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Magnetocaloric properties of Fe and Ge doped Ni$_2$Mn$_{1-x}$Cu$_x$Ga

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The magnetocaloric properties of Fe and Ge doped Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga Heusler alloys have been investigated. Using Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga as the parent material, the Fe doped system (Ni$_2$Mn$_{1-x}$(Cu$_x$−Fe)$_x$Ga) and a Ge doped system (Ni$_2$Mn$_{1-x}$Cu$_x$Ge$_{1-x}$Ga) 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 magnetostuctural transition temperature. In both cases the giant magnetocaloric effect is successfully preserved. © 2007 American Institute of Physics.

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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 recent discoveries, interest in the magnetocaloric cooling 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$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga) and on a Ge doped system (Ni$_2$Mn$_{0.70}$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 $\Delta S_m$ peak value.

Polycrystalline buttons of approximately 5 g of Ni$_2$Mn$_{0.77}$Cu$_{0.23}$Fe$_{0.02}$Ga and Ni$_2$Mn$_{0.70}$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 minimaaterials 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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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$_2$MnGa results in a decrease of $T_M$\textsuperscript{19} and so when Ga is replaced by partial Ge in Ni$_2$Mn$_{0.70}$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 3.16$\mu_B$/f.u. for Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga, Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga, and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.05}$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$_2$Mn$_{0.75}$Cu$_{0.25}$Ga system can be increased by Fe doping.

The $\Delta S_m$ 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 $\Delta S_m$ 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.\textsuperscript{3} The majority of the reported $\Delta S_m$ values of Ni–Mn–Ga, and other ferromagnetic systems 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$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.05}$Ge$_{0.05}$, respectively. The changes of magnetic entropies of Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga, Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga, and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.05}$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 $\Delta S_m$. Peak values of 32 and 58 J/kg K for Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and 23 and 57 J/kg K for Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.05}$Ge$_{0.05}$ are obtained at 2 and 5 T fields, respectively. The values compare well to those of Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga (28 and 64 J/kg K at 2 and 5 T fields, respectively). As shown in Fig. 5, the $\Delta S_m$ peak values of Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.05}$Ge$_{0.05}$ are found to be linearly dependent on the applied fields, whereas the $\Delta S_m$ peak values of Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga are not linear with field. Due to this, at 2 T field the $\Delta S_m$ peak value of...
Ni$_2$Mn$_{0.7}$Cu$_{0.27}$Fe$_{0.02}$Ga is observed to be larger than those of Ni$_2$Mn$_{0.75}$Cu$_{0.25}$Ga and Ni$_2$Mn$_{0.70}$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$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga. The isothermal magnetization curves near magnetostructural transition temperature of Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.95}$Ge$_{0.05}$ are found to be very linear.

We have studied magnetocaloric effects in Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.95}$Ge$_{0.05}$. The manipulation of the Mn–Cu subsystem of Ni$_2$Mn$_{0.71}$Cu$_{0.27}$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$_2$MnGa Heusler 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.

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![Graph](image1)

**FIG. 3.** Isothermal magnetization curves of (a) Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and (b) Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.95}$Ge$_{0.05}$ at temperature increments of 1 and 0.5 K.

![Graph](image2)

**FIG. 4.** Magnetic entropy changes ($\Delta S_m$) as a function of temperatures of Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.95}$Ge$_{0.05}$ for a field changes ($\Delta H$) of 5 T (closed symbols) and 2 T (open symbols).

![Graph](image3)

**FIG. 5.** Maximum magnetic entropy changes ($\Delta S_m$ max) as a function of fields of Ni$_2$Mn$_{0.71}$Cu$_{0.27}$Fe$_{0.02}$Ga and Ni$_2$Mn$_{0.70}$Cu$_{0.30}$Ga$_{0.95}$Ge$_{0.05}$.