4-1-2011

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Arjun K. Pathak
Southern Illinois University Carbondale

Igor Dubenko
Southern Illinois University Carbondale

Yimin Xiong
Louisiana State University

Philip W. Adams
Louisiana State University

Shane Stadler
Louisiana State University

See next page for additional authors

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Pathak, A., Dubenko, I., Xiong, Y., Adams, P., Stadler, S., & Ali, N. (2011). Effect of partial substitution of Ni by Co on the magnetic and magnetocaloric properties of Ni₅₀Mn₃₅In₁₅ Heusler alloy. *Journal of Applied Physics*, 109 (7) <https://doi.org/10.1063/1.3540696>

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Authors

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Louisiana State University

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Published in *Journal of Applied Physics*, Vol. 109 No. 7 (2011) at [10.1063/1.3540696](https://doi.org/10.1063/1.3540696)

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Pathak, Arjun K., Dubenko, Igor, Xiong, Yimin, Adams, Philip W., Stadler, Shane and Ali, Naushad. "Effect of Partial Substitution of Ni by Co on the Magnetic and Magnetocaloric Properties of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ Heusler Alloy." (Apr 2011).

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Authors

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

Arjun K. Pathak,^{1,a)} Igor Dubenko,¹ Yimin Xiong,² Philip W. Adams,² Shane Stadler,² and Naushad Ali¹

¹Department of Physics, Southern Illinois University Carbondale, Carbondale, Illinois 62901, USA

²Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, USA

(Presented 16 November 2010; received 23 September 2010; accepted 8 November 2010; published online 25 March 2011)

The magnetic and magnetocaloric properties of $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ were studied using magnetization and heat capacity measurements. The magnetic entropy change (ΔS_M) was evaluated from both magnetizing and demagnetizing fields. An inverse ΔS_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 ΔS_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 adiabatic temperature change to be 4.93 states/eV f.u., 314 K, and -3.7 K, respectively, from the measured heat capacity data. © 2011 American Institute of Physics. [doi:10.1063/1.3540696]

The off-stoichiometric $\text{Ni}_2\text{Mn}_{1+y}\text{X}_{1-y}$ ($X = \text{In}, \text{Sb}, \text{Sn}$) 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).¹ 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 (ΔS_M), adiabatic temperature change (ΔT_{ad}), and refrigeration capacity (RC)] should be significant at reasonable applied magnetic field values. It was reported earlier that the ΔS_M and net RC [after accounting for hysteresis loss (HL)] of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ 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.² Recent studies show that substitution of Ni by Co in $\text{Ni}_2\text{Mn}_{1+y}\text{X}_{1-y}$ strongly affects the magnetic, magnetocaloric, and magnetoelastic properties.^{3–6} 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 (ΔS_M , ΔT_{ad} , RC, and HL) for the partial substitution of Ni by Co in $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ using magnetization and heat capacity measurements.

A 5 g polycrystalline $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ ingot was fabricated by conventional arc melting in an argon atmosphere. A part of the same sample was used in other previous measurements.⁷ 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.⁸ Although this equation is technically valid only for second-order

magnetic transitions, it is conventionally employed to calculate ΔS_M in the vicinity of FOT, a practice that is justified in cases where problematic discontinuities are not present in the phase transition.⁸ The RC was calculated by integrating the $\Delta S_M(T, H)$ curves over the full-width at half-maximum (FWHM).⁸

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 ΔT_{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):

FIG. 1. (Color online) (a) Zero field cooled magnetization as a function of temperature $[M(T)]$ for $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$. The inset shows the linear dependence of the martensitic transition temperature as a function of external magnetic field.

^{a)} Author to whom correspondence should be addressed. Electronic mail: pathak@siu.edu.

FIG. 2. (Color online) (a) Heat capacity (C_p) of $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ as a function of temperature at $H=0$ and 5 T [(inset) the magnified version of low temperature C_p]. (b) Low temperature C_p/T vs T^2 linear fit data for $H=0$ and 5 T.

$$S(T)_{0,H} = \int_0^T \frac{C(T)_{0,H}}{T} dT, \quad (1)$$

where $S(T)_{0,H}$ and $C(T)_{0,H}$ are, respectively, the entropy and heat capacity as a function of temperature at zero field and at magnetic field H . From $S(T)_0$ and $S(T)_H$, ΔT_{ad} was calculated as⁸

$$\Delta T_{\text{ad}}(T)_H = T(S)_H - T(S)_0. \quad (2)$$

The zero field cooled magnetization $M(T)$ curves for $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ at different magnetic fields are 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 $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$, 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 $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ in 0 and 5 T external magnetic fields is shown in Fig. 2. The λ -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 λ -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 ($H=5$ T) shift of T_M to 245 K obtained from $M(T)$ 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)Co₂ compounds was explained by a nuclear contribution.¹⁰

Low-temperature heat capacity data for 0 and 5 T magnetic fields were fitted to the equation: $C_p(T) = \gamma T + \beta T^3$, where γT , and βT^3 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, γ and β , were found to be 0.04418 mJ/g K², 0.000950 mJ/g K⁴ for zero field (0 T) (and 0.04104 mJ/g K², 0.000881 mJ/g K⁴ for 5 T), respectively. The observed value of γ is similar to that observed in single-crystal $\text{Ni}_{50}\text{Mn}_{33.7}\text{In}_{16.3}$ (0.054 mJ/g K²)¹¹ and polycrystalline $\text{Ni}_2\text{Mn}_{1.4}\text{Sb}_{0.6}$ (0.04862 mJ/g K²).¹² Based on the fitted values of γ and β we estimated the density of states, $g(E_F)$, at the Fermi level and the Debye temperature, Θ_D , using the following equations:¹³

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

where N_A and k_B are Avogadro's number and Boltzmann constant, respectively. The values of $g(E_F)$ and Θ_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].

FIG. 3. (Color online) Isothermal magnetization curves $M(H)$ for both magnetizing (for magnetic field changes from 0 to 5 T, closed symbols) and demagnetizing fields (for magnetic field changes from 5 to 0 T, open symbols) of $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ in the vicinity of (a) the FOT and (b) the SOT.

FIG. 4. (Color online) (a) Magnetic entropy change (ΔS_M) as a function of temperature for $\text{Ni}_{48}\text{Co}_2\text{Mn}_{35}\text{In}_{15}$ in the vicinity of the FOT, and the SOT for (a) magnetizing [inset] the hysteresis loss (HL) as a function of temperature] and (b) demagnetizing fields.

ΔS_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) ΔS_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) ΔS_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 ΔS_M was found to be 81 J/kg [see Fig. 4(a), inset].

As shown in Fig. 4, the inverse ΔS_M for the magnetizing and demagnetizing processes were, respectively, found to be 20.5 and 18.5 $\text{J kg}^{-1} \text{K}^{-1}$ for $\Delta H = 5$ T. The normal ΔS_M was found to be $-5.4 \text{ J kg}^{-1} \text{K}^{-1}$ for both magnetizing and demagnetizing fields. However, the inverse ΔS_M for the Co-substituted $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ sample is slightly lower when compared to the parent compounds ($35 \text{ J kg}^{-1} \text{K}^{-1}$), and ΔS_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 ΔS_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 $268 + 243 = 511 \text{ J/kg}$ and $285 + 274 = 559 \text{ J/kg}$ 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 $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$,² $\text{Ni}_{50-x}\text{Mn}_{35+x}\text{In}_{15}$,¹⁴ and $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$,¹⁵ $\text{Ni}_{50}\text{Mn}_{34}\text{X}_{16}$ (X = In, Sn).¹⁶

The ΔT_{ad} is one of the most important parameters to determine the potential for magnetocaloric materials. The estimated ΔT_{ad} from 0 and 5 T heat capacity data is shown in Fig. 5. Inverse ΔT_{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 ($\sim 4\%$) in Ni site in $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{35}\text{In}_{15}$ ($x = 2$) significantly

FIG. 5. Adiabatic temperature change as a function of temperature obtained from heat capacity data.

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 ΔT_{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 $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ by Co significantly enhanced the magnetoresistance in the vicinity of T_M . Therefore, the $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{35}\text{In}_{15}$ Heusler alloys could be promising magnetic materials for ongoing research in a multifunctional application.

This research was supported by the Research Opportunity Award from Research Corporation (RA-0357) and by the Office of Basic Energy Sciences of the U.S. Department of Energy (Contract No. DE-FGP2-06ER46291). P.W.A. acknowledges support of the DOE Office of Basic Energy Sciences under Grant No. DE-FG02-07ER46420

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