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Magnetism and magnetocaloric effects in $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ Heusler alloysArjun K. Pathak,^{1,a)} Igor Dubenko,¹ Christopher Pueblo,¹ Shane Stadler,² and Naushad Ali¹¹*Department of Physics, Southern Illinois University, Carbondale, Illinois 62901, USA*²*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, USA*

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The effects of the partial substitution of Mn by Co on the magnetic, magnetoelastic, and magnetocaloric properties of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ Heusler alloys were studied using x-ray diffraction, temperature and field dependences of the magnetization $[M(T,H)]$, and strain gauge techniques. It was observed that the presence of $\approx 3\%$ Co atoms in Mn sites strongly affected the magnetic and magnetoelastic behaviors of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$. At $H=5$ T, a maximum magnetoelastic strain of $\approx 0.6\%$ was observed for $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$. It was found that Co substituted into the Mn position does not affect the ΔS_M in the vicinity of the second order transitions (SOTs), however ΔS_M near the first order transitions (FOTs) it slightly decreases. The net refrigeration capacities in the vicinity of both the FOT and SOT were found to significantly increase by introducing Co into Mn sites. The net refrigeration capacity in the vicinity of the FOT and SOT was found to be 167 J/kg ($T=277-293$ K) and 229 J/kg ($T=305-354$ K), respectively, at a magnetizing field of 5 T. These values of the magnetocaloric parameters are comparable to that of the largest values reported for metallic magnets near room temperature. © 2010 American Institute of Physics.

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In condensed matter physics, magnetic materials that show large changes in magnetic properties associated with first order phase transitions around room temperature are of significant interest because of their potential applications in spintronics, magnetic refrigeration, and magnetomechanical devices such as actuators and transducers.¹⁻³ There are several classes of materials that have shown such properties. The Mn-based Heusler alloys, Ni-Mn-X ($X=\text{Ga}, \text{Sb}, \text{Sn}, \text{or In}$), and Fe-based intermetallic compounds, La-Fe-Si, are particular examples.⁴⁻⁷

The off-stoichiometric $\text{Ni}_2\text{Mn}_{1+y}\text{X}_{1-y}$ ($X=\text{In}, \text{Sb}, \text{or Sn}$) Heusler alloys that undergo martensitic transformations at T_M below the ferromagnetic (FM) ordering temperature (T_C) have attracted attention because of their giant magnetocaloric effect (MCE), and therefore demonstrate their possible employment as working materials in environmentally friendly magnetic refrigerators.^{5,6,8} 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 (HL), (ii) the effect must occur near room temperature for room temperature application, and (iii) the MCE [magnetic entropy changes and refrigeration capacity (RC)] must be significant at reasonable applied magnetic field values. It was reported earlier that the magnetic entropy changes (ΔS_M) and net RC (after accounting for 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.⁶ The phase transition temperatures and crystal phase magnetizations responsible for magnetocaloric proper-

ties can be controlled either by changing the valence electron concentration (e/a ratio) or through atomic substitution by other elements.^{9,10} Recent studies show that substitution of Ni by Co Ni-Mn-X ($X=\text{In}, \text{Sb}, \text{and Sn}$) strongly affects the magnetic and magnetoelastic properties.¹¹⁻¹³ However, the effect of partial substitution of Mn by Co on the magnetic and MCEs has not been studied. Therefore, in this work we have studied the magnetic, magnetoelastic, and magnetocaloric properties for the substitution of $\sim 3\%$ Co on Mn sites in $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$.

Approximately 5 g polycrystalline $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ alloys were prepared and the magnetization measurements were performed by the methods described in Ref. 9. Before the magnetization $[M(T)]$ measurements were made, the samples were cooled from 380 to 5 K at 0 applied external magnetic field. A non-0 magnetic field was then applied and the measurements were done from 5 to 400 K [i.e., zero field cooled (ZFC)] and then from 400 to 5 K [i.e., field cooled cooling (FCC)]. Subsequently, without removing the field, the measurements were done from 5 to 400 K [i.e., field cooled warming (FCW)]. The transition temperatures were determined from the local maxima of dM/dT of the FCW $M(T)$ curves.

The $M(H)$ for $\Delta S_M(T,H)$ was carried out both for increasing and decreasing magnetic field from 0 to 5 T in temperature increments of 1 and 4 K in the vicinity of FOT and SOT, respectively. The magnetic entropy change $\Delta S_M(T,H)$ was estimated from isothermal magnetization curves $M(H)$ using the Maxwell equation.¹⁴ Although this equation is valid only for second order magnetic transitions, it is conventionally employed to calculate ΔS_M in the vicinity of FOTs, a practice which is justified in cases where problematic discontinuities are not present in the phase transition,¹⁴ or where the applied field is high enough to complete the

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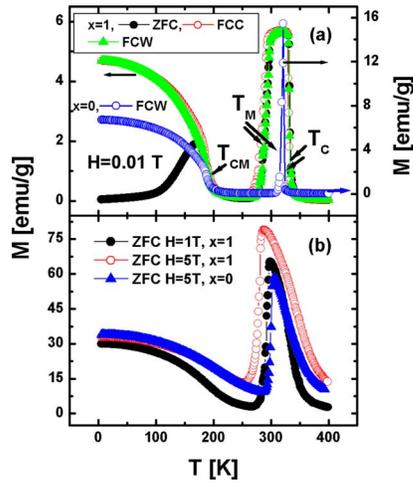


FIG. 1. (Color online) (a) ZFC, FCC, and FCW magnetization $M(T)$ for $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ ($x=0, 1$) at $H=0.01$ T and (b) ZFC $M(T)$ for $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ for $H=1$ and 5 T.

transition.¹⁵ The error in the estimation of ΔS_M which accounts for errors in H , T , and $M(T,H)$ measurements was approximately 30%.¹⁶ The RC was estimated by the method described in Ref. 14. The temperature-induced strains $[\epsilon(T)]$ parallel to the external magnetic field direction were measured using a strain gauge in magnetic fields up to 5 T.

Room temperature XRD measurements revealed that the samples were in the martensitic phase. As shown in Fig. 1(a), the $M(T)$ curves (ZFC, FCC, and FCW) for Co substituted samples split at $T \approx 175$ K. As in the parent compound [$x=0$, see Fig. 1(a)], when temperature increases, the sample undergoes multiple transitions: (i) at the Curie temperature of the martensitic phase (T_{CM}) at ≈ 185 K; (ii) from a low magnetic state [paramagnetic (PM) or antiferromagnetic (AF)] to the FM austenitic phase at the martensitic transition temperature $T_M \approx 295$ K; and (iii) from the FM austenitic to a PM austenitic phase at the Curie temperature of the austenitic phase at $T_C \approx 331$ K. The decrease in magnetization in the low-temperature martensitic state results from the increase of AF exchange interaction, and therefore an exchange bias effect can be expected in this compound.^{17–19} The irreversibility of $M(T)$ below T_{CM} is also evidence of pinning due to AF interactions in the martensitic phase. Detailed studies of the similar systems are presented in Ref. 20. Recent polarization-analysis experiments in Ni–Mn–Sb/Sn suggest that the low magnetic state at $T_{CM} < T < T_M$ is AFM.²¹ Therefore the sharp jump of magnetization at T_M may be due to a FOT from an AFM to an FM austenitic phase. It is shown in Fig. 1(a) that, compared to those of the parent compound, $\approx 3\%$ substitution of Co for Mn increases T_C by 10 K and decreases T_M by 24 K. Similar results are also observed in substitution of Ni by Co in Ni–Mn–X ($X=\text{In}, \text{Sb}, \text{or Sn}$) alloys.^{13,22,23} As shown in Fig. 1(b), partial substitution of Mn by Co significantly increases the difference in magnetization $\Delta M=63$ emu/g for $H=1$ T at T_M and provides a shift of T_M of about 13 K toward lower temperature for an external magnetic field of 5 T. This increase in ΔM at T_M could be attributed to the increase of FM alignment due to substitution of Co in Mn position.

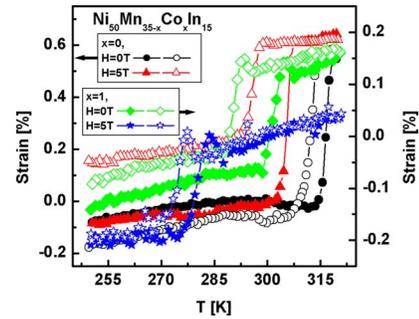


FIG. 2. (Color online) (a) Temperature dependence of the strain for $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ in heating (closed symbols) and cooling (open symbols) cycles at 0 and 5 T external magnetic fields.

Magnetoelastic strain is another property that is connected to the phase transitions in $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$. Figure 2 shows that temperature dependence of the strain measured in parallel 0 and 5 T external magnetic fields. As shown in Fig. 2, the strain increases with increasing temperature and shows a sharp jump in the strain ($\approx 0.6\%$) in the vicinity of T_M for the parent compound. This value of strain is higher than that found in polycrystalline Ni–Mn–X ($X=\text{Sb}, \text{Sn}, \text{In}, \text{and Ga}$).^{24,25} The jumplike strain changes and large temperature hysteresis obtained at T_M are indicative of a FOT. The substitution of Co in Mn positions decreases the strain. The decrease in strain with Co substitution could be due to the change in crystallographic structure of the martensitic phase. The details of magnetoelastic behavior in Ni–Mn–In will be discussed elsewhere.

Figure 3 shows the magnetization curves at discrete temperatures in increasing and decreasing fields up to 5 T. As shown in Fig. 3(a), the magnetization curves show a gradual transition to metamagnetism, starting at 271–293 K and are associated with a field-induced reverse martensitic transformation. From 293 to 356 K, the magnetization curves show

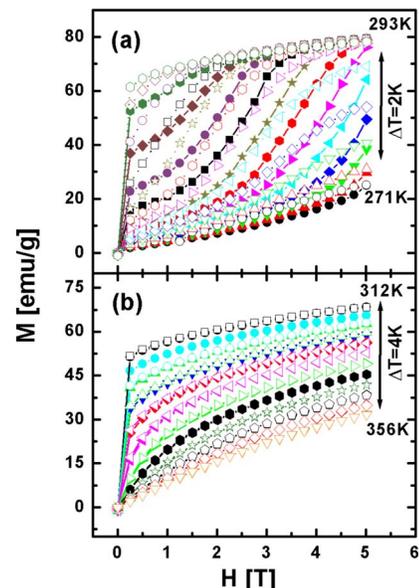


FIG. 3. (Color online) Isothermal magnetization curves $M(H)$ for both magnetizing (for magnetic field changes from 0 to 5 T, closed symbols) and demagnetizing fields (for magnetic field changes from 5 to 0 T, open symbols) of $\text{Ni}_{50}\text{Mn}_{34}\text{CoIn}_{15}$ in the vicinity of (a) the FOT and (b) the SOT.

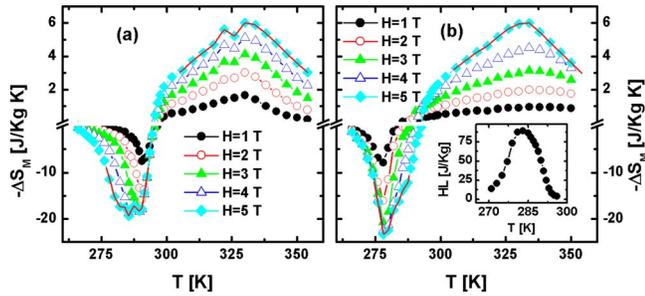


FIG. 4. (Color online) (a) Magnetic entropy change (ΔS_M) as a function of temperature for $\text{Ni}_{50}\text{Mn}_{34}\text{Co}_{16}\text{In}_{15}$ in the vicinity of the FOT, and the SOT for (a) magnetizing and (b) demagnetizing field. Inset in (b) shows the HL as the function of temperature.

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 field overlap]. Beyond 356 K, the $M(H)$ curves show PM behavior (not shown in Fig. 3). The ΔS_M was estimated by using the Maxwell equation¹⁴ for both magnetizing and demagnetizing $M(H)$ curves presented in Fig. 3. Figure 4 shows the positive (i.e., inverse) entropy change in the range of 264–296 K, followed by the negative (i.e., normal) entropy change in the range of 296–356 K. This suggests that both magnetizing and demagnetizing processes can be employed for magnetizing refrigeration processes which can improve their efficiency.⁸ As shown in Fig. 4, the inverse ΔS_M for the magnetizing and demagnetizing process were, respectively, found to be 19.4 and 23.3 $\text{J kg}^{-1} \text{K}^{-1}$ for $\Delta H=5$ T. The normal ΔS_M was found to be $-6 \text{ J kg}^{-1} \text{K}^{-1}$ for both magnetizing and demagnetizing fields. However, the inverse ΔS_M for Co substituted samples are slightly lower when compared to the parent compounds ($35 \text{ J kg}^{-1} \text{K}^{-1}$), and ΔS_M expands over the large temperature interval. This is one of the requirements for good MCE materials as discussed in the introduction. In Co substituted samples, the decrease in ΔS_M is related to the decrease in strain which could be attributed to a decrease in the magnetic anisotropy.

HL estimated from the enclosed area between the magnetizing and demagnetizing $M(H)$ curves, is another parameter to quantify the potential of MCE materials. It was found that, compared to the parent compounds; the substitution of Co decreased the HL (see in inset of Fig. 4(b) and Ref. 6). The RC in the vicinity of FOT and SOT were found to be, respectively, 256 and 229 J/kg for a magnetizing field of 5 T. Similarly, for a demagnetizing field, RC in the vicinity of FOT and SOT were found to be 235 and 231 J/kg, respectively. Taking into account HL [see inset of Fig. 4(b)] in the vicinity of FOT, the net RC was calculated by subtracting the maximum HL from the uncorrected RC value. The corresponding net RC value at FOT was found to be 167 J/kg when hysteretic losses are taken into account. Roughly then, the *total* effective RC on a complete refrigeration cycle (assuming it effectively exploits both effects) would be $229 + 167 = 396 \text{ J/kg}$ and $231 + 146 = 377 \text{ J/kg}$ for magnetizing and demagnetizing field, respectively, over the wide temperature range. This value of RC is comparable to some of the best prototypical magnetocaloric materials, Gd (400 J/kg)

(Ref. 14) and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (240 J/kg) (Ref. 26) alloys. Therefore, we hope these results will attract the attention of researchers who are developing magnetic refrigeration cycles (and corresponding devices) that can exploit both normal and inverse MCEs.

In conclusion, we found that a small amount ($\approx 3\%$) of Co in Mn position improves the MCE properties (RC, T_C , and HL) of $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$. Therefore, $\text{Ni}_{50}\text{Mn}_{35-x}\text{Co}_x\text{In}_{15}$ with higher Co concentrations could be an attractive potential magnetic refrigerant material for further study.

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