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2004 J. Phys.: Condens. Matter 16 L39

(http://iopscience.iop.org/0953-8984/16/6/L02)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) L39–L44 PII: S0953-8984(04)73728-5

LETTER TO THE EDITOR

A criterion for enhancing the giant magnetocaloric effect: (Ni–Mn–Ga)—a promising new system for magnetic refrigeration

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Received 19 December 2003
Published 30 January 2004
Online at stacks.iop.org/JPhysCM/16/L39 (DOI: 10.1088/0953-8984/16/6/L02)

Abstract

This letter reports a giant magnetocaloric effect (GMCE) in a novel series of materials based on the shape memory alloy Ni_2MnGa. The origin of an enhanced GMCE is traced to the coincidence of a first-order magnetic transition and its attendant structural phase transition with a second-order magnetic transition. This coincidence is achieved by careful compositional tuning and is a technique which provides a criterion for enhancing the GMCE in this system. Thus, for $Ni_{55.2}Mn_{18.6}Ga_{26.2}$, we report an entropy change $\Delta S_m = -20.4\ J\ kg^{-1}\ K^{-1}$ at 317 K in a field of 5 T. This shape memory system also has the added advantage of being formed from inexpensive, non-toxic constituents. With a working temperature at and above room temperature, it appears to be a most promising candidate for practical room temperature magnetic refrigeration.

The magnetocaloric effect (MCE)—an isothermal entropy/adiabatic temperature change accompanying the application of an external magnetic field to a material—has been the subject of much recent interest. This interest is of both a fundamental and an applied nature, the latter being driven by growing environmental concerns. However, while magnetic refrigeration has long been utilized to produce ultra-low temperatures (<1 K) since its development in 1926 [1], its general application was seen as limited—until the 1990s—because most candidate materials displayed a small magnetocaloric effect and had a low operating/magnetic ordering temperature (T_c). Such considerations notwithstanding, the intrinsically higher efficiency of this technique (60%, compared with 40% for conventional methods) and its environmental friendliness has resulted in it becoming the focus of this recently renewed interest. Thus Gd, with a T_c near 293 K and a relatively large MCE [2], became the first possible candidate for room temperature magnetic refrigeration.

More recently, several systems displaying a first-order magnetic phase transition were found to exhibit a large—indeed a giant—magnetocaloric effect (GMCE); such materials

Table 1. The measured results for the four selected samples. T_m and T_c are the first-order and the second-order transition temperatures, respectively. The ΔT ($=T_c - T_m$) is the temperature difference between T_c and T_m. ΔS_m is magnetic entropy change in a field of 5 T.

Sample	Composition	T_m (K)	T_c (K)	ΔT (K)	ΔS_m (J kg^{-1} K^{-1})
1	$Ni_{50.9}Mn_{24.7}Ga_{24.4}$	280	363	83	−3.5 at 274 K
2	$Ni_{51.6}Mn_{24.7}Ga_{23.8}$	296	368	72	−7.0 at 290 K
3	$Ni_{52.7}Mn_{23.9}Ga_{23.4}$	338	354	16	−15.6 at 325 K
4	$Ni_{55.2}Mn_{18.6}Ga_{26.2}$	320	320	0	−20.4 at 317 K

include the Gd-based compound $Gd_5Si_2Ge_2$ [3], $MnFeP_{0.45}As_{0.55}$ [4] and $MnAs_{1-x}Sb_x$ [5]. In fundamental terms the large change in entropy (S) underlying such a GMCE originates from the substantially different contributions to S in the magnetically ordered and disordered regimes separated by this first-order/discontinuous phase change. There also exists a number of systems that display sequential magnetic transitions on cooling: specifically a continuous paramagnetic to ferromagnetic transition followed by a first-order/discontinuous (order–order) transition, both of which involve entropy changes. While previous experience suggests that the dominant entropy change accompanies the first-order phase change, it appeared possible that if these transitions could be merged—or at least brought into close proximity—an enhancement of the separate entropy changes—and hence the MCE—could be accomplished. In this letter we report the presence of a GMCE in a novel series of materials based on the shape memory alloy Ni_2MnGa; indeed for $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ an entropy change of $\Delta S_m = -20.4$ J kg^{-1} K^{-1} is observed at 317 K in a field of 5 T, one of the larger values measured at or above room temperature. This enhancement is traced to the coincidence of a first-order magnetic transition and its attendant structural phase change with a second-order magnetic transition. Such coincidence is achieved by careful compositional tuning. Indeed, as anticipated above, when the first- and second-order transitions are separate, there is a significantly smaller entropy change (and hence a smaller MCE) which occurs in the vicinity of the first-order transition, while if the composition is tuned so that a second-order transition alone occurs, the MCE is also much diminished.

The Heusler alloy Ni_2MnGa is known to undergo a first-order magnetic transition at a (lower) temperature $T_m \approx 200$ K and a second-order transition at a (higher) temperature, $T_c \approx 376$ K. It is also well established that the transition temperatures T_m and T_c are both compositionally sensitive [6, 7]. As part of an investigation into this latter compositional variation and its effect on the MCE, it was found that, as the temperature difference between T_m and T_c became smaller, the entropy change ΔS_m was enhanced. Indeed when the first- and second-order transitions merged at 317 K for the composition $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ the associated entropy change exceeded -20.4 J kg^{-1} K^{-1} in a field of 5 T, well above that measured with separated transitions and even higher than that for the single crystal $Ni_{52.6}Mn_{23.1}Ga_{24.3}$ [8].

A series of polycrystalline specimens of varying composition based on Ni_2MnGa was prepared by arc melting appropriate amounts of Ni (99.95% purity), Mn (spectrographic grade) and Ga (99.99% purity). Each sample was inverted and remelted several times to ensure homogeneity prior to being sealed in Ar filled Vycor tubing and annealed for nine days at 850 °C. They were subsequently quenched into iced water. The magnetic properties were measured in a Quantum Design PPMS Model 6000 system on samples cut from each ingot; the composition of each sample was verified using a Cameca SX100 electron microprobe while the crystal structure was found from power x-ray diffraction data obtained using Cu Kα radiation. Table 1 summarizes the physical data from four selected samples with differing T_m and T_c. For samples 1 ($Ni_{50.9}Mn_{24.7}Ga_{24.4}$) and 2 ($Ni_{51.6}Mn_{24.7}Ga_{23.8}$), T_m is below

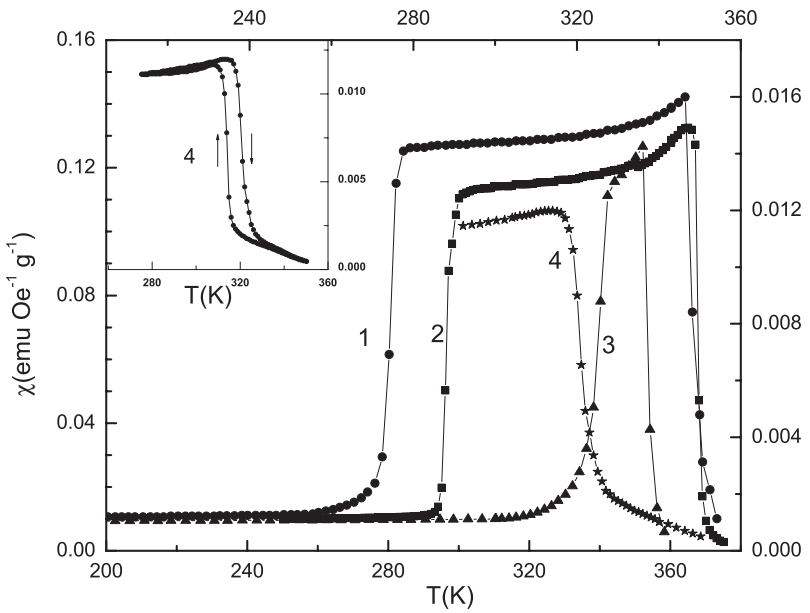

Figure 1. The ac susceptibility χ as a function of temperature measured during heating for the samples with different composition listed in table 1. The inset shows hysteresis of the ac susceptibility χ for sample 4 on heating and cooling.

room temperature and they display the expected cubic structure at 300 K; by contrast samples 3 ($Ni_{52.7}Mn_{23.9}Ga_{23.4}$) and 4 ($Ni_{55.2}Mn_{18.6}Ga_{26.2}$) are tetragonal at room temperature as T_m exceeds 300 K in them. In particular, for sample 4 (the focus of the present study), x-ray diffraction confirmed that it was single phased tetragonal structure with room temperature unit cell dimensions of $a = b = 5.980$ Å and $c = 5.485$ Å, in general agreement with previous reports at similar compositions [6].

The general magnetic behaviour of the four samples selected is summarized in figure 1, which shows the temperature dependence of the zero-field ac susceptibility (measured at 2.4 kHz in an ac driving field of 30 mOe rms). This figure illustrates that on passing through samples 1–4 the first-order transition temperature (T_m) increases while the second-order transition temperature (T_c) decreases. The feature that needs to be noted in this figure is that sample 4 displays only a single transition at $T_m(T_c) = 320$ K. Here it is appropriate to note the presence of a thermal hysteresis of some 7 K on subsequently cooling this sample, as shown in the inset in figure 1. Such hysteresis is a signature that the first-order nature of the transition persists. The dual character—each of two features separately linked to a first- and second-order/continuous transition respectively—will be presented elsewhere.

Figure 2 reproduces the data on which one of the principal results of this letter is based, namely the variation of the magnetization with field at various (fixed) temperatures for sample 4 in the vicinity of its ordering temperature. Before each isotherm (field sweep at constant temperature) was recorded, the sample was heated above $T_c(T_m)$ to produce a demagnetized state before zero-field cooling to below $T_c(T_m)$ and measuring at a new temperature. To ensure equilibrium was maintained during each measuring sequence, a sufficiently slow sweep rate was adopted. The data in figure 2 confirm that the sample is ferromagnetic and easy to saturate below $T_c(T_m)$; in particular the 'S'-shape of the magnetization curve in the temperature interval 317–324 K is clear; this is a feature generally characterizing a metamagnetic first-order transition [9].

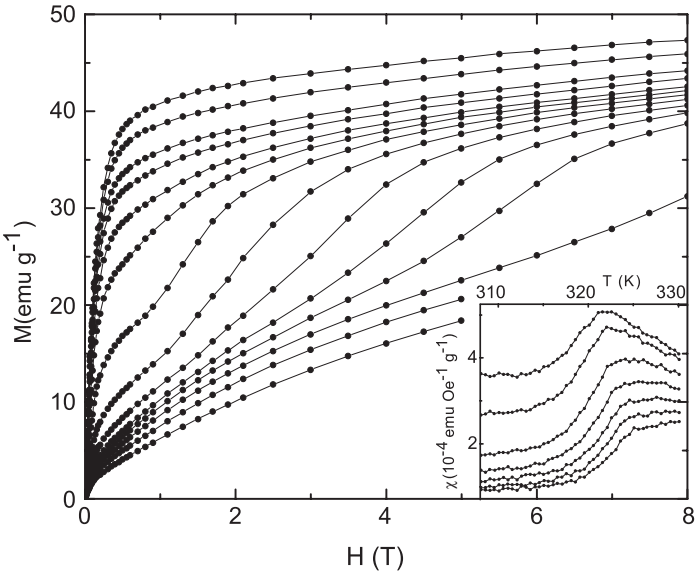

Figure 2. The magnetization dependence of $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ (sample 4) on applied magnetic field measured at various temperatures: from top to bottom 300, 305, 310 and 312 K, then 314 to 320 K in steps of 1 K; the bottom three lines are 322, 325 and 330 K. The inset shows the temperature dependence of the ac susceptibility in fixed fields of 0.8, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 T from top to bottom. The behaviour of the peak structure with increasing field is a characteristic feature of a second-order magnetic phase transition.

Such a first-order magnetic transition is accompanied by an entropy change. This change, ΔS_{m}, can be estimated from the appropriate Maxwell relation(s), namely [2]

$$\Delta S_{\mathrm{m}}(T, H) = S_{\mathrm{m}}(T, H) - S_{\mathrm{m}}(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \tag{1}$$

in the usual notation. The resulting ΔS_{m} calculated based on equation (1) and the data in figure 2 are reproduced in figure 3 for fields of 1.5 and 5 T; the corresponding values for Gd are included for comparison. Table 1 lists the estimates of ΔS_{m} similarly obtained in a 5 T field for the four samples selected.

As is evident from this table, there is a clear correspondence between $\Delta T = T_{\mathrm{c}} - T_{\mathrm{m}}$ (the temperature difference between the first- and second-order transitions) and the magnitude of ΔS_{m}; the latter increases as ΔT decreases for samples 1–4. When T_{m} and T_{c} merge—as in sample 4—the magnetic entropy change reaches its maximum value in this system, $\Delta S_{\mathrm{m}} = -20.4$ J kg^{-1} K^{-1} at $T = 317$ K (just below $T_{\mathrm{c}}(T_{\mathrm{m}})$) in a field of 5 T. In a low field of 1.5 T the change is $\Delta S_{\mathrm{m}} = -9.2$ J kg^{-1} K^{-1}; while both of these values are substantially larger than those for Gd, the latter result has a particular significance, as is discussed below.

For the other samples listed in table 1, the peak value for ΔS_{m} appears near the *first*-order transition temperature, T_{m}, indicating that the principal source of this entropy change is derived from this—the first-order phase change. This provides indirect support for the first-order character of the transition in sample 4. Direct evidence supporting this assignment is the metamagnetic nature of the magnetization—field curves in this sample close to $T_{\mathrm{c}}(T_{\mathrm{m}})$. The inset in figure 2 reproduces data that support the contention of a concomitant second-order transition. Isokaps of the ac susceptibility reveal a series of peaks, the amplitudes of which decrease while the peak temperatures increase with increasing applied field. Such features are

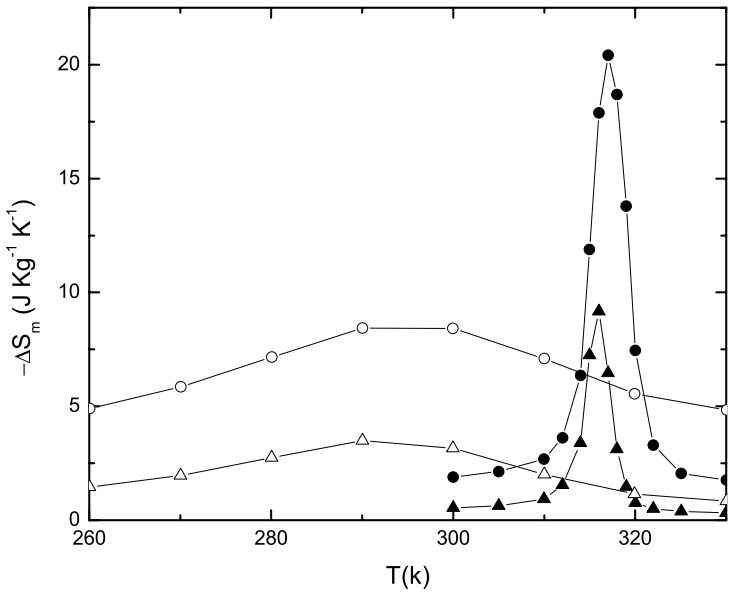

Figure 3. The magnetic entropy change of $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ (sample 4) and Gd with temperature at fields of 1.5 T (triangles) and 5 T (circles), calculated from the magnetization data. The solid circles and triangles are for $Ni_{55.2}Mn_{18.6}Ga_{26.2}$ and the open circles and triangles are for Gd.

linked unequivocally to the presence of a second-order/continuous magnetic phase transition, as numerous previous studies on a wide range of systems have demonstrated [10]. This, however, is not the principal focus here. Rather, the focus is to demonstrate that while a large—likely the dominant—entropy change does occur at a first-order magnetic transition accompanied by a structural phase change (in this system, from tetragonal to cubic on warming), this entropy change can be further enhanced through the (essential) coincidence of a second-order magnetic transition. The data in table 1 indicate that the increasing entropy change is *not* the result of a simple monotonic increase in T_m, but rather the decrease in $\Delta T = T_m - T_c$, ΔS_m becoming a maximum as ΔT approaches zero. By contrast, in the opposite extreme where compositional adjustments result in a second-order transition *alone*, the magnetic entropy change is in fact quite small (the latter will be discussed in detail elsewhere).

In summary, the polycrystalline alloy, $Ni_{55.2}Mn_{18.6}Ga_{26.2}$, displays an enhanced GMCE with $\Delta S_m = -20.4$ and -9.2 J kg^{-1} K^{-1} in fields of 5 and 1.5 T respectively at 317 K. The origin of the enhancement is traced to the essential coincidence of first-order magnetic transition and its attendant tetragonal to cubic structural phase change with a second-order magnetic transition. This coincidence is achieved through careful compositional tuning, and an investigation of this enhancement criterion for other GMCE candidate systems is currently being undertaken. Indeed, the nature of the entropy change in Ni–Mn–Ga, although enhanced, is otherwise similar to that in other GMCE materials such as $Gd_5Si_2Ge_2$ [3], $MnFeP_{0.45}As_{0.55}$ [4] and $MnAs_{1-x}Sb_x$ [5]. However, the Ni–Mn–Ga system, in addition to displaying excellent physical properties for magnetic refrigeration, possesses several practical advantages that might favour its future application. These include the low cost of its constituents, an ease of processing for mass production, and its environmental friendliness. In contrast with other GMCE materials, this system does not contain the expensive rare-earth element Gd (as in the GdSiGe family) or the toxic constituent As (present in the MnFePAs and

MnAsSb systems); for Ni–Mn–Ga the components are abundant in nature and inexpensive. Most importantly the phase transition temperatures can be tuned by compositional adjustments to not only produce an enhanced GMCE (through the coincidence of T_m and T_c) but also to yield a working temperature at and above room temperature. Indeed, the significant entropy change ($\Delta S_m = -9.2$ J kg^{-1} K^{-1} at 317 K) in a relatively low field of 1.5 T could enable this material to operate in fields produced by permanent magnets (as opposed to the more restrictive technology utilizing superconducting magnets). All of these factors combine to make Ni–Mn–Ga a most promising candidate for practical room-temperature magnetic refrigeration utilizing an enhancement technique that might have more general applicability.

This work was supported, in part, through grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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