Experimental and theoretical investigations of the magnetocaloric effect of Ni$_{2.15}$Mn$_{0.85-x}$Cu$_x$Ga ($x=0.05,0.07$) alloys

J. F. Duan,$^1$ Y. Long,$^{1,4}$ B. Bao,$^1$ H. Zhang,$^1$ R. C. Ye,$^1$ Y. Q. Chang,$^1$ F. R. Wan,$^1$ and G. H. Wu$^2$

$^1$School of Materials Science and Engineering, University of Science and Technology of Beijing 100083, People’s Republic of China
$^2$Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People’s Republic of China

(Received 16 May 2007; accepted 24 January 2008; published online 21 March 2008)

Magnetocaloric effects of Ni$_{2.15}$Mn$_{0.85-x}$Cu$_x$Ga ($x=0.05,0.07$) alloys were investigated with both experimental and theoretical approaches. The experiments show that these alloys have large entropy changes and refrigeration capacities with the field change of 2 T. Further theoretical analysis indicates that both magnetic entropy changes and lattice entropy changes have the same sign during heating, while the main entropy change arises from the magnetic entropy change. © 2008 American Institute of Physics. [DOI: 10.1063/1.2899041]

I. INTRODUCTION

In recent years, there has been an increasing awareness toward incorporating an alternate technology for refrigeration that would replace the conventional gas compression/expansion technique. In this respect, the promising candidates are the magnetic materials that exhibit an inherent magnetocaloric effect (MCE). Fundamentally, MCE is a process in which an isothermal variation in the magnetic entropy change takes place with an adiabatic temperature change of the system on the application of magnetic field. Some recently reported systems with a distinct MCE at room temperature include Gd–Si–Ge,$^{1,2}$ Mn–Fe–P–As,$^{3,4}$ Mn–As–Sb,$^{5,6}$ La–Fe–Si,$^{7,8}$ and Ni–Mn–Ga (Refs. 9 and 10) alloys. The MCE here is mainly due to magnetostructural transitions. Among these alloys, the Ni–Mn–Ga alloy offers a number of advantages in being biocompatible, relatively easy to synthesize and fabricate in specific shapes, and especially because its transition temperature is around room temperature. Thus, it is an important candidate for commercial applications at room temperature.

Stoichiometric Ni$_2$MnGa undergoes two separate transitions: one is a magnetic transition at $T_C=376$ K, the other is a structural transition at $T_M=220$ K. By appropriate tuning of the composition, a Ni–Mn–Ga alloy will simultaneously undergo the structural and magnetic transitions and show a distinct magnetic entropy change $\Delta S_M$.\(^{9,10}\)

In addition to the compositional change of Ni$_{2+x}$Mn$_{1-x}$Ga, both the magnetic and martensitic transitions can be tuned through atomic substitution with either or both of Mn or Ga. Stadler et al. found that replacing Mn with Co or Cu in Ni$_2$Mn$_{1-x}$M$_x$Ga ($M=Co$, Cu) resulted in a decrease in $T_C$ and an increase in $T_M$. For a specific composition, these two values coincide and the alloy will exhibit a distinct $S_M$.\(^{11,12}\)

When Ni–Mn–Ga alloy undergoes the first-order magnetostuctural transition, a structural transition takes place in the vicinity of the magnetic transition. This implies possible changes in lattice and electron entropies accompanying the phase transition. It is very important to distinguish the magnetic, lattice, and electron contributions.

For the Gd$_5$Si$_4$Ge$_x$ alloy, the total entropy change should be the sum of $\Delta S_M$ and the difference of the entropies in the two crystallographic modifications joined by the first-order transition.\(^{13}\) For the LaFeSi alloy, the magnetic entropy change dominates but the lattice entropy change is not negligible and cancels out most of the magnetic change.\(^{14}\) There has been a few investigation of this aspect of Ni–Mn–Ga alloy, and here, the contribution of both the magnetic entropy change and lattice entropy change to the total entropy change in Ni$_{2.15}$Mn$_{0.85-x}$Cu$_x$Ga alloy was investigated.

The magnetic entropy change $\Delta S_M$ and the adiabatic temperature change $\Delta T_{ad}$ are two important measured parameters that can be used to quantify the MCE of a material. Pecharsky and Gschneidner have pointed out that the combined heat capacity at constant field and $\Delta S_M(T)\Delta T_{ad}$ from the magnetization data can be used to accurately calculate $\Delta T_{ad}(T)\Delta S_M$.\(^{15}\) So, in this work, we studied the $\Delta S_M$ with experimental and theoretical approaches.

II. EXPERIMENTS

Polycrystalline alloys with a nominal composition of Ni$_{2.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{2.15}$Mn$_{0.78}$Cu$_{0.07}$Ga were prepared by arc melting in Ar. The weight loss after melting was less than 0.5%. The samples were homogenized at 1173 K for 3 days with subsequent quenching in ice water. The x-ray diffraction using Cu $\bar{K}\alpha$ radiation was applied to determine the crystalline structure. Magnetic properties were determined with a vibrating sample magnetometer with a field change of 0–2.0 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the ac susceptibility as a function of temperature for Ni$_{2.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{2.15}$Mn$_{0.78}$Cu$_{0.07}$Ga. The figure shows that there is only one ac-susceptibility anomaly and it indicates that these two alloys undergo a direct first-order magnetostuctural transition...
from ferromagnetic martensite to paramagnetic austenite during heating and then a reverse transition during cooling.

Figures 2 and 3 show isothermal magnetization curves of Ni$_{2.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{2.15}$Mn$_{0.78}$Cu$_{0.07}$Ga alloys at selected temperatures during heating. In both alloys, the magnetization decreases with increasing temperature and displays an appreciable discontinuous decrease in the vicinity of the transition temperatures. The magnetization change of Ni$_{2.15}$Mn$_{0.78}$Cu$_{0.07}$Ga during the phase transition is sharper than that of Ni$_{2.15}$Mn$_{0.80}$Cu$_{0.05}$Ga. The entropy change $\Delta S$ is calculated from the magnetization isotherms in Figs. 2 and 3 using the Maxwell relation

$$\Delta S(T, \Delta H) = \int_0^\Delta H \left( \frac{dM}{dT} \right)_H \, dH,$$

where $M$ is the magnetization at field $H$ and temperature $T$. The results are shown in Fig. 4 (solid symbols). With $\Delta H = 2$ T, the maximum $\Delta S$ of Ni$_{2.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{2.15}$Mn$_{0.78}$Cu$_{0.07}$Ga are $-15.6$ and $-22.9$ J/kg K, respectively.

To theoretically calculate the $\Delta S_M$, the magnetic moments of the Mn and Ni atoms in the alloy are considered first. Moriya have noted that in Ni$_3$Mn$_X$ Heusler alloys, the distance between the atoms is sufficiently large for a direct overlap of electron orbitals to be negligible and the delocalization effects are of secondary importance. Therefore, in the first approximation, a localized moment model can be applied to the description of the magnetic properties of these alloys. Ooiwa et al. stated that the magnetic moment of Mn atoms is localized and the magnetic moment of Ni is induced by the molecular field from local Mn atoms and directly depends on the magnetization. The magnetic properties of the alloy can be determined from the magnetic moments of the constituting atoms and their effective magnetic moments. Then $\Delta S_M$ at a specific temperature can be calculated as

$$\Delta S_M = S_M(\sigma) - S_M(0)$$

$$= Nk_B \left[ \ln(2J + 1) - \ln \left( \frac{\sinh(2J + 1)y/2J}{\sinh(y/2J)} \right) + y\sigma \right]$$

where $\sigma = M / g \mu_B J N$ is the normalized magnetization, $M$ is the experimentally determined magnetization at the temperature, $N$ is the number of effective magnetic atoms per gram, $J$ is the total angular momentum, and the expression for $y$ is
In the expression for $y$, $g$ is the Landé factor, $\mu_B$ is Bohr magneton, $k_B$ is Boltzmann’s constant, $M$ is the saturation magnetization of the alloy, $T_c$ is the Curie temperature of Ni$_{1.15}$Mn$_{0.85}$Cu$_{0.05}$Ga alloys, and $H$ is the maximum applied magnetic field. In the Ni$_{1.15}$Mn$_{0.85}$Cu$_{0.05}$Ga alloy, both the Ni and Mn atoms contribute to the magnetic moment, but the major contribution is from Mn. The magnet moment of the Mn and Ni atoms is 2.99 and 0.43 $\mu_B$, respectively. $M_{Mn} = 6.95 M_{Ni}$. The number of effective magnetic atoms $N$ may thus be as 2.75 $\times$ 10$^{21}$/g of Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga alloy, when the magnetic moments of both Ni and Mn atoms have been considered. A saturation magnetization of 75 $\text{emu/kg}$ was set, assuming that the effective magnetic moment is 2.99 $\mu_B$. By fitting the saturation magnetization to $NgJ\mu_B$, we get $J = 1.4$.

With these parameters, Eq. (2) yields a theoretical $\Delta S_M$ in a field of 2 T, as shown by the empty symbols (triangles and circles), where the maximum $\Delta S_M$ in Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga is $-14.9$ J/kg K and in Ni$_{1.15}$Mn$_{0.78}$Cu$_{0.07}$Ga is $-21.7$ J/kg K. The calculated results agree well with the experiments and indicate that the main contribution to $\Delta S$ is from the magnetic entropy change.

Next, the contribution of the lattice entropy change $\Delta S_L$ will be considered. The electron contribution is disregarded as it is trivial. The resultant $\Delta S_L$ can be estimated from the Debye temperature approximation

$$S_L(\Theta) = -3Nk_B\ln\left[1 - \exp(-\Theta/T)\right]$$

$$+ 12Nk_B\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3 dx}{\exp(x) - 1}.$$  

(3)

Here, $N$ is the number of atoms in Ni$_{1.15}$Mn$_{0.85}$Cu$_{0.05}$Ga per gram and $\Theta$ is the Debye temperature. The Debye temperature $\Theta$ of Ni$_{1.15}$Mn$_{0.84}$Ga alloy is reported as 377 K. The composition of the alloy here is slightly different but $\Theta = 377$ K is used in the discussion as the small deviation in composition does not change the atomic cohesive force in the similar crystal structures of these alloys. As the compositions of Ni$_{1.15}$Mn$_{0.8}$Cu$_{0.05}$Ga and Ni$_{1.17}$Mn$_{0.79}$Cu$_{0.06}$Ga are similar and they have the same structure, the number of atoms $N$ and Debye temperature $\Theta$ of these two alloys are nearly identical, only Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga will be used to evaluate $\Delta S_L$. After the phase transition, $\Theta$ can be approximated by $\Theta = \Theta_0(1 - \eta V/V_0)$, where $\eta$ is the Grüneisen parameter. From Eq. (3), $S_L(\Theta) = S_L(\Theta_0) - 3.0$ J/kg K is obtained for $\eta = 1$, $\Delta V/V = 4\%$, and $T = 330$ K. Generally, $\eta$ will take a value between 1 and 3 for solid compounds. A $\Delta V/V = 4\%$ of Ni$_{1.15}$Mn$_{0.08}$Cu$_{0.02}$Ga alloy was assumed as this is a kind of magnetic shape memory alloys. This shows that the structural transition can cause $\Delta S_L = -3.0$ J/kg K, further, it is found that both $\Delta S_L$ and $\Delta S_M$ are negative.

The refrigeration capacity (RC) is another important parameter to evaluate in a magnetic refrigerator. The RC is defined as:

$$q = -\int_{T_{cold}}^{T_{hot}} \Delta S_M dT.$$  

Under a field change of 2 T, the RC of Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{1.15}$Mn$_{0.78}$Cu$_{0.07}$Ga are 59.2 and 58.6 J/kg, respectively. The RC values are larger than those for Ni$_{1.15}$Mn$_{0.75}$Cu$_{0.25}$Ga under a similar field change of 2 T (49 J/kg), although Ni$_{1.15}$Mn$_{0.75}$Cu$_{0.25}$Ga showed a much larger magnetic entropy. This is because the saturation magnetizations of Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{1.15}$Mn$_{0.78}$Cu$_{0.07}$Ga are very similar to that of Ni$_{2}$Mn$_{0.75}$Cu$_{0.25}$Ga but the phase transition temperature span is much wider than that of Ni$_{2}$Mn$_{0.75}$Cu$_{0.25}$Ga.

**IV. CONCLUSION**

This report investigated the magnetic entropy change of NiMnCuGa alloys with both experimental and theoretical approaches. With a field change of 2 T, the experiments showed maximum entropy changes of Ni$_{1.15}$Mn$_{0.80}$Cu$_{0.05}$Ga and Ni$_{1.15}$Mn$_{0.78}$Cu$_{0.07}$Ga are $-15.6$ and $-22.9$ J/kg K. The theoretical calculations indicate that $\Delta S_M$ of the two alloys are $-14.9$ and $-24.7$ J/kg K and that $\Delta S_L$ is $-3$ J/kg K. Although both lattice and magnetic entropy changes are negative, the magnetic entropy change causes the major contribution to the total entropy change.

**ACKNOWLEDGMENTS**

This work is supported in part by the National Science Foundation of China (No. 50571008) and the National Basic Research Program of China (No. 2006CB601100).