Effect of partial substitution of Ni by Co on the magnetic and magnetocaloric properties of Ni$_{50}$Mn$_{35}$In$_{15}$ Heusler alloy

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The magnetic and magnetocaloric properties of Ni$_{48}$Co$_2$Mn$_{35}$In$_{15}$ were studied using magnetization and heat capacity measurements. The magnetic entropy change ($\Delta S_M$) was evaluated from both magnetizing and demagnetizing fields. An inverse $\Delta S_M$ for the magnetizing and demagnetizing processes were found to be 20.5 and 18.5 J kg$^{-1}$ K$^{-1}$, respectively, for $\Delta H = 5$ T at the martensitic transition ($T = T_M$). The normal $\Delta S_M$ was found to be $-5.4$ J kg$^{-1}$ K$^{-1}$ for both fields at the paramagnetic/ferromagnetic transition ($T = T_C$). The effective refrigeration capacity at $T_M$ and $T_C$ for magnetizing field was found to be 268 and 243 J/kg (285 and 243 J/kg for the demagnetizing field), respectively. We have also estimated the density of states, the Debye temperature, and the inverse magnetizing field was found to be 268 and 243 J/kg (285 and 243 J/kg for the demagnetizing field), respectively.

The off-stoichiometric Ni$_2$Mn$_{1+y}$X$_{1-y}$ (X = In, Sb, Sn) Heusler alloys that possess extreme changes in magnetic properties linked to magnetic or structural phase transitions near room temperature are of great importance in the study of the magnetocaloric effect (MCE). There are at least three important characteristics to consider in order to evaluate a good magnetocaloric material: (i) the process must be reversible with respect to changing/reversing magnetic field and show low hysteresis loss, (ii) the effect must occur near room temperature (RT) for RT applications, and (iii) the MCE [magnetic entropy change ($\Delta S_M$), adiabatic temperature change ($\Delta T_{ad}$), and refrigeration capacity (RC)] should be significant at reasonable applied magnetic field values. It was reported earlier that the $\Delta S_M$ and net RC [after accounting for hysteresis loss (HL)] of Ni$_{50}$Mn$_{35}$In$_{15}$ in the vicinity of the first-order transition (FOT) and second-order transition (SOT) were, respectively, 35 J kg$^{-1}$ K$^{-1}$, 57 J/kg, and $-5.7$ J kg$^{-1}$ K$^{-1}$, 123 J/kg for $\Delta H = 5$ T. Recent studies show that substitution of Ni by Co in Ni$_2$Mn$_{1+y}$X$_{1-y}$ strongly affects the magnetic, magnetocaloric, and magnetoelastic properties. However, additional studies are required to fully evaluate the MCE properties of Ni–Co–Mn–In. In this study, we report a detailed study of the MCE ($\Delta S_M$, $\Delta T_{ad}$, RC, and HL) for the partial substation of Ni by Co in Ni$_{50}$Mn$_{35}$In$_{15}$ using magnetization and heat capacity measurements.

A 5 g polycrystalline Ni$_{48}$Co$_2$Mn$_{35}$In$_{15}$ ingot was fabricated by conventional arc melting in an argon atmosphere. A part of the same sample was used in other previous measurements. The magnetic properties were measured by the method described in Ref. 7. The $\Delta S_M(T, H)$ was estimated from isothermal magnetization curves using the Maxwell relation. Although this equation is technically valid only for second-order magnetic transitions, it is conventionally employed to calculate $\Delta S_M$ in the vicinity of FOT, a practice that is justified in cases where problematic discontinuities are not present in the phase transition. The RC was calculated by integrating the $\Delta S_M(T, H)$ curves over the full-width at half-maximum (FWHM).

The heat capacity ($C_P$) measurements were carried out by physical properties measurements systems (PPMS) by Quantum Design, Inc. For each measurement, the sample was cooled in zero fields from a temperature above the magnetic transition temperature. All heat capacity measurements were conducted during the warming process, from 0.4 K to above RT. The $\Delta T_{ad}$ was estimated from the heat capacity data using an indirect method. The entropy as a function of temperature $S(T)$ was calculated from the heat capacity using the following relation (Ref. 8, and references therein):

$S(T) = \int_0^T C_P(T') \, dT'$

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FIG. 1. (Color online) (a) Zero field cooled magnetization as a function of temperature $M(T)$ for Ni$_{48}$Co$_2$Mn$_{35}$In$_{15}$. The inset shows the linear dependence of the martensitic transition temperature as a function of external magnetic field.
increase in field dependence of the martensitic and austenitic phases at external magnetic fields is shown in Fig. 1. As the temperature increases, the M(T) curve with $H = 0.01$ T shows evidence of multiple phase transitions: (i) at the Curie temperature of the martensitic phase ($T_{CM}$), (ii) at the martensitic transition at $T_M$, and (iii) at the Curie temperature of the austenitic phase at $T_C$. As reported by other research groups, it was found that the substitution of Co for Ni decreases both $T_{CM}$ and $T_M$, and increases $T_C$ relative to that of ternary Ni–Mn–In alloy.\(^9\) The substitution of Co in the Ni position results in an enhancement of the magnetization jump (up to 77 emu/g) across the martensitic transition (MT). It was found that $T_M$ is much more sensitive to the magnetic field in the case of Ni$_{48}$Co$_2$Mn$_{33}$In$_{15}$, and $T_M$ decreases linearly with an external magnetic field at a rate of 7 K/T [see Fig. 1(inset)]. The increase in field dependence of $T_M$ with Co substitution could be due to the enhancement of the difference in the magnetization of martensitic and austenitic phases at $T_M$.

The temperature dependence $C_p(T)$ for Ni$_{48}$Co$_2$Mn$_{33}$In$_{15}$ in 0 and 5 T external magnetic fields is shown in Fig. 2. The $\lambda$-type anomaly in $C_p(T)$ represents the first-order M(T) from the low magnetization martensite to the ferromagnetic (FM) austenite phase at $T \approx 275$ K, which is close to the $T_M$ observed from M(T) (see Fig. 1). The $C_p(T)$ slope change observed at $T \approx 350$ K is typical for a second-order phase transition. The $\lambda$-type anomaly peak at $C_p(T)$ at zero fields shifted to $T \approx 244$ K with the application of an external magnetic field of 5 T. The field-induced $(H = 5T)$ shift of $T_M$ to 245 K obtained from $C_p(T)$ is close to that observed from $C_p(T)$. The $C_p(T)$ at $T < 1$ K shows an upturn [see Fig. 2(inset)]. Similar behavior in the $C_p(T)$ of (Er, Y)Co$_2$ compounds was explained by a nuclear contribution.\(^16\)

Low-temperature heat capacity data for 0 and 5 T magnetic fields were fitted to the equation: $C_p(T) = \gamma T + \beta T^2$, where $\gamma T$ and $\beta T^2$ are the electronic and phonon contributions to the specific heat capacity, respectively. We observed that $C_p(T)$ is a linear function of $T^2$ [see Fig. 2(b)]. The electronic and phonon coefficients, $\gamma$ and $\beta$, were found to be 0.04418 mJ/g K$^2$, 0.000950 mJ/g K$^4$ for zero field (0 T) (and 0.04104 mJ/g K$^2$, 0.000881 mJ/g K$^4$ for 5 T), respectively. The observed value of $\gamma$ is similar to that observed in single-crystal Ni$_{50}$Mn$_{33.7}$In$_{16.3}$ (0.054 mJ/g K$^2$)\(^11\) and polycrystalline Ni$_{33}$Mn$_{67}$Sb$_{15}$ (0.04862 mJ/g K$^2$)\(^12\). Based on the fitted values of $\gamma$ and $\beta$, we estimated the density of states, $g(E_F)$, at the Fermi level and the Debye temperature, $\Theta_D$, using the following equations:\(^13\)

$$g(E_F) = \frac{3\gamma}{\pi^2 N_A k_B^2}, \quad \Theta_D = \sqrt{\frac{12\pi^4 N_A k_B^2}{5\beta}},$$

where $N_A$ and $k_B$ are Avogadro’s number and Boltzmann constant, respectively. The values of $g(E_F)$ and $\Theta_D$ were found to be 4.93 states/eV f.u. and 314 K, respectively, at zero external magnetic field.

The isothermal magnetization $M(H)$ was carried out for both magnetizing (from 0 to 5 T) and demagnetizing (5 to 0 T) fields in 1 and 5 K increments in the vicinity of $T_M$ and $T_C$, respectively. For clarity, only typical $M(H)$ curves are shown in Fig. 3. In the vicinity of $T_M$ [Fig. 3(a)], the magnetization curves show a gradual transition to metamagnetism (from 245 to 275 K), and are associated with a field-induced reverse martensitic transformation. The $M(H)$ curve in the vicinity of $T_M$ is associated with a large-field hysteresis. From 300 to 380 K, the magnetization curves show FM behavior and no hysteresis was obtained in this temperature region [see in Fig. 3(b) that the $M(H)$ curves for both increasing and decreasing fields overlap].
\[ \Delta S_M \] was estimated for both magnetizing and demagnetizing \( M(H) \) curves and are shown in Fig. 4. Figure 4 shows the positive (i.e., inverse) \( \Delta S_M \) in the FWHM temperature range of 250–274 K for a magnetizing field (and 242–269 K for the demagnetizing field), followed by the negative (i.e., normal) \( \Delta S_M \) in the range of 311–376 K for a magnetizing field (and 309–377 K for the demagnetizing field). This suggests that both magnetizing and demagnetizing processes can be employed for the magnetic refrigeration, which could potentially improve the efficiency of the process. The average HL over the FWHM temperature range of \( \Delta S_M \) was found to be 81 J/kg [see Fig. 4(a), inset].

As shown in Fig. 4, the inverse \( \Delta S_M \) for the magnetizing and demagnetizing processes were, respectively, found to be 20.5 and 18.5 J kg\(^{-1}\) K\(^{-1}\) for \( \Delta H = 5 \) T. The normal \( \Delta S_M \) was found to be \(-5.4\) J kg\(^{-1}\) K\(^{-1}\) for both magnetizing and demagnetizing fields. However, the inverse \( \Delta S_M \) for the Co-substituted Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) sample is slightly lower when compared to the parent compounds (35 J kg\(^{-1}\) K\(^{-1}\)), and \( \Delta S_M \) expands over a large temperature interval. The RC in the vicinity of FOT and SOT were found to be 324 and 268 J/kg, respectively, for a magnetizing field of 5 T. Similarly, for a demagnetizing field, RC in the vicinity of the FOT and SOT was found to be 366 and 274 J/kg, respectively. Taking into account the HL [see Fig. 4(a), inset] in the vicinity of the FOT, the net RC was calculated by subtracting the average HL, calculated over the same temperature range as that of the FWHM of the \( \Delta S_M \), from the uncorrected RC value. The corresponding net RC value for the magnetizing process at the FOT was found to be 243 J/kg when HL was taken into account. Roughly then, the total effective RC on a complete refrigeration cycle (assuming it effectively exploits both effects) would be 268 + 243 = 511 J/kg and 285 + 274 = 559 J/kg for magnetizing and demagnetizing processes, respectively, over the wide temperature range. These values of RC are larger than that observed for other Heusler alloys such as Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\), Ni\(_{50}\)Sn\(_{35}\)+Co\(_{15}\), and Ni\(_{50}\)Mn\(_{35}\)Sn\(_{35}\)+X\(_{15}\) (\( X = \text{In, Sn} \)).

The \( \Delta T_{ad} \) is one of the most important parameters to determine the potential for magnetocaloric materials. The estimated \( \Delta T_{ad} \) from 0 and 5 T heat capacity data is shown in Fig. 5. Inverse \( \Delta T_{ad} \) of \(-3.7\) K was found for a magnetic field change 5 T.

It was found that the substitution of a small amount of Co (~4%) in Ni site in Ni\(_{50}\)-Co\(_{5}\)Mn\(_{35}\)In\(_{15}\) (\( x = 2 \)) significantly increases the RC in the vicinity of both \( T_M \) and \( T_C \). The phase transition temperatures, \( T_M \) and \( T_C \), were found to be close to those obtained from \( C_p(T) \) measurements. The indirect inverse \( \Delta T_{ad} \) was found to be \(-3.7\) K in the vicinity of \( T_M \) at \( \Delta H = 5 \) T. In previous studies, it was also shown that the partial substitution of Ni in Ni\(_{50}\)Mn\(_{35}\)In\(_{15}\) by Co significantly enhanced the magnetoresistance in the vicinity of \( T_M \). Therefore, the Ni\(_{50}\)-Co\(_{5}\)Mn\(_{35}\)In\(_{15}\) Heusler alloys could be promising magnetic materials for ongoing research in a multifunctional application.

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