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A less expensive NiMnGa based Heusler alloy for magnetic refrigeration

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We present a study of the substitution of Mn by Cu on the compound $Ni_2Mn_{1-x}Cu_xGa_{0.9}Al_{0.1}$, showing that the substitution of a small amount of Al on the Ga site does not affect the magnetic and magnetocaloric potential compared to Ni_2(Mn,Cu)Ga alloy. The samples were prepared with 10% substitution of Al and with Cu concentrations of $x = 0.0$, 0.2, and 0.3. Magnetization measurements as a function of temperature performed from 10 to 400 K, with an applied field of 0.02 T showed a ferromagnetic state, with critical temperature $T_c = 295$ and 300 K for the samples with Cu, $x = 0.2$ and 0.3, respectively. For the sample without Cu, a complex behavior is observed at $T_c = 370$ K, with martensitic transition at 220 K and a premartensitic at 250 K. Analysis of x-rays diffractograms at room temperature show a $L2_1$ structure for $x = 0.0$, while for $x = 0.2$ a mixture of $L2_1$ and martensitic is present, and the sample with $x = 0.3$ it is in a fully martensitic phase. Heat capacity measurements were performed in order to calculate magnetocaloric effect in the samples. The results indicate that in Ni(Mn,Cu)Ga alloys, a partial substitution of Ga by Al still produce a high refrigerant capacity while reducing the costs of fabrication. © *2012 American Institute of Physics*. [doi:10.1063/1.3675064]

Ni-Mn-Ga Heusler alloys have been attracting considerable interest for presenting attractive properties as magnetocaloric effect (MCE)[1] and shape memory effect.[2] The Ni_2MnGa alloys present a ferromagnetic to paramagnetic transition around $T_c = 380$ K and a martensitic transition at $T_M \approx 220$ K from a cubic $L2_1$-type structure to a tetragonal martensitic structure.[3] A small excess of Ni in this alloy leads to an increase of the magnetocaloric effect due the concurrence of the structural and magnetic transitions.[4] On the other hand, it has been shown that the magnetic (T_c) and martensitic (T_M) transitions can be tuned through atomic substitution of Cu on Mn site, leading to a giant magnetocaloric effect (GMCE) in $Ni_2Mn_{1-x}Cu_xGa$ alloy at room temperature[5] for the ideal $x = 0.25$ composition. Recently, the partial substitution of Ga for Al has been studied as a way to improve the ductility and cost of Ni-Mn-Ga alloys. However, a 30% aluminum concentration on the $Ni_2MnGa_{1-x}Al_x$ is sufficient to suppress the martensitic transition,[6,7] possibly due to the coexistence of $L2_1$- and $B2$-type structures that leads to a predominant antiferromagnetic behavior. As reported by Ishikawa *et al*., the fabrication process of these alloys is a key point in their magnetic properties, as the martensitic transformation temperature is dependent on the annealing temperature. In the present work, we show our study to produce a less expensive magnetocaloric material based on a 10% Al substitution on $Ni_2Mn_{1-x}Cu_xGa$ Heusler alloys. We have studied the effect of Al substitution in the magnetic and structural properties of $Ni_2Mn_{1-x}Cu_xGa_{0.9}Al_{0.1}$ with $x = 0.0$, 0.2, and 0.3. Our results indicate that the martensitic and structural phase transition occurs almost at the same temperature for the sample with $x = 0.2$, with the same mechanism responsible for the GMCE as in the Ni(Mn,Cu)Ga and also on other magnetocaloric materials as $Gd_5Ge_2Si_2$ (Ref. 8) and MnAs.[9] Heat capacity measurements were performed in order to calculate magnetocaloric potential of the samples and the results show that less expensive Heusler alloys can be produced and used as a magnetic refrigerant at ambient temperatures. In particular, the substitution of Ga by Al is of large interest due to the large difference in prices between them.[10] In our case, we found that a substitution of 10% in Ga reduces the costs of about 26% when compared to the alloy without Al, for quantities of each material with the same refrigerant capacity (RC).

$Ni_2Mn_{1-x}Cu_xGa_{0.9}Al_{0.1}$ samples, with $x = 0.0$, 0.2, and 0.3, were prepared using a standard arc-melting method with high purity metallic elements in an argon atmosphere. The samples were remelted four times to assure homogeneity and annealed at 1273 K for 3 days followed by quenching in room temperature water at the end of the process. An additional annealing at 673 K for one day was also performed. The annealing process was made in quartz ampoules with a partial Ar atmosphere. Identification of crystal structure of the samples was achieved by x-ray powder diffraction (XPD) made in a Bruker D8 Advanced equipment, using Cu Kα radiation. Magnetization and heat capacity measurements were performed in a physical property measurement system (PPMS) and a SQUID magnetometer, both from Quantum Design, Inc.

X-rays measurements performed at room temperature are presented on Fig. 1. Due to the small differences in the scattering factors between the 3d-metals Mn, Ni, and Cu,

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and also between Ga, x-rays diffractograms are not as good as could be expected. The diffraction peaks are not well defined and the intensities are small, even with a 10 s measuring-time at each point. The annealing temperatures and treatment duration where chosen following Ref. 7 as heat treatment solution to obtain the $L2_1$-type structure in the $Ni_2MnGa_{1-x}Al_x$ alloys. The crystallographic phase for the sample with $x=0.0$ coincide with a $L2_1$-type structure (space group $Fm\bar{3}m$, number 225) at room temperature. The sample with $x=0.2$ have a mixture of orthorhombic martensitic structure (space group *Fmmm*, number 69) and $L2_1$ as can be seen on Fig. 1(b), where all the diffractograms peaks are marked as a martensitic or $L2_1$ reflections. Finally, $x=0.3$ compound displays a martensitic orthorhombic structure at room temperature. The space group of the martensitic phase on this alloy is also *Fmmm*, but the cell parameters seem to be a little different comparing Fig. 1(b) with Fig. 1(c). The main diffraction peaks for $L2_1$-type structure and orthorhombic *Fmmm* are also show on Figs. 1(a) and 1(c), respectively. Additional x-rays diffractograms were performed on samples $x=0.2$ and $x=0.3$ for a temperature of 360 K. These measurements revealed that the austenite phase of the sample $x=0.2$ is a cubic $L2_1$-type structure. The sample with $x=0.3$ has the same crystallographic structure at room temperature and at 360 K, indicating that the martensitic transition temperature might be higher than 360 K.

Magnetization measurements as a function of temperature were performed from 10 to 400 K, with an applied field of 0.02 T following zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) procedures. Figure 2 presents the results obtained on cooling. For the sample without Cu the magnetization curves show a ferromagnetic state, with a Curie temperature of the austenite phase at $T_{CA}=370$ K and a martensitic transition at $T_M=220$ K. A premartensitic transition is also present at $T_{PM}=250$ K, as previously reported for a similar composition.[6] It was also verified that an applied magnetic field of 5 T does not change the martensitic transition temperature for this sample. The ZFC measurements indicate that some antiferromagnetic component is also present on all the samples, but this component is eliminated by cooling with an applied field, as shown by the FCC measurements (Fig. 2). From the FCW curve on the $x=0.0$ sample it was found that the martensitic transition has a thermal hysteresis of approximately 7 K. For the sample with $x=0.2$, it can be inferred from the results presented in Fig. 2 that the paramagnetic to ferromagnetic transition of the austenite phase is overlapping with the martensitic transition at $T_M=T_{CA}=295$ K. The FCW curve reveal a thermal hysteresis for this transition of the order of 4 K. For the sample with $x=0.3$ only one magnetic transition is observed between 10 and 400 K. According to x-rays results the sample is at the martensitic phase in this temperature interval, therefore, the critical temperature of the paramagnetic-ferromagnetic transition observed, called Curie temperature of the martensitic phase (T_{CM}) is around 300 K. The martensitic start and finishing temperatures, T_{Ms} and T_{Mf}, are also indicated in the figure for the samples with $x=0.0$ and $x=0.2$.

Isothermal magnetization measurements performed at 10 K (not shown) confirm the ferromagnetic order of the samples. An applied magnetic field of 5 T is enough for the sample to reach the 96% of the magnetic saturation, M_{sat}, of the $x=0.0$ sample, 98% of the $x=0.2$ sample and 99% of the $x=0.3$ sample. $M_{sat}=97.8$, 73.0, and 60.4 emu/g for $x=0.0$, 0.2, and 0.3, respectively.

Heat capacity measurements were perform from 2 to 385 K in zero magnetic field and in an applied field of 5 T for all the samples. Figure 3 presents the results for the $x=0.0$ and $x=0.2$ samples. The measurement for the sample with $x=0.3$ is not shown, but has all the characteristics of a second-order transition as expected for the magnetization measurements. As also expected, the martensitic transition temperature for this $x=0.3$ compound is higher than

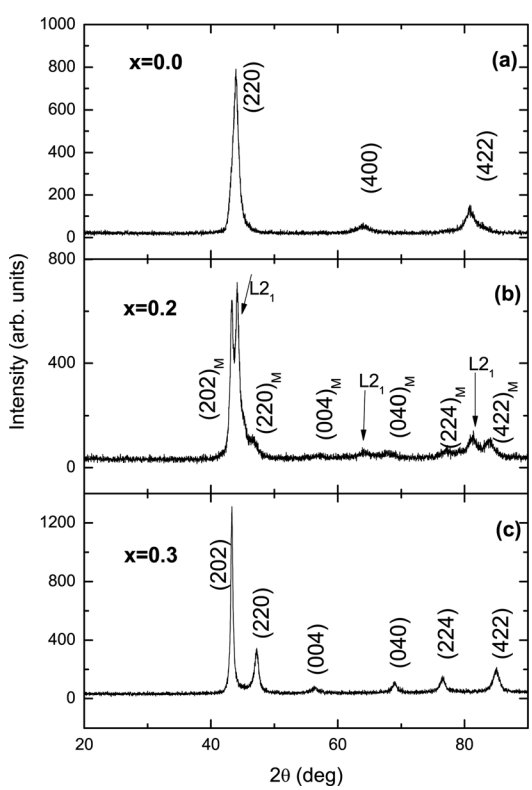

FIG. 1. X-ray diffractograms at room temperature for (a) $x=0.0$, (b) $x=0.2$, and (c) $x=0.3$.

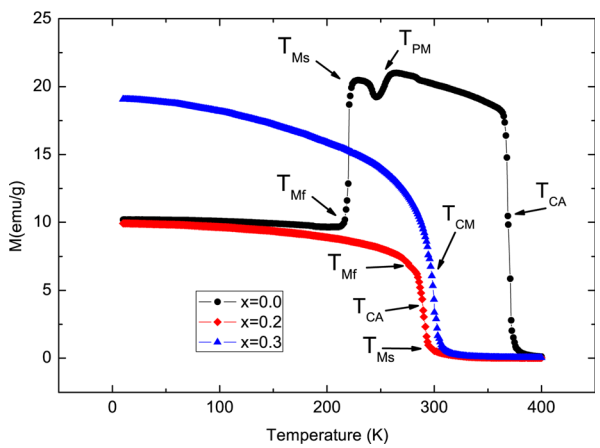

FIG. 2. (Color online) Magnetization vs. temperature curves, for $x=0.0$, $x=0.2$, and $x=0.3$ under a magnetic applied field of 0.02 T. For FCC routine.

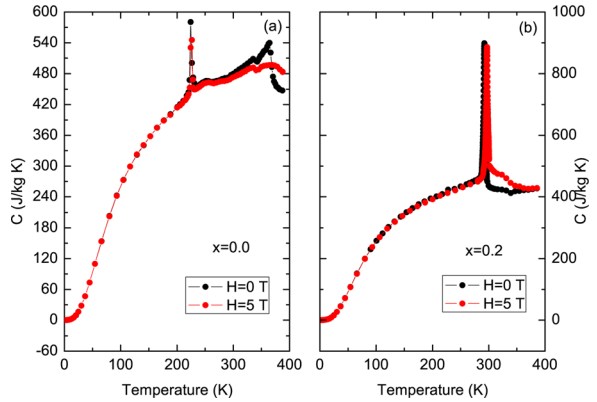

FIG. 3. (Color online) Heat capacity data for the samples with $x = 0.0$ (a), and $x = 0.2$ (b), for applied fields of 0 and 5 T.

400 K, and no first-order transiton peak was found at heat capacity measurements for $T > T_{CM}$. A similar behavior was reported for $Ni_2Mn_{1-x}Cu_xGa$ for higher Cu concentration of $x \geq 0.35$.[11] For the $x = 0.0$ sample the peak of the first-order martensitic transition is nearly nonfield-dependent, since the peaks for $H = 0$ T and $H = 5$ T occur almost at the same temperature. The premartensitic transition is also present on the heat capacity curves as second-order peak at 250 K. For the sample with $x = 0.2$ only one first-order transition peak is observed without an applied magnetic field, indicating that the structural transition is concurrent with the magnetic one, in other words, $T_M = T_{CA} = 295$ K. The curves for $H = 5$ T show a shoulder around 330 K that indicates that for at a high magnetic field the structural transition is decoupled from the magnetic one.

The magnetic entropy change, ΔS_M, for a field change $\Delta H = 5$ T, was calculated from the heat capacity data using the relation:[12]

$$\Delta S_M(T, \Delta H = 5T) = \int_{T_I}^{T_F} \frac{C(T, H = 5T) - C(T, H = 0)}{T} dT \quad (1)$$

and the results for the 3 samples are present on Fig. 4. The results for the sample with $x = 0.3$ are presented in the inset of the figure for clarity.

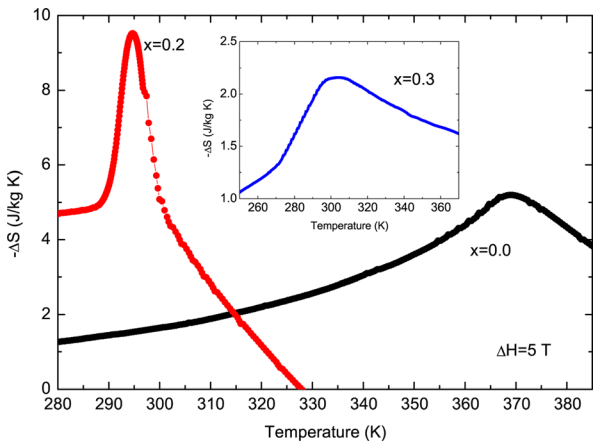

FIG. 4. (Color online) Magnetic entropy change for a magnetic field change $\Delta H = 5$ T for the samples $x = 0.0$ and $x = 0.2$. The inset shows the ΔS_M for the sample with $x = 0.3$.

As the martensitic transition is low-field dependent on the sample without Cu, the magnetocaloric effect at T_M is not significant. For the sample without Cu, $x = 0.0$, the maximum value found for ΔS_M was found around the ferromagnetic to paramagnetic transition of the austenite phase, $\Delta S_M = -5.3$ J/(kg K) $= -1.25$ J/(mol K). For the sample with $x = 0.2$, the maximum of ΔS_M is present around the structural-magnetic transition, $\Delta S_M = -9.5$ J/(kg K) $= -2.3$ J/(mol K). And finally, for the sample with $x = 0.3$, $\Delta S_M = -2.2$ J/(kg K) $= -0.52$ J/(mol K) around the ferromagnetic-paramagnetic transition of the martensitic phase. The refrigerant capacity, RC, was calculated for the sample with $x = 0.2$ by integrating the ΔS_M curve over the full-width at half-maximum (FWHM)[13] and the value found for $x = 0.2$ was 110 J/kg. Compared with the reported RC value for $Ni_2Mn_{0.75}Cu_{0.25}Ga$ alloy (84 J/kg, Ref. 5) it can be said that the Al substitution does not affect the magnetocaloric properties of these compounds. It is also important to emphasize that the thermal hysteresis for these samples is low, reducing losses on thermal cycles.

The Cu substitution on $Ni_2Mn_{1-x}Cu_xGa_{0.9}Al_{0.1}$ samples leads to a decrease of the ferromagnetic transition temperature T_c and an increase of the martensitic transition temperature T_M as previously reported.[5,11] However the transition temperatures are slightly different due to the presence of Al. The Cu concentration where the magnetic and structural transition overlap was found to be $x = 0.2$. This amount of substitution is considered as ideal due to the higher magnetic entropy change value found for that sample. The high RC value found on these compounds and the advantage of lower fabrication costs made these materials highly desirable for application in magnetic refrigeration.

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