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Magnetic properties and magnetocaloric effects of $Mn_5Ge_{3-x}Ga_x$*

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We report on the magnetic properties and magnetocaloric effects of $Mn_5Ge_{3-x}Ga_x$ compounds with x=0.1, 0.2, 0.3, 0.4, 0.6 and 0.9. All samples crystallize in the hexagonal Mn_5Si_3-type structure with space group $P6_3/mcm$ and order ferromagnetically. The Curie temperature of these compounds decreases with increasing x, from 306K (x=0.1) to 274K (x=0.9). The average Mn magnetic moments increases with increasing Ga content, reaching a maximum value at x=0.6. The magnetic entropy changes in these compounds are determined from the temperature and field dependence of the magnetization using the thermodynamic Maxwell relation. The Ga substitution has two kinds of influence on the magnetocaloric effect (MCE) of Mn_5Ge_3. One is that the magnitude of the magnetic entropy change decreases, the other is that the MCE peak becomes broadened.

Keywords: magnetic properties, magnetic entropy change
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1. Introduction

Magnetic refrigeration is based on the magnetocaloric effect (MCE). This is an isothermal magnetic-entropy change, $\Delta S_{\rm M}(T,\Delta H)$, or an adiabatic temperature change, $\Delta T_{\rm ad}(T,\Delta H)$, of a magnetic material upon application/removal of a magnetic field. It is becoming a promising technology to replace the conventional gas-compression/expansion technique. The efficiency of magnetic refrigeration depends on many variables, one of which is the magnitude of $\Delta S_{\rm M}(T,\Delta H)$ of the material. For realizing magnetic refrigeration, a large magnetic entropy change is very important, especially near room temperature. Generally, heavy-rare-earth elements and their compounds are considered as the best candidate materials for finding a large MCE due to their high magnetic moments. The highest MCE involving a second-order transition known so far is produced by the rare-earth metal Gd, which has been demonstrated to be used to achieve cooling between 270 and 310K.[1] Many other materials have been studied with respect to their MCEs, such as $Gd_5Si_2Ge_2$,[2] $La_{1-x}Ca_xMnO_3$,[3] $Gd_3Al_{2-x}Ga_x$,[4] $Ce_{2-x}Dy_xFe_{17}$,[5] FeRh,[6] $MnFeP_{1-x}As_x$,[7] and the Heusler alloys Ni-Mn-Ga.[8] Most recently, magnetic-entropy changes comparable with that in Gd have been observed in $La(Fe,Co)_{11.83}Al_{1.17}$,[9] $LaFe_{11.4}Si_{1.6}$ [10,11] and $LaFe_{11.5}Si_{1.5}H_{1.3}$ [12] compounds, which are 3d-transition-metal-rich systems. These results are of significant importance because these compounds can be used as excellent candidates for working material in magnetic refrigeration and open a new class of materials to study with respect to MCE and their applications. All of these results show that large MCEs are not restricted to materials with very large magnetic moments but that, in the vicinity of a phase transition, the MCE depends strongly on the type of the magnetic phase transition. This is important for further improvement of the MCEs in given materials and for exploring new materials with large MCEs.

According to thermodynamic theory, ferromagnetic materials give rise to large magnetocaloric effects in the vicinity of their Curie temperatures due to the rapid change of the magnetization. The intermetal-

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lic compound Mn_5Ge_3 is ferromagnetic with a Curie temperature in the range of 300–320K. Favourable large MCE might be expected in Mn_5Ge_3 due to the high density of the ferromagnetically aligned moments of the Mn^{2+} and Mn^{3+} ions present.[13] Although Mn_5Ge_3 has only an adiabatic temperature change of 1.7K for a field change of 2T,[14] the replacement of Ge by other elements such as Si, Sn, Pb and Sb showed that substitution can have some effects on the magnetic and structural properties. For Si substitution, the Curie temperature of $Mn_5Ge_{3-x}Si_x$ decreases from 296 K (x=0) to 151 K (x=0.75) and the average Mn magnetic moment decreases from $2.6\mu_B$ to $2.15\mu_B$ due to the volume effect.[13,15] The $Mn_5Ge_{3-x}Sb_x$ compounds show enhanced Curie temperatures but decreasing average magnetic Mn moments with increasing Sb content.[16] Carbon doping of the Mn_5Ge_3 lattice leads to a strongly enhanced Curie temperature due to a change in the electronic structure.[17] These studies suggest that the structural and magnetic properties are not only influenced by the volume effect but also by electronic structure. The aim of this work is to study the effect of substitution of Ga for Ge in Mn_5Ge_3 on the magnetic properties, especially on the magnetocaloric effects.

2. Experiments

Samples of $Mn_5Ge_{3-x}Ga_x$ with x=0.1, 0.2, 0.3, 0.4, 0.6 and 0.9 were prepared from 99.9wt.% pure Mn, 99.999wt.% pure Ge, and 99.99wt.% pure Ga. Stoichiometric amounts of materials were alloyed by arc melting in an argon atmosphere. In order to obtain homogeneous alloys, each sample was melted three to four times. Mass losses during melting totalled about 3%. The samples were sealed in evacuated quartz tubes and annealed at 700°C for 10 days followed by quenching into ice water. The crystal structure was deduced from x-ray diffraction patterns, registered on a Rigaku Rint 1400 diffractometer with an automatic divergence slit (Cu $K\alpha$ radiation λ=0.15406nm). The magnetization of the samples were measured in fields up to 5T using a superconducting quantum interference device (SQUID) magnetometer.

The magnetocaloric effect can be characterized by the isothermal magnetic entropy change $\Delta S_M(T, \Delta H)$upon application of a magnetic field H. The value of $\Delta S_M(T, \Delta H)$ can be determined using the Maxwell relation [18]

$$\Delta S_M(T, \Delta H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right) \mathrm{d}H. \quad (1)$$

3. Results and discussion

The x-ray diffraction patterns of the compounds show that all samples crystallize in the hexagonal Mn_5Si_3-type structure but with a very small amount of $Ni_2In(hp6)$ structure phase. For x larger than 0.9 the desired compounds are difficult to form. Replacement of Ge by Ga, which has a larger atomic radius, leads to changes of the lattice parameters of the crystal. Table 1 shows the concentration dependence of the lattice parameters of the $Mn_5Ge_{3-x}Ga_x$ compounds. It appears that the lattice parameter a increases slightly with x whereas the lattice parameter c remains almost constant, resulting in a decrease of the ratio c/a and an increase of the unit cell volume.

Table 1. The structural lattice parameters, Curie temperatures and average moment per Mn atom at 5K of $Mn_5Ge_{3-x}Ga_x$.

$Mn_5Ge_{3-x}Ga_x$ x	a/nm	c/nm	v/nm^3	c/a	T_c/K	Average moment per Mn atom (μ_B)
0.1	0.7202	0.5034	0.22608	0.699	306	2.38
0.2	0.7210	0.5035	0.22666	0.698	304	2.36
0.3	0.7211	0.5033	0.22667	0.698	302	2.38
0.4	0.7222	0.5037	0.22753	0.697	299	2.60
0.6	0.7230	0.5045	0.22838	0.698	292	2.63
0.9	0.7233	0.5037	0.22823	0.696	274	2.51

Figure 1 shows the temperature dependence of the magnetization measured in a field of 0.01T for $Mn_5Ge_{3-x}Ga_x$ with x=0.1, 0.2 , 0.3, 0.4, 0.6 and 0.9 in the temperature range from 5 to 350K. It is clear that these compounds retain their ferromagnetic order. The Curie temperature of these compounds are listed in Table 1, which decreases with increasing x, from 306K (x=0.1) to 274K (x=0.9). The decrease of the Curie temperature is probably due to the lattice expansion or the change of the number of 4p electrons

which results in the modification in the 3d band structure induced by 3d–4p hybridization.

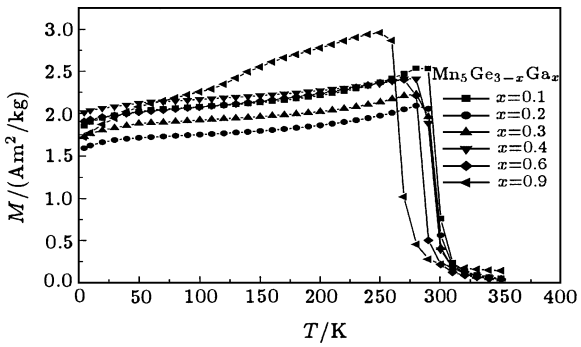


Fig.1. Temperature dependence of the magnetization at 0.01T for $Mn_5Ge_{3-x}Ga_x$.

Figure 2 shows the magnetization of $Mn_5Ge_{3-x}Ga_x$ with x=0.1, 0.2, 0.3, 0.4, 0.6 and 0.9 measured at 5K in a maximum field of 5T. It can be seen that the magnetization curves are characteristic of a ferromagnet. It also can be seen that the average magnetic moment per Mn atom remains nearly constant when $x \leq 0.3$, showing a minimum and then increases, reaching a maximum value of 2.63 μ_B at x=0.6, after which it decreases as x goes to 0.9. This is probably due to mixing of the 3d electron states of the Mn atoms and the 4p electron states of the Ga atoms.

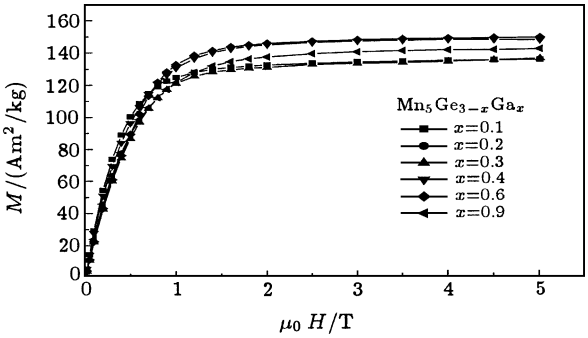


Fig.2. Field dependence of the magnetization at 5K of $Mn_5Ge_{3-x}Ga_x$ compounds.

The field dependence of the magnetization of the $Mn_5Ge_{3-x}Ga_x$ compounds with x=0.3, 0.6, 0.9 was measured at a series of temperatures around the transition temperature. As a representative plot, the magnetization isotherms of $Mn_5Ge_{2.4}Ga_{0.6}$ are shown in Fig.3. In the temperature ranges of 260–280K and 310–340K, the interval of temperature is 5K. In the temperature range of 280–310K, the interval of temperature is 2K. From the magnetization isotherms, we calculated the values of $-\Delta S_M^{max}(T, \Delta H)$ as a function of temperature and field changes. The results are presented in Figs.4 and 5. The characteristic parameters, the magnitude of $-\Delta S_M^{max}(T, \Delta H)$ and its full width at half maximum δT_{FWHM}, were determined and have been listed in Table 2. δT_{FWHM} is defined as the temperature interval corresponding to the half maximum of the $-\Delta S_M(T, \Delta H)$ peak. This is an important parameter related to the relative cooling power (RCP) by the product [7]

$$\mathrm{RCP}(T, \Delta H) = -\Delta S^{max}(T, \Delta H) \times \delta T_{FWHM}. \quad (2)$$

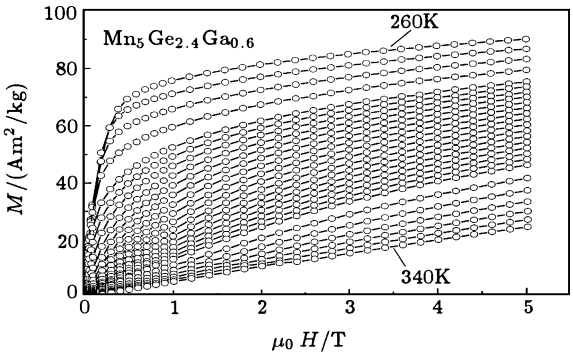


Fig.3. Field dependence of the magnetization of $Mn_5Ge_{2.4}Ga_{0.6}$ at various temperatures.

The cooling capacity in the temperature interval δT_{FWHM} can be estimated by taking 3/4 of the RCP value. It is clear that the larger the δT_{FWHM}, the better the cooling capacity. For Mn_5Ge_3, the values of $-\Delta S_M^{max}(T, \Delta H)$ and δT_{FWHM} are 3.8 J/kg·K and 35 K for ΔH=2 T, 9.3 J/kg·K and 46 K for ΔH=5T [13], respectively. The Ga substitution leads to a decrease of the magnitude of $-\Delta S_M^{max}(T, \Delta H)$, but results in a broadening of δT_{FWHM}. These results are similar to those obtained from Sb substitution.[13]

Table 2. Maximum magnetic entropy changes for field changes of 2 and 5 T, full width at half maximum obtained from the experimental magnetization of $Mn_5Ge_{3-x}Ga_x$ with x=0, 0.3, 0.6 and 0.9.

$Mn_5Ge_{3-x}Ga_x$	$-\Delta S_M^{max}(T,\Delta H)/(J/kg\cdot K)$		$\delta T_{FWHM}/K$	
x	ΔH=2T	ΔH=5T	ΔH=2T	ΔH=5T
0.3	3.2	6.1	35	56
0.6	3.5	6.6	35	54
0.9	3.2	6.2	40	61

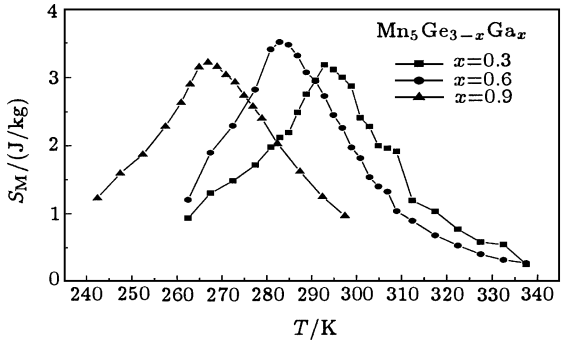


Fig.4. Magnetic-entropy changes of $Mn_5Ge_{3-x}Ga_x$ compounds with x=0.3, 0.6, 0.9 for field changes from 0 to 2T.

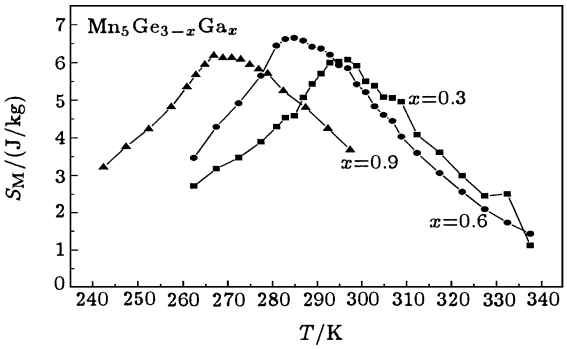


Fig.5. Magnetic-entropy changes of $Mn_5Ge_{3-x}Ga_x$ compounds with x=0.3, 0.6, 0.9 for field changes from 0 to 5T.

4. Summary

In the present investigation on $Mn_5Ge_{3-x}Ga_x$, it has been shown that the $P6_3/mcm$ structure of Mn_5Si_3-type is maintained up to x=0.9 with a slight increase of the lattice parameter a. All samples are ferromagnetic and the Curie temperature decreases with increasing Ga content. In general, the average Mn magnetic moment increases when $x \leq 0.6$ and then decreases a little at x=0.9. The largest magnetic-entropy changes in this system are obtained in $Mn_5Ge_{2.4}Ga_{0.6}$ with a maximum value of about 6.6J/(kg·K) for a field change of 5T. We attribute this large MCE to the relatively large value of the Mn moment. In addition, the replacement of Ge by Ga results in a broadening of full width at half maximum δT_{FWHM}, especially when the field change is 5T. These results suggest that the $Mn_5Ge_{3-x}Ga_x$ compounds have a potential for room temperature magnetic refrigeration applications.

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