}\text{K}^{-1}$ for Co-free $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ [5]. The substitution of Co for Mn in $\text{Ni}_{43}\text{Mn}_{46-x}\text{Co}_x\text{Sn}_{11}$ considerably increases ΔS_M^{peak} from about $10 \text{ Jkg}^{-1}\text{K}^{-1}$ to $19.1 \text{ Jkg}^{-1}\text{K}^{-1}$ and raises its working temperature range to around room temperature [6]. Ito *et al.* [7] suggested that to significantly enhance the ferromagnetic coupling between the Mn atoms, the Co content should exceed about 6 at. %. However, the addition of Co also spurs the formation of a second phase [10, 11]. In fact, our previous work on Ni-Co-Mn-Sn bulk alloys shows that if Co exceeds 10 at. %, a large amount of γ phase particles form [12]. In $\text{Ni}_{37.7}\text{Co}_{12.7}\text{Mn}_{40.8}\text{Sn}_{8.8}$ melt-spun ribbon ΔS_M^{peak} decreased from $15 \text{ JK}^{-1}\text{kg}^{-1}$ to $2.2 \text{ J K}^{-1}\text{kg}^{-1}$ because of the formation of γ phase particles [13]. Liu *et al.* [4] suggested that the γ phase widens the range of transformation temperatures and, thus, smears the magnetic-field induced

transformation reducing the MCE. Thus, the Co content must be controlled to avoid the formation of the γ phase as a precondition to keep a high magnetization for the austenitic phase in the quaternary alloy system (i.e., the Co content has to be chosen between 6 % and 10 at. %).

For ideal Ericsson cycle based magnetic refrigeration, magnetocaloric material should possess a constant ΔS_M in the working refrigeration temperature range [14]. This means the full-width at half-maximum of $\Delta S_M(T)$ curve (δT_{FWHM}) should be large. A composite material [15, 16] showing two or more successive magnetic phase transitions is, from the experimental point of view, a promising approach to this problem. The starting point is the selection of an appropriate synthesis method. Considering that in Ni-Mn-Z Heusler alloys the structural transition temperatures are highly sensitive to small composition changes the attainment of successive martensitic transformations can be obtained by creating chemical segregation or composition gradient. Segregations typically occur with directional solidification, most prominently in the growth of unidirectional [17] crystal or single crystal [18, 19].

With this idea in mind, a unidirectional crystal of $\text{Ni}_{40.6}\text{Co}_{8.5}\text{Mn}_{40.9}\text{Sn}_{10}$ was expected to be grown using the Bridgman-Stockbarger method, which leads to chemical segregation [18, 19]. It was found that the prepared sample had a crystallographic growth direction of [110] and exhibited a step-like phase transition resulting in a remarkable increase in δT_{FWHM} . The effect of such a transformation on various magnetocaloric properties is also discussed.

2. Experimental procedure

The unidirectional crystal was fabricated from an induction melted polycrystalline alloy with the nominal composition $\text{Ni}_{41}\text{Co}_9\text{Mn}_{40}\text{Sn}_{10}$. The alloy was hand-grounded into a powder that was re-melted in a custom-made furnace and a crystal with 6.3 mm diameter was grown by means of the Bridgman-Stockbarger technique; we used as seed a Ni-Mn-Ga single crystal with [001]

parallel to the growth direction [19]. After growth, the sample was homogenized at 900 °C for 72 h under an argon atmosphere.

Microstructural studies were carried out on slices cut from the same ingot next to the samples used for the magnetic measurements. The average composition determined by energy dispersive X-ray spectroscopy (EDS) in a LEO model 1430VP scanning electron microscope was $\text{Ni}_{40.6}\text{Co}_{8.5}\text{Mn}_{40.9}\text{Sn}_{10}$. The microstructure was characterized with an optical microscope. XRD analysis was performed at room temperature using copper K_α radiation.

Magnetic properties were measured by vibrating sample magnetometry in a Quantum Design PPMS[®] EverCool[®] -9T platform. The sample studied had a parallelepiped shape with dimensions $0.8 \times 4.5 \times 4.0 \text{ mm}^3$; the major length was parallel to the axial direction of the ingot (i.e., [110]). The magnetic field $\mu_0 H$ was applied along the latter in order to reduce the influence of the demagnetizing field. The low-field (5 mT) and high-field (5 T) magnetization as a function of temperature, $M(T)$, curves were measured between 10 and 400 K (data were obtained by first cooling the sample from room temperature in zero applied magnetic field to an initial measuring temperature of 10 K. Then, the magnetic field was applied and the variation of magnetization was continuously measured while the temperature was increased continuously up to 400 K (ZFC process) at a rate of 1.0 K/min. After the last point was measured, the sample is cooled to 10 K keeping the same static field (FC process). Finally, the M vs T data were measured again for increasing temperatures under a constant magnetic field (FH process). The phase transformation and magnetic transition temperatures were obtained from the differential scanning calorimetric (DSC) curves measured in a TA Instruments model Q200 with a heating/cooling rate of 10 K/min and the minimum of the dM/dT vs. T curve measured under $\mu_0 H = 5 \text{ mT}$. The temperature dependence of magnetic entropy change $\Delta S_M(T)$ was determined by numerical integration of the

Maxwell relation (i.e., $\Delta S_M(T, \mu_0 H) = \mu_0 \int_0^{\mu_0 H} \left[\frac{\partial M(T, \mu_0 H')}{\partial T} \right] dH'$). For such a purpose, a set of isothermal magnetization curves, $M(\mu_0 H)$, were measured in increasing the temperature across MST $\rightarrow$ AST phase transition [temperature steps are indicated in Figure 4(a)]. Taking into account that in the temperature range where phase transformation occurs the shape of the $M(\mu_0 H)$ curves may strongly depend on the thermal history, we applied a fixed thermal protocol throughout MST $\rightarrow$ AST as follows: (1) heating to 400 K to stabilize austenite, (2) cooling to 210 K to completely form martensite, and (3) heating to the selected measuring temperature T_{meas} . This procedure was repeated for each T_{meas} to ensure that, prior to applying the magnetic field at a given T_{meas} , the sample consistently had the phase constitution corresponding to the thermally induced structural transition.

3. Results and discussion

Figure 1 shows an XRD pattern and optical image taken at room temperature from the cross section of the rod-shaped sample. The XRD result indicates that the sample has a preferred orientation of [110] parallel to the solidification direction. It is different from the seed orientation, [001], indicating that the preferred growing direction of the Ni-Co-Mn-Sn **unidirectional crystal** is [110]. The inset shows three domains with two different martensite variants. The martensite laths in the top left corner of the image have the same orientation as the martensite laths in the bottom right corner. No second phase particles are present in good agreement with the XRD analysis.

Fig. 2(a) shows the $M(T)$ curves measured in zero-field-cooling (ZFC), field-cooling (FC) and field-heating (FH) modes under static magnetic fields $\mu_0 H$ of 5 mT and 5 T. At large, the main characters and the effect of magnetic field on the $M(T)$ curve are similar to those reported for other Ni-Mn-Z Heusler alloys [1, 3, 5, 20]. The almost zero value of the low-field $M(T)^{5\text{mT}}$ curve

from 10 to around 280 K reflects the weak magnetic character of martensite; this is a favorable precondition for a large inverse magnetocaloric effect. The top-left inset in Fig. 2(b) zooms into the low-temperature range of the curve to show the occurrence of a weak and broad peak with maximum at 86 K. Above this temperature the magnetic behavior of MST has been referred as superparamagnetic [21]. For the $M(T)$ curve at $\mu_0 H = 5$ T [Fig. 2(a)], the structural transition temperatures are shifted to lower temperatures by almost 40 K, i.e. by 8 K/T. Starting at around 290 K the MST $\rightarrow$ AST transition leads to a large and wide stepwise magnetization change that altogether at 5 T is around $75 \text{ Am}^2\text{kg}^{-1}$. However, the magnetization increases (and decreases) in successive stages suggesting the occurrence of a **step-like** thermoelastic martensitic transformation; this is also evident in the bottom-right inset of Fig. 2(b) by the successive peaks shown by the dM/dT vs T curves at 5 mT. The heating and cooling DSC curves [Fig. 2(c)] show multiple peaks in the same temperature range further confirming the **step-like** nature of the structural transition. **This behaviour is completely different from multi-step intermartensitic transformations, a phenomenon that has been observed in (Ni-Mn)-based Heusler alloys such as Ni-Mn-Ga [22-31], and Ni-Mn-Sn [32-34] systems. The latter corresponds to two or three separate martensitic transformation occurring between martensites with different structures. As a result, each separate martensitic transformation is accompanied by a number of effects, including changes in latent heat, magnetization, electrical resistivity and so on. Usually, these changes detected by DSC or $M(T)$ curves are sudden and abrupt rather than flat and successive for the present martensitic transformation. Therefore, step-like martensitic transformation occurs in the present sample.** It has been reported that Bridgman growth may lead to substantial compositional variation in Ni-Mn-Ga single crystals [18, 19]. Our results suggest that a similar phenomenon occurs in Ni-Mn-Co-Sn alloys, whose martensitic transition temperatures strongly depend on the alloy composition [21], giving rise to the **step-like** phase transitions revealed by both the DSC and

$M(T)$ curves. Fig. 3 shows the composition profiles for all the four alloy elements determined from EDS along the growth direction. The first measurement was taken just after the Ni-Mn-Ga seed and henceforward every 2 mm. The approximate position of the specimen studied is indicated in the graph. The component concentration of the grown crystal varies monotonically over the length and differs from the starting one as the distance from the seed increases. In particular, the contents of Ni and Sn decreased, while that of Mn and Co increased along the growth direction.

Figure 4(a) shows the set of isothermal magnetization curves $M(\mu_0 H)$ measured around the MST $\rightarrow$ AST structural transition to determine the thermal dependence of the magnetic entropy change. The curves can be divided into three stages as follows. Below 315 K and above 345 K, they tend to show typical ferromagnetic behaviour (i.e., saturation upon increasing of the magnetic field strength above the saturation field). Between 320 and 345 K (within the MST $\rightarrow$ AST transition interval), a metamagnetic-like behavior occurs, i.e., with increasing field, the magnetization initially tend to saturates quickly by applying a low $\mu_0 H$ followed by a distinct increase of the slope dM/dH above a critical field, $\mu_0 H_{CR}$ (e.g. $\mu_0 H_{CR} \cong 3.2$ T for 325 K as estimated by tangent method as shown in the figure). This is due to the field-induced reverse martensitic transition from a low magnetization MST to a high magnetization AST. In Ni-Mn-Z Heusler alloys such metamagnetic-like behavior makes an important contribution to ΔS_M^{peak} across the MST $\rightarrow$ AST transition [9]. Fig. 4(b) displays the ΔS_M dependence on the temperature ($\Delta S_M(T)$ curve) at 2 and 5 T, whereas a summary of the magnetocaloric properties for these two field change values is given in Table 1. The entropy change curve shows a wide “hump-like” peak as a function of temperature. This peak shape and field dependence contrast with those reported for other Ni-Mn-Z alloys which often exhibit a narrow spike-like shaped $\Delta S_M(T)$ curve [2, 3, 5, 6, 35]. We attribute this difference to the **step-like martensitic**

transformation. For $\mu_0\Delta H = 5$ T, the ΔS_M^{peak} reaches $16.0 \text{ JK}^{-1}\text{kg}^{-1}$ which is slightly larger than that found for $\text{Ni}_{40}\text{Co}_{10}\text{Mn}_{40}\text{Sn}_{10}$ ($\Delta S_M^{\text{peak}}=14.9$ under 5 T of field change) [36]. The enhancement of ΔS_M in our alloy may be also due to the 1.5% reduction of Co, which circumvents the formation of γ phase owing to its non ferromagnetic character would reduce $\Delta M_{\text{M-A}}$ with the consequent weakening of the MCE [13]. The peak position ΔS_M^{peak} shifts to lower temperatures upon increasing $\mu_0\Delta H$ (as indicated in the figure by the curved arrow). This shift results from the magnetic-field-induced shift of the phase transition temperatures. The inset of Fig. 4(c) shows the trend of the temperatures T_{hot} and T_{cold} that define the full-width at half-maximum δT_{FWHM} of the $\Delta S_M(T)$ curve. This shift also reflects the magnetic-field-induced shift of the martensitic starting and finishing temperatures (M_s and M_f). The field dependence of T_{cold} is stronger than that of T_{hot} . The widening of the temperature range enhances the refrigerant capacity, RC . In addition to this, the enlargement of the working temperature range is also a consequence of the occurrence of successive structural phase transitions. RC quantifies the amount of heat that might be transferred between the cold and the hot reservoir through an ideal refrigeration cycle [14, 37, 38]. The value of RC depends on $|\Delta S_M^{\text{peak}}|$ and on the temperature width of the ΔS_M curve [39]. From the practical viewpoint, three different criteria have been defined to estimate RC from the $\Delta S_M(T)$ curve [14, 37, 38]: (a) by the product $|\Delta S_M^{\text{peak}}| \times \delta T_{\text{FWHM}}$ (usually referred to as $RC-1$); (b) by the integral under the $\Delta S_M(T)$ curve between T_{hot} and T_{cold} (referred to as $RC-2$); and (c) by maximum of the product $|\Delta S_M^{\text{peak}}| \times \delta T$ below the $\Delta S_M(T)$ curve (referred to as $RC-3$). The dependence of $RC-1$, $RC-2$, and $RC-3$ and the temperatures T_{cold} and T_{hot} (T_{cold} and T_{hot} are the limiting temperatures for δT_{FWHM}) on $\mu_0\Delta H$ are depicted in Fig. 4(c). $RC-1$, $RC-2$, and $RC-3$ increase monotonically with increasing magnetic field change. For $\mu_0\Delta H=5$ T, the $RC-1$ value (366 Jkg^{-1}) attained not considering the hysteresis losses is comparable to that reported for $\text{Gd}_5\text{Ge}_2\text{Si}_2$ (360

Jkg⁻¹) [40] and only 60 Jkg⁻¹ smaller than that in Ni₄₀Co₁₀Mn₄₀Sn₁₀ which has heretofore the largest *RC* reported in Ni-Mn-Z Heusler alloys [36]. In addition, *RC*-1 is much higher than other Ni-Mn-Sn alloys (*RC*-1=80 Jkg⁻¹ for Ni₅₀Mn₃₆Sn₁₄ [35], 202 J kg⁻¹ for Ni₄₄Fe₂Mn₄₃Sn₁₁, and about 220 J kg⁻¹ for Ni₄₃Mn₄₆Sn₁₁C₂ [41]). All the above *RC* represents the value of *RC*-1 obtained under a field change of 5 T.

Nevertheless, for a more precise evaluation of the effective *RC*, the effect of the hysteresis losses originated in the field-induced reverse martensitic transformation must be considered. They were estimated up to a maximum applied magnetic field of 2 T from the set of isothermal magnetization curves measured on increasing and decreasing the field shown in Fig. 5(a) (The value of 2 T was chosen because this is the field change value of interest from a technological point of view). Fig. 5(b) displays the hysteresis loss dependence on the temperature at $\mu_0\Delta H=2$ T. Thus, the effective refrigerant capacity *RC*_{eff} is found by subtracting the average hysteresis loss $\langle HL \rangle$ from the corresponding *RC* value at 2 T. For the studied alloy we found $\langle HL \rangle = 19$ Jkg⁻¹, which caused a reduction of about 17% for the totla *RC* value. Thus the *RC*_{eff} is 94 Jkg⁻¹. It is much higher than Ni₄₉Mn₃₉Sn₁₂ (58 Jkg⁻¹) [17] and Mn₅₀Ni₄₀In₁₀ (76.72 Jkg⁻¹) [42] unidirectional crystals grown using a modified high-pressure optical zone-melting technique. It should be noted that, *RC*_{eff} for Ni₄₉Mn₃₉Sn₁₂ and Mn₅₀Ni₄₀In₁₀ unidirectional crystals are caused only by martensitic transformation as the present Ni_{40.6}Co_{8.5}Mn_{40.9}Sn₁₀ alloy, while at a higher field of $\mu_0\Delta H=3$ T.

4. Conclusions

A high Co content unidirectional crystal of composition Ni_{40.6}Co_{8.5}Mn_{40.9}Sn₁₀ alloy, without γ phase precipitates as a secondary phase, was fabricated with the Bridgman-Stockbarger technique. It shows a large magnetic entropy change and refrigerant capacity above room temperature (16 J K⁻¹ kg⁻¹ and 366 Jkg⁻¹, respectively, at 5 T), along with a wide working

1 temperature range of 23 K resulting from a **step-like** structural transition. Composition
2 segregation, seemingly a shortcoming, during crystal growth by Bridgman-Stockbarger method
3 causes **step-like** structural transition and then widens the working temperature range for the
4 magnetic entropy change.

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Table 1. Magnetocaloric properties associated to the MST to AST structural transition along the [110] direction for the $\text{Ni}_{40.6}\text{Co}_{8.5}\text{Mn}_{40.9}\text{Sn}_{10}$ **unidirectional crystal** studied under magnetic field changes of 2 and 5 T. Samples were grown by the Bridgman-Stockbarger technique.

	$\mu_0\Delta H$ (T)	
	2	5
$ \Delta S_M^{\text{peak}} $ (J kg ⁻¹ K ⁻¹)	9.7	16.0
$RC-1$ (J kg ⁻¹)	113	366
δT_{FWHM} (K)	11	23
T_{hot} (K)	343	343
T_{cold} (K)	332	320
$RC-2$ (J kg ⁻¹)	89	302
$RC-3$ (J kg ⁻¹)	57	191

Figure captions

Fig. 1 XRD trace and optical image (**inset**) obtained at room temperature. The XRD trace shows a strong 202 reflection. The microstructure presents three domains containing two martensite variants.

Fig. 2 (a) Temperature dependence of magnetization under static magnetic fields of 5 mT and 5 T. **(b)** Low-field $M(T)$ curves in ZFC, FC and FH regimes between 10 and 400 K. **Top-left inset:** zoom-in of the $M(T)$ curve at 5 mT in the temperature range 10-300 K. **Bottom-right inset:** dM/dT vs. T curve at 5 mT in the temperature range 320-380 K. **(c)** Heating and cooling DSC scans across the structural transition (sweep rate: 10 K/min).

Fig. 3 Composition profiles determined by EDS along the growth direction for the Ni-Mn-Co-Sn **unidirectional crystal**. The grey rectangle shows the approximate location of **unidirectional crystal** specimen studied.

Fig. 4 (a) Isothermal magnetization curves obtained in the temperature range of 300-352.5 K. **(b)** $\Delta S_M(T)$ curves under various magnetic field. **Inset:** ΔS_M^{peak} as a function of $\mu_0 \Delta H_{\text{max}}$. **(c)** Refrigerant capacity ($RC-1$, $RC-2$, and $RC-3$) as a function of the magnetic field change. **Inset:** field dependence of the temperatures T_{cold} and T_{hot} that define the δT_{FWHM} .

Fig. 5 (a) Isothermal magnetization curves on increasing (field-up) and decreasing (field-down) the magnetic field. **(b)** Hysteresis loss across the MST to AST transition up to $\mu_0 \Delta H_{\text{max}} = 2$ T.

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