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Magnetocaloric properties of the $Ni_2Mn_{1-x}(Cu,Co)_xGa$ Heusler alloys

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We have investigated the magnetocaloric properties on the $Ni_2Mn_{1-x}A_xGa$ Heusler alloys with partial substitution of Mn by A=Co (x=0.10, 0.20, and 0.30) and Cu (x=0.15 and 0.20) in the vicinity of the martensitic transition by measuring magnetization curves at magnetic field up to 20 kOe and in the temperature range of 250–300 K. The changes of the magnetic part of entropy dependence on magnetic field and temperature have been evaluated. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2164415]

The interest on the magnetocaloric properties of materials have renewed attention on the last decade since Brown[1] has shown that magnetic materials can be successfully applied to magnetic refrigeration at room temperature. The magnetocaloric effect is intrinsic to all materials and is remarkable at phase transitions when the magnetic order of the materials is changed. A decrease in the magnetic part of entropy at the phase transition from ferromagnetic to paramagnetic state at the Curie temperature (T_C) is compensated by the increase in the lattice entropy.[2] Structural and magnetic transitions occurring concurrently at the same temperature are responsible for the giant magnetocaloric effect in $Gd_5Si_2Ge_2$ (Ref. 3) and some recent reports indicate that the same effect occurs in the Ni_2MnGa-based system.[4]

The Ni_2MnGa-based Heusler alloys are known as a magnetic shape-memory material which undergo a first-order structural transition, the martensitic transition, at $T=T_M$ below T_C.[5] The variation in stoichiometry and composition of Ni–Mn–Co–Ga Heusler alloys can result in noticeable changes of T_C and T_M.[6]

The concentration dependencies of T_M and T_C for $Ni_2Mn_{1-x}Co_xGa$ and $Ni_2Mn_{1-x}Cu_xGa$ systems are shown in Fig. 1. The increasing concentration of doped metals leads to the increase of T_M and decrease of T_C, and as a result, only the transition from paramagnetic cubic to ferromagnetic martensitic phase is observed at $T_M=T_C$ starting from x=0.25 and 0.30 for $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2Mn_{1-x}Co_xGa$ systems, respectively.[5] Thus, these two systems provide the opportunity to study the magnetocaloric effect (MCE) at three different types of phase transitions.

Stoichiometric polycrystalline ingots of $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2Mn_{1-x}Co_xGa$ were prepared by conventional arc-melting technique in argon atmosphere from high-purity Ni, Mn, Ga, Co, and Cu. X-rays-diffraction measurements at room temperature were conducted for phase composition and lattice-constant determination. The samples were annealed

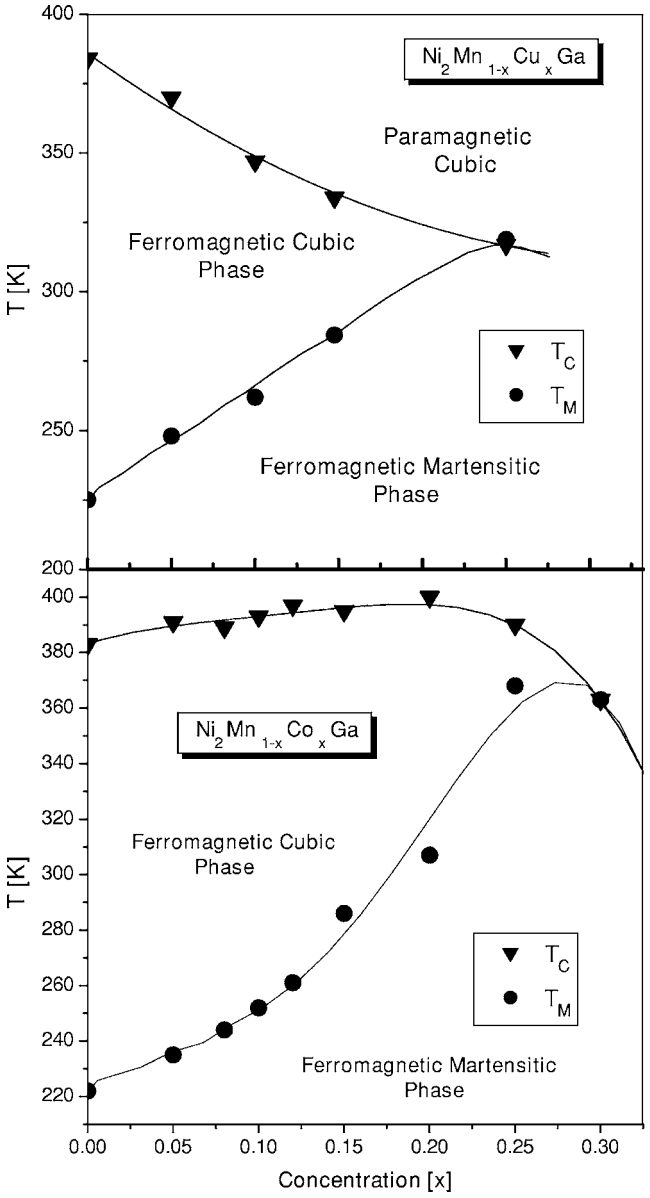

FIG. 1. (T-x)-phase diagram for $Ni_2Mn_{1-x}Cu_xGa$ and $Ni_2Mn_{1-x}Co_xGa$.

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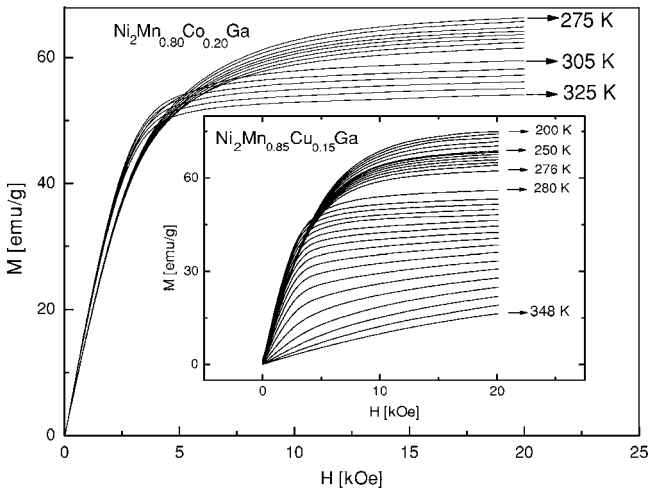

FIG. 2. The typical results of isothermal magnetization measurements $M(H)$ for the $Ni_2Mn_{0.80}Co_{0.20}Ga$. Inset: $M(H)$ for the $Ni_2Mn_{0.85}Cu_{0.15}Ga$.

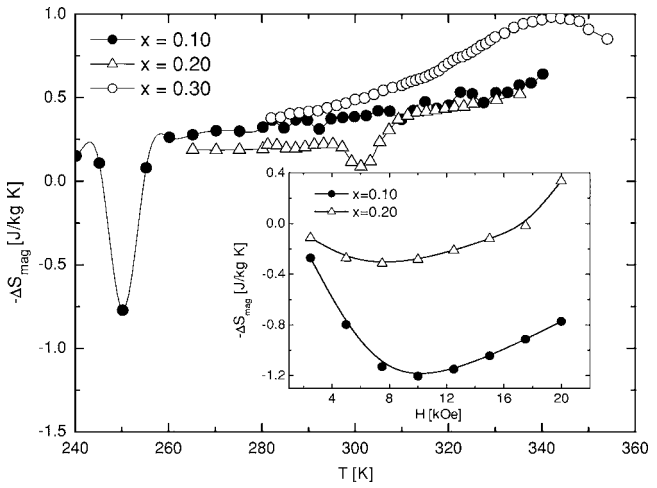

FIG. 3. $Ni_2Mn_{1-x}Co_xGa$ magnetic entropy change for $\Delta H=+20$ kOe and compounds with $x=0.10$, 0.20, and 0.30. Inset: field dependence of ΔS_{mag} at $T=T_M$.

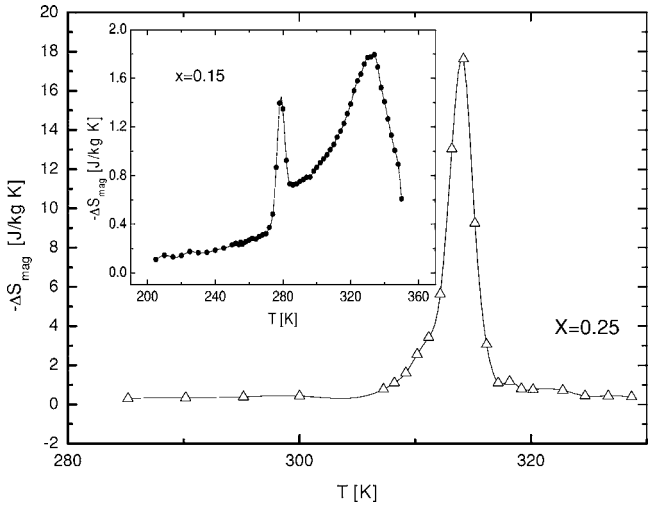

FIG. 4. $Ni_2Mn_{1-x}Cu_xGa$ magnetic entropy change for $\Delta H=+20$ kOe and compounds with $x=0.15$ and 0.25.

under dynamic vacuum at $T=900\,^{\circ}C$ for 72 h and slowly cooled down to room temperature.

Typical magnetization isotherms $M(H)$ of $Ni_2Mn_{1-x}A_xGa$ for $A=Co$ and Cu are shown in Fig. 2. As it can be seen from Fig. 2 the lowering of temperature results in jumplike decrease or increase of the magnetization at low- and high-magnetic-field regions respectively, for both systems below T_M. Due to the higher magnetocrystalline anisotropy, the parent cubic phase is more easily oriented by the magnetic field than the tetragonal martensitic phase. This effect occurs at magnetic fields $H<5$ kOe; after that, its behavior is reversed. For the Co sample with $x=0.30$, not shown here, a typical ferromagnetic to paramagnetic transition was observed.

For the Cu-doped sample, we have T_M and T_C approaching to each other as the Cu concentration increases, as shown in Fig. 1. The optimal concentration occurs for the Cu sample with $x=0.25$, where the martensitic and magnetic transition temperatures coincide at (314 ± 1) K.

From the $M(H)$ curves we calculate the magnetic entropy changes using Maxwell thermodynamic relation as follows:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H, \tag{1}$$

that can be rewritten as

$$\Delta S_{\mathrm{mag}} = \int \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{2}$$

The integration in Eq. (2) has been replaced by a numerical integration. Each experimental $M(H)$ curve was obtained with 2.5 kOe steps and the isothermal curves were separated by at least 2 K around the transition temperature. The magnetic entropy change calculated for the three Co concentrations and the field dependence of the positive ΔS_{mag} for $x=0.10$ and 0.20 are shown in Fig. 3. The same procedure was also applied to determine ΔS_{mag} in the vicinity of the martensitic transition of the $Ni_2Mn_{1-x}Cu_xGa$ system for Cu concentrations $x=0.15$ and 0.20. The ΔS_{mag} for both samples is considerably higher than that for the Co-doped samples, and particularly with $x=0.25$, we obtain a giant magnetocaloric effect ($\Delta S_{\mathrm{mag}}=-17.2$ J/kg K) at $T_C=T_M$, as shown in Fig. 4. For the Cu sample with $x=0.15$ the magnetic entropy change shows similar behavior as the Co-doped samples, with the martensitic ferromagnetic phase showing an inverse magnetocaloric effect up to $H_C=12.5$ kOe. The maximum value of ΔS_{mag} at T_M is negative and has lower intensity compared to the maximum at T_C. The results for both samples are summarized in Table I. The low values of ΔS_{mag} at T_C are in agreement to second-order mag-

TABLE I. The temperatures of the phase transitions and variation of magnetic part of entropy for $Ni_2Mn_{1-x}A_xGa$ (A=Co,Cu) Heusler alloys. T_M is the martensitic transition temperature. $\Delta S_{mag}(T_M)$ is the magnetic entropy change at T_M for a magnetic-field change of 20 kOe. $\Delta S^{inv}_{mag}(T_M)$ is the maximum inverse magnetocaloric effect at T_M obtained in a field change from 0 up to H_M. H_M is the magnetic field where the inverse magnetocaloric effect start to decrease. T_C is the magnetic transition temperature and $\Delta S_{mag}(T_C)$ is the magnetic entropy change at T_C for a magnetic-field change of 20 kOe.

Composition (x)	T_M (K)	$-\Delta S_{mag}(T_M)$ (J/kg K)	$-\Delta S^{inv}_{mag}(T_M,H_M)$ (J/kg K)	H_M (kOe)	T_C (K)	$-\Delta S_{mag}(T_C)$ (J/kg K)
0.10 of Co	250	−0.77	−1.2	10.0	395	···
0.20 of Co	307	+0.33	−0.31	7.5	390	···
0.30 of Co	362	+0.31	···	···	362	···
0.15 of Cu	290	+1.39	···	···	333	1.79
0.25 of Cu	315	···	···	···	315	17.6

netic phase transitions, while a first-order martensitic transition at T_C observed for the Cu concentration x=0.25 results in the giant magnetocaloric effect.

In conclusion, we have shown that magnetic entropy change in Ni–Mn–(Co,Cu)–Ga presents interesting details to understand the mechanisms associated with martensitic transition in Heusler alloys. The low-field inverse magnetocaloric effect is associated with the increase of the magnetic crystalline anisotropy in the martensitic phase. The giant magnetocaloric effect observed in the x=0.25 Cu-doped sample indicates a route for studies of Heusler alloys as magnetic refrigerant.

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