Magnetic hysteresis and refrigeration capacity of Ni–Mn–Ga alloys near Martensitic transformation*

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This paper studies the magnetic hysteresis and refrigeration capacity of Ni–Mn–Ga alloys in detail during heating and cooling isothermal magnetisation processes. The Ni–Mn–Ga alloys show larger magnetic hysteresis when they transform from austenite to martensite, but smaller magnetic hysteresis when they transform from martensite to austenite. This behaviour is independent of either the pure Ni–Mn–Ga alloys or the alloys doped with other elements. Because of the existence of the magnetic hysteresis, the relation between the magnetic entropy change and refrigeration capacity is not simply linear. For practical consideration, magnetocaloric effect of Ni–Mn–Ga alloys should be investigated both on cooling and heating processes.

Keywords: magnetic refrigeration capacity, first-order magnetic transition, Heusler alloys
PACC: 7530S, 7550

1. Introduction

Recently, interest in the study of magnetocaloric effects (MCE) in Heusler alloys has grown due to variety of their MCE and phase transition processes. A large magnetic entropy change has been observed in Heusler alloys with the concurrence of magnetic and structural phase transitions.[1−11] Meanwhile, the phase transition process of Heusler alloys with the first-order magnetic transition is much more complicated than the process of other MCE materials with the same transition. It has been reported that although both $Ni_{55.5}Mn_{20}Ga_{24.5}$ and $Ni_{55}Mn_{20.5}Ga_{24.5}$ undergo the first-order magnetic transition and show large magnetic entropy change, their phase transition processes are different.[5] Further studies show that the temperature span of the structural transition has great effect on the peak value and shape of the magnetic entropy change curve.[6]

Large magnetic entropy change is caused by a first-order magnetic transition which brings magnetic hysteresis loss inevitably. Therefore, the depression of hysteresis loss, which undermines the efficiency of magnetic refrigeration, becomes important for the practical application of materials with the first-order magnetic transition. A reduction of hysteresis loss was found in $Gd_5Si_2Ge_2$ with the addition of Fe, which results in a very small hysteresis loss by suppressing the formation of the orthorhombic phase.[12] As for $La(FeSi)_{13}$ compounds, partly replacing La by Pr could decrease the magnetic hysteresis efficiently.[13,14] For Heusler alloy Ni–Mn–Ga, Stadler *et al.*[4] reported that the hysteresis loss in $Ni_2Mn_{0.75}Cu_{0.25}Ga$ is 12 J/kg during heating, meanwhile Pasquale *et al.*[3] and Cherechukin *et al.*[1] pointed out that isothermal magnetisations exhibit the magnetic hysteresis in Ni–Mn–Ga alloys during cooling. However, magnetic refrigeration cycle includes both heating and cooling processes and our previous studies have indicated that the magnetic entropy change could be different during heating and cooling.[15] Therefore comprehensive evaluation of hysteresis loss in Ni–Mn–Ga alloys cannot be given by research of heating or cooling process independently. Unfortunately, reports on the magnetic hysteresis of Heusler alloys usually focused on only one process, heating and cooling isothermal magnetisation processes are rarely studied together. The present work investigates in detail the magnetic hysteresis of pure Ni–Mn–Ga and alloys doped with Cu or Gd elements during two processes. All of the alloys have the first-order magnetic transition and could be used in magnetic refrigeration technology.

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2. Experimental procedure

The pure Ni–Mn–Ga alloys and alloys doped with other elements Cu or Gd were prepared. The preparation and subsequent heat treatment of the polycrystalline ingots are the same as those in Refs. [15] and [16]. The x-ray powder diffraction measurements were investigated with Cu $K\alpha$ radiation to prove the present samples crystallised in the non-modulated tetragonal martensitic structure at room temperature without secondary phase.[15,16] Magnetisation data were measured in fields from 0 to 2 T by vibrating sample magnetometer (VSM). The measurements of heating and cooling isothermal magnetisation curves were carried out by the following steps: at first, the sample was cooled to temperatures far below the Curie temperature $T_{\rm C}$ and then heated to temperature near $T_{\rm C}$, after that the measurement of the isothermal magnetisation (M–H) curve began. When the measurement of M–H curves in heating process was finished, measurement of cooling process was carried out by the same way as above. The step of magnetic field is 24 Oe/s (1 Oe = 79.5775 A/m) for both heating and cooling processes. The constant temperature with fluctuation less than ±0.02 °C was maintained during measurement of each isothermal magnetisation curve. The measurements were repeated at least two times to ensure repeatability. The magnetic entropy change was calculated from the M–H curves by using the integrated Maxwell relation, which, for magnetisation measurements made at constant temperature and at discrete H intervals, ΔS_M can be approximated by:

$$\Delta S \approx \frac{1}{\Delta T}\left[\int_0^H M(T+\Delta T,H)\,\mathrm{d}H - \int_0^H M(T,H)\,\mathrm{d}H\right].$$

3. Results and discussion

Figure 1 shows the magnetisation as a function of temperature (M–T) of $Ni_{54.7}Mn_{20.2}Ga_{25.1}$, $Ni_{55.2}Mn_{18.6}Ga_{26.15}Gd_{0.05}$ and $Ni_{53.75}Mn_{19.5}Cu_{1.75}Ga_{25}$ alloys during heating and cooling under a magnetic field of 0.05 T. These M–T curves had been discussed in the previous papers.[15,16] It indicates that these alloys undergo the first-order magnetic transition during heating and cooling. In heating process, they transform from ferromagnetic martensite to paramagnetic austenite, and a reverse transformation can be found during cooling process.

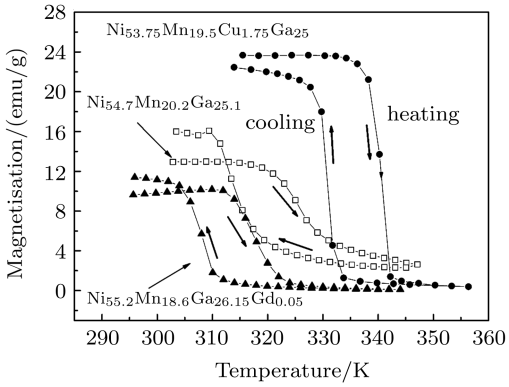


Fig. 1. The magnetisation curves under a field change of 0.05 T.

Figure 2 shows the typical isothermal magnetisation curves for $Ni_{54.7}Mn_{20.1}Ga_{25.2}$ alloy measured with increase and decrease of the field. It can be found that small magnetic hysteresis occurs in the vicinity of the transition temperatures during heating, but large magnetic hysteresis occurs during cooling. The magnetic hysteresis loss was obtained by calculating the area between the increasing and decreasing magnetic field segments of isothermal magnetisation curves. The magnetic hysteresis loss during heating is just 5 J/kg, while it reaches the value of 16 J/kg during cooling.

Figure 3 gives isothermal magnetisation curves for $Ni_{53.75}Mn_{19.5}Cu_{1.75}Ga_{25}$ alloy. Similar to $Ni_{54.7}Mn_{20.1}Ga_{25.2}$ alloy, small magnetic hysteresis is observed during heating, but large one occurs during cooling in the vicinity of the transition temperature. The magnetic hysteresis loss during heating is only 2 J/kg, while it is as large as 11 J/kg during cooling.

Figure 4 gives the isothermal magnetisation curves for $Ni_{55.2}Mn_{18.6}Ga_{26.15}Gd_{0.05}$ alloy. The magnetic hysteresis loss during heating is 1.2 J/kg, and the magnetic hysteresis loss during cooling reaches 24.0 J/kg. The magnetic hysteresis loss of $Ni_{55.2}Mn_{18.6}Ga_{26.15}Gd_{0.05}$ during cooling is the largest in these alloys.

The above results indicate that for Ni–Mn–Ga alloys with first-order magnetostructural transition, isothermal magnetisations show small magnetic hysteresis during heating, while large magnetic hysteresis during cooling. The same phenomenon has also been found in other Ni–Mn–Ga alloys.[1,3] Therefore, this behaviour is independent of either the pure Ni–Mn–Ga alloys or the alloys doped with other elements. Moreover, multiple isothermal magnetisation curves show larger magnetic hysteresis near the Curie temperature $T_{\rm C}$ during cooling processes. The different magnetic

hysteresis between heating and cooling is due to the different processes between the positive and reverse martensite-austenite transition. The twin boundary motion may be the cause of larger magnetic hysteresis during cooling.[17,18] So, much attention should be paid to the cooling isothermal magnetisation process in the research of Ni–Mn–Ga alloys when it is used as the magnetic refrigerators in refrigeration cycle.

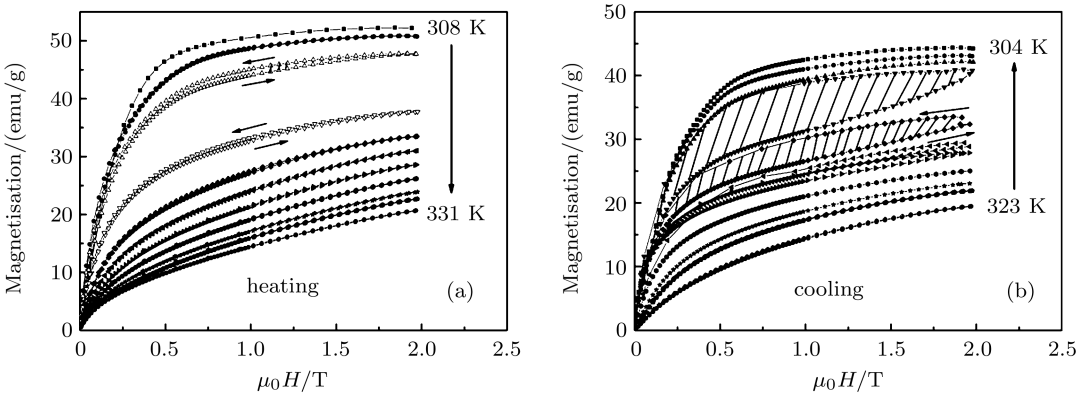


Fig. 2. Isothermal magnetisation curves of $Ni_{54.7}Mn_{20.1}Ga_{25.2}$ alloy in heating (a) and cooling (b) processes.

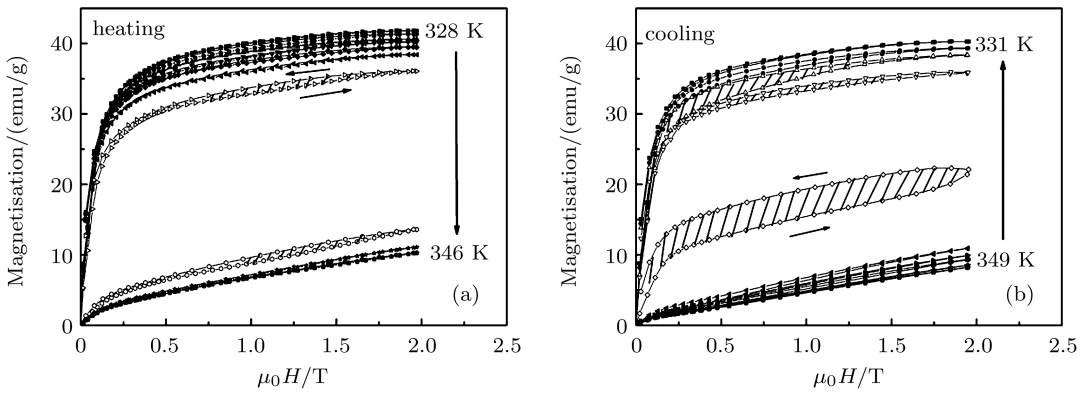


Fig. 3. Isothermal magnetisation curves of $Ni_{53.75}Mn_{19.5}Cu_{1.75}Ga_{25}$ alloy in heating (a) and cooling (b) processes.

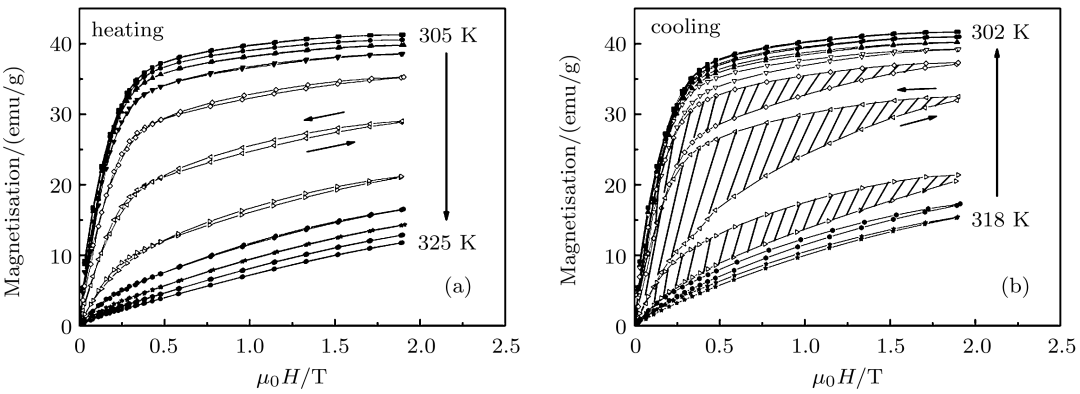


Fig. 4. Isothermal magnetisation curves of $Ni_{55.2}Mn_{18.6}Ga_{26.15}Gd_{0.05}$ alloy in heating(a) and cooling(b) processes.

The numerical integration of the area under the $-\Delta S_{\rm M}(T)$ curve between T_1 and T_2 leads to the cooling capacity $q = -\int_{T_1}^{T_2} \Delta S_{\rm M}(T) {\rm d}T$. The way to take into account the hysteresis loss is to simply subtract it from the corresponding q and obtain the net refrigeration capacity $q_{\rm N}$. The values of $q_{\rm N}$ of all three alloys were calculated and shown in Table 1.

The results in Table 1 indicate that large $\Delta S_{\rm M}$ does not mean large magnetic refrigeration capacity. Because of the existence of the magnetic hysteresis, the relation between the magnetic entropy change and refrigeration capacity is not simply linear. All of the alloys show larger $q_{\rm N}$ during heating. From the viewpoint of practical application, it is of fundamental importance that hysteresis should be reduced as much as possible.

Table 1. The $\Delta S_{\rm M}, q$ and $q_{\rm N}$ of $Ni_{54.7}Mn_{20.2}Ga_{25.1}$, $Ni_{53.75}Mn_{19.5}Cu_{1.75}Ga_{25}$, and $Ni_{55.2}Mn_{18.6}Ga_{25.15}Gd_{0.05}$ alloys.

alloys	$\lvert\Delta S_{\rm M}\rvert$/(J/kg K)		q/(J/kg)		$q_{\rm N}$/(J/kg)	
	heating	cooling	heating	cooling	heating	cooling
$Ni_{54.7}Mn_{20.2}Ga_{25.1}$	8.8	12.7	68.8	57.5	59.5	52.7
$Ni_{53.75}Mn_{19.5}Cu_{1.75}Ga_{25}$	22.5	16.3	60.5	61.1	66.1	45.2
$Ni_{55.2}Mn_{18.6}Ga_{25.15}Gd_{0.05}$	7.7	8.6	55.7	51.1	54.5	27.1

4. Conclusions

The present work indicates that Ni–Mn–Ga alloys show larger magnetic hysteresis when they transform from austenite to martensite during cooling, but smaller magnetic hysteresis when they transform from martensite to austenite during heating. From this cause, hysteresis loss leads to larger $q_{\rm N}$ and smaller $q_{\rm N}$ during heating and cooling processes in Ni–Mn–Ga alloys, respectively. Therefore, the MCE of Ni–Mn–Ga alloys should be investigated on both cooling and heating if Ni–Mn–Ga alloys are considered to be used in the magnetic refrigeration technology.

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