Pressure effects on the magnetocaloric properties of Ni-rich and Mn-rich Ni$_2$MnGa alloys

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Abstract

The pronounced magnetocaloric properties of Ni$_{2\pm x}$Mn$_{1\pm y}$Ga$_{1\pm z}$ alloys are strongly dependent on both the composition and the inter-atomic distances. Moreover, the off-stoichiometric Mn- and Ni-rich Ni$_2$MnGa compounds exhibit mutually different magnetocaloric behaviour under high hydrostatic pressure. A pressure-induced co-occurrence of martensitic transformation and magnetic transition was found for Mn-rich compounds, resulting in a substantial increase of magnetocaloric effect. In contrast to this, the magnetocaloric effect was partially suppressed in the Ni-rich compounds under high pressure. These results reflect the specific role of Ni in the martensitic transformation of Ni$_2$MnGa alloys.
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Ni$_2$MnGa alloys have drawn a great deal of interest for the giant magnetoelastic and magnetocaloric effects (MCE). Magnetic-field-induced strains (up to 9% in Mn-rich single crystals) and, more recently, MCE (up to 20 J/(kg K) for a field span 0–1.6 T in Ni-rich polycrystals) have been found [1,2]. These extraordinary properties arise from the strong interplay between magnetic and structural degrees of freedom, due to the occurrence of a martensitic transformation (MT) between a cubic and a lower-symmetry phase in a ferromagnetic alloy. It is worth noticing that martensitic transformation, Curie temperature, and magnetic anisotropy are strongly influenced by the alloy composition, making the material very attractive for the possibility to maximise the above mentioned effects in a wide temperature range (from 200 to 400 K) [3–5].

Although some papers are present in the literature, the pressure effects on magnetic and structural properties of this compound have not yet been thoroughly studied and some discrepancies between different works can also be found (e.g., [6,7]). This fact is likely to be due to the strong dependence of pressure effects on sample composition [8,9]. Reliable data on the main properties of the Ni$_{2\pm x}$Mn$_{1\pm y}$Ga$_{1\pm z}$ alloys under hydrostatic pressure would play an important role for making light on magnetism and martensitic properties of this system of the Heusler alloys. It is also worth recalling that the basic effect of hydrostatic pressure is a reduction of the volume of elementary crystal cell. Even if the action of chemical pressure may be different from that of a cell contraction, the possibility to modify the giant effects exploitable in applications by applying a hydrostatic pressure is a topic of interest. The relevant pressure effect on magnetocaloric behaviour of GdSiGe has been reported in a recent work [10].

Aim of the present paper was to study the pressure effect on the magnetocaloric properties of Ni$_{2\pm x}$Mn$_{1\pm y}$Ga$_{1\pm z}$ alloys with Ni- and Mn-rich compositions that display large MCE above room temperature.

Samples of composition Ni$_{2.15}$Mn$_{0.85}$Ga (a) and Ni$_{1.9}$Mn$_{1.3}$Ga$_{1.8}$ (b) were prepared by melting techniques

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followed by a thermal annealing. Powder X-ray diffraction (PXRD) analysis carried out on these samples confirms that both are in the martensitic phase at room temperature. The sample (a) is mainly constituted by a martensitic phase showing the orthorhombic 7M structure ($a = 5.822$ Å, $b = 6.118$ Å, and $c = 5.546$ Å, related to the typical $L2_1$ super-lattice) with a secondary tetragonal phase $a = 5.506$ Å and $c = 6.535$ Å. Also for sample (b) the principal phase is the orthorhombic 7M structure ($a = 5.845$ Å, $b = 6.191$ Å and $c = 5.531$ Å) and secondary phase is observed with tetragonal lattice $a = 5.505$ Å and $c = 6.539$ Å. Compositional measurements performed by microprobe analysis confirmed a very good homogeneity of samples with a low lack of Ga (~ 1.5 at% for Ni-rich compound and ~ 0.75 at% for Mn-rich). Isothermal magnetisation and susceptibility measurements were done from ambient pressure up to 1.2 GPa using a CuBe pressure cell in a SQUID magnetometer with magnetic field up to 5 T in the temperature range 5–400 K.

Fig. 1 reports AC susceptibility plots as a function of temperature at ambient pressure for the noticed two different compositions. The structural transformation, characterized by a thermal hysteresis, is displayed in the plot as an increase of AC susceptibility at temperature T_{MA} of the transformation between low-symmetry (low temperature) phase and high-symmetry (high temperature) phase that is followed by a sharp decrease of AC susceptibility at the Curie temperature T_C.

An increase of both the structural transformation temperatures (T_{MA} for the martensite–austenite transition and T_{AM} for the reverse) and the Curie temperature (T_C) was observed for $Ni_{2.15}Mn_{0.85}Ga$ under hydrostatic pressure. This is shown in Fig. 2a, where DC susceptibility measurements are reported at ambient and high pressure. The structural and the magnetic transitions
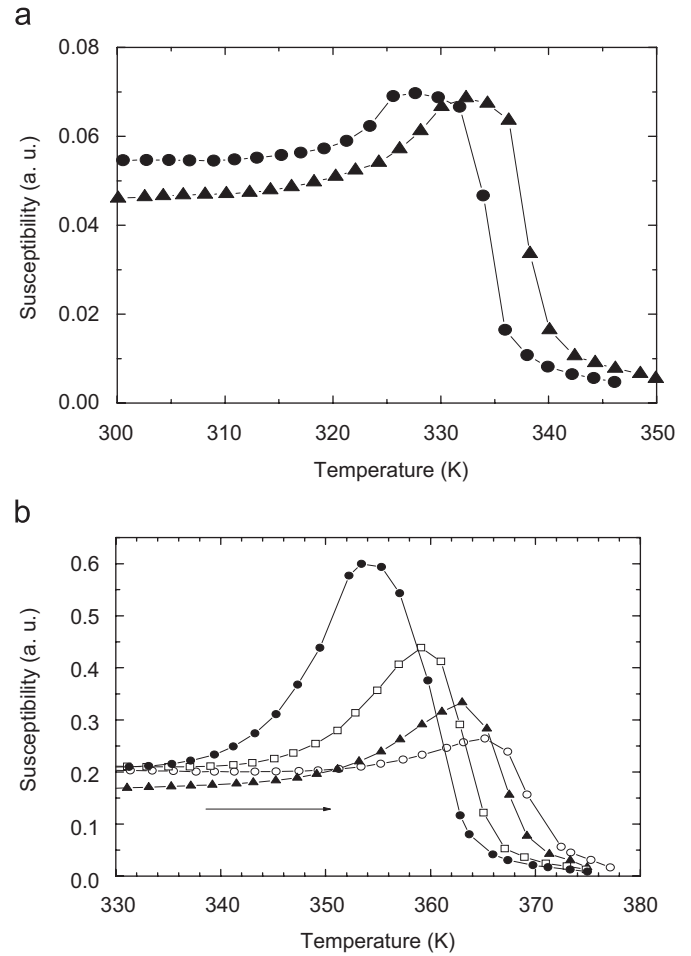

Fig. 2. Magnetic DC susceptibility measured on heating with applied field $\mu_0 H = 0.02$ at different pressure: (a) $Ni_{2.15}Mn_{0.85}Ga$ ambient pressure (filled circles) and $P = 0.81$ GPa (filled triangles); (b) $Ni_{1.9}Mn_{1.3}Ga_{1.8}$ ambient pressure (filled circles), $P = 0.47$ GPa (open squares), $P = 0.81$ GPa (filled triangles), and $P = 1.22$ GPa (open circles).
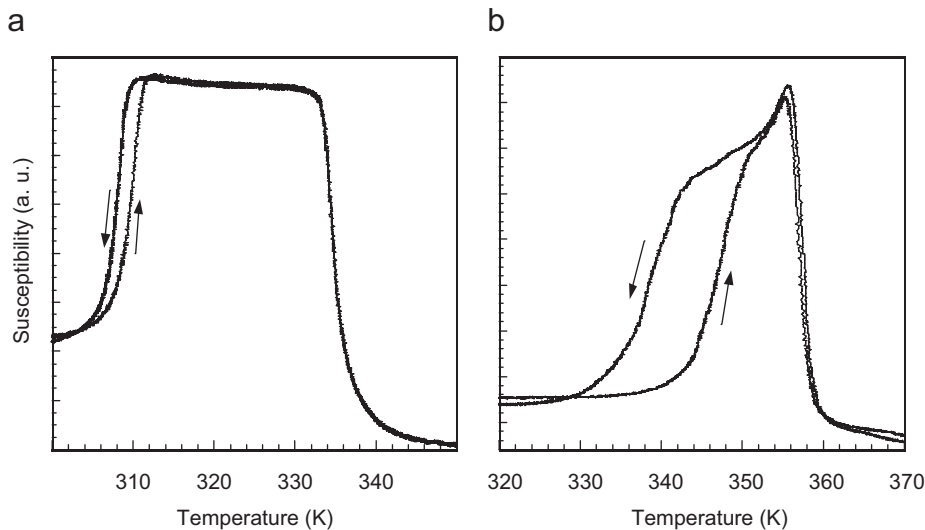

Fig. 1. Temperature variation of magnetic AC susceptibility of $Ni_{2.15}Mn_{0.85}Ga$ (a) and $Ni_{1.9}Mn_{1.3}Ga_{0.8}$ (b) compounds.

become slightly closer under high pressure but they are still well separated.

The DC susceptibility measurements for $Ni_{1.9}Mn_{1.3}Ga_{0.8}$ under different pressures are shown in Fig. 2b. In this case, the pressure dependence of the structural transformation temperature is much stronger than in the previous one. This fact is evident in Fig. 2b where martensite–austenite transformation coincides with magnetic transition at T_C under high pressure and sample exhibits a first order transformation from ferromagnetic-martensite state to the paramagnetic-austenite one.

The transformation temperatures and their pressure dependences are reported in Table 1. It is clearly seen that the increase of T_{MA} under pressure is much faster in the Mn-rich than in the Ni-rich compounds. T_{MA} and T_{AM} are practically independent on pressure in the stoichiometric compound [9]. T_C increases under pressure in all compounds. The increase of T_C of the same magnitude was observed for the stoichiometric Ni_2MnGa compound [9].

The co-occurrence of magnetic and structural transitions has also been recently induced in Ni–Mn–Ga alloys by performing suitable changes in composition of both the Ni-rich and the Mn-rich alloys [4,11,12] to enhance MCE.

MCE was evaluated by the magnetic entropy change ΔS_{mag}, obtained by applying Maxwell relations to isothermal magnetisation measurements (see [2]) performed at ambient pressure and under pressures up to 1.2 GPa. Magnetisation isotherms were measured at temperatures that increased with steps from 2 to 5 K in temperature range of about 40 K around the structural transformation in a field span 0–5 T. The saturation magnetisation at 5 K is 56.9 A m^2/kg for sample (a) and 64.9 A m^2/kg for sample (b) confirming a partial antiferromagnetic ordering of Mn in Mn-rich compound [13].

A decrease of MCE in the Ni-rich alloy (a) of about 18% has been observed under pressure 1.17 Gpa (Fig. 3). This fact agrees with predictions presented in Ref. [9] taking into account an increase of magnetisation under pressure at temperature above T_{MA}. This behaviour is consistent with the specific role of Ni in the martensitic transformation of Ni_2MnGa alloys [9,14].

Magnetic entropy change was calculated also for Mn-rich compound by applying Maxwell relations to magnetisation isotherms in a temperature range including both magnetic and structural transitions. Magnetisation isotherms measured at ambient pressure and at $P = 1.22$ GPa are reported in Fig. 4.
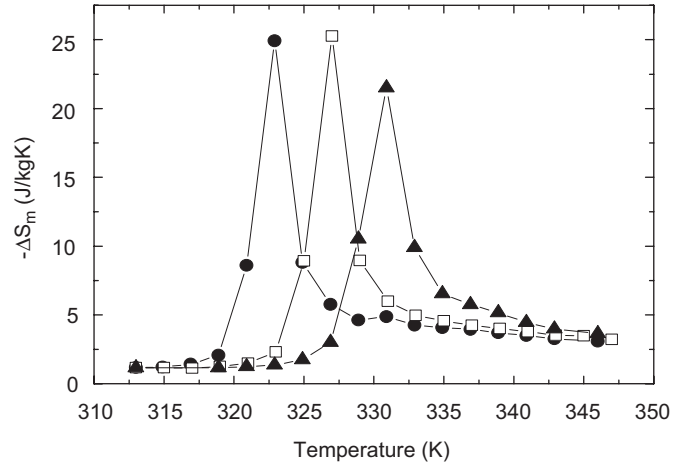

Fig. 3. Magnetic entropy change $-\Delta S_{mag}$ as a function of the average temperature between two next magnetic isotherms, with a field span from 0 to 5 T for $Ni_{2.15}Mn_{0.85}Ga$ at room pressure (filled circles), $P = 0.57$ GPa (open squares) and $P = 1.17$ GPa (filled triangles).
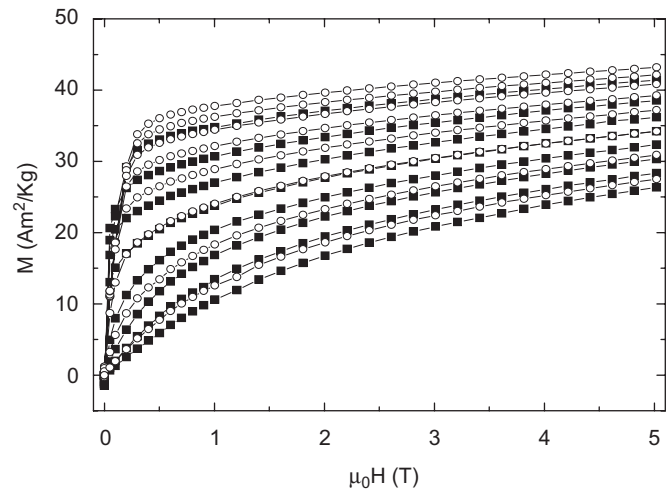

Fig. 4. Magnetisation isotherms of $Ni_{1.9}Mn_{1.3}Ga_{0.8}$ in temperature range from 346 to 374 K ($\Delta T = 4$ K) at ambient pressure (open circles) and under $P = 1.22$ GPa (filled stars).

Magnetic entropy change is reported in Fig. 5 and shows a completely different behaviour for Mn-rich compounds in comparison with Ni-rich ones. The pressure-induced co-existence of structural and magnetic transitions at T_C is the cause of increase of MCE. $|\Delta S_{mag}|$ (in a field span of 5 T) increases to about ~22% with increasing pressure up to 1.22 GPa. The co-occurrence of magnetic and structural transitions obtained by changing stoichiometry led to a similar enhancement of MCE.

Beside the main peak on the $|\Delta S_{mag}|$ vs. temperature curve (corresponding to the structural transformation), a second peak is also evident as a reflection of the magnetic transition at T_C under ambient pressure (filled circles in Fig. 5). With increasing pressure, the magnetic entropy
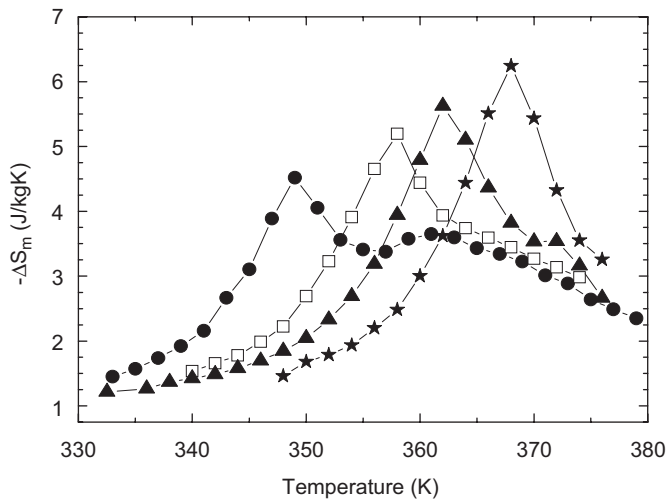
Table 1
Transition temperatures and their pressure dependence

Sample	T_{AM} (K)	T_{MA} (K)	T_C (K)	dT_{MA}/dP (K/GPa)	dT_C/dP (K/GPa)
(a)	308	310	335	5.8	4.7
(b)	338	348	361	17.0	6

Fig. 5. Magnetic entropy change $-\Delta S_{mag}$ in $Ni_{1.9}Mn_{1.3}Ga_{0.8}$ as a function of average temperature between two next magnetic isotherms (field span = 5 T) at ambient pressure (filled circles), $P = 0.47$ GPa (open squares), $P = 0.81$ GPa (filled triangles) and $P = 1.22$ GPa (filled stars).

changes of both transitions flow into the main peak (filled stars in Fig. 5).

Some doubts have recently been raised on a possible overestimation of the isothermal magnetic entropy change using the Maxwell relations in the case of the first-order transitions, but a discussion is still open ([2] and references

therein). Nevertheless, our data can be well compared with most of the values in literature (e.g., [15]).

In conclusion, the magnetocaloric properties of Ni_2Mn Ga alloys are strongly dependent on hydrostatic pressure. Moreover, MCE behaviour under pressure is substantially different for Mn-rich with respect to Ni-rich compounds.

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