7-2007

Phase Transitions and Corresponding Magnetic Entropy Changes in Ni2Mn0.75Cu0.25−xCoxGa Heusler Alloys

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Published in *Journal of Applied Physics*, Vol. 102 No. 2 (2007) at doi: 10.1063/1.2753587

Phase transitions and corresponding magnetic entropy changes in $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ Heusler alloys

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(Received 21 February 2007; accepted 30 May 2007; published online 16 July 2007)

Detailed studies of room temperature crystal structures, phase transitions, and related magnetic entropy changes (ΔS_m) in shape memory alloys $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ (x=0.0, 0.01, 0.02, 0.025 0.03, 0.05) have been carried out by x-ray diffraction, magnetization, and thermal expansion measurements in magnetic fields of up to 5 T and in a temperature interval of 5–400 K. The high temperature austenitic cubic phase passes through a magnetic transition to ferromagnetic state and a structural transition to martensitic phase at the same temperature for all samples of the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ system. The first order magnetostructural transition temperature increases from 308 to 345 K with increasing Co concentration. All of the alloys in the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ system were found to possess large magnetic entropy changes. The maxima in the magnetic entropy changes ranged from $\Delta S_m^{max}=-48$ J/kg K to −64 J/kg K in a temperature range of 308–345 K. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2753587]

I. INTRODUCTION

Recent discoveries of ferromagnetic materials that undergo first order magnetic transitions and exhibit large magnetocaloric effects (MCE) have triggered a significant growth of interest in magnetocaloric cooling technology.[1–3]

Magnetocaloric cooling technology, when compared to the currently employed gas cooling technology, has enhanced efficiency, and therefore the recent discoveries and continuing research on magnetocaloric materials may lead to the development of environmentally friendly cooling technologies.[4–7] The MCE is a result of the alignment of magnetic moments with an external magnetic field. The alignment causes a reduction in the magnetic randomness, i.e., the magnetic component of the total entropy. The reduction of magnetic entropy is compensated by an increase in the other components of the total entropy. In the case of magnetocaloric materials, the compensation results in the heating of the material. A detailed discussion of the thermodynamics of the MCE is presented in Ref. 8.

The Heusler alloy Ni_2MnGa, an alloy that possesses shape memory properties, is well known to have potential applications as an actuator material. Lately it has gained additional interest due to its possible application as a magnetic refrigerant material.[9–13] Stoichiometric Ni_2MnGa has an $L2_1$ crystal structure at room temperature and, upon cooling, it undergoes a first order martensitic structural phase transition (at $T_M \approx 220$ K) from the parent cubic (austenitic) phase to a low temperature (LT) complex tetragonal structure.[14] The Curie temperature of the austenitic phase of this is alloy is T_C=376 K.[14] The substitution of Ni for Mn in the $Ni_{2+x}Mn_{1-x}Ga$ system results in an increase in T_M and a decrease of T_C and, for $0.17 \le x \le 0.20$, the coincidence of T_M and T_C results in an apparent first order magnetostructural phase transition.[15] As a result of this first order transition, a large magnetic entropy change of $|\Delta S_m|=15$ J kg^{-1} K^{-1} at a 1.8 T field is observed in $Ni_{2.19}Mn_{0.81}Ga$.[10] In $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ a magnetic entropy change of $\Delta S_m=-20.4$ J kg^{-1} K^{-1} at 317 K in a field of 5 T has been reported.[9] In polycrystalline Ni-Mn-Ga, the highest value of $\Delta S_m=-66.2$ J kg^{-1} K^{-1} at 350.25 K in a field change of 5 T is observed in $Ni_{2.19}Mn_{0.81}Ga$.[13] The coincidence of T_M and T_C is also reported to be the result of Cu substitution on the Mn sites of Ni_2MnGa.[16] In a recent study a magnetic entropy change of $\Delta S_m \approx -64$ J kg^{-1} K^{-1} at 308 K is observed in $Ni_2Mn_{0.75}Cu_{0.25}Ga$.[17] Close to room temperature, this is the highest ΔS_m value reported so far for any polycrystalline Heusler alloy. Since the giant magnetic entropy change occurs very close to room temperature, further research and development on this alloy might result in a potential magnetic refrigerant material that could be very cheap and efficient. To be able to tune the magnetostructural transition temperature while preserving the large magnetic entropy changes would be an interesting and significant outcome of further research. This is because tunability of the large magnetic entropy changes over a wide temperature range will open possibilities of developing magnetic refrigerant composites for near room temperature magnetic cooling applications.

In Ref. 16, it is shown that the substitution of Cu on the Mn sites of Ni_2MnGa results in an increase of T_M and a decrease of T_C, and the substitution of Co results in an increase of both T_M and T_C. Therefore, in $Ni_2Mn_{0.75}Cu_{0.25}Ga$, where $T_M=T_C$, the partial substitution of Co on the Cu sites could increase both T_M and T_C, resulting their shift to higher temperature as one single magnetostructural transition.

As an attempt to test this idea conjecture hypothesis, in this article we present a study on the magnetostructural phase transition and the corresponding giant magnetic entropy changes of $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$ ($0 \le x \le 0.05$). The aim is to control the magnetostructural phase transition temperature while preserving the high ΔS_m value.

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TABLE I. Compositions of $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$ system obtained from the EDX measurements.

x	% Ni	% Mn	% Cu	% Co	% Ga	Composition determined from EDX
0	48.05	17.68	6.12	⋯	28.16	$Ni_{1.92}Mn_{0.707}Cu_{0.245}Ga_{1.126}$
0.01	48.95	17.08	6.08	0.54	27.35	$Ni_{1.958}Mn_{0.683}Cu_{0.243}Co_{0.022}Ga_{1.094}$
0.02	48.27	17.46	5.47	0.81	27.98	$Ni_{1.931}Mn_{0.698}Cu_{0.219}Co_{0.032}Ga_{1.119}$
0.025	48.21	17.61	5.30	0.89	27.98	$Ni_{1.928}Mn_{0.704}Cu_{0.212}Co_{0.036}Ga_{1.119}$
0.3	48.54	16.12	5.22	1.11	29.01	$Ni_{1.942}Mn_{0.645}Cu_{0.209}Co_{0.044}Ga_{1.160}$
0.5	48.37	17.42	4.69	1.51	28.02	$Ni_{1.935}Mn_{0.697}Cu_{0.188}Co_{0.060}Ga_{1.121}$

II. EXPERIMENTAL TECHNIQUE

The fabrication of approximately 5 g of polycrystalline buttons of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ (x=0.00, 0.01, 0.02, 0.025 0.03, 0.05) was done by conventional arc melting in an argon atmosphere using Ni, Mn, Cu, Co, and Ga of 4*N* purity. The elements were melted four times and the weight loss after melting was found to be less than 0.3%. For homogenization, the samples were wrapped in Ta foil, annealed in vacuum for 144 h at 800 °C, and subsequently slowly cooled down to room temperature. The final compositions of the alloys, as summarized in Table I, were determined by energy dispersive x-ray photoluminescence (EDX) analysis. The average estimated errors in determining the concentrations were ±0.18%, ±0.10%, ±0.0.15%, 0.07%, and ±0.22% for Ni, Mn, Cu, Co, and Ga, respectively.

For phase identification and lattice constants determination, x-ray diffraction measurements were conducted at room temperature using a GBC minimaterials analyzer x-ray diffractometer that employed Cu $K\alpha$ radiation and Bragg–Brentano geometry.

The magnetization measurements were performed using a superconducting quantum interference device made by Quantum Design, Inc. The measurements were performed in a temperature range of 5–400 K and magnetic field of up to 5 T. The saturation moments were estimated by extrapolation of magnetization curves, $M(H)$, at 5 K to infinite magnetic field. Effective paramagnetic moments (p_{eff}) and paramagnetic Curie temperatures were obtained from the linear parts of inverse susceptibility χ^{-1} vs T curves at magnetic field of 1000 Oe. The magnetic entropy change, ΔS_m, was calculated from the isothermal magnetization data using the relation

$$\Delta S_{\text{mag}} = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{1}$$

Thermal expansion measurements were performed using a high resolution capacitance dilatometry method in the temperature range of 150–350 K.[18]

III. RESULT AND DISCUSSION

The room temperature powder x-ray diffraction (XRD) patterns of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ (x=0.0, 0.01, 0.02, 0.025, 0.03, 0.05) are shown in Fig. 1(a). The XRD pattern of the sample with x=0 suggests that there is a coexistence of the martensitic and austenitic phases in this sample at room temperature. As Cu is partially replaced by Co, the fraction of austenitic phases decreases until $x>0.02$, where the samples are found to possess near-pure typical martensitic body-centered-tetragonal (space group I_4/mmm) structures at room temperature. Figures 1(b) and 1(c) shows how the lattice parameters, **a** and **c**, and the cell volumes change with increasing Co concentration, respectively. It is observed that Co slightly increases the lattice parameters and the corresponding cell volume of the samples. This is because the

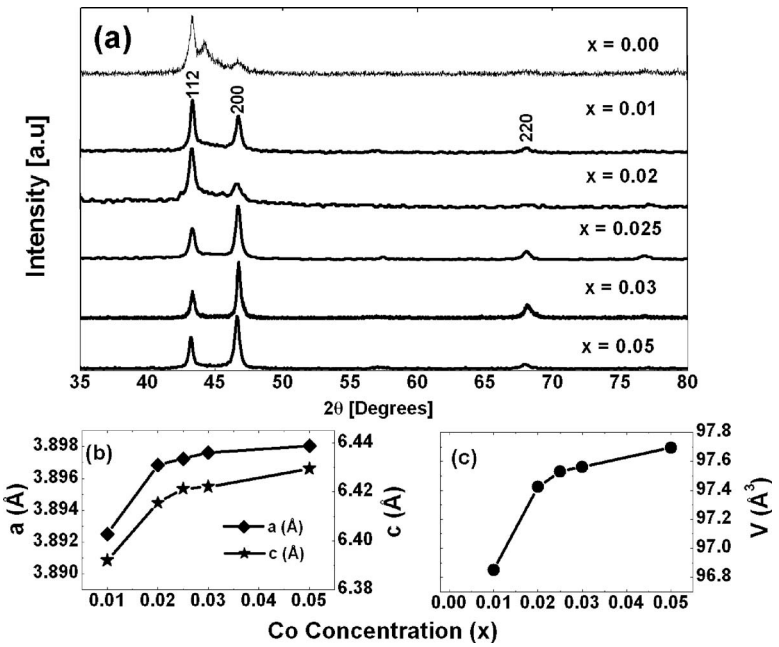

FIG. 1. (a) Powder XRD patterns of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$, (b) lattice parameters as a function of Co concentration, and (c) cell volumes as a function of Co concentration.

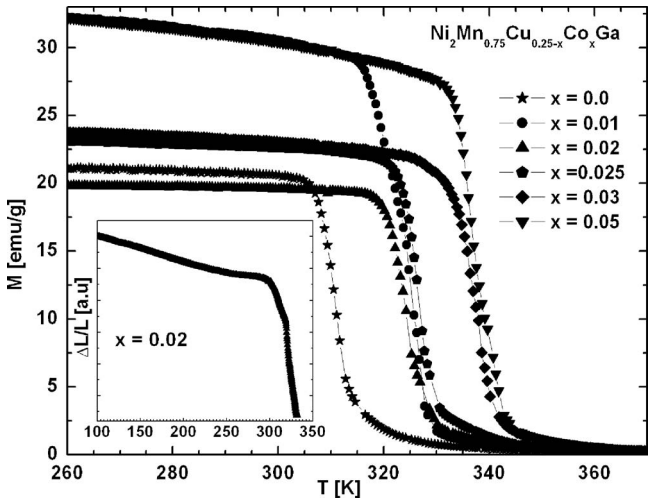

FIG. 2. Magnetization as a function of increasing temperature of $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$, obtained at a field of 1 kOe. The inset shows the thermal expansion as a function of temperature for the alloy with $x=0.02$.

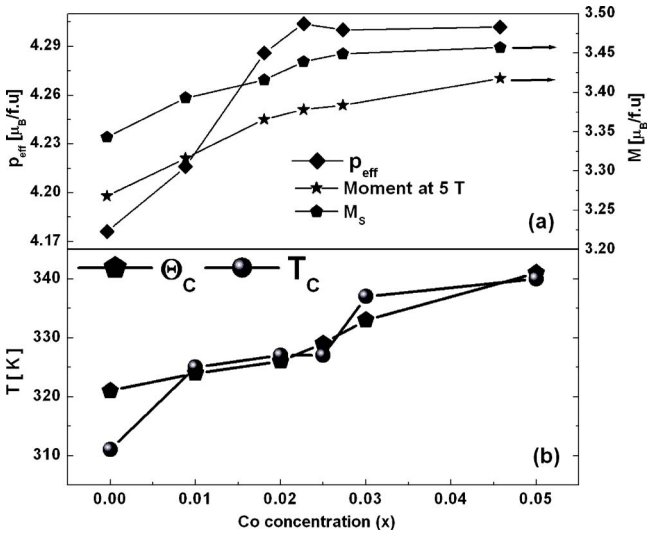

FIG. 3. (a) Magnetic moment (μ_B/f.u.) at 5 T, estimated saturation magnetic moment, and effective paramagnetic moment (p_{eff}) and (b) paramagnetic Curie temperature, Θ_C, and the Curie temperature, T_C, as a function of Co concentration of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$.

atomic radius of Co is a slightly larger than Cu. The lattice parameters for the samples with $x=0.01$ and 0.05 are **a** =3.892 Å, 3.898 Å and **c**=6.392 Å, 6.429 Å, respectively. The average cell volumes of the samples, and the corresponding densities are found to be approximately 97.4 $Å^3$ and $\rho=8.3$ g/cm^3, respectively.

The magnetization curves as a function of temperature of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ at a field of 1 kOe are shown in Fig. 2. Similar to the $Ni_2Mn_{0.75}Cu_{0.25}Ga$ alloy, the only transition observed in the magnetization curves of each Co doped sample is a sharp jump of magnetization at T_C. The increase of T_C with increasing Co concentration is also clear in the figure. The thermal expansion curve of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ with $x=0.02$, as a function of temperature is shown in the inset of Fig. 2. The step-like changes in the thermal expansion curves (typical for a first order phase transition) provides further evidence that the transition at T_C is of first order. Thus, as it was found for $Ni_2Mn_{0.75}Cu_{0.25}Ga$,[17] all the Co doped samples of the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ system pass through the magnetic transition to the ferromagnetic state and a structural transition to the martensitic phase at the same temperature. This explains the coexistence of both austenitic and martensitic phases (as observed in the XRD patterns in Fig. 1) in the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ samples, where martensitic transformations take place near room temperature. As shown in Figs. 3(a) and 3(b),the effective paramagnetic moment (p_{eff}), the magnetic moments at 5 T, saturation moments (M_S) at 5 K, Curie temperatures (T_C), and the paramagnetic Curie temperatures (Θ_C) are found to increase with increasing Co concentration. This suggests that Co substitution results in an increase of the positive exchange interaction in the system. In Ref. 16, it was shown that the substitution of Cu and Co on the Mn sites of Ni_2MnGa results in the decrease of the alloy's cell volume and in an increase of conduction electron concentrations. When compared to Co doping, Cu doping resulted in a more pronounced increase of the conduction electrons and decrease of the cell volume. Thus little decrease of the conduction electron and increase of the cell parameters by Co doping in $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ results in an increase of the positive exchange interactions and the values of $T_M=T_C$.

The magnetic entropy changes (ΔS_m) were evaluated from isothermal magnetization curves using Eq. (1). The use of this equation is more appropriate in evaluating ΔS_m at second order magnetic transition, however, most often this equation has been employed to calculate ΔS_m in the vicinity of first order phase transition which, according to Gschneidner *et al.*, is justified in cases where problematic discontinuities are not present in the phase transition.[3] The majority of the reported ΔS_m values of Ni-Mn-Ga, and other ferromagnetic systems[3] exhibiting first order phase transitions, are calculated using Eq. (1). Figure 4(a) shows the isothermal magnetization curves as a function of field for $Ni_2Mn_{0.75}Cu_{0.20}Co_{0.05}Ga$. In Fig. 4(b) the hysteresis loops are shown for the same sample at temperatures where the maximum ΔS_m value is obtained. The area between the increasing and decreasing field segments of the magnetization isotherms represents the hysteresis loss of the sample [see shaded part of Fig. 4(b)]. As can be seen in this figure, some hysteresis loss (17.9 J/kg at 332 K) exists in the sample with $x=0.05$. The hysteresis loss is considered to be one of the main obstacles for the practical application of a magnetocaloric material, as it directly opposes the refrigeration capacity. Therefore, reduction of the hysteresis loss in this system could be subject of further studies.

The change of magnetic entropy of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ as a function of temperature is presented in Fig. 5. As show in this figure, all the samples possess peak values of ΔS_m that are well comparable with the highest value of 28 J/kg K (227 mJ/cm^3 K) at 2 T and 64 J/kg K (513 mJ/cm^3 K) at 5 T obtained for $x=0.00$. The MCE values in (mJ/cm^3 K) units were evaluated because for application development the (mJ/cm^3 K) unit is more appropriate.[3] Although the ΔS_m values in the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ system are very high, it occurs in

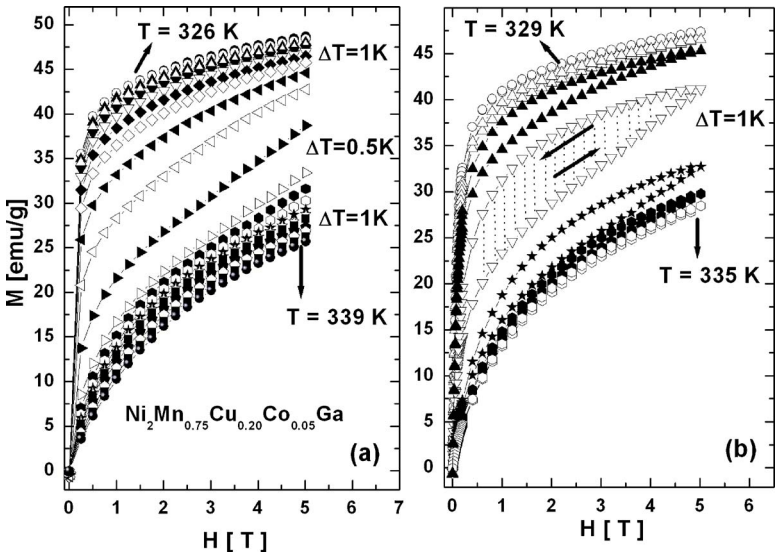

FIG. 4. (a) Isothermal magnetization curves of $Ni_2Mn_{0.75}Cu_{0.20}Co_{0.05}Ga$ at temperature increments of 1 and 0.5 K and (b) the hysteresis loops of $Ni_2Mn_{0.75}Cu_{0.20}Co_{0.05}Ga$ at temperatures where the maximum entropy is observed.

only a very narrow range of temperature, and therefore might not be that useful from application point of view. However, the results demonstrate that the magnetostructural transitions and the related large magnetic entropy changes in the $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ system can be tuned over a wide range of temperatures between 308 and 345 K. So it might be possible to develop composites based on this system that will exhibit giant MCE in wider range of temperature. As demonstrated in Fig. 6, the peak ΔS_m values of $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$ are found to depend linearly with the applied magnetic field of up to 5 T. Thus, higher values of ΔS_m can be expected in higher magnetic fields.

IV. CONCLUSION

We have studied the magnetic entropy changes in $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$ (x=0.01, 0.02, 0.025 0.03, 0.05). In $Ni_2Mn_{0.75}Cu_{0.25}Ga$, T_M and T_C are equal. Partial substitution of Co in the Cu sites results in a concerted increase in both T_M and T_C, preserving the first order magnetostructural transition. High ΔS_m peak values have been observed for all the alloys with the highest value (for x=0.00) of 28 J/kg K (227 mJ/cm^3 K) at 2 T and 64 J/kg K (513 mJ/cm^3 K) at 5 T. These experimental results suggest the possibility of tuning the first order magnetostructural transition temperatures while preserving the large magnetic entropy changes in $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$ Heulser alloys. We believe that these results will significantly contribute to the understanding of the fundamental phenomenon of the phase transitions and related MCE in Ni-Mn-Ga based Heusler alloys, and thus will facilitate the development of promising magnetic refrigerants for near room temperature magnetic refrigeration applications.

ACKNOWLEDGMENTS

This research was supported by the Research Opportunity Award from Research Corporation (RA0357), and by the Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy (Contract No. DE-FG02-06ER46291). The authors are thankful to James Mabon and Timothy Spila for conducting the EDX measurements carried out at the Center for Microanalysis of Materials, University

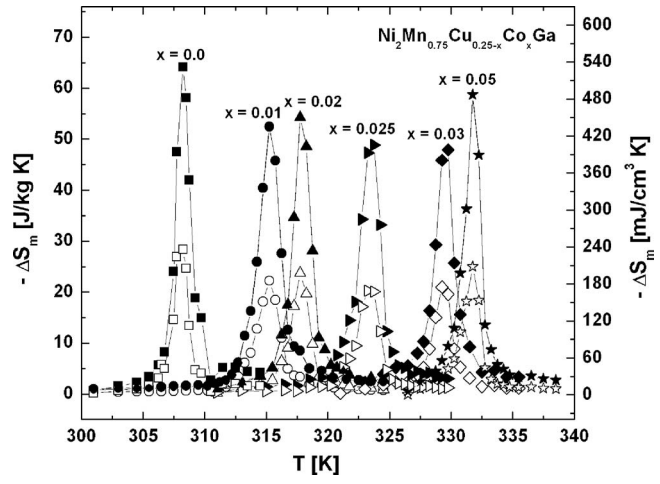

FIG. 5. Magnetic entropy changes (ΔS_m) as a function of temperature of $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$ for a field change (ΔH) of 5 T (closed symbols) and 2 T (open symbols).

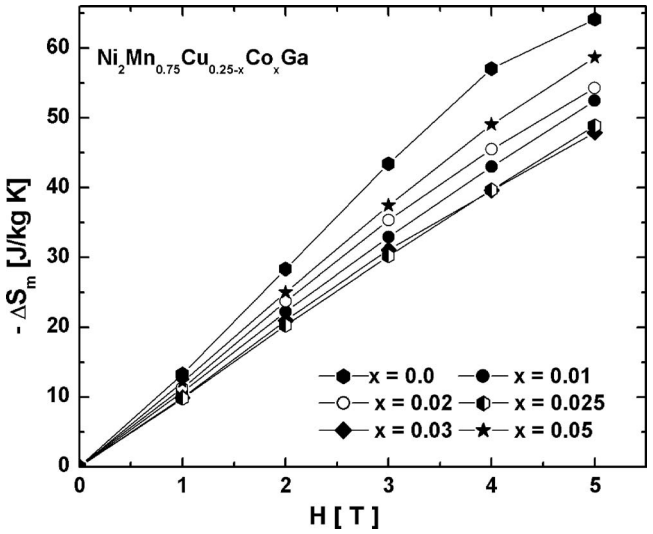

FIG. 6. Magnetic entropy changes (ΔS_m) as a function of field change (ΔH) of $Ni_2Mn_{0.75}Cu_{.25-x}Co_xGa$.

of Illinois, which is partially supported by the U.S. Department of Energy under Grant No. DEFG02-91-ER45439.

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