Large reversible magnetocaloric effect and magnetoresistance by improving crystallographic compatibility condition in Ni(Co)-Mn-Ti all-d-metal Heusler alloys

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Recently, all-d-metal Ni(Co)-Mn-Ti Heusler systems have become the research hotspot due to their magnetoresponsive properties associated with a tunable first-order magnetostructural transformation (MST) and excellent mechanical stability for potential applications. However, the presence of large thermal hysteresis acts as an obstacle to the cyclic operation of this novel material. In this present paper, we investigate a large reversible magnetocaloric effect (MCE) and magnetoresistance (MR) in Ni$_{37}$Co$_{13}$Mn$_{34.5}$Ti$_{15.5}$ all-d-metal Heusler alloys that undergo a first-order MST accompanied by a large magnetization change between ferromagnetic austenite and antiferromagnetic martensite phases. Tuning the small at% of Co doping in Ni$_{37-x}$Co$_{13.4}$Mn$_{34.5}$Ti$_{15.5}$ systems, we achieved an optimum composition with $x = 1$ where low thermal hysteresis of $\sim 4.7$ K, a narrow transformation interval of $\sim 11.2$ K, and improved sensitivity of transformation temperature $\sim 2.8$ K/T is observed. In addition, the origin of small hysteresis is studied based on geometric compatibility between cubic austenite and monoclinic martensite phases, calculated from the powder x-ray diffraction data. These optimized parameters lead to a reversible magnetic field-induced inverse martensitic transition under the field cycling, yielding a large reversible magnetic entropy change ($\Delta S_M$) of $\sim 17.78$ J kg$^{-1}$ K$^{-1}$ at 277 K in a field change of 5 T. Moreover, a large reversible magnetoresistance (MR) of $\sim 14$% out of 32.6% is also obtained under 5-T magnetic field for $x = 1$ sample in all-d-metal Heusler alloys. These reversible magnetoresponsive properties are comparable to other Ni-Mn-based Heusler alloys and have not been reported so far in the all-d-metal Heusler system. Therefore our present work demonstrates a pathway to design new cyclically stable multifunctional materials in all-d-metal Heusler systems for solid-state cooling devices and magnetic recording applications.

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I. INTRODUCTION

Caloric materials with first-order magnetostructural transitions (MST) are a key element of solid-state-based cooling applications which is deemed as a substitute of conventional cooling technology owing to its higher energy efficiency and environment friendly nature [1]. Since the discovery of room-temperature (RT) giant magnetocaloric effect (MCE) across MST in Gd$_5$(Si$_2$Ge$_2$) [2]. RT magnetic refrigeration has attracted a lot of attention as a reliable and significant energy conversion technology. Furthermore, several classes of materials displaying coupled MST, such as La(Fe, Si)$_{13}$-based materials [3–5], Mn-Ni (Ge, Si) systems [6], and Ni-Mn-X ($X =$ Ga, In, Sn, Sb) metamagnetic Heusler alloys [7–10] have also been widely investigated for RT solid-state-based applications.

Among the above mentioned systems, Ni-Mn-X Heusler alloys are extensively investigated due to their multifunctional properties like inverse MCE [11–13], magnetic shape memory effect [14], and magnetoresistance (MR) [15–17]. In general, to induce first-order phase transition, the energy is required to overcome the potential barrier between austenite and martensite phases. This energy leads to the intrinsic irreversibilities in the MCE properties during the subsequent field cycling operations. These irreversible behaviors are originated from friction of interface motion, formation of defects and thereby, results both thermal and magnetic hysteresis. Therefore most attempts have been explored to the reduction of hysteresis through improving the compatibility condition between the austenite and martensite phases [7,18–21], modifying the chemical compositions, physical pressure, annealing conditions, minor loops, and measurement of cyclical way [22–24]. However, in those systems, brittleness nature due to field cycling is a challenging issue towards their use in technological applications.

In this regard, all-d-metal Ni–Mn-Ti Heusler alloys were developed with excellent ductility using the concept of $d$-$d$ hybridization between transition metals instead of $p$-$d$ hybridization between main group and transition metal of conventional Heusler alloys [25,26]. In the stoichiometric form, Ni$_2$MnTi alloy usually displays an antiferromagnetic (AFM) like ordering at low temperature $\sim 120$ K in the austenite phase, originating from Mn(B)-Mn(D) interaction. Further studies indicated the conversion of AFM interaction into a strong ferromagnetic (FM) Mn(B)-Co/Fe(A,C)-Mn(D) exchange exchange interaction due to the partial Co/Fe exchange interactions.
substitution in Ni site. Hence, MST occurs from a high-
temperature strong FM cubic B2-type austenite (spatial group
$Pm
to a low temperature weak-magnetic monoclinic
(spatial group $P2_1/m$) or tetragonal (spatial group $I4/mmm$)
martensite phases [25]. These systems have received enorm-
ous interest due to their magnetofunctionalities caused by
magnetic field-induced inverse martensitic transition (IMT).
For instance, large magnetic entropy change ($\Delta S_{\text{hys}}$) of 38
J kg$^{-1}$ K$^{-1}$ driven by a relatively low magnetic field of 2 T
across the MST of Ni$_{37}$Co$_{13}$Mn$_{34}$Ti$_{15}$ alloy is reported [27].
Recently, we reported a giant conventional exchange bias field
of 3.68 kOe in Ni$_{40}(\text{FeCo})_4$Mn$_{36}$Ti$_{20}$ all-$d$-metal Heusler alloy
[28]. In addition, a colossal elastocaloric effect with a large
reversable adiabatic temperature change ($\Delta T_{\text{ad}}$) up to 31.5 K
is achieved in (Ni$_{30}$Mn$_{31.5}$Ti$_{18.5}$)$_9$$_H_2$. 2 bulk polycrystalline
system [29]. Subsequently, a giant barocaloric effect with a large
$\Delta S$ of 74 J kg$^{-1}$ K$^{-1}$ in the same system is also ob-
tained [30]. Therefore, from the above experimental point of
view, the attainable of reversible MCE during subsequent field
cycling has not yet been addressed in this particular system,
which is important for the technological applications.

From the Clausius Clapeyron (CC) relation, the minimum
field required to achieve a complete reversible field-induced
IMT and corresponding MCE is

$$\Delta(MH)_{\text{min}} = (\Delta T_{\text{hys}} + \Delta T_{\text{int}})/(\Delta M/\Delta S_{\text{tr}}),$$

where $\Delta M$ is the magnetization change between austenite and
martensite phase, $\Delta T_{\text{hys}}$ is the thermal hysteresis, $\Delta T_{\text{int}}$, the
transformation interval, and $\Delta S_{\text{tr}}$ is the transformation
entropy change across the transition. Based on the above Eq. (1),
the reversibility of field-induced functional properties would be
achieved for the smaller $\Delta T_{\text{hys}}$, $\Delta S_{\text{tr}}$, and narrower $\Delta T_{\text{int}}$
in NiCo-Mn-Ti all-$d$-metal systems. Furthermore, $\Delta M/\Delta S_{\text{tr}}$
is closely related to the distance between Curie and inverse
MT temperature, i.e., $(T_C - T_A)$ [31–33]. Hence, it is feasible
to modulate $\Delta M/\Delta S_{\text{tr}}$ through the tailoring of $(T_C - T_A)$
in order to improve the reversible magnetoresponsive properties
in IMT under subsequent field cycling in all-$d$-metal NiCo-
Mn-Ti systems.

In the present study, we aim to improve the reversibility of
magnetoresponsive properties associated with the IMT in
Ni$_{37-x}$Co$_{13+x}$Mn$_{34.5}$Ti$_{15.5}$ all-$d$-metal Heusler systems. Moti-
vating by the work of Taubel et al. [27], our starting material
is Ni$_{37}$Co$_{21}$Mn$_{34.5}$Ti$_{15.5}$ which exhibits smaller $\Delta T_{\text{hys}}$ (5.5 K)
and $\Delta T_{\text{int}}$ (11.7 K), while the presence of large $\Delta S_{\text{tr}}$ (~30
J kg$^{-1}$ K$^{-1}$) and weak sensitivity $dT_d/d\mu_B H$ (~1.6 K/T)
hinders them in technological application. Thus we substituted
a small amount of Co in Ni$_{37}$Co$_{21}$Mn$_{34.5}$Ti$_{15.5}$, aiming to
improve the reversible properties associated with the mag-
netostructural transformation. To illustrate the origin of the
reversible properties, we used powder x-ray diffraction experi-
ment in order to analyze geometrical compatibility condition
which is calculated using the lattice parameters between
austenite and martensite phase [21,34,35]. We suggest from
experimental results that the obtained geometrical compatibil-
ity conditions of martensite and austenite phases could be the
basis of lower hysteresis and reversible magnetoresponsive
properties in NiCo-Mn-Ti all-$d$-metal-Heusler systems.

II. EXPERIMENTAL DETAILS

Ni$_{37-x}$Co$_{13+x}$Mn$_{34.5}$Ti$_{15.5}$ ($x = 0, 1, \text{and } 2$) polycrystalline
samples were prepared by arc melting technique under a
4 N purity argon atmosphere using high purity constituent
elements from Sigma Aldrich. The samples were re-melted
five to six times on each side to ensure homogenization.
The melted ingots were wrapped with a tantalum foil and sealed
in a quartz tube under a high vacuum and annealed at 1323 K.
Past 4 days of heat treatment, samples were quenched into ice
water. The actual compositions of the studied samples were
verified by energy dispersive x rays (EDX). The temperature-
dependent of x-ray diffraction (XRD) patterns of the sample
in powder form was investigated using SmartLab9KW, Rigaku
with Cu-K$_\alpha$ radiation. Magnetic measurements were per-
formed in a vibrating sample magnetometer (VSM) using
physical property measurement system (PPMS, Quantum de-
sign). Differential scanning calorimetry (DSC, TA Instrument,
Q2000) was performed to measure the heat flow curve of the
sample with a constant heating/cooling rate of 10 K/min. The
specific heat capacity ($C_P$) was measured by modulated-DSC
technique. The transport measurements were performed in the
PPMS (Quantum Design, USA) using the ac-transport option.
For both the resistivity and MR measurements, the electrical
contacts were made in the standard four-probe configuration
using conducting silver epoxy and copper wires.

III. RESULTS AND DISCUSSIONS

A. Composition optimization by magnetic properties analysis

DSC heat flow measurement is carried out during the
heating and cooling sequence at a ramp rate of 10 K/min
for all the samples, as exhibited in Fig. 1(a). All samples
exhibit endothermic and exothermic peaks, associated with
IMT and MT, respectively. The presence of thermal hysteresis ($\Delta T_{\text{hys}}$)
between endothermic and exothermic peaks confirms
the first-order phase transition. The characteristic transition
temperatures of the first-order MST namely, austenite start ($T_s$), austenite finish ($T_f$), martensite start ($M_s$), martensite
finish ($M_f$) determined by the tangent method from the DSC
curves and corresponding austenite to martensite transition
$\Delta T_m = (M_f - M_s)/2$ and the martensite to austenite phase
transition $\Delta T_s = (A_s + A_f)/2$, and ($\Delta T_{\text{hys}} = T_h - T_m$) of all
the samples are tabulated in Table I. Notice that the Co
doping in Ni site transformation temperatures decrease con-
siderably which is in agreement with the decrease in e/a
ratio of Co with respect to that Ni [36]. Further, due to the
interaction between structural and magnetic contributions to
the total transformation entropy change ($\Delta S_{\text{tr}}$), $\Delta S_{\text{tr}}$
across the first-order structural transition during heating is measured
following the equation:

$$\Delta S_{\text{tr}} = \int_{T_s}^{T_f} dQ / dT \left( dT / dt \right)^{-1} \frac{1}{T} dT,$$

where $dQ/dT$ is the heat flow changes of the sample. $T_s$ and
$T_f$ are the starting and finishing temperatures of the first-order
phase transition, respectively. The obtained $\Delta S_{\text{tr}}$ for all the
samples is gathered in Table I.

Figures 1(b)–1(d) represents the temperature-dependent
magnetization data for all the samples. On decreasing the
FIG. 1. (a) DSC heat-flow measurement for all the alloys. Isofield-magnetization $M(T)$ curve of Ni$_{37-x}$Co$_{13+x}$Mn$_{34.5}$Ti$_{15.5}$ for (b) $x = 0$, (c) 1, and (d) 2 samples at magnetic field of 0.05 and 5 T. (Inset shows minor hysteresis loop of $x = 1$ sample during heating.)

temperature, all samples exhibit a first-order MST from FM austenite to weak magnetic martensite below the Curie temperature $T_C$. With increasing magnetic field, the $T_M$ and $T_A$ move towards lower temperature, in agreement with the magnetic field stabilizing the FM cubic austenite phase with high magnetization. A shift in $T_M$ of $\sim$9, $\sim$12, and $\sim$16 K towards low temperature and the corresponding shift of $T_A$ of $\sim$8, $\sim$10, and $\sim$15 K is observed for $x = 0, 1,$ and $2$ samples, respectively towards lower temperature due to the change in magnetic field change from 0.05 to 5T. Hence, the sensitivity of transition temperatures to the magnetic field obtained from linear fitting of $T_M$ versus field (see Fig. S1 of Ref. [37]) are mentioned in Table I. This value is rather weak compared to the Ni-Mn-In alloys [34,35,38] yet higher than the Ni-Mn-Ti all-$d$-metal Heusler alloys [39], and Mn-Ni-Ge-based system [40]. On the basis of the CC equation $dT_M/d\mu_0H = \Delta M/\Delta S_{tr}$, the sensitivity not only depends on the magnetization change but also $\Delta S_{tr}$ [13] and corresponding to $(T_C - T_A)$, i.e., larger the $(T_C - T_A)$, weaker the $\Delta S_{tr}$ at the transition, which leads to a larger $dT_M/d\mu_0H$ (and thus reversible MCE) [31–33]. In view of this, Co substitution for Ni site in Ni$_{37-x}$Co$_{13+x}$Mn$_{34.5}$Ti$_{15.5}$ all-$d$-metal Heusler alloys, increases the value of $(T_C - T_A)$ and decreases $\Delta S_{tr}$. Clearly, $x = 1$ possess relatively smaller $\Delta T_{sys}$, $\Delta T_{int}$, and lower critical field $\Delta(\mu_0H)_{min}$ of about 4.5 T. On the contrary, the $x = 2$ shows much larger $\Delta T_{sys}$ + $\Delta T_{int}$ as well as $\Delta(\mu_0H)_{min}$, which is about 5.7 T and hence it is hard to achieve a complete phase transformation under 5 T, hence resulting in a small magnetoresponsive properties. Therefore the alloy with $x = 1$ is more favorable for the further reversible magnetoresponsive properties studies.

It is reported that the reversible field-induced IMT in presence of certain magnetic field $\mu_0H$ is occurred when the shift of $M(T)$ curve is higher than the thermal hysteresis [41]. Consequently, the reversible MCE across the field-driven IMT is expected over a temperature window between $\Delta S$ under $\mu_0H$ and $\Delta S$ under zero field [42]. Therefore the reversible MCE can be obtained in a large temperature window from

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$M_s$ (K)</th>
<th>$M_f$ (K)</th>
<th>$A_s$ (K)</th>
<th>$A_f$ (K)</th>
<th>$T_M$ (K)</th>
<th>$T_A$ (K)</th>
<th>$\Delta T_{int}$ (K)</th>
<th>$\Delta T_{sys}$ (K)</th>
<th>$\Delta S_{tr}$ (J kg K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>283.2</td>
<td>274.3</td>
<td>286.1</td>
<td>292.3</td>
<td>278.6</td>
<td>289.2</td>
<td>8.9</td>
<td>10.6</td>
<td>22.5</td>
</tr>
<tr>
<td>$x = 1$</td>
<td>286.1</td>
<td>272.9</td>
<td>278.5</td>
<td>290.1</td>
<td>280.5</td>
<td>285.2</td>
<td>11.2</td>
<td>4.7</td>
<td>19.89</td>
</tr>
<tr>
<td>$x = 2$</td>
<td>250.3</td>
<td>235.3</td>
<td>244.6</td>
<td>261.1</td>
<td>242.8</td>
<td>252.9</td>
<td>15</td>
<td>10.1</td>
<td>18.89</td>
</tr>
</tbody>
</table>
267.5 K ($A_3$) at 5 T to 286.1 K ($M_S$) from DSC for $x = 1$ sample, as shown in the Fig. 1(c).

B. Geometric compatibility condition from structural analysis

In magnetic shape memory alloys (SMAs), the presence of small thermal hysteresis is strongly related to the austenite and martensite phases and their interfaces (known as habit plane) [20,21,43,44]. Recently, it has been widely reported that not only small hysteresis yet narrow transformation interval is resulted by improving the geometrical compatibility condition between both phases and established certain condition for it [18–20]. Mathematically, the condition, $\lambda_2 = 1$, where $\lambda_1 \geq \lambda_2 \geq \lambda_3$ are the order eigenvalues of the transformation stretch matrix $U$, represents the existence of an invariant plane between both phases. The $U$ is defined as a homogeneous 3×3 deformation matrix. In the case of complete reversible MCE, the $\lambda_2$ of $U$ is 1. To determine $U$ for our system, the temperature dependent powder XRD experiment is carried out for $x = 1$ sample and depicted in Fig. 2(a). Noticeably, the sample experiences the transition from a martensitic phase with a five-modulated (5M) monoclinic structure to a cubic austenite phase during heating and the crystal orientation relation between the 5M martensite and B2 austenite phases: $\sqrt{2}a_M = a_c; b_M = a_c; \sqrt{2}c_M/5 = a_c$, and $2V_M = V_a$ [45]. A small fraction of martensite at 300 K can be appeared due to the residual stress generated during the grinding of the ingot into powder [46]. From the Fig. 2(b), the refined lattice parameters, at 277 K where both phases coexist, are $a_M = 4.342 \text{ Å}, b_M = 5.5136 \text{ Å}, c_M = 21.0359 \text{ Å},$ and $\beta_M = 90.95$ for martensite and $a_c = 5.921 \text{ Å}$ for the austenite phase. Theoretically, in the cubic to monoclinic transformation, there are 12 corresponding variants for monoclinic structure of martensitic phase, where these variants have the same eigenvalue, eigen energy, and volume changes [35]. The transformation stretch matrix of one of the corresponding variants of martensite phase is given by

$$U = \begin{pmatrix} \tau & \sigma & 0 \\ \rho & \sigma & 0 \\ 0 & 0 & \delta \end{pmatrix},$$

where the deformations are given by

$$\tau = \frac{\alpha^2 + \gamma^2 + 2\alpha\gamma (\sin \beta - \cos \beta)}{2\sqrt{\alpha^2 + \gamma^2 + 2\alpha\gamma \sin \beta}},$$

$$\rho = \frac{\alpha^2 + \gamma^2 + 2\alpha\gamma (\sin \beta + \cos \beta)}{2\sqrt{\alpha^2 + \gamma^2 + 2\alpha\gamma \sin \beta}},$$

$$\delta = \frac{b_M}{a_c},$$

with $\alpha = \sqrt{2}a_M/a_c$ and $\gamma = \sqrt{2}c_M/Na_c$ [47,48], $a_c$ is the lattice parameter of a cubic austenite phase and $a_M$, $b_M$, $c_M$, and the angle $\beta$ denote the lattice parameters of a monoclinic unit cell. Now the transformation matrix of the $x = 1$ sample is

$$U = \begin{pmatrix} 1.0293 & 0.0161 & 0 \\ 0.0161 & 1.0124 & 0 \\ 0 & 0 & 0.9311 \end{pmatrix}.$$
magnetic field-induced IMT from weak magnetic martensite to FM austenite. At the temperature (∼268 K) close to $A_S$, the $M(\mu_0 H)$ curves of both cycles match with each other, suggesting the MST is completely reversible. However, from the temperature ∼271 to 280 K, the low field magnetization in $M(\mu_0 H)$ curves of the second cycle is higher than the first one. It is also noted that the $M(\mu_0 H)$ curves recorded during the third and following field cycles coincide with the second field cycle. This yields a good reversibility of IMT in the system after the first field cycle. At 283 K, no martensite phase is recovered after the first cycle, exhibiting that IMT does not occur after 283 K, upon the field cycling [41,55].

Now we quantitatively explain the above results based on the reversible effect in the Ni-(Co)-Mn-Ti all-d-metal system. When the field of 5 T is applied above $A_S$, the $M(\mu_0 H)$ curves of both cycles match with each other, suggesting the MST is completely reversible. However, from the field cycling [41,55], and the Clausius-Clapeyron relation [CC$_H$ $\Delta S_M$ vs $T$] during the first and second field cycles of the $x = 1$ sample (d) of $x = 2$ sample, where the second cycle $\Delta S_M$ is reversible.

Isothermal magnetic entropy change ($\Delta S_M$) is an important parameter to quantify MCE response of the investigated alloys which can be computed across $T_A$, using Maxwell relation [1],

$$\Delta S_M(T, \Delta H) = \mu_0 \int_0^H \left( \frac{\partial M(H, T)}{\partial T} \right)_H dH$$  \hspace{1cm} (7)

where $\mu_0$, $M$, $H$, and $T$ are the permeability of free space, magnetization, applied magnetic field, and instantaneous temperature, respectively. The maximum value of $\Delta S_M$ ∼19.78 J kg$^{-1}$ K$^{-1}$ at 281.5 K is obtained for $x = 1$ under 5 T, shown in Fig. 3(b) which is in good agreement with $\Delta S_m$, determined from the DSC curve (in Table I).

For a more comprehensive and reliable analysis, the $\Delta S_M$ is also deduced using different methods. Clausius-Clapeyron equation using transformation fraction method is appropriate for the first-order MST and is employed here to deduce $\Delta S_M$ values from isofield $M$-$T$ measurements for the different field changes [56].

$$\Delta S_M = -\Delta f \Delta M \left( \Delta T_{f} \Delta H_{0} \right)^{-1},$$  \hspace{1cm} (8)

where $\Delta f$ is the change of phase fraction of austenite induced by the change of magnetic field that can be defined as $\Delta f(T, \mu_0 \Delta H) = f(T, \mu_0 H_f) - f(T, \mu_0 H_0)$, $\mu_0 H$, and $\mu_0 H_f$ are the initial and final applied magnetic field, respectively. The phase volume fraction of austenite can be assumed as proportional to the total magnetization and can be
TABLE II. Comparison of reversible magnetic entropy change ($\Delta S_M$) at 5 T and their respective transition temperatures ($T_{\text{peak}}$) of all-$d$-Ni$_{37-x}$Co$_{13+x}$Mn$_{34}$Ti$_{15.5}$ Heusler alloys, and other related promising systems.

| Materials                  | $|\Delta S_M^{\text{peak}}|$ (J/kg$^{-1}$K$^{-1}$) | $T_{\text{peak}}$ (K) | References |
|----------------------------|-----------------------------------------------|------------------------|------------|
| Gd                        | 10.2                                         | 294                    | [59]       |
| Gd$_3$(Si$_2$Ge$_2$)       | 18.5                                         | 278                    | [2]        |
| Ni$_{49}$Co$_{13}$Mn$_{34}$In$_{15.5}$ | 14.6                                         | 235                    | [60]       |
| Ni$_{49}$Co$_{13}$Mn$_{34}$In$_{14}$ | 16.5                                         | 268                    | [38]       |
| Ni$_{50}$V$_{0.3}$Mn$_{14.4}$In$_{15.6}$ | 18.9                                         | 276                    | [61]       |
| Ni$_{41.3}$Co$_{2.9}$Mn$_{36}$Ga$_{0.4}$In$_{1}$ | 11                                           | -                      | [62]       |
| Ni$_{41}$Ti$_{3.1}$Co$_{0.9}$Mn$_{39}$Sn$_{10}$ | 18.7                                         | 287                    | [9]        |
| Ni$_{1.9}$Pt$_{0.3}$Mn$_{14}$In$_{0.6}$ | 12                                           | 262                    | [47]       |
| Mn$_{0.87}$Co$_{0.13}$Si$_{0.95}$Ga$_{0.05}$ | 5.2                                          | 280                    | [63]       |
| Ni$_{37-x}$Co$_{13+x}$Mn$_{34}$Ti$_{15.5}$ | $x=1$                                        | 277                    | Present work |

estimated as [56]

$$f(T) = \frac{M(T) - M_M(T)}{M_A(T) - M_M(T)},$$

where $M_M(T)$ and $M_A(T)$ represent the magnetization of the low-temperature and high-temperature phases, respectively. The maximum $\Delta S_M$ for the field changes from H$_f$ ~ 5 T to $H_f$ ~ 5 T is 19.66 J kg$^{-1}$K$^{-1}$, plotted in Fig. 3(b). The result obtained from both Maxwell relation and CC equation confirms that our $\Delta S_M$ values are reliable [57].

Furthermore, from the viewpoint of practical application, to achieve reversible and reproducible MCE, the transformation fraction method based on $M(\mu_0H)$ curve is a feasible and reliable procedure [9]. The phase fraction of austenite is determined from the $M(\mu_0H)$ curve of both cycles at the respective temperatures using the following equation:

$$f(T) = \frac{M(H) - M_M(H)}{M_A(H) - M_M(H)},$$

where $M_M(H)$ and $M_A(H)$ represent the magnetization of the martensite and austenite phase which can be deduced by the extrapolating of $M(\mu_0H)$ curve at 250 and 300 K of pure martensite and austenite phases, respectively [58]. Figure 3(b) renders the $\Delta S_M$ value based on the various methods as a function of temperature during the first field cycle for $x = 1$ sample under the field changes of 5 T. Evidently, the value of $\Delta S_M$ estimated from TF-$M(\mu_0H)$ is almost consistent with the CC-$M(T)$ and Maxwell equation. As mentioned earlier, the field-induced transformation is reversible during second and subsequent field cycles in the temperature range from 265 to 280 K and in Fig. 3(c) we compared $\Delta S_M$ using TF-$M(\mu_0H)$ method for first and second cycles (details are shown in Fig. S3 of Ref. [37]). It is seen that $\Delta S_M$ value of second cycle is quite close to that of the first one, indicating good reversibility of the MCE. Hence, a large reversible $\Delta S_M$ of 17.78 J kg$^{-1}$K$^{-1}$ over a broad temperature window ~12 K is achieved upon 5 T, since a large fraction of IMT is involved to contribute in the MCE. For comparison, similar measurements are carried out for $x = 2$ sample and illustrated in Fig. S4 in Ref. [37]). Here, the $\Delta S_M$ value at 243 K of $x = 2$ sample obtained from TF-$M(\mu_0H)$ method for first and second cycles are 18.76 and 16.72 J kg$^{-1}$K$^{-1}$, respectively, depicted in Fig. 3(d). The $\Delta S_M$ value of second field cycles are about 11% smaller than the first cycle because of the relatively large residual austenite formed during first field ascending does not take part in the transformation during subsequent field cycles. Therefore $x = 1$ sample produces large reversible entropy change which represent nearly 90% of total magnetic entropy change obtained at the first field cycle. The magnitude of reversible $\Delta S_M$ is comparable with the highest value reported in the other related promising systems (shown in Table II) which is indeed beneficial in potential application.

Adiabatic temperature change ($\Delta T_{ad}$) is another important parameter to quantify the MCE. It is reported that the reversible $\Delta T_{ad}$ is roughly estimated using the measuring temperature-dependent specific heat capacity ($C_p$) following the equation:

$$\Delta T_{ad} = -\frac{T}{C_p} \times \Delta S_M.$$  

$C_p$ has been recorded in zero field condition using modulated DSC technique as shown as a function of temperature in Fig. 4(a). The reversible $\Delta T_{ad}$ is deduced from the reversible $\Delta S_M$ data in Fig. 3(c) and the $C_p$ values presented in Fig. 4(a), which is plotted as a function of temperature in Fig. 4(b). A maximum reversible $\Delta T_{ad}$ ~6.7 K is obtained in Ni$_{37-x}$Co$_{13+x}$Mn$_{34}$Ti$_{15.5}$ all-$d$-metal alloys and this magnitude is comparable to other Ni-Mn-X Heusler alloys [9,38,40,55,64].

It is well known that the cyclic behavior of phase transformation plays a significant role on the mechanical stability of the MCE materials. We plotted in Fig. 5(a) the thermal cycling behavior for the alloy with $x = 1$ measured by DSC and their respective characteristic temperatures vs. cycle are presented in Fig. 5(b). Clearly, the peak positions remain almost unchanged and no significant shift of the characteristic temperatures is observed over 35 thermal cycles. Therefore this observation demonstrates that the phase transition possesses a good reversibility and stability in our system.

**D. Magnetoresistance**

The structural transformations in the Heusler alloys are realized by the band John-Teller effect. They are accompanied
by the change of fundamental ordering of spins and consequently the crystal and magnetic structure which causes to a significant change in the electrical resistance. To investigate the magnetoresistive properties and their reversibility, we measured the temperature and magnetic field dependent electrical resistivity of $x = 1$ sample and are shown in Fig. 6. It is seen [in Fig. 6(a)] that on cooling, $\rho(T)$ exhibits an abrupt increase around the MST. This is caused by the change in the electronic density of state in the vicinity of Fermi level due to the lattice distortion of the phase transformation [65]. On the application of a magnetic field of 5 T, $\Delta S$ is reduced by $\sim 11$ K with the reduction rate of 2.2 K/T. Hence, there exists a certain temperature gap between the resistivity at 259.6 K ($A_S$) upon 5 T to that at 277.3 K ($M_S$) under 0 T, which indicates that a partial reversible behavior of MR is expected in the above-mentioned temperature range.

The inset of Fig. 6(a) exhibits the temperature dependence of MR under a magnetic field change of $\mu_0 H$ during heating is obtained from the following equation:

$$MR = \left[ \frac{R(\mu_0 H) - R(0)}{R(0)} \right] \times 100\%,$$

where $R(\mu_0 H)$ and $R(0)$ stand for the electrical resistance under $\mu_0 H$ and zero field. A maximum MR value of $-32.6\%$ is observed across the IMT under the field of 5 T which is comparable to other Ni-Mn-based Heusler alloys [66–68]. This large negative MR is developed as the electrical resistance in the austenite state is much lower than that of martensite phase. On applying the magnetic field, a field-induced inverse transformation from weak magnetic martensitic state to FM austenite state is developed, leading to the negative MR.

To get a further insight of reversible MR, the isothermal resistivity versus field is studied upon subsequent field cycling and the corresponding field dependent MR is depicted Figs. 6(c) and Fig. 6(e), respectively. At 300 K, the sample is in the fully austenite state and no significant change in MR is observed when a field is applied. One can observe that with increasing temperature in the reverse IMT region, for example, at 265, 270, and 277 K, the critical field decreases with increasing field because reverse IMT is induced by the field from the martensite to austenite state. Notably, the peak value of MR increases with the measured temperature because of the enhancement of the volume fraction of martensite by the application of magnetic field of 5 T. After that, upon removal of the field, the MR does not reverse entirely into the initial state. As a consequence, a reduced reversible MR of about 14% is obtained at 277 K for the second and subsequent field cyclic measurements. Compared to the reversible MR of sample $x = 1$, the analogous $\rho(T)$ and $\rho - \mu_0 H$ measurements are illustrated in Figs. 6(b), 6(d) and 6(f) for $x = 2$ sample. An applied of magnetic field 5T resulted in a decrease of $A_F$ by 17.1 K with the reduction rate of 3.4 K/T, which is well consistent with the result from M(T) curve. Hence, the partial reversible field-induced IMT may occurs between 232.8 K

FIG. 4. (a) Specific heat capacity ($C_P$) as a function of temperature under zero field for the Ni$_{36}$Co$_{14}$Mn$_{34.5}$Ti$_{15.5}$ alloy recorded during heating mode. (b) Reversible $\Delta T_{ad}$ vs $T(K)$ under 5 T obtained from Eq. (10).

FIG. 5. (a) DSC heat-flow curves during heating and cooling cycles (b) The characteristic transformation temperatures under 35 thermal cycles of $x = 1$ sample.
FIG. 6. [(a) and (b)] Temperature-dependent electrical resistivity ($\rho - T$) curves of $x = 1$ and $x = 2$ samples upon heating and cooling with 0 and 5 T. Inset shows the corresponding temperature dependence of MR during heating and cooling cycles. [(c) and (d)] Field-dependent resistivity ($\rho - \mu_0H$) at various temperatures upon heating mode across the transition of $x = 1$ and $x = 2$ samples. The green hollow circle represents the second cycle ($\rho - \mu_0H$) at 277 K after the first cycle of magnetic field. [(e) and (f)] The corresponding field dependence of MR of those samples, respectively in the inverse martensitic region. (AS) upon 5 T and 250.3 K ($M_s$) under 0 T. Figures 6(d) and 6(f) show the field-dependent resistivity and corresponding MR in the reverse IMT region. It is observed from Fig. 6(d) that at 250 and 235 K, the resistivity decreases with increasing temperature and very weak field-induced transition occurs with increasing the magnetic field. The same phenomena is observed in the $M - \mu_0H$ curve (in Fig. S4 in Ref. [37]). So, for the evaluation of reversible MR, second cycle of $\rho - \mu_0H$ curve are record with the first one at 243 K. It is seen that at 243 K, large fraction of residual austenite of the first field descending cycle persists for subsequent field cycling [69]. As a consequence of that, a relatively small reversible MR of about 13.1% during the second cycle of the total MR $\sim 31.2\%$ during first cycle at 243 K is obtained. Therefore relatively large temperature window of the reversible MR and near room temperature working temperature highly favors the sample $x = 1$ as magnetic actuator for technological application.

IV . CONCLUSIONS

In summary, the reversibility of both the MCE and MR has been experimentally investigated using different measurement protocols. The reversibility of magnetoresponsive properties depend upon the two competing factors, field-induced shift of the transformation temperatures and the width of the hysteresis. Thus systematically tuning with the small at.% of Co addition in Ni site, a small $\Delta T_{hyp}$, narrow $\Delta T_{int}$ and improved sensitivity of $\sim 2.8$ K/T is observed in the $x = 1$ sample. The origin of the small ($\Delta T_{hyp} + \Delta T_{int}$) is related to the middle eigenvalue i.e., $\lambda_2 \approx 1.0065$ of the transformation stretch matrix U which is closed to one, confirming good geometrical compatibility between two phases in all-d-metal Heusler alloys. In addition, the minor hysteresis loop has been done in order to enhance the reversibility of our system. A large reversible $\Delta S_M$ of $\sim 17.78$ J kg$^{-1}$ K$^{-1}$ at 277 K over a broad temperature window $\sim 12$ K has been deduced in the studied alloy. Moreover, due to partial reversible field-induced inverse MT, a large reversible MR of 14% out of 32.6% is obtained. The present work also demonstrates that narrower hysteresis loop in $x = 1$ sample is more beneficial for reversible multifunctional properties than the larger magnetization difference in $x = 2$ sample. These reversible magnetoresponsive properties are comparable to other Ni-Mn-based Heusler alloys and have not been reported so far in the all-d-metal Heusler system. Therefore these findings illuminate new potential functionalities in Ni(Co)-Mn-Ti all-d-metal Heusler alloys and make them attractive candidates as a cyclically stable caloric material with small hysteresis for magnetic refrigeration and magnetic recording applications.

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