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Manipulation of magnetostructural transition and realization of prominent multifunctional magnetoresponsive properties in NiCoMnIn alloys

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Abstract

Promising multifunctional magnetoresponsive effects such as magnetoresistance, magnetostrain and magnetocaloric effect have recently been extensively studied in Ni-Mn-based metamagnetic shape memory alloys, but large reversible magnetoresponsive effects are usually obtained under high magnetic fields, which is an obstacle for practical applications. Here, through manipulating magnetostructural transition, we achieved large reversible magnetoresponsive effects under a relatively low magnetic field of 3 T in a Ni-Co-Mn-In alloy. By systematically tuning the Mn/In ratio and Co substitution, an optimum composition Ni49Co3Mn34In14 with a low thermal hysteresis (8 K), a narrow transformation interval (7 K) and a high sensitivity of transformation temperature to field change (6 K T⁻¹), was obtained. Good geometric compatibility between austenite and martensite was revealed by in-situ
synchrotron high-energy X-ray diffraction experiment, which accounts for the low hysteresis and narrow transformation interval. A reversible transformation between pure austenite and pure martensite is induced by a relatively low field of 3 T, which was directly evidenced by in-situ neutron diffraction experiment. As a result, a large reversible magnetocaloric effect with entropy change of 16.5 J kg\(^{-1}\) K\(^{-1}\), a large reversible magnetostrain of 0.26% and a large reversible magnetoresistance of 60%, under a relatively low field of 3 T, were simultaneously achieved. These reversible magnetoresponsive effects are comparable to the maximum reversible values obtained under high fields in other Ni-Mn-based alloys, but the magnetic field we applied is much lower. This study may guide the design of metamagnetic shape memory alloys with low-field-induced magnetoresponsive properties for magnetic refrigeration, magnetic sensing and magnetic recording applications.

Keywords: Metamagnetic shape memory alloy; Martensitic transformation; Magnetocaloric effect; Magnetostrain; Magnetoresistance
I. INTRODUCTION

In recent years, Heusler-type Ni-Mn-based Ni-(Co)-Mn-X (X = Sb, Sn, In) metamagnetic shape memory alloys (MSMAs) undergoing solid-to-solid martensitic transformation have aroused great interest due to their multifunctional magnetoresponsive effects such as magnetoresistance [1–3], magnetostrain [4–6], magnetocaloric effect [7–10] and magnetothermal conductivity [11]. Among these magnetoresponsive effects, magnetoresistance, magnetostrain and magnetocaloric effect show promising prospects for applications in magnetoresistive heads for magnetic recording devices [12], high-performance actuators [13] and environment-friendly magnetic refrigerators [14], respectively. The magnetoresponsive effects in Ni-Mn-based MSMAs stem from the magnetic-field-induced first-order magnetostructural transformation from the low-symmetry and weak magnetic martensite to the high-symmetry and ferromagnetic austenite, accompanied with abrupt change of lattice parameters. The first-order nature of the magnetic-field-induced transformation, on the one hand, leads to much enhanced magnetoresponsive effects, but on the other hand, makes it difficult to transform completely and reversibly between the two phases under low fields owing to the pronounced transformation hysteresis and transformation interval.

Great efforts have been devoted to investigating the magnetoresponsive properties in Ni-Mn-based MSMAs in the past decade. Large magnetoresistance under a magnetic field of 5 T was reported in the Ni_{41}Co_{9}Mn_{39}Sb_{11} [15], Ni_{41}Co_{9}Mn_{40}Sn_{10} [16] and Ni_{50}Mn_{34}In_{16} [17] MSMAs, where the magnetoresistance
was up to 60%, 53.8% and 64%, respectively. Large magnetostrains were obtained under high magnetic fields in a Ni$_{50}$Mn$_{34}$In$_{16}$ alloy (0.12% under 5 T) [6] and in a Ni$_{43}$Co$_7$Mn$_{39}$Sn$_{11}$ alloy (0.56% under 8 T) [18], whose magnetic work output was considered to be higher than that of the Ni-Mn-Ga alloys [19]. Large magnetocaloric effect under high magnetic fields (above 5 T), with considerable magnetic refrigeration capacity, was reported in various Ni-Mn-based MSMAs [6–8,20,21]. However, almost all of the large and reversible magnetoresponse properties were obtained under high magnetic fields above 5 T [1–3,6,20–27]. If the magnetic field is low, the magnetic-field-induced transformation in Ni-Mn-based MSMAs is largely irreversible due to the coexistence of austenite and martensite across the field-induced transformation, leading to the significant irreversibility of the magnetoresponsive effects which deteriorates the performance during cyclic operation. For practical applications, it is extremely difficult and costly to generate high magnetic fields. Therefore, it is highly desirable to achieve large and reversible magnetoresponsive effects under low magnetic fields. This is the motivation of our present work.

For the sake of realizing complete and reversible transformation and large reversible magnetoresponsive effects under low magnetic fields, it is important to manipulate the magnetostructural transition in MSMAs. In particular, the thermal hysteresis ($\Delta T_{hys}$), phase transformation interval ($\Delta T_{int}$) and sensitivity of transformation temperature to field change are of great relevance [20]. In practice, $\Delta T_{hys}$ and $\Delta T_{int}$ can be estimated as $A_f - M_s$ and $M_s - M_f$ ($M_s$, $M_f$, $A_s$ and $A_f$ are the martensitic and austenitic transformation start and finish temperatures), respectively.
[21,27], and the sensitivity of transformation temperature to field change can be estimated with the Clausius-Clapeyron relation [4], which approximately equals $\Delta M/\Delta S_A$ ($\Delta M$ is the magnetization difference between the two phases and $\Delta S_A$ is the transformation entropy change for austenitic transformation). The minimum field required to induce the complete and reversible transformation between austenite and martensite is [21]:

$$\Delta(\mu_0 H)_{\text{min}} = (\Delta T_{\text{hys}} + \Delta T_{\text{int}})/(\Delta M/\Delta S_A)$$

(1)

Apparently, to obtain large reversible magnetoresponsive effects under a low field, the MSMAs should have low $\Delta T_{\text{hys}}$, narrow $\Delta T_{\text{int}}$, and high $\Delta M/\Delta S_A$. It was reported that the value of $\Delta M/\Delta S_A$ is closely related to the relative temperature distance between the Curie temperature ($T_c$) and austenitic transformation temperature ($T_A$, the temperature corresponding to the transformation peak) [28–30]; the larger the $T_c - T_A$, the larger the $\Delta M/\Delta S_A$. Hence, it is viable to tune $\Delta M/\Delta S_A$ via tailoring $T_c - T_A$. In addition, to facilitate practical applications, the large reversible magnetoresponsive effects should occur around room temperature [1,4,31–35]. Since chemical modification has been proved to be an instructive and effective way used to manipulate magnetostructural transition in MSMAs [1,21,26,36–40], in this work we will use this method to synergistically optimize the magnetostructural transition parameters, with a final goal to achieve large reversible magnetoresponsive effects under low fields.

Among Ni-Mn-based MSMAs, Ni-(Co)-Mn-In alloys have been viewed as a very promising candidate for multifunctional magnetoresponsive applications [4,9,14].
The magnetostructural transition in Ni-(Co)-Mn-In alloys can occur within a narrow transformation interval and with a low transformation hysteresis, beneficial for attaining excellent magnetoresponsive properties [1,4,6,9]. Nevertheless, up to now, most studies on the Ni-(Co)-Mn-In system are focused on the Ni-Mn-In alloys with 50 at.% Ni or the Ni-Co-Mn-In alloys in which Co is added to substitute for Ni and the sum of Ni and Co is 50 at.% [1,4,6,9,11,17,22,28,29,41]. Unfortunately, these Ni-(Co)-Mn-In alloys always require high magnetic fields to induce a complete and reversible phase transformation, which severely limits their practical applications. Increasing the Ni content in Ni-(Co)-Mn-In alloys could increase the electron concentration (e/a) and thus raise the martensitic transformation temperature, because in this kind of alloys the martensitic transformation temperature is strongly correlated with e/a: the higher the e/a, the higher the martensitic transformation temperature [42–44]. This allows substitution of more Co for Ni to get a composition with transformation temperature around room temperature, since substitution of Co for Ni results in decrease of e/a and thus decrease of transformation temperature [34]. Substitution of more Co for Ni could also lead to higher $T_c$ and larger $T_c - T_A$, and thus greater sensitivity of transformation temperature to field change, as mentioned above. Moreover, it was recently reported that the Ni-Mn-In alloys with Ni content higher than 50 at.% possess a relatively small $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ [45,46]. Therefore, we envisage that, through manipulating the magnetostructural transition, prominent magnetoresponsive properties could be achieved in the Ni-(Co)-Mn-In alloys with higher Ni content. Here in this work, we selected Ni$_{52}$Mn$_{35}$In$_{13}$ as the starting material.
and systematically tuned the magnetostructural transition parameters via simultaneously tailoring the Mn/In ratio and the amount of Co substitution for Ni. Optimized magnetostructural transition parameters were obtained in the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy. As a result, large reversible near-room-temperature magnetocaloric effect, magnetostrain and magnetoresistance were successfully achieved under a relatively low magnetic field of 3 T.

II. EXPERIMENT

A total number of 21 polycrystalline button ingots (each of ~40 g) with compositions of Ni$_{52-x}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2, 3$ and $4$), Ni$_{52-y}$Co$_y$Mn$_{35}$In$_{13}$ ($y = 1, 2, 3, 4, 5$ and $5.2$), Ni$_{52-y}$Co$_y$Mn$_{34}$In$_{14}$ ($y = 1, 2, 3, 4$ and $4.5$), Ni$_{52-y}$Co$_y$Mn$_{33}$In$_{15}$ ($y = 1, 2$ and $3$), and Ni$_{52-y}$Co$_y$Mn$_{32}$In$_{16}$ ($y = 1$ and $2$), were prepared by repeated melting (for five times) of the high-purity raw elements (Ni, Co and In) mixed with the master alloy Ni$_{40}$Mn$_{60}$ in an arc furnace protected under Ar. Since the master alloy Ni$_{40}$Mn$_{60}$ was used to alleviate the Mn evaporation during melting, no additional elements were added. The weight loss during repeated melting was less than 0.5 wt.%. For homogeneity, the ingots were sealed into an evacuated quartz tube and then annealed at 1173 K for 24 h followed by quenching into water. The actual composition of the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy was measured with an electron probe microanalyzer (EPMA-1720H, SHIMADZU); the composition was determined by averaging the compositions of five randomly measured points, and it turns out to be Ni$_{48.9}^{\pm 0.1}$Co$_{3.2}^{\pm 0.5}$Mn$_{34.2}^{\pm 0.8}$In$_{13.7}^{\pm 0.4}$.

The phase transformation temperatures and transformation entropy change were analyzed by differential scanning calorimetry (DSC) experiments performed with
heating and cooling rates of 10 K min\(^{-1}\). The specific heat capacity \(C_p\) was measured with the modulated DSC technique using a standard sapphire sample with a well-known \(C_p\). The microstructure was characterized by scanning electron microscopy (SEM). The magnetic measurements and electrical resistivity measurements were conducted in a physical property measurement system (PPMS, Quantum Design). The magnetostrain was measured by using a strain gauge and a data logger (TDS 150, Tokyo Sokki Kenkyujo Co., Ltd.) under magnetic field up to 3 T provided by PPMS.

The crystal structure evolution during phase transformation was investigated during cooling and heating in the temperature range between 250 K and 290 K by \textit{in-situ} synchrotron high-energy X-ray diffraction (HEXRD) experiments carried out at the 11-ID-C beam line of Advanced Photon Source, Argonne National Laboratory, USA; A monochromatic X-ray beam with a wavelength of 0.1173 Å was used and the diffraction Debye rings were collected by a two-dimensional (2D) large area detector while the sample (\(\Phi 2 \times 1 \text{ mm}^3\)) was rotated at high speed. The crystal structure evolution during magnetic-field-induced transformation was studied during increasing and decreasing magnetic field at 268 K and 270 K by \textit{in-situ} neutron diffraction experiments, performed on the high intensity diffractometer WOMBAT [47] at the Australian Nuclear Science and Technology Organisation (ANSTO). A wavelength of 2.41 Å was used. The diffracted neutrons were collected on the cylindrical position-sensitive area detector that subtends an angle of 120° on the sample in the diffraction plane and \(~15°\) in the vertical, out of plane direction. For the \textit{in-situ}
experiments, WOMBAT was equipped with a vertical field magnet (0 – 11 T) with a temperature range of 1.5 – 300 K. The disc sample of $\Phi 2 \times 1 \text{ mm}^3$ was glued to a pure aluminum bolt for the \textit{in-situ} experiments. Considering that the sample possesses a coarse-grained microstructure and there are only a limited number of grains within this sample, reciprocal space mapping was conducted to provide sufficient structural information.

III. RESULTS AND DISCUSSION

A. Magnetostructural transition manipulation

To manipulate magnetostructural transition for optimal magnetoresponsive properties, we systematically tuned both the Mn/In ratio and the amount of Co substitution for Ni. The DSC curves of Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2, 3$ and $4$) alloys are plotted in Fig. 1(a). As can be seen, the phase transformation temperatures decrease rapidly with increasing $x$ ($0 \leq x \leq 3$). When it comes to $x = 4$, martensitic transformation cannot be detected within the measured temperature range between 110 K and 500 K. For easy visualization, the composition dependence of $M_s$, $T_M$, $M_f$, $A_s$, $T_A$, and $A_f$ ($T_M$ is the peak temperature of martensitic transformation) is shown in Fig. 1(b) (see Table I for detailed values). It is worth noting that, for the alloys showing martensitic transformation, even the one (Ni$_{52}$Mn$_{32}$In$_{16}$, $x = 3$) with the lowest transformation temperature presents phase transformation above room temperature, which is much higher than the phase transformation temperature (around 220 K) reported for the Ni$_{50}$Mn$_{34}$In$_{16}$ alloy [1,6,17,48]. The higher phase transformation temperature of Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2$ and $3$) offers opportunities
for substituting more Co for Ni to attain higher sensitivity of transformation temperature to field change while bringing down the transformation temperature to around room temperature, as mentioned before. The transformation entropy changes for the austenitic transformation ($\Delta S_A$) and martensitic transformation ($\Delta S_M$) estimated from DSC results are also shown in Table I, from which one can see that both $\Delta S_A$ and $\Delta S_M$ decrease with increasing $x$ ($0 \leq x \leq 3$). The influence of transformation entropy change on magnetoresponsive effects will be taken into consideration when manipulating magnetostructural transition. Fig. 1(b) also shows the variation of $\Delta T_{hys}$ and $\Delta T_{int}$ as a function of $x$ for the Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ alloys. Overall, all the Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2$ and $3$) alloys have relatively small $\Delta T_{hys} + \Delta T_{int}$, beneficial for obtaining low-field-induced transformation [see Eq. (1)].

Based on the Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2$ and $3$) alloys, we further substituted Co for Ni to optimize magnetostructural transition parameters. In practice, we increased the amount of Co continuously until no martensitic transformation could be detected in the measurement temperature range between 110 K and 500 K. Figs. 2(a)–2(d) show the DSC curves of the Ni$_{52-y}$Co$_y$Mn$_{35}$In$_{13}$ ($y = 0, 1, 2, 3, 4, 5$ and $5.2$), Ni$_{52-y}$Co$_y$Mn$_{34}$In$_{14}$ ($y = 0, 1, 2, 3, 4$ and $4.5$), Ni$_{52-y}$Co$_y$Mn$_{33}$In$_{15}$ ($y = 0, 1, 2$ and $3$) and Ni$_{52-y}$Co$_y$Mn$_{32}$In$_{16}$ ($y = 0, 1$ and $2$) alloys, respectively. For each series of alloys, the phase transformation temperatures decrease with increasing the Co content $y$, until martensitic transformation disappears in the measurement temperature range at $y = 5.2$ for Ni$_{52-y}$Co$_y$Mn$_{35}$In$_{13}$ [Fig. 2(a)], $y = 4.5$ for Ni$_{52-y}$Co$_y$Mn$_{34}$In$_{14}$ [Fig. 2(b)], $y = 3$ for Ni$_{52-y}$Co$_y$Mn$_{33}$In$_{15}$ [Fig. 2(c)] and $y = 2$ for Ni$_{52-y}$Co$_y$Mn$_{32}$In$_{16}$ [Fig. 2(d)]. The detailed
phase transformation characteristic parameters of these series of alloys, determined from the DSC curves [Figs. 2(a)–2(d)], are shown in Table II. As can be seen, for each series of alloys, the Curie temperature $T_c$ tends to increase and thus $T_c - T_A$ becomes larger, with increasing $\gamma$.

As discussed above, to achieve reversible near-room-temperature magnetoresponsive effects under low magnetic field, the alloys should have a small $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$, a large $T_c - T_A$ and a $T_A$ around room temperature. In addition, an appropriate $\Delta S_A$ is essential for achieving reversible magnetocaloric effect. If $\Delta S_A$ is too large, the sensitivity of transformation temperature to field change is low; if $\Delta S_A$ is too small, the magnetocaloric effect as a result of magnetic-field-induced transformation is small. Taking into consideration the above criteria, we plotted $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ and $T_c - T_A$ together in Fig. 3(a) and $\Delta S_A$ and $T_A$ together in Fig. 3(b) for the Co-substituted alloys (shown in Table II), to guide the selection of an optimum composition for large and reversible magnetoresponsive effects under low magnetic fields. Clearly, among all the alloys shown in Fig. 3(a), the alloy H (Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$) shows the smallest $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ (15 K) and a relatively large $T_c - T_A$ (84 K). As seen from Fig. 3(b), the alloys H (Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$) and J (Ni$_{51}$Co$_1$Mn$_{33}$In$_{15}$) both exhibit an appropriate $\Delta S_A$ (18.8 J kg$^{-1}$ K$^{-1}$ for Ni$_{51}$Co$_1$Mn$_{33}$In$_{15}$ and 17.6 J kg$^{-1}$ K$^{-1}$ for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$) and a near-room-temperature $T_A$ (283 K for Ni$_{51}$Co$_1$Mn$_{33}$In$_{15}$ and 279 K for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$). Nevertheless, the alloy J (Ni$_{51}$Co$_1$Mn$_{33}$In$_{15}$) shows a much larger $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ and a smaller $T_c - T_A$ as compared with the alloys H (Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$) [see Fig. 3(a)]. Therefore, we selected Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ (H) as the
optimum composition. Through magnetostructural transition manipulation, this Ni_{49}Co_{3}Mn_{34}In_{14} alloy possesses a small $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ (15 K), a large $T_c - T_A$ (84 K), a near-room-temperature $T_A$ (279 K) and an appropriate $\Delta S_A$ (17.6 J kg^{-1} K^{-1}) and thus we expect that large reversible magnetocaloric effect, magnetostrain and magnetoresistance could be achieved under a low magnetic field in this alloy. The following investigation will be focused on this alloy.

**B. Reversibility of temperature-induced transformation studied by in-situ synchrotron HEXRD**

To trace the structural evolution and the reversibility of phase transformation during cooling and heating in the Ni_{49}Co_{3}Mn_{34}In_{14} alloy, *in-situ* synchrotron HEXRD experiments were carried out. The sample was first cooled from room temperature to 290 K and 250 K, and then heated to 290 K. Figs. 4(a)–4(c) show the 2D HEXRD patterns collected at 290 K reached by cooling, 250 K and 290 K reached by heating, respectively. By integrating the 2D patterns along the azimuth angle from 0° to 360°, 1D diffraction patterns were obtained and shown in Fig. 4(d). At 290 K, the sample shows an austenitic structure. When cooled to 250 K, the sample transforms into martensite. As can be seen, the 2D HEXRD patterns collected at 290 K reached by cooling [Fig. 4(a)] and 290 K reached by heating [Fig. 4(c)] are almost the same, indicating that the transformation is fully reversible. The 1D diffraction pattern at 250 K [Fig. 4(d)] can all be well indexed according to the six-layered modulated monoclinic martensitic structure (space group No.10, $P2_1/m$) [21,49] with the lattice parameters of $a_M = 4.4$ Å, $b_M = 5.616$ Å, $c_M = 26.014$ Å and $\beta = 92.95°$. No residual
austenite could be observed at this temperature. This suggests that the transformation is complete. Therefore, during the cooling and heating process, the transformation between austenite and martensite is complete and reversible. Indexation of the 1D diffraction pattern at 290 K [Fig. 4(d)] reveals that the austenite shows a cubic L2₁ Heusler structure (space group No. 225, Fm\(\overline{3}m\)) with the lattice parameter of \(a_A = 5.99 \text{ Å}\).

Utilizing the crystalline symmetry and the lattice parameters of austenite and martensite determined by *in-situ* synchrotron HEXRD experiments, we evaluated the geometric compatibility between austenite and martensite, which can be characterized by the middle eigenvalue (\(\lambda_2\)) of the phase transformation stretch matrix \(U\) [50–56]. It should be noted that HEXRD has high resolution, which ensures the accuracy of the crystal structure information. Our calculation reveals that the \(\lambda_2\) for the Ni\(_{49}\)Co\(_{3}\)Mn\(_{34}\)In\(_{14}\) alloy is 1.0033, which is fairly close to 1. The comparison of the \(\lambda_2\) for the present alloy with the values for other Ni-Mn-based MSMAs reported in the literature [9,21,23,36,54] is shown in Fig. 4(e). Usually, good geometric compatibility leads to small thermal hysteresis (\(\Delta T_{\text{hys}}\)) [51]. Besides, recently it was reported that good geometric compatibility also results in narrow transformation temperature interval (\(\Delta T_{\text{int}}\)) and completeness of phase transformation [36,55]. In the present alloy, the excellent geometric compatibility between austenite and martensite accounts for the small \(\Delta T_{\text{hys}} + \Delta T_{\text{int}}\) and the completeness of phase transformation, facilitating a reversible and cyclically stable phase transformation.

To check the reversibility and cyclic stability of phase transformation, which
plays a significant role in the functional fatigue of MSMAs, we carried out thermal
cycling test across austenitic transformation and martensitic transformation. Fig. 5
shows the DSC curves recorded during 100 thermal cycles for the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$
alloy. Clearly, no significant shift of the DSC peaks can be observed during 100
thermal cycles. The migration of the martensitic transformation temperatures is within
1 K and the latent heat remains almost unchanged during the cycling test. After the
100 thermal cycles, $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ still keeps a small value of 15 K, which is the same
as that before thermal cycling. Moreover, the sample remains intact with no cracks
observed after 100 thermal cycles (see the inset of Fig. 5). Taken together, these
observations indicate good reversibility and cyclic stability of phase transformation in
the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy.

C. Magnetic-field-induced complete and reversible transformation evidenced by

in-situ neutron diffraction

As mentioned before, the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy shows a small $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ and
a large $T_c - T_A$; thus, magnetic-field-induced complete and reversible transformation
could be expected under a low magnetic field. Fig. 6(a) shows the temperature
dependence of magnetization [$M(T)$] measured under magnetic fields of 0.02 T and 3
T for the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy. From the $M(T)$ curve under 0.02 T, $M_s$, $M_f$, $A_s$, $A_f$, and
$T_c$ are determined to be 274 K, 267 K, 275 K, 282 K and 363 K, respectively, which
are well consistent with the transformation temperatures determined from DSC
measurements. As seen from the $M(T)$ curve under 3 T, there is a large magnetization
difference ($\Delta M$) of 98 emu g$^{-1}$ between austenite and martensite across transformation.
Comparing the $M(T)$ curves under 0.02 T and 3 T, one can see that applying a relatively low magnetic field of 3 T dramatically decreases $A_s$ by about 18 K, with the sensitivity of transformation temperature to field change $\Delta A_s/\Delta(\mu_0H) \approx 6$ K T$^{-1}$. This is in good agreement with the $\Delta M/\Delta S_A$ value (5.6 K T$^{-1}$) estimated based on the results obtained from DSC and $M(T)$ measurements. It is known that if the magnetic-field-induced shift of transformation temperature is larger than $\Delta T_{hys} + \Delta T_{int}$, a reversible magnetic-field-induced transformation can occur in the temperature range between $A_s$ under the magnetic field and $M_f$ under zero field [20,21,27,57]. In order to get insights into the magnetic-field-induced transformation and its reversibility, isothermal magnetization [$M(H)$] curves were measured during cyclically increasing and decreasing magnetic field in the temperature range from 258 K to 270 K with an interval of 2 K and the results are shown in Fig. 6(b). For measurement at each temperature, firstly the sample was zero-field cooled to 258 K to get a full martensitic state and then heated to the desired temperature for measurement; the field change of 0 T – 3 T – 0 T was repeated twice for each measurement. As seen from the $M(H)$ curves in Fig. 6(b), this alloy shows a strong metamagnetic transformation behavior between 262 K and 270 K, indicating a magnetic-field-induced transformation from weak magnetic martensite to ferromagnetic austenite. At each temperature, the $M(H)$ curves measured during the two cycles of field change almost overlap with each other, suggesting that the magnetic-field-induced transformation is reversible [58]. In the temperature range between 264 K and 270 K, the magnetization saturates under the magnetic field of 3 T, implying that the magnetic-field-induced transformation is
complete. Therefore, it is inferred that complete and reversible transformation occurs under a relatively low field of 3 T at temperatures between 264 K and 270 K. Notably, the magnetic hysteresis ($\Delta H_{hy}$) of the magnetic-field-induced transformation is quite narrow, which is about 1 T. This is the smallest $\Delta H_{hy}$ value among those reported for Ni-Mn-based MSMAs [3,4,34,59,60]. Such a narrow $\Delta H_{hy}$ will substantially minimize the energy loss during magnetic field cycles [20,35], beneficial for attaining high magnetocaloric performance (especially effective magnetic refrigerant capacity).

To provide direct evidence on the magnetic-field-induced phase transformation as well as its completeness and reversibility, we employed in-situ neutron diffraction technique to trace the crystal structure evolution during applying and removing magnetic field. Reciprocal space mapping was carried out during magnetic field change of 0 T – 3 T – 0 T at 268 K and 270 K, respectively. The sample was initially cooled down from room temperature to 250 K to get a full martensitic state and then heated to 268 K for the in-situ neutron diffraction experiment. The reciprocal space maps measured during increasing and decreasing magnetic field at 268 K are shown in Figs. 7(a)–7(c). The coordinates of the figures are expressed with respect to the scattering vector $\mathbf{Q}$ with its length $Q = 2\pi/d = 4\pi \sin \theta / \lambda$, with $d$ being the interplanar spacing and $2\theta$ the diffraction angle. To better illustrate the structural evolution during the field change of 0 T – 3 T – 0 T, in Fig. 7 we only focused on the representative diffraction spots within the $Q$ range from 1.3 Å$^{-1}$ to 2.5 Å$^{-1}$, but the other spots out of this range were also taken into consideration when we analyzed the results. Analysis of the diffraction spots in Fig. 7(a) shows that the sample is in fully
martensitic state before applying magnetic field. When the magnetic field is increased to 3 T, all of the diffraction spots of martensite disappear while the diffraction spot of austenite emerges [Fig. 7(b)], clearly showing the complete magnetic-field-induced transformation from pure martensite to pure austenite. When the magnetic field is decreased from 3 T to 0 T, the diffraction spots of martensite reappear and the diffraction spot of austenite completely vanishes [Fig. 7(c)]. The diffraction spots of martensite before applying magnetic field [Fig. 7(a)] and after removing magnetic field [Fig. 7(c)] are almost identical, demonstrating that the magnetic-field-induced transformation is fully reversible. Overall, Figs. 7(a)–7(c) unambiguously confirm that the sample can transform completely and reversibly between austenite and martensite under a relatively low magnetic field of 3 T at 268 K. This corresponds well to the $M(H)$ curve at 268 K shown in Fig. 6(b). After the in-situ neutron diffraction experiment at 268 K, the sample is heated to 270 K where all of the diffraction spots still indicate a fully martensitic structure [Fig. 7(d)]. Upon applying a magnetic field of 3 T at 270 K, the martensite transforms completely into austenite [Fig. 7(e)]. After removing the magnetic field, the field-induced austenite mostly transforms back to martensite [Fig. 7(f)], but there is still a tiny amount of residual austenite as suggested by the weak intensity of the (200)$_A$ diffraction spot in Fig. 7(f).

For a more comprehensive analysis, the evolution of the one-dimensional (1D) diffraction patterns, obtained by azimuthal integration of the reciprocal space maps, during applying and removing magnetic field at 268 K and 270 K are shown in Figs. 7(g) and 7(h), respectively. Based on the 1D diffraction patterns, the completeness
and reversibility of magnetic-field-induced transformation under 3 T at 268 K and 270 K are clearly presented. The above in-situ neutron diffraction experiment clearly evidences that a complete and reversible magnetic-field-induced transformation occurs under a relatively low magnetic field of 3 T in the Ni_{49}Co_{3}Mn_{34}In_{14} alloy. Thus, large reversible multifunctional magnetoresponsive effects can be expected under a relatively low field of 3 T in this alloy.

**D. Magnetocaloric effect**

To examine the magnetocaloric effect under a magnetic field of 3 T, we first evaluated the magnetic entropy change (ΔS_m) which is one important characteristic parameter for magnetocaloric effect [9,20,35]. Based on the M(H) curves shown in Fig. 6(b) (for clarity, the M(H) curves recorded during increasing magnetic field in the second cycle are displayed in the inset of Fig. 8), ΔS_m is estimated using the Maxwell relation:

\[
\Delta S_m = S_m(T, H) - S_m(T, 0) = \int_0^{\mu_0 H} \frac{\partial M}{\partial T} d\mu_0, H
\]

(2)

It should be noted that ΔS_m is usually overestimated with the Maxwell relation if there is a phase-coexistence of the weak magnetic martensite and ferromagnetic austenite before applying magnetic field [61,62]. Fortunately, our Ni_{49}Co_{3}Mn_{34}In_{14} alloy is in the pure martensitic state before applying magnetic field at each temperature at which the M(H) curves in Fig. 6(b) were recorded; in this case, the ΔS_m estimated with the Maxwell relation is reliable [20,62]. The estimated ΔS_m under 3 T is shown as a function of temperature in Fig. 8. Clearly, the maximum value of ΔS_m under 3 T is ~16.5 J kg^{-1} K^{-1}, which is very close to the transformation entropy change ΔS_A (17.6 J
kg\(^{-1}\) K\(^{-1}\)) determined from the DSC curve in Fig. 2(b) (see Table II). Since the magnetic-field-induced transformation is reversible (as demonstrated above in Section III. C.), the \(\Delta S_m\) as a result of such transformation is also reversible. Therefore, a large reversible \(\Delta S_m\) of 16.5 J kg\(^{-1}\) K\(^{-1}\) is achieved under a relatively low field of 3 T in the Ni\(_{49}\)Co\(_3\)Mn\(_{34}\)In\(_{14}\) alloy. Table III lists the reversible \(\Delta S_m\) obtained in Ni-Mn-based MSMAs [20,21,27,63,64]. As can be seen, the magnitude of the reversible \(\Delta S_m\) we achieved is comparable to that obtained under higher fields (above 5 T) in other Ni-Mn-based alloys [20,21,27,63,64], but the magnetic field we applied is significantly lower, which is indeed beneficial for practical applications.

The adiabatic temperature change \(\Delta T_{ad}\) is another important characteristic parameter for magnetocaloric effect. It was reported that the reversible \(\Delta T_{ad}\) can be estimated on the basis of the reversible \(\Delta S_m\) data by using the following relation [9]:

\[
\Delta T_{ad} = -\frac{T}{C_p} \cdot \Delta S_m
\]  

(3)

where \(C_p\) is the specific heat capacity obtained at the temperature \(T\). The \(C_p\) in the Ni\(_{49}\)Co\(_3\)Mn\(_{34}\)In\(_{14}\) alloy is determined by using the modulated DSC technique and it is shown as a function of temperature in Fig. 9(a). Using the reversible \(\Delta S_m\) data shown in Fig. 8 and the \(C_p\) values presented in Fig. 9(a), the reversible \(\Delta T_{ad}\) is computed with Eq. (3) and shown as a function of temperature in Fig. 9(b). As can be seen, the maximum reversible \(\Delta T_{ad}\) under 3 T is about –9.7 K, which actually is a large reversible \(\Delta T_{ad}\) under such a relatively low field.

For magnetic refrigeration, the refrigerant capacity \((RC)\) is often used to evaluate the potential magnetic cooling efficiency of the magnetocaloric materials for practical
applications [34,35]. The $RC$ for a reversible refrigeration cycle is defined as [35,65]:

$$RC = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_m dT$$

(4)

where $T_{\text{cold}}$ (the temperature of the cold reservoir) and $T_{\text{hot}}$ (the temperature of the hot reservoir) correspond to the temperatures at full width half maximum of the $\Delta S_m$ peak [65]. Using Eq. (4), the $RC$ under 3 T is estimated to be $\sim$116.6 J kg$^{-1}$. It should be noted that, for magnetocaloric materials with negligible hysteresis loss, Eq. (4) can be used to reasonably evaluate the magnetic cooling efficiency [20,65–67], but for the materials with apparent magnetic hysteresis (e.g. Ni-Mn-based MSMAs), it is more reliable to use the effective refrigerant capacity $RC_{\text{eff}}$, computed by taking the average hysteresis loss away from the $RC$ value, to evaluate the final cooling efficiency for cyclic applications [68]. In the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy, a narrow $\Delta H_{\text{hy}}$ of $\sim$1 T [Fig. 6(b)] leads to a relatively small hysteresis loss of $\sim$42.1 J kg$^{-1}$. Consequently, a $RC_{\text{eff}}$ value of $\sim$74.5 J kg$^{-1}$ is obtained under 3 T in the present alloy. Considering that the magnetic-field-induced transformation is reversible and repeatable (as inferred from Fig. 6), the magnetic hysteresis loss and thus the $RC_{\text{eff}}$ is consistent during magnetic cycling. Actually, this large repeatable $RC_{\text{eff}}$ ($\sim$74.5 J kg$^{-1}$) under 3 T is comparable to that obtained under a high magnetic field of 5 T ($\sim$76.6 J kg$^{-1}$) in other Ni-Mn-based alloys [20]. As demonstrated above, a large reversible magnetocaloric effect, with $\Delta S_m$ of 16.5 J kg$^{-1}$ K$^{-1}$ and $RC_{\text{eff}}$ of $\sim$74.5 J kg$^{-1}$, is achieved under a relatively low field of 3 T in the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy.

E. Magnetostrain

The magnetic-field-induced transformation in Ni-Co-Mn-In alloys usually results
in a magnetostrain effect [4]. We investigated the magnetostrain under a magnetic field of 3 T in the Ni_{49}Co_{3}Mn_{34}In_{14} alloy by measuring the strain during increasing and decreasing magnetic field. A cubic sample with the size of 7 × 7 × 7 mm³ was used for the magnetostrain measurements. It was cut from the button ingot, with four edges parallel to the solidification direction of the ingot, as illustrated in Fig. 10(a). Owing to the temperature gradient along the solidification direction when the ingot was prepared in a water-cooled copper crucible, preferred crystallographic orientation forms in the ingot. The annealed ingot consists of columnar grains showing a texture with <001> of austenite parallel to the solidification direction [25,26,68]. For the magnetostrain measurements, the magnetic field is always applied along the solidification direction, while the strain is measured in the directions both parallel and perpendicular to the solidification direction (Fig. 10). The magnetostrain is defined as:

\[ \frac{\Delta L}{L_0} = \frac{L(H) - L_0}{L_0} \]  

where \( L_0 \) is the length under zero field and \( L(H) \) is the length under a magnetic field \( \mu_0 H \). Before the measurement at each temperature, the sample was first cooled down to 256 K under zero field to ensure a full martensitic state and then heated to the measurement temperature.

Fig. 10(b) shows the magnetostrain parallel to the solidification direction measured at 260 K, 264 K and 268 K in the polycrystalline Ni_{49}Co_{3}Mn_{34}In_{14} alloy. One can see that at each temperature the strain shows an obvious increase above a critical magnetic field, which is owing to the magnetic-field-induced transformation, and recovers fully to the initial state after removing the field. The magnetostrain under
3 T is about 0.025% at 260 K, and it increases to about 0.07% at 264 K. This is because of the increased fraction of magnetic-field-induced transformation. The magnetostrain under 3 T reaches 0.26% at 268 K, at which the complete transformation is induced. Therefore, a large reversible magnetostrain up to 0.26% is achieved under a relatively low magnetic field of 3 T in the polycrystalline Ni$_{49}$Co$_{3}$Mn$_{34}$In$_{14}$ alloy. The magnetostrain perpendicular to the solidification direction in the same sample is also measured and the results are shown in Fig. 10(c). At all the measurement temperatures (265 K, 267 K and 268 K), the magnetic-field-induced transformation is reversible and complete at 3 T, and hence the magnetostrain at 3 T (which is fully reversible) is approximately the same at these temperatures, i.e. −0.12%. Apparently, the magnetostrain perpendicular to the solidification direction shows a negative sign and has a magnitude much smaller than that parallel to the solidification direction [Fig. 10(b)]. This is attributed to the anisotropy of microstructure and crystallographic orientation in the button ingot solidified in a water-cooled copper crucible [25,26,68–70].

To evaluate the repeatability of magnetostrain during different magnetic cycles, we continued to examine the magnetostrain during cyclic application and removal of magnetic field after the measurement shown in Fig. 10(c). The magnetostrain perpendicular to the solidification direction measured during two field cycles at different temperatures is displayed in Fig. 11. At 267 K [Fig. 11(a)] and 268 K [Fig. 11(b)], the magnetostrain exhibits almost the same field dependence during the first and second cycles of increasing and decreasing magnetic field. Further measurements
at 268 K shows that the magnetostrain vs. field curves recorded during the third and fourth cycles (for clarity, not shown here) coincide well with those recorded during the first and second field cycles. This clearly demonstrates the excellent repeatability of magnetostrain in the Ni$_{40}$Co$_{3}$Mn$_{34}$In$_{14}$ alloy. As seen from Figs. 11(c) and 11(d), when the measurement temperature increases to 270 K and 271 K, the magnetostrain during the first field cycle could not fully recover after removing field, which is attributed to the residual field-induced austenite as revealed by our in-situ neutron diffraction experiment [Fig. 7(f)]. Fortunately, the magnetostrain (−0.1% at 3 T) becomes fully reversible and repeatable from the second cycle [Figs. 11(c) and 11(d)].

As demonstrated above, a large reversible magnetostrain of up to 0.26% is achieved under a relatively low field of 3 T in the polycrystalline Ni$_{40}$Co$_{3}$Mn$_{34}$In$_{14}$ alloy. Table IV lists the reversible magnetostrain obtained in Ni-Mn-based MSMAs [5,6,24,26,71]. Since only the reversible magnetostrain is useful for cyclic actuation, the irreversible magnetostrain reported in the literature is not included in this table. As can be seen, the large reversible magnetostrain can only be obtained with a high magnetic field above 5 T in the literature. In contrast, we only applied a relatively low magnetic field of 3 T to attain a large reversible strain of 0.26%, thanks to the optimized magnetostructural transition parameters in the studied alloy. The reduction of the actuation magnetic field is important for practical applications. It is worth mentioning that pre-deformation or thermal-mechanical training [4,5,24] is not needed to get the large reversible magnetostrain in the present work. In addition, the large reversible magnetostrain is achieved in the polycrystals, which are easier to synthesize.
as compared with single crystals, which, from the technological point of view, facilitates the applications of this material.

F. Magnetoresistance

Owing to the difference in the resistivity of austenite and martensite in Ni-Mn-based MSMAs, there is a change in resistivity during magnetic-field-induced transformation, giving rise to a magnetoresistance effect. To examine the magnetoresistance under a magnetic field of 3 T, we studied the variation of electrical resistance with temperature and magnetic field in the Ni_{49}Co_{3}Mn_{34}In_{14} alloy. Fig. 12(a) illustrates the temperature dependence of the electrical resistance \([\rho(T)]\) measured under 0 T and 3 T. As seen from the \(\rho(T)\) curves, during cooling the electrical resistance undergoes an abrupt increase upon martensitic transformation. This is related with the variation of the density of electronic states in the vicinity of the Fermi surface during phase transformation [1,17,72]. Remarkably, the electrical resistance of martensite is three times as large as that of austenite. Comparing the \(\rho(T)\) curves under 0 T and 3 T [Fig. 12(a)], one can see that the transformation temperature \(A_s\) is significantly decreased by 17 K under a field of 3 T, with \(\Delta A_s/\Delta(\mu_0H) = 5.7 \text{ K T}^{-1}\), which is well consistent with the result obtained from the \(M(T)\) curves [Fig. 6(a)]. If a magnetic field of 3 T is applied at a temperature close to \(A_s\) (under 0 T), there will be a magnetic-field-induced transformation from martensite to austenite leading to a significant decrease of electrical resistance, and thus a large magnetoresistance can be expected.

The electrical resistance during increasing and decreasing magnetic field was
measured and the magnetoresistance under a magnetic field $\mu_0H$ was obtained from the following relation:

$$\frac{\Delta R}{R_0} = \frac{(R_H - R_0)}{R_0}$$

(6)

where $R_0$ is the electrical resistance under zero field and $R_H$ is the electrical resistance under $\mu_0H$. Fig. 12(b) displays the magnetoresistance as a function of magnetic field [$\rho(H)$] at 240 K, 260 K, 264 K and 268 K for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$, where the sample is in the fully martensitic state before applying magnetic field at each temperature. As can be seen, the magnetoresistance abruptly increases above a critical magnetic field at 260 K, 264 K and 268 K, which is attributed to the magnetic-field-induced transformation from martensite to austenite; the magnetoresistance recovers to zero after removing the field, indicating that the magnetoresistance in the present alloy is fully reversible. The magnetoresistance shows a negative value owing to the lower electrical resistance of austenite, and it amounts to 19% and 38% (under 3 T) at 260 K and 264 K, respectively. Notably, the magnetoresistance under 3 T reaches a high value of 60% at 268 K. Thus, a large reversible magnetoresistance is achieved under a relatively low magnetic field of 3 T in the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy. For comparison, Table V lists the reversible magnetoresistance obtained in Ni-Mn-based MSMAs [1,3,73–75]. As can be seen, the large reversible magnetoresistance we achieved under a relatively low field of 3 T is comparable to that obtained under higher fields (e.g. 9 T) in other Ni-Mn-based alloys. Moreover, the large reversible magnetoresistance in the present work is achieved around room temperature whereas that reported in the literature is usually obtained at temperatures much lower than room temperature.
(below 240 K, see Table V). The lower actuation magnetic field and the near-room-temperature working temperature benefit the applications of the magnetoresistance in the present Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy.

IV. CONCLUSIONS

The magnetostructural transition in the Ni-(Co)-Mn-In MSMAs was manipulated via systematically tuning the Mn/In ratio and the Co substitution in a series of compositions. An optimum composition Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ with best combination of magnetostructural transition parameters was singled out. This Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy shows a small $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ of 15 K and a high sensitivity of transformation temperature to field change, 6 K T$^{-1}$. A reversible magnetic-field-induced transformation between pure martensite and pure austenite occurs under a relatively low magnetic field of 3 T in this alloy, which is directly evidenced by our in-situ neutron diffraction experiment. Based on this magnetic-field-induced transformation, large reversible multifunctional magnetoresponsive effects were obtained. A large reversible magnetocaloric effect with $\Delta S_m$ of 16.5 J kg$^{-1}$ K$^{-1}$, a large reversible magnetostrain of 0.26% and a large reversible magnetoresistance of 60%, under a relatively low magnetic field of 3 T, were simultaneously achieved in this Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy. The magnitudes of these reversible magnetoresponsive effects are comparable to those reported under high magnetic fields (above 5 T) in other Ni-Mn-based MSMAs, but the magnetic field required to induce the magnetoresponsive effects in the present work is drastically lower. Moreover, the large reversible magnetoresponsive effects in Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ were obtained around
room temperature. The reduced actuation magnetic field and the near-room-temperature working temperature of Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ are quite beneficial for the practical applications of the magnetoresponsive effects. The present work may guide the design of high-performance MSMAs with extraordinary low-field-induced multifunctional magnetoresponsive properties.

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References

TABLE I
Martensitic and austenitic transformation characteristic temperatures (K), phase transformation interval $\Delta T_{\text{int}}$ (K), transformation thermal hysteresis $\Delta T_{\text{hys}}$ (K), and the entropy change for austenitic ($\Delta S_A$) and martensitic ($\Delta S_M$) transformations (J kg$^{-1}$ K$^{-1}$) for the Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2$ and $3$) alloys. The letters “M” and “A” denote martensitic and austenitic transformations, respectively.

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<th>$M_f$</th>
<th>$A_s$</th>
<th>$A_f$</th>
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<th>$T_A$</th>
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<th>$\Delta T_{\text{hys}}$</th>
<th>$\Delta S_A$</th>
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TABLE II

The martensitic and austenitic transformation characteristic temperatures (K), phase transformation interval $\Delta T_{\text{int}}$ (K), transformation thermal hysteresis $\Delta T_{\text{hys}}$ (K), $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$ (K), and the entropy change for austenitic ($\Delta S_A$) and martensitic ($\Delta S_M$) transformations (J kg$^{-1}$ K$^{-1}$) for the Co doped Ni-Co-Mn-In alloys. The letters “M” and “A” denote martensitic and austenitic transformations, respectively.

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<th>Alloys</th>
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<th>$M_f$</th>
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### TABLE III

Magnetic-field-induced reversible $\Delta S_m$ in the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy (this work) compared with that reported in other Ni-Mn-based alloys. "$T$" denotes the temperature at which the reversible $\Delta S_m$ is obtained.

<table>
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<th>Alloys</th>
<th>$\Delta S_m$ (J kg$^{-1}$ K$^{-1}$)</th>
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<td>5</td>
<td>[64]</td>
</tr>
</tbody>
</table>
TABLE IV
Magnetic-field-induced reversible magnetostrain in the Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy (this work) compared with that reported in other Ni-Mn-based alloys. “T” denotes the temperature at which the reversible magnetostrain is obtained. The letters “S” in the bracket denotes single crystal; the other alloys are all polycrystalline.

<table>
<thead>
<tr>
<th>Ni-Mn-based alloys</th>
<th>Magnetostrain (%)</th>
<th>$T$ (K)</th>
<th>Applied field (T)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{49}$Co$<em>3$Mn$</em>{34}$In$</em>{14}$</td>
<td>0.26</td>
<td>268</td>
<td>3</td>
<td>This work</td>
</tr>
<tr>
<td>Ni$<em>{43}$Co$<em>7$Mn$</em>{39}$Sn$</em>{11}$</td>
<td>0.3</td>
<td>310</td>
<td>8</td>
<td>[5]</td>
</tr>
<tr>
<td>Ni$<em>{50}$Mn$</em>{34}$In$_{16}$</td>
<td>0.12</td>
<td>195</td>
<td>5</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni$<em>{30}$Cu$<em>6$Co$</em>{12}$Mn$</em>{37}$Ga$_{13}$ (S)</td>
<td>0.47</td>
<td>264</td>
<td>9</td>
<td>[24]</td>
</tr>
<tr>
<td>Ni$<em>{50}$Mn$</em>{33}$In$_{13}$Ga$_4$</td>
<td>0.49</td>
<td>194</td>
<td>7</td>
<td>[26]</td>
</tr>
<tr>
<td>Ni$<em>{46}$Co$<em>4$Mn$</em>{39}$Sn$</em>{11}$</td>
<td>0.012</td>
<td>225</td>
<td>3</td>
<td>[71]</td>
</tr>
</tbody>
</table>
TABLE V
Magnetic-field-induced reversible magnetoresistance in the Ni<sub>49</sub>Co<sub>3</sub>Mn<sub>34</sub>In<sub>14</sub> alloy (this work) compared with that reported in other Ni-Mn-based alloys. “T” denotes the temperature at which the reversible magnetoresistance is obtained.

<table>
<thead>
<tr>
<th>Ni-Mn-based alloys</th>
<th>Magnetoresistance (%)</th>
<th>T (K)</th>
<th>Applied field (T)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;49&lt;/sub&gt;Co&lt;sub&gt;3&lt;/sub&gt;Mn&lt;sub&gt;34&lt;/sub&gt;In&lt;sub&gt;14&lt;/sub&gt;</td>
<td>60</td>
<td>268</td>
<td>3</td>
<td>This work</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;50&lt;/sub&gt;Mn&lt;sub&gt;35&lt;/sub&gt;In&lt;sub&gt;15&lt;/sub&gt;</td>
<td>80</td>
<td>150</td>
<td>9</td>
<td>[1]</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;41&lt;/sub&gt;Co&lt;sub&gt;9&lt;/sub&gt;Mn&lt;sub&gt;39&lt;/sub&gt;Sb&lt;sub&gt;11&lt;/sub&gt;</td>
<td>70</td>
<td>230</td>
<td>13</td>
<td>[3]</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;46.4&lt;/sub&gt;Mn&lt;sub&gt;32.8&lt;/sub&gt;Sn&lt;sub&gt;20.8&lt;/sub&gt;</td>
<td>5</td>
<td>239</td>
<td>12</td>
<td>[73]</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;47&lt;/sub&gt;Fe&lt;sub&gt;3&lt;/sub&gt;Mn&lt;sub&gt;36&lt;/sub&gt;Sn&lt;sub&gt;14&lt;/sub&gt;</td>
<td>10</td>
<td>75</td>
<td>9</td>
<td>[74]</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;50&lt;/sub&gt;Mn&lt;sub&gt;34&lt;/sub&gt;In&lt;sub&gt;15.5&lt;/sub&gt;Al&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>50</td>
<td>215</td>
<td>5</td>
<td>[75]</td>
</tr>
</tbody>
</table>
Figures

**FIG. 1.** (a) DSC curves for the Ni$_{52}$Mn$_{35-x}$In$_{13+x}$ ($x = 0, 1, 2, 3$ and $4$) alloys. (b) Phase transformation temperatures, transformation thermal hysteresis ($\Delta T_{\text{hys}}$) and transformation interval ($\Delta T_{\text{int}}$) as a function of $x$. 
FIG. 2. DSC curves for (a) Ni$_{52-y}$Co$_y$Mn$_{35}$In$_{13}$ ($y = 0, 1, 2, 3, 4, 5$ and $5.2$), (b) Ni$_{52-y}$Co$_y$Mn$_{34}$In$_{14}$ ($y = 0, 1, 2, 3, 4$ and $4.5$), (c) Ni$_{52-y}$Co$_y$Mn$_{33}$In$_{15}$ ($y = 0, 1, 2$ and $3$) and (d) Ni$_{52-y}$Co$_y$Mn$_{32}$In$_{16}$ ($y = 0, 1$ and $2$) alloys, respectively.
FIG. 3. (a) The sum of phase transformation thermal hysteresis and transformation interval, $\Delta T_{\text{hys}} + \Delta T_{\text{int}}$, and the relative temperature distance between the Curie temperature and austenitic transformation temperature, $T_c - T_A$, plotted together for the Co-substituted Ni-Mn-In alloys. (b) Austenitic transformation entropy change $\Delta S_A$ and austenitic transformation temperature $T_A$, plotted together for the Co-substituted Ni-Mn-In alloys. The letters “A–L” denote the designed alloys shown in Table II; A: Ni$_{51}$Co$_1$Mn$_{35}$In$_{13}$, B: Ni$_{50}$Co$_2$Mn$_{35}$In$_{13}$, C: Ni$_{49}$Co$_3$Mn$_{35}$In$_{13}$, D: Ni$_{48}$Co$_4$Mn$_{35}$In$_{13}$, E: Ni$_{47}$Co$_5$Mn$_{35}$In$_{13}$, F: Ni$_{51}$Co$_1$Mn$_{34}$In$_{13}$, G: Ni$_{50}$Co$_2$Mn$_{34}$In$_{13}$, H: Ni$_{49}$Co$_3$Mn$_{34}$In$_{13}$, I: Ni$_{48}$Co$_4$Mn$_{34}$In$_{13}$, J: Ni$_{51}$Co$_1$Mn$_{33}$In$_{13}$, K: Ni$_{50}$Co$_2$Mn$_{33}$In$_{13}$, L: Ni$_{51}$Co$_1$Mn$_{32}$In$_{16}$. 
FIG. 4. (a–c) Two-dimensional (2D) high-energy X-ray diffraction (HEXRD) patterns experimentally collected at 290 K (reached by cooling) (a), 250 K (reached by cooling) (b), and 290K (reached by subsequent heating) (c) for Ni$_{49}$Co$_{3}$Mn$_{34}$In$_{14}$. (d) One-dimensional (1D) HEXRD patterns obtained by integrating the 2D patterns in (b) and (c), corresponding to martensitic state and austenitic state, respectively. (e) Correlation between the $\lambda_2$ and the thermal hysteresis in typical Ni-Mn-based MSMAs.

The compositions corresponding to the reference numbers are: [9]–Ni$_{50.4}$Mn$_{34.8}$In$_{15.8}$, [21]–Ni$_{41}$Ti$_{3}$Co$_{9}$Mn$_{39}$Sn$_{10}$, [23]–Ni$_{50}$Mn$_{31.5}$In$_{16}$Cu$_{2.5}$, [36]–Ni$_{40}$Co$_{10}$Mn$_{40}$Sn$_{9}$Al$_{1}$, [54]–Ni$_{45}$Co$_{3}$Mn$_{40}$Sn$_{10}$.
FIG. 5. DSC curves recorded during 100 thermal cycles across martensitic transformation and austenitic transformation for $\text{Ni}_{49}\text{Co}_{3}\text{Mn}_{34}\text{In}_{14}$. The inset shows the microstructure of the sample after 100 thermal cycles.
FIG. 6. (a) Temperature dependence of magnetization \([M(T)]\) measured under magnetic fields of 0.02 T and 3 T, respectively, for Ni_{49}Co_{3}Mn_{34}In_{14}. (b) Two cycles of isothermal magnetization \([M(H)]\) curves recorded at constant temperatures from 258 K to 270 K with an interval of 2 K for Ni_{49}Co_{3}Mn_{34}In_{14}. 
FIG. 7. (a–c) Reciprocal space maps measured at 268 K during increasing magnetic field from 0 T (a) to 3 T (b) and then decreasing magnetic field to 0 T (c) for Ni_{49}Co_{3}Mn_{34}In_{14}. (d–f) Reciprocal space maps measured at 270 K during increasing magnetic field from 0 T (d) to 3 T (e) and then decreasing magnetic field to 0 T (f) for Ni_{49}Co_{3}Mn_{34}In_{14}. (g, h) One-dimensional (1D) diffraction patterns obtained by azimuthal integration of the reciprocal space maps shown in (a) – (c) measured at 268 K (g) and (d) – (f) measured at 270 K (h), respectively. The letters “A” and “M” in the indices denote austenite and martensite, respectively. The coordinates of the figures are expressed with respect to the scattering vector $Q$ with its length $Q = 2\pi / d = 4\pi \sin \theta / \lambda$, with $d$ being the interplanar spacing and $2\theta$ the diffraction angle.
FIG. 8. Reversible magnetic entropy change ($\Delta S_m$) under a magnetic field of 3 T shown as a function of temperature. The inset shows the $M(H)$ curves extracted from Fig. 6b; for clarity, only the curves recorded during increasing magnetic field in the second cycle are displayed.
FIG. 9. (a) Specific heat capacity $C_p$ measured by using the modulated DSC technique shown as a function of temperature for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$. The result is for the heating process. (b) Reversible adiabatic temperature change $\Delta T_{ad}$ under a magnetic field of 3 T, estimated with Eq. (3), shown as a function of temperature.
FIG. 10. (a) Illustration of how the cubic sample (7 × 7 × 7 mm³) for magnetostrain measurements was cut from the button ingot. (b) Magnetostrain parallel to the solidification direction measured at 260 K, 264 K and 268 K in the polycrystalline Ni₄₉Co₃Mn₃₄In₁₄ alloy. (c) Magnetostrain perpendicular to the solidification direction measured at 265 K, 267 K and 268 K in the polycrystalline Ni₄₉Co₃Mn₃₄In₁₄ alloy.
FIG. 11. Magnetostrain perpendicular to the solidification direction measured during two field cycles at (a) 267 K, (b) 268 K, (c) 270 K and (d) 271 K in the polycrystalline Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$ alloy.
FIG. 12. (a) Temperature dependence of electrical resistance $[\rho(T)]$ measured under 0 T and 3 T, respectively, for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$. (b) Variation of magnetoresistance as a function of magnetic field $[\rho(H)]$ measured at 240 K, 260 K, 264 K and 268 K, respectively, for Ni$_{49}$Co$_3$Mn$_{34}$In$_{14}$. 