

## Magnetocaloric properties of $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$

Shane Stadler,<sup>a)</sup> Mahmud Khan, Joseph Mitchell, and Naushad Ali  
 Department of Physics, Southern Illinois University, Neckers 483A, Carbondale, Illinois 62901

Angelo M. Gomes  
 Instituto de Física, Universidade Federal do Rio de Janeiro, C. P. 68528, Rio de Janeiro 21941-972, Brazil

Igor Dubenko, Armando Y. Takeuchi, and Alberto P. Guimarães  
 Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Rio de Janeiro 22290-180, Brazil

(Received 12 January 2006; accepted 29 March 2006; published online 11 May 2006)

We present the magnetocaloric properties of the substituted Heusler alloy  $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$ , which shows a maximum magnetic entropy change of  $\Delta S_M \approx -64 \text{ J/Kg K} = -532 \text{ mJ/cm}^3 \text{ K}$  at 308 K for a magnetic field change  $\Delta H = 5 \text{ T}$ . The dependence of  $\Delta S_M$  on  $\Delta H$  is approximately linear and does not reach saturation at 5 T. It is demonstrated that the temperature at which  $\Delta S_M$  occurs can be tuned through subtle variations in composition. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2202751]

Interest in magnetocaloric cooling technology has grown recently due to significant advances in the design of magnetic cooling devices,<sup>1</sup> and in the development of working materials that exhibit large magnetocaloric effects (MCEs) near room temperature.<sup>2-4</sup> These recent developments may lead to profound global consequences due to, among many other things, the significantly enhanced efficiency that solid state cooling systems have over the currently employed compressed gas systems.<sup>5</sup>

The MCE occurs as the result of the alignment of magnetic moments with an external applied magnetic field. This alignment reduces the magnetic randomness or the magnetic component of the total entropy. The reduction of magnetic entropy must be compensated by an increase in other components of the total entropy and, in the case of magnetocaloric materials, is channeled into electronic entropy and lattice entropy, or *heat*. A full discussion of the thermodynamics of the MCE is presented in the work by Pecharsky *et al.*<sup>6</sup> The magnetocaloric effect occurs in all magnetic materials; the most appreciable effect occurs at temperatures near magnetic transitions, and depends strongly on the type of transition (being strongest for first-order transitions).<sup>6,7</sup> Some of the recently reported systems that exhibit a large MCE near room temperature include  $\text{Gd}_5(\text{SiGe})_4$ ,<sup>2,8</sup>  $\text{La}(\text{FeSi})$ ,<sup>9</sup>  $\text{MnFeP}_{1-x}\text{As}_x$ ,<sup>4</sup> and  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ .<sup>10-16</sup> The phase transitions responsible for the large MCE in these systems are generally magnetocrystalline, i.e., a magnetic and a structural phase change occurs at the same temperature. Stoichiometric  $\text{Ni}_2\text{MnGa}$  is a full Heusler alloy that undergoes two separate transitions: (i) A magnetic (order-disorder) transition at  $T_C \approx 376 \text{ K}$ , and (ii) a structural (martensitic) transition at  $T_M \approx 220 \text{ K}$ . At  $T_C > T > T_M$ ,  $\text{Ni}_2\text{MnGa}$  is ferromagnetic and has a cubic (austenic)  $L2_1$  crystal structure. Upon cooling through  $T_M$ , the system undergoes a structural phase transition to a complex tetragonal (martensitic) structure that is also ferromagnetic. By altering the stoichiometry of the alloy such that it becomes Ni rich, i.e.,  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ,  $T_M$  and  $T_C$  can be tuned such that each structural phase can be either paramagnetic or ferromagnetic at room temperature, depending on the transi-

tion temperatures.<sup>16-18</sup> The largest changes in magnetic entropy ( $\Delta S_M$ ) have been observed in  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  where the second order magnetic and first-order structural transitions are tuned to coincide in temperature. The most recent demonstrations of this are in single crystalline  $\text{Ni}_{55}\text{Mn}_{20}\text{Ga}_{25}$  ( $\Delta S_M = -86 \text{ J/kg K}$ ).<sup>16</sup>

We have found that, rather than varying the stoichiometry of the  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  system, the magnetic ( $T_C$ ) and martensitic ( $T_M$ ) transitions can be tuned through atomic substitution in either the manganese or gallium (or both) sites. In the case of the substitution of gallium with indium, i.e.,  $\text{Ni}_2\text{MnGa}_{1-x}\text{In}_x$ , both  $T_M$  and  $T_C$  were found to decrease in temperature with increasing indium concentration.<sup>19</sup> In another study, Mn was partially substituted with Fe ( $\text{Ni}_{50.5}\text{Mn}_{25-x}\text{Fe}_x\text{Ga}_{24.5}$ ) which resulted in a reduction in  $T_M$  and an increase in  $T_C$ .<sup>20</sup> Replacing Mn with Co or Cu in  $\text{Ni}_2\text{Mn}_{1-x}\text{M}_x\text{Ga}$  ( $M = \text{Co}, \text{Cu}$ ), resulted in a decrease in  $T_C$  and an increase in  $T_M$  and, for  $x \approx 0.25$ , the two transition temperatures were found to coincide ( $T_M = T_C = T_{MC}$ ).<sup>21</sup> Fortunately, the resulting magnetostructural transition occurs at  $T_{MC} = 308 \text{ K}$ , for  $x \approx 0.25$ , i.e., near room temperature, and we have found that this transition temperature can be tuned through subtle variations of Cu concentration. In this letter we report our results on the magnetocaloric effects in  $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$ .

The magnetic entropy change,  $\Delta S_M$ , is one measured parameter that can be used to quantify the MCE of a material. However,  $\Delta S_M$  alone does not fully characterize or verify the effectiveness of a material for refrigeration applications. For instance, the adiabatic temperature change  $\Delta T_A$  is an important extrinsic property that can be measured through direct means or from indirect ones, such as from heat capacity measurements as a function of temperature and field.<sup>22</sup> Another helpful parameter is the refrigeration capacity (RC), which is proportional to the area under the  $\Delta S_M(T)$  curve and is calculated using at least two different conventions.<sup>3,23</sup> In the present study, we have calculated the magnetic entropy  $\Delta S_M$  from magnetic isotherms and the RC by integrating  $\Delta S_M(T)$ . The magnetic entropy change has been calculated from the magnetization isotherms using the integrated Maxwell relation,

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: sstadler@physics.siu.edu

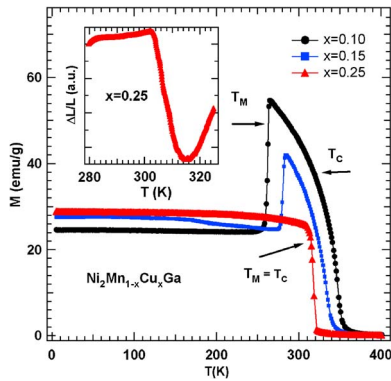


FIG. 1. (Color online) Magnetization ( $M$ ) vs temperature ( $T$ ) at an applied field of 1 kOe as a function of Cu concentration. The transition temperatures,  $T_M$  and  $T_C$ , coincide for  $x=0.25$ . (Inset) Thermal expansion ( $\Delta L/L$ ) vs temperature ( $T$ ) near the phase transition.

$$\Delta S_M(T, \Delta S) = \int_0^{H'} \left( \frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

which, for magnetization measurements made at constant temperature and at discrete  $H$  intervals, can be approximated by<sup>22</sup>

$$\Delta S_M \approx \frac{1}{\Delta T} \left[ \int_0^{H'} M(T + \Delta T, H) dH - \int_0^{H'} M(T, H) dH \right]. \quad (2)$$

Technically, this expression for the magnetic entropy change may not be appropriate for perfect first-order transitions due to discontinuities. Gschneidner *et al.*,<sup>22</sup> in reference to using this method to calculate the magnetic entropy change, state that “In reality, these changes occur over a few Kelvin wide temperature range, and both functions [specifically the integrand in Eq. (1)] can be measured experimentally.” The use of this expression to calculate  $\Delta S_M$  at nonideal first-order transitions is also justified by Tishin and Spichkin.<sup>24</sup>

Polycrystalline  $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$  alloy ingots (approximately 5 g) with nominal concentrations in the range of  $0.245 \leq x \leq 0.260$  were fabricated from high purity (4N) Ni, Mn, Cu, and Ga components using conventional arc melting in an argon atmosphere. The weight loss after melting was found to be less than 0.3%. For homogenization, the samples were wrapped in tantalum foil and annealed at 800 °C for six days in a vacuum furnace, and slowly cooled to room temperature. In order to determine the crystalline structure and phase purity, x-ray diffraction (XRD) measurements were done on a GBC DiffTech mini-materials analyzer (MMA) x-ray diffractometer using  $\text{Cu } K\alpha$  radiation and Bragg-Brentano geometry. Magnetization data were acquired in the temperature range of 5–400 K in fields from 0 to 5 T with a superconducting quantum interference device (SQUID) magnetometer by Quantum Design, Inc. Thermal expansion measurements were made using a high-resolution capacitance dilatometry method in the temperature range of 300–355 K.<sup>25</sup>

XRD patterns for all of the samples  $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$  with nominal concentrations,  $x=0.245, 0.250, 0.255,$  and  $0.260$ , were measured at room temperature. The data showed that the samples were of mixed austenetic and martensitic phases, which is a consequence of  $T_M$  being very close to room temperature. This is consistent with previously reported results, where the XRD patterns clearly evolve from the austenetic to martensitic structure with increasing Cu

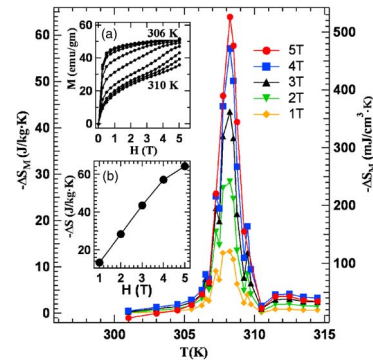


FIG. 2. (Color online)  $\Delta S_M$  as a function of temperature ( $T$ ) for  $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$  for various changes in applied magnetic field  $\Delta H$ . (a) Some representative magnetization isotherms. (b)  $\Delta S_M^{\text{max}}$  as a function of applied field.

concentration at room temperature.<sup>21</sup> The density was calculated from measured lattice parameters and had a value of about  $8.2 \text{ g/cm}^3$ .

Magnetization as a function of temperature ( $M$  vs  $T$ ) curves for various concentrations is shown in Fig. 1. All magnetization curves were measured in an applied field of 1 kOe. The transition temperatures,  $T_M$  and  $T_C$ , gradually merge as the Cu concentration increases from zero to about  $x=0.25$ . A series of samples was fabricated in the nominal concentration range of  $0.245 < x < 0.260$ , and each one exhibited a single transition as that shown for  $x=0.25$ , albeit at slightly different temperatures. Thermal expansion measurements [Fig. 1 (inset)] show a steplike jump at the transition temperature which alone clearly indicates that the transition is first order. Although not shown, a similar jump was observed in the resistivity near the same temperatures.

The magnetic entropy change  $\Delta S_M$  has been calculated as a function of change in applied field  $\Delta H$  (Fig. 2) for  $x=0.250$  from magnetization isotherms [Fig. 2(a)].  $\Delta S_M$  has been plotted in both mass ( $\text{J/kg K}$ ) and volume ( $\text{mJ/cm}^3 \text{ K}$ ) units in order to more easily compare materials. The  $\Delta S_M^{\text{max}}$  increases almost linearly with  $\Delta H$ , and does not saturate for  $\Delta H=5 \text{ T}$  [Fig. 2(b)], as is the case for many other materials.  $\Delta S_M^{\text{max}}$  ( $\Delta H=5 \text{ T}$ ) is about  $-65 \text{ J/kg K}$ , or about  $-533 \text{ mJ/cm}^3 \text{ K}$  for a mass density of about  $8.2 \text{ g/cm}^3$ . This value can be put into perspective by comparing it with values reported for other polycrystalline Heusler alloy systems using the same procedure as applied in this letter [e.g., using Eqs. (1) and (2)]. Hu *et al.*<sup>26</sup> measured the MCE of the off-stoichiometric alloy,  $\text{Ni}_{51.5}\text{Mn}_{22.7}\text{Ga}_{25.8}$ , and observed a  $\Delta S_M$  of approximately  $-4 \text{ J/kg K}$  near the martensitic transition  $T_M \sim 197 \text{ K}$  ( $T_C=351 \text{ K}$ ) for a field change of 0.9 T. An improvement of the MCE in Ni–Mn–Ga was observed in the off-stoichiometric alloy  $\text{Ni}_{55.2}\text{Mn}_{18.6}\text{Ga}_{26.2}$ , where the transition temperatures  $T_M$  and  $T_C$  merged into a single magnetostructural transition at  $T_M=T_C=T_{MC}$ , resulting in a  $\Delta S_M$  of  $-20.4 \text{ J/kg K}$  at 317 K in a magnetic field change of 5 T.<sup>10</sup> As stated above, a large entropy change of  $\Delta S_M=-86 \text{ J/kg K}$  was reported for a  $\text{Ni}_{55}\text{Mn}_{20}\text{Ga}_{25}$  single crystal.<sup>16</sup> Working materials in magnetic refrigeration systems will likely be chosen for, among many other things, ease of fabrication, and will therefore unlikely utilize single crystal materials. We have also found that the size of the magnetic entropy change, and the magnetic properties in general, observed in these systems depends significantly on the fabrication and annealing conditions. We have reported

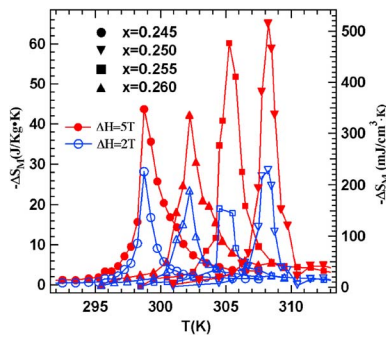


FIG. 3. (Color online)  $\Delta S_M$  as a function of temperature for various nominal Cu concentrations and magnetic field changes of 5 and 2 T.

here the largest values that we have observed, and which correspond to fabrication procedure as described.

By varying the nominal Cu concentration, the peak magnetic entropy change can be tuned in temperature without a severe reduction in the magnitude of the maximum  $\Delta S_M$  value (Fig. 3). This property is important when considering devices that are designed to operate over some extended temperature range. The width of the  $\Delta S_M(T)$  curve is quite narrow in these systems; one proposed method to extend the temperature range is to fabricate composites of these alloys with different Cu concentrations.

Another important aspect of evaluating the magnetocaloric properties of a given material is the hysteretic loss at the phase transition. The hysteretic loss directly opposes the RC, and is therefore an unwanted characteristic in any magnetocaloric system that is to be used in real devices. The RC can be calculated by integrating the  $\Delta S_M(T)$  curve over the full width at half maximum, which yields a value of about 84 J/kg for  $x=0.250$ . The loss was calculated by calculating the area between the increasing and decreasing temperature segments of the magnetization curves (Fig. 4). The hysteretic loss has a maximum at the same temperature as the maximum of the  $\Delta S_M(T)$  curve [Fig. 4 (Inset)]. The average loss ( $\sim 12$  J/kg) was calculated over the same temperature range as that of RC [full width at half maximum (FWHM)], and then subtracted from RC to obtain the net refrigeration constant,  $RC^* = 72$  J/kg. This value is significantly lower than that reported for  $Gd_5(SiGe)_4$ ,<sup>2,9</sup> however, it is evaluated over a much narrower temperature range.

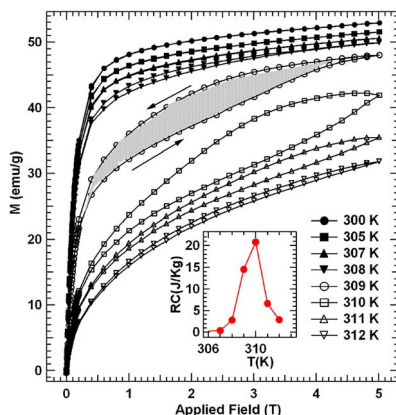


FIG. 4. (Color online) Hysteresis curves for the  $Ni_2Mn_{0.75}Cu_{0.25}Ga$  magnetization isotherms. The arrows indicate the direction of change of the applied field, and the shaded area represents the hysteresis loss for that particular isotherm. (Inset) The hysteresis loss as a function of temperature for the displayed magnetization isotherms.

A strong interest in  $Ni_2Mn_{1-x}Cu_xGa$  and related alloys is justified since many of these systems have intriguing characteristics that are relevant for potential applications in magnetocaloric devices. The alloys are easily fabricated, and the constituent materials are more affordable than many of the rare-earth based systems, and are generally nontoxic and environmentally friendly. The demonstrated control of the phase transitions through atomic substitution and the relatively large and tunable magnetic entropy change will hopefully attract attention to these systems and open new vistas for research in the field.

This research was supported by the Petroleum Research Fund (Grant No. 42068-GB5), the Research Corporation (Grant No. CC5967), the Southern Illinois University Materials Technology Center (MTC), and CNPq/CT-Petro, Faperj (Brazil).

- <sup>1</sup>C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner, Jr., M. Osborne, and I. Anderson, *Adv. Cryog. Eng.* **43**, 1759 (1998).
- <sup>2</sup>V. K. Pecharski and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- <sup>3</sup>V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature (London)* **429**, 853 (2004).
- <sup>4</sup>O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, *Nature (London)* **415**, 150 (2002).
- <sup>5</sup>J. Glanz, *Science* **279**, 2045 (1998).
- <sup>6</sup>V. K. Pecharsky, K. A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, *Phys. Rev. B* **64**, 144406 (2001).
- <sup>7</sup>O. Tegus, E. Brück, L. Zhang, O. Dagula, K. H. J. Buschow, and F. R. de Boer, *Physica B* **319**, 174 (2002).
- <sup>8</sup>F. Casanova, X. Batlle, A. Labarta, J. Marcos, L. Manosa, and A. Planes, *Phys. Rev. B* **66**, 100401(R) (2002).
- <sup>9</sup>S. Fujieda, A. Fujita, and K. Fukamichi, *Appl. Phys. Lett.* **81**, 1276 (2002).
- <sup>10</sup>X. Zhou, W. Li, H. P. Kunkel, and G. Williams, *J. Phys.: Condens. Matter* **16**, L39 (2004).
- <sup>11</sup>A. N. Vasil'ev, A. D. Bozhko, V. V. Khovailo, I. E. Dikshstein, V. G. Shavrov, V. D. Buchelnikov, M. Matsumoto, S. Suzuki, T. Takagi, and J. Tani, *Phys. Rev. B* **59**, 1113 (1999).
- <sup>12</sup>Chengbao Jiang, Gen Feng, and Huibin Xu, *Appl. Phys. Lett.* **80**, 1619 (2002).
- <sup>13</sup>F. Albertini, F. Canepa, S. Cirafici, E. A. Franceschi, M. Napolitano, A. Paoluzi, L. Pareti, and M. Solzi, *J. Magn. Magn. Mater.* **272–276**, 2111 (2004).
- <sup>14</sup>L. Pareti, M. Solzi, F. Albertini, and A. Paoluzi, *Eur. Phys. J. B* **32**, 303 (2003).
- <sup>15</sup>V. V. Khovailo, T. Takagi, J. Tani, R. Z. Levitin, A. A. Cherechukin, M. Matsumoto, and R. Note, *Phys. Rev. B* **65**, 092410 (2002).
- <sup>16</sup>M. Pasquale, C. P. Sasso, L. H. Lewis, L. Giudici, T. Lograsso, and D. Schlager, *Phys. Rev. B* **72**, 094435 (2005).
- <sup>17</sup>V. V. Khovailo, T. Takagi, J. Tani, R. Z. Levitin, A. A. Cherechukin, M. Matsumoto, and R. Note, *Phys. Rev. B* **65**, 092410 (2002).
- <sup>18</sup>V. A. Chernenko, E. Cesari, V. V. Kokorin, and I. N. Vitenko, *Scr. Metall. Mater.* **33**, 1239 (1995).
- <sup>19</sup>M. Khan, I. Dubenko, S. Stadler, and N. Ali, *J. Phys.: Condens. Matter* **16**, 5259 (2004).
- <sup>20</sup>Z. H. Liu, M. Zhang, W. Q. Wang, W. H. Wang, J. L. Chen, G. H. Wu, F. B. Meng, H. Y. Liu, B. D. Liu, J. P. Qu, and Y. X. Li, *J. Appl. Phys.* **92**, 5006 (2002).
- <sup>21</sup>Mahmud Khan, Igor Dubenki, Shane Stadler, and Naushad Ali, *J. Appl. Phys.* **97**, 10M304 (2005).
- <sup>22</sup>K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- <sup>23</sup>M. E. Wood and W. H. Potter, *Cryogenics* **25**, 667 (1985).
- <sup>24</sup>A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (IOP, Bristol, 2003), p. 82.
- <sup>25</sup>M. O. Steinitz, J. Genossar, W. Schnepfand, and D. A. Tindall, *Rev. Sci. Instrum.* **57**, 297 (1986).
- <sup>26</sup>Feng-Xia Hu, Bao-Gen Shen, and Ji-Rong Sun, *Appl. Phys. Lett.* **76**, 3460 (2000).
- <sup>27</sup>T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, *Nat. Mater.* **4**, 450 (2005).