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Field dependence of the magnetic entropy change in typical materials with a second-order phase transition

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Abstract

Magnetic field dependence of the magnetic entropy change (ΔS) is the key for magnetic refrigeration. For magnetic materials with a second-order phase transition, the experimental data can be well fitted by the formula of $\Delta S = -kM_s(0)h^{2/3} - S(0,0)$ for a practical field change from 0 to h (the reduced field), where $M_s(0)$ is the spontaneous magnetization at 0 K. The constant k is approximately equal to 1.00 T/K, and $S(0,0)$ is interestingly found to be negative. The formula is discussed based on the renormalization group approach to scaling. The attempts have also been made using the formula for $NaZn_{13}$-type $La(Fe,Si)_{13}$ compounds with a magnetic first-order phase transition.

Keywords: Magnetic entropy change; Second-order magnetic phase transition; First-order magnetic phase transition

Since a large magnetocaloric effect (MCE) was found in $Gd_5Si_2Ge_2$ compound in 1997 [1], much effort has been paid to find a good room-temperature magnetic refrigerant with a large MCE [2]. Currently, the large MCE has been found in materials with a magnetic first-order phase transition (FOPT), such as $R_5(Si,Ge)_4$ [1,2], MnAs [3,4], $La(Fe,Si)_{13}$ [5,6], MnFe (P,As) [7] and Ni_2MnGa [8]-based compounds. On the other hand, a proof-of-principle magnetic refrigerator is working in Ames Laboratory. At room temperature, this machine achieves a cooling power of 600 W with an efficiency reaching to 60% of Carnot [9].

It is well known that the MCE is an intrinsic thermodynamic property of magnetic solid, and may manifest itself as an isothermal magnetic entropy change (ΔS). The intensity of the magnetic field (H) plays an important role in magnetic cooling. The larger the magnetic field is, the bigger the magnetic entropy change shall be. In other words, the increase of the field will result in high efficiency. For household applications, the field offered by a permanent magnet is up to 1.5 T. The largest static field of several teslas is achieved by a superconducting magnet. Thus, for practical purpose, the range of the field change is about 1–10 T. Therefore, the investigation on the field dependence of ΔS in the commercial field range is of fundamental and practical importance. Additionally, gadolinium is used as the magnetic refrigerant in the proof-of-principle machine because some problems, such as hysteresis and time dependence, should be overcome to apply materials with a magnetic FOPT. In this work, we will report on the dependence of ΔS on H in materials with a magnetic second-order phase transition, and then that with a magnetic FOPT.

The polycrystalline samples Gd, $LaFe_{10.8}Si_{2.2}$, $LaFe_{11}Al_2C_{0.5}$, $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$, $TbCo_2$, $Mn_5Ge_{2.7}Sn_{0.3}$, $Mn_5Ge_{2.7}Al_{0.3}$ and $Nd_2AlFe_{13}Mn_3$ were prepared by arc melting in high-purity argon atmosphere. The purities of the starting elements were all better than 99.9%. After annealing, nearly single-phase samples were obtained by X-ray diffraction analysis. Magnetic measurements were performed on a commercial superconducting quantum interference device (SQUID) magnetometer, MPMS-7. The value of ΔS was calculated from magnetization data using the integrated Maxwell relations.

Up to now, there are two different theoretic relationships between ΔS and H for materials with a magnetic second-

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order transition given in the literature [10–12]. Here, the magnetic field change is chosen from zero to H for convenience. One is based on the Curie–Weiss law as follows [10,11]:

$$\Delta S = -\frac{C}{2(T-T_C)^2}H^2, \tag{1}$$

where T_C is the Curie temperature, C is the Curie constant. The other is based on the framework of molecular field approximation as follows [12]:

$$\Delta S \simeq -1.07\, q\mathrm{R}\left(\frac{g\mu_B JH}{k_B T_C}\right)^{2/3}, \tag{2}$$

where q is the number of magnetic ions per mole, R is the gas constant, the others have the conventional meanings.

For commercial applications, the maximum ΔS, i.e. ΔS in the vicinity of T_C, is preferred. Thus, in the following part, ΔS represents the maximum entropy change at T_C. For example, Fig. 1 shows the field dependence of the experimental ΔS for Th_2Zn_{17}-type $Nd_2Fe_{13}Mn_3Al$, Mn_5Si_3-type $Mn_5Ge_{2.7}Sn_{0.3}$, $NaZn_{13}$-type $LaFe_{10.8}Si_{2.2}$ and HCP-type Gd. Here, $h = (\mu_0\mu_B H)/(k_B T_C)$ is used instead of H for convenience. Obviously, Eq. (1) is not valid for the data shown in Fig. 1, which means that the preconditions of low magnetic field and high temperature for Eq. (1) are not satisfied. Clearly, there is a linear relationship between $H^{2/3}$ and ΔS as shown in Fig. 1. As expected in Eq. (2), ΔS should be equal to zero if H becomes zero. However, it is interesting that the fitting lines do not pass the origin. On the other hand, the slope of the fitting line given in Fig. 1 is much different from that expected by Eq. (2).

Based on the renormalization group approach to scaling [13], the relationship between ΔS and H can be obtained.

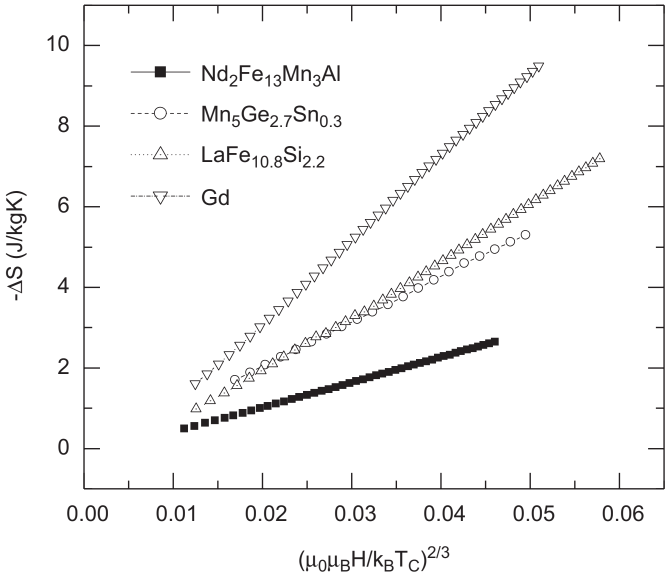

Fig. 1. Field dependence of the experimental ΔS for Th_2Zn_{17}-type $Nd_2Fe_{13}Mn_3Al$, Mn_5Si_3-type $Mn_5Ge_{2.7}Sn_{0.3}$, $NaZn_{13}$-type $LaFe_{10.8}Si_{2.2}$ and HCP-type Gd.

However, to date, we do not find any expression. Thus, we give a brief deduction here. The magnetic entropy ($S(t,h)$) can be obtained by the differential of free energy ($F(t,h)$) with respect to the temperature as follows:

$$\begin{aligned} S(t,h) &= -\frac{\partial F(t,h)}{\partial t} \\ &= -\frac{\partial(l^{-d}F(t_l,h_l))}{\partial t_l}\frac{\partial t_l}{\partial t} = l^{x-d}S(t_l,h_l), \end{aligned}$$

where $t = (T-T_C)/T_C$, $t_1 = tl^x$ and $h_l = hl^y$. Setting $h_l = 1$, we can get

$$S(t,h) = h^{(d-x)/y}S(th^{-x/y},1). \tag{3}$$

For $T = T_C$, we get

$$S(0,h) = h^{(d-x)/y}S(0,1). \tag{4}$$

According to three-dimensional mean-field model, $(d-x)/y$ equals 2/3. Thus,

$$\Delta S = S(0,h) - S(0,0) = h^{2/3}S(0,1) - S(0,0). \tag{5}$$

We must mention that $S(0,0)$ is used only as a reference parameter because Eq. (4) is invalid for $h = 0$. In other words, $S(0,0)$ may not be equal to zero. Therefore, Eq. (5) sounds more reasonable than Eq. (2) for the experimental results in the commercial field range.

Based on Eq. (5), the experimental data are examined for materials such as HCP-type Gd, $NaZn_{13}$-type $LaFe_{10.8}Si_{2.2}$, $LaFe_{11}Al_2C_{0.5}$ and $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$, $MgCu_2$-type $TbCo_2$, Mn_5Si_3-type $Mn_5Ge_{2.7}Sn_{0.3}$ and $Mn_5Ge_{2.7}Al_{0.3}$, and Th_2Zn_{17}-type $Nd_2AlFe_{13}Mn_3$. The experimental data from literature are also used for Th_2Zn_{17}-type Pr_2Fe_{17} [11], Mn_3GaC-type $Mn_3GaC_{0.78}$ [14], Pr_2Ni_2Al-type Gd_2Co_2Ga [15] and $MgCu_2$-type $Er_{0.4}Gd_{0.6}Co_2$ [16]. It is found that all the experimental data can be well fitted by Eq. (5). Table 1 lists the fitting results.

As given in Table 1, all the materials show a nonzero $S(0,0)$ varying from −0.20 to −1.06 J/kg K. The physical origin of $S(0,0)$ is still open for future investigation. In addition, $S(0,1)$ seems to be connected with the spontaneous magnetization ($M_s(0)$) at 0 K (the saturation magnetization at 5 K is used as $M_s(0)$ in this work) as $-S(0,1) = kM_s(0)$, here k is a constant. Using the values of $S(0,1)$ and $M_s(0)$, the value of k is obtained and listed in Table 1. The average value of k ($\bar{k}$) is about 1.00 (J/kg K) × (kg)/(A m²), i.e. 1.00 T/K with the standard deviation $\left(\overline{(k-\bar{k})^2}\right)^{1/2} \simeq 0.07$ T/K. If the reduced magnetization $m(t,h)$ ($M(T,H)/M_s(0)$) is identical for all materials in the vicinity of T_C, the linear relationship between $S(0,1)$ and $M_s(0)$ can be understood according to the Maxwell relation $\Delta S = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$. Therefore, based on the experimental results, we get the following equation:

$$\Delta S = -kM_s(0)h^{2/3} - S(0,0) \tag{6}$$

in the commercial field range. Although we do not really set up a connection between $S(0,1)$ and $kM_s(0)$

Table 1
Crystal structure, saturation magnetization at 5 K, Curie temperature, S(0,0) and S(0,1) for the given materials

Compound	Structure	M_s(Am^2/kg)	T_C(K)	S(0,0) (J/kgK)	−S(0,1) (J/kgK)	$k = -S(0,1)/M_s(0)$ (T/K)
$LaFe_{10.8}Si_{2.2}$	$NaZn_{13}$	135	242	−0.83	136	1.01
$LaFe_{11}Al_2C_{0.5}$	$NaZn_{13}$	146	291	−0.67	136	0.93
$La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$	$NaZn_{13}$	187	303	−0.76	195	1.04
Gd	HCP	234	293	−1.06	209	0.89
$TbCo_2$	$MgCu_2$	117[a]	231	−0.23	112	0.96
$Er_{0.4}Gd_{0.6}Co_2$	$MgCu_2$	70[b]	296	−0.29	70	1.00
$Mn_5Ge_{2.7}Sn_{0.3}$	Mn_5Si_3	117	305	−0.23	113	0.97
$Mn_5Ge_{2.7}Al_{0.3}$	Mn_5Si_3	133	292	−0.56	132	0.99
$Mn_3GaC_{0.78}$	Mn_3GaC	75[c]	295	−0.20	75	1.00
Pr_2Fe_{17}	Th_2Zn_{17}	135[d]	286	−1.03	128	0.95
$Nd_2AlFe_{13}Mn_3$	Th_2Zn_{17}	72	340	−0.23	63	0.88
Gd_2Co_2Ga	Pr_2Ni_2Al	125[e]	76	−1.04	99	0.79

[a] M_s in Ref. [17] is used.
[b] According to the results in Ref. [18].
[c] M_s of Mn_3GaC in Ref. [19] is used as reference.
[d] The magnetization at 270 K under 25 T in Ref. [11] is used as M_s.
[e] The magnetization at 50 K under 5 T in Ref. 15 is used as M_s.

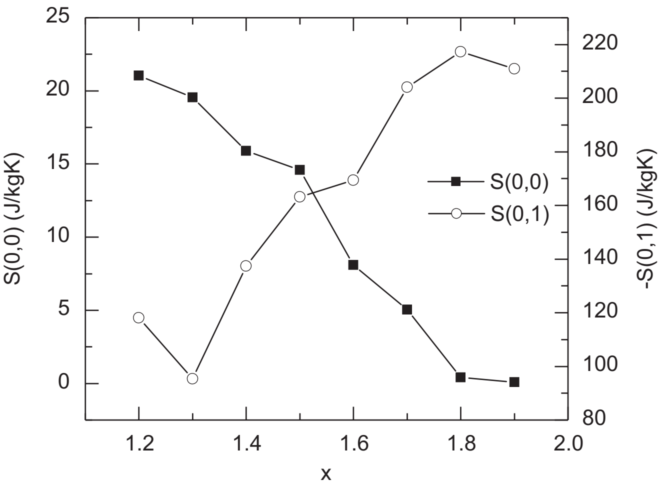

Fig. 2. The variation of S(0,0) and S(0,1) with x for $LaFe_{13-x}Si_x$ compounds.

theoretically, Eq. (6) is at least an empirical formula for the field dependence of ΔS, which will be helpful to design the magnetic refrigerant.

All Eqs. (1), (2), (5) and (6) work on the magnetic second-order transition. It is essential to get a formula to describe the relationship between ΔS and H for materials with a magnetic FOPT. Fortunately, we find that Eq. (5) also fits well the experimental results for $LaFe_{13-x}Si_x$ ($x = 1.2$–1.9) with a magnetic FOPT [20–23]. Fig. 2 shows the obtained S(0,0) and S(0,1) for $LaFe_{13-x}Si_x$ with $x = 1.2$–1.9. Note that $-S(0,1) = kM_s(0)$ is no longer satisfied. S(0,0) is found to become positive instead of negative and increase rapidly with decreasing x. The spontaneous magnetization shows a discontinuous change $\Delta M_s(T_C)$ at T_C, which is the characteristic of a magnetic first-order transition. The giant ΔS is mainly determined by the value of $\Delta M_s(T_C)/M_s(0)$ [24,25]. In $LaFe_{13-x}Si_x$ compounds, the value of ΔS increases with the decrease of x [21–23], indicating that $\Delta M_s(T_C)/M_s(0)$ increases with decreasing x. Thus, S(0,0) is somewhat related to $\Delta M_s(T_C)/M_s(0)$. Note that a parameter in Ref. [26] as well as $\Delta M_s(T_C)/M_s(0)$ can be used to separate the first-order and second-order phase transition. However, it is impossible to get the parameter in Ref. [26] or $\Delta M_s(T_C)/M_s(0)$ directly in experiments. Therefore, combining the data as given in Table 1 for $LaFe_{10.8}Si_{2.2}$ with those for $x = 1.2$–1.9, it is found that S(0,0) may characterize the magnetic first-order transition and distinguish the magnetic first-order and second-order transition.

In summary, the relationship between ΔS and H can be well described by Eq. (6) for the reported materials with a magnetic second-order transition, which is useful for the application of magnetic cooling. The effort to explain the obtained H dependent of ΔS is made based on the renormalization group approach to scaling. Whether the results presented in this paper can be generalized to other materials is still an open question, which will be interesting for further analysis.

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