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Magnetocaloric properties of Fe and Ge doped $Ni_2Mn_{1-x}Cu_xGa$

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The magnetocaloric properties of Fe and Ge doped $Ni_2Mn_{0.75}Cu_{0.25}Ga$ Heusler alloys have been investigated. Using $Ni_2Mn_{0.75}Cu_{0.25}Ga$ as the parent material, the Fe doped system $(Ni_2Mn_{1-x}(Cu-Fe)_xGa)$ and a Ge doped system $(Ni_2Mn_{1-x}Cu_xGa_{1-x}Ge_x)$ were studied. The manipulation of the Mn–Cu subsystem with Fe doping results in a decrease of the first order magnetostructural transition temperature, whereas the substitution of Ge for the Mn–Cu–Ga subsystems results in an increase of the magnetostructural transition temperature. In both cases the giant magnetocaloric effect is successfully preserved. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2712304]

Recently many ferromagnetic materials have been discovered that undergo first order magnetic transitions and exhibit large magnetocaloric effects (MCE).[1–3] Due to these recent discoveries, interest in the magnetocaloric cooling technology has grown significantly. When compared to the currently employed gas cooling technology, the magnetocaloric cooling technology has considerably enhanced efficiency, and therefore the recent discoveries and continuing research on magnetocaloric materials may lead to intense universal consequences.[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 or 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 is a well known shape memory alloy that has potential application as a magnetic actuator material. Lately it has gained additional interest due to its possible candidacy 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 $T_M=202$ K) from the parent cubic (austenitic) phase to a low temperature (LT) complex tetragonal structure. The Curie temperature for 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 decrease of T_C and, for $0.17 \leqslant x \leqslant 0.20$, the coincidence of T_M and T_C results in a first order magnetostructural phase transition.[15] As a result of this first order transition, a giant MCE of $|\Delta S_m|=15$ J kg^{-1} K^{-1} at 1.8 T field was observed in $Ni_{2.19}Mn_{0.81}Ga$.[10] In stoichiometric $Ni_{55.2}Mn_{18.6}Ga_{18.6}$ a magnetic entropy change of $\Delta S_m=-20.4$ J kg^{-1} K^{-1} at 317 K in a field change 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 giant MCE of $\Delta S_m \approx -64$ J kg^{-1} K^{-1} at 308 K was observed in $Ni_2Mn_{0.75}Cu_{0.25}Ga$.[17] Since the giant MCE occurs very close to room temperature, further research on and development of this alloy might result in the outcome of a potential magnetic refrigerant material that would be affordable and efficient. The ability to tune the magnetostructural transition temperature while preserving the high MCE value would be an interesting and significant outcome of further research. This is because the tunability of the high MCE value over a wide temperature range will open possibilities of developing magnetic refrigerant composites for near room temperature magnetic cooling applications.

In this work we report our experimental results of MCE studies on the Fe doped system $(Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga)$ and on a Ge doped system $(Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05})$. The objective was to be able to tune the first order magnetostructural transition temperature through various substitutions while preserving the high ΔS_M peak value.

Polycrystalline buttons of approximately 5 g of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ were fabricated by conventional arc melting in an argon atmosphere using Ni, Mn, Cu, Fe, Ga, and Ge 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 and annealed in vacuum for 72 h at 800 °C, and subsequently slowly cooled down to room temperature.

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

The magnetization measurements were performed using a superconducting quantum interference device (SQUID) made by Quantum Design, Inc. The measurements were performed in a temperature range of 5–400 K and magnetic

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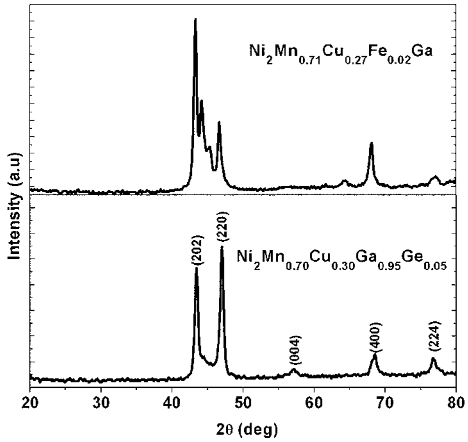

FIG. 1. Room temperature powder XRD patterns of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$.

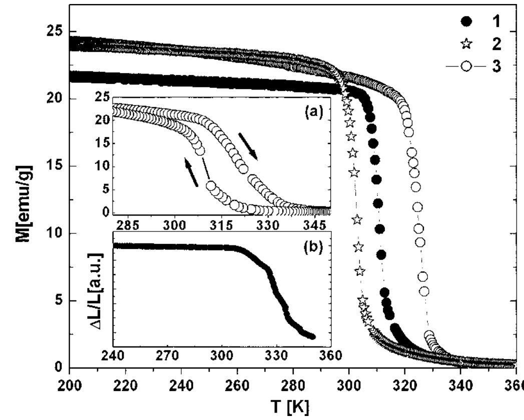

FIG. 2. Magnetization as a function of temperature of (1) $Ni_2Mn_{0.75}Cu_{0.25}Ga$, (2) $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$, and (3) $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ obtained at a field of 1 kOe. The inset (a) and (b) represents the temperature hysteresis and thermal expansion curves, respectively, of $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$.

field of up to 5 T. The magnetic entropy change ΔS_m was calculated from the isothermal magnetization data using the relation,

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

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

Figure 1 represents the room temperature x-ray diffraction (XRD) patterns of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$. The XRD patterns indicate that $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ possess a typical tetragonal structure at room temperature with $a=b=5.46$ Å and $c=6.41$ Å. In the $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ sample, both martenstic and austenitic phases seem to coexist. This coexistence of both phases is due to the martensitic transition taking place at $T_M=302$ K, which is very close to room temperature. A similar XRD pattern was observed for $Ni_2Mn_{0.75}Cu_{0.25}Ga$.[16]

The magnetization curves as a function of temperature $M(T)$ of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$, $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ at a field of 1 kOe are presented in Fig. 2. As shown in this figure, the only transition observed in each alloy is a sharp jump of magnetization at T_C. The temperature hysteresis observed in the $M(T)$ curves at 1 kOe, obtained for increasing and decreasing temperature, of $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ [see inset (a) of Fig. 2] suggests that the transition at T_C is a first order phase transition. The sharp steplike change in the thermal expansion curve (typical for a first order phase transition) of $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ shown in inset (b) of Fig. 2 further verifies that the transition is a first order phase transition. It is clear from the figure that the magnetostructural transition temperature, represented by T_C, increases in the Ge doped sample and decreases in the Fe doped sample. It has been reported previously that Fe substitution on the Mn sites of Ni_2MnGa results in decrease of T_M and increase of T_C.[18] In $Ni_2Mn_{0.75}Cu_{0.25}Ga$, $T_M=T_C$, and therefore as suggested in Ref. 16, the further partial substitution of Cu on the Mn sites results in the increase of T_M and decreases of T_C. Additional substitution of Fe on the Mn site increases the T_C and decreases of T_M, bringing back the two transitions at the same temperature. Ge substitution on the Ga site in Ni_2MnGa results in a decrease of T_M,[19] and so when Ga is replaced by partial Ge in $Ni_2Mn_{0.70}Cu_{0.30}Ga$, T_M decreases resulting in the overlap of T_M and T_C. The saturation moments of the samples at 5 K are 3.32, 3.27, and 3.16μ_B/f.u. for $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$, $Ni_2Mn_{0.75}Cu_{0.25}Ga$, and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$, respectively. It is apparent that the sample with Fe possesses a higher saturation moment than the other two samples, suggesting that the moment of the $Ni_2Mn_{0.75}Cu_{0.25}Ga$ system can be increased by Fe doping.

The ΔS_m values were evaluated from isothermal magnetization curves using Eq. (1). This equation is more appropriate to calculate MCE in the vicinity of a second order phase transition. However, its employment in calculating ΔS_m in the vicinity of first order phase transitions is very common 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). Figures 3(a) and 3(b) show the isothermal magnetization curves as a function of fields of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$, respectively. The changes of magnetic entropies of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$, $Ni_2Mn_{0.75}Cu_{0.25}Ga$, and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$, as a function of temperature, are shown in Fig. 4. As shown in this figure, all of the samples possess comparable peak values of ΔS_m. Peak values of 32 and 58 J/kg K for $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and 23 and 57 J/kg K for $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ are obtained at 2 and 5 T fields, respectively. The values compare well to those of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ (28 and 64 J/kg K at 2 and 5 T fields, respectively). As shown in Fig. 5, the ΔS_m peak values of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ are found to be linearly dependent on the applied fields, whereas the ΔS_m peak values of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ are not linear with field. Due to this, at 2 T field the ΔS_m peak value of

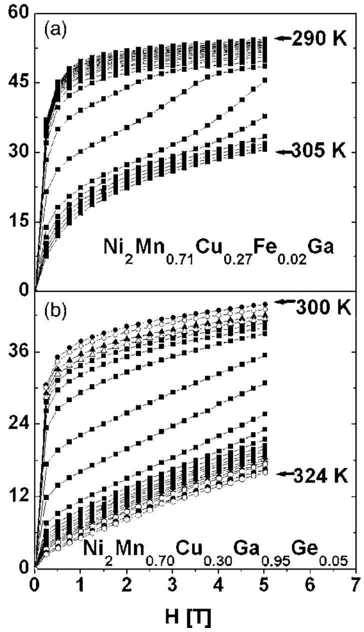

FIG. 3. Isothermal magnetization curves of (a) $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and (b) $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ at temperature increments of 1 and 0.5 K.

$Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ is observed to be larger than those of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$. This could be attributed to the nonlinear isothermal magnetization curves near the magnetostructural transition temperature of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$. The isothermal magnetization curves near magnetostructural transition temperature of $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ are found to be very linear.

We have studied magnetocaloric effects in $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$. The manipulation of the Mn–Cu subsystem of $Ni_2Mn_{0.75}Cu_{0.25}Ga$ with Fe doping results in a decrease of the first order magnetostructural transition temperature, whereas the substitution of Ge in the Mn–Cu–Ga subsystems results in an increase of the magnetostructural transition temperature. In both cases the giant magnetocaloric effect is successfully preserved. These experimental results suggest the possibility of tuning the first order magnetostructural transition temperatures while preserving the high MCE values in Ni_2MnGa 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.

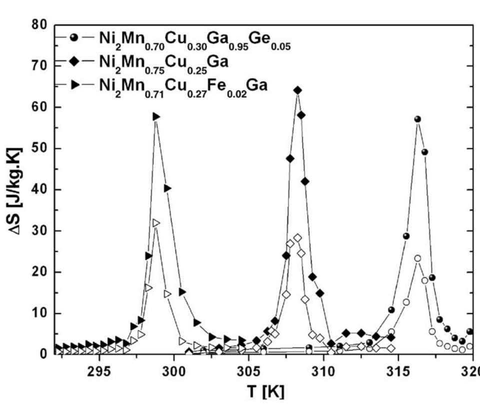

FIG. 4. Magnetic entropy changes (ΔS_M) as a function of temperatures of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$ for a field changes (ΔH) of 5 T (closed symbols) and 2 T (open symbols).

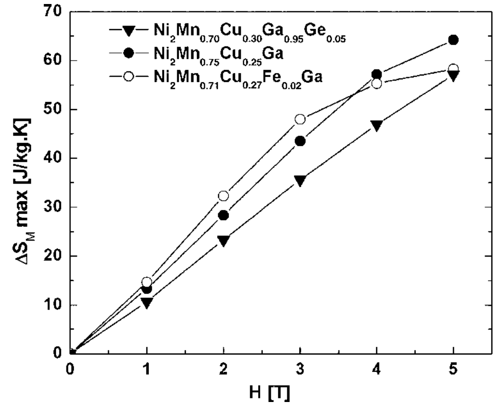

FIG. 5. Maximum magnetic entropy changes (ΔS_M max) as a function of fields of $Ni_2Mn_{0.71}Cu_{0.27}Fe_{0.02}Ga$ and $Ni_2Mn_{0.70}Cu_{0.30}Ga_{0.95}Ge_{0.05}$.

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