Magnetic field dependence of the maximum magnetic entropy change

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The maximum isothermal entropy change in a magnetic refrigerant with a second-order phase transition is shown to depend on applied magnetic field H as follows: $(-\Delta S)_{max} = A(H + H_0)^{2/3} - A H_0^{2/3} + B H^{4/3}$. Here A and B are intrinsic parameters of the cooling material and H_0 is an extrinsic parameter determined by the purity and homogeneity of the sample. This theoretical prediction is confirmed by measurements on variously pure poly- and single-crystalline samples of Gd. The Curie point of pure Gd is found to be 295(1) K; however, the maximum of $-\Delta S_M$ is attained at a lower temperature: The higher the quality of the sample, the closer the peak position to 295 K. Further tests are reported for a series of melt-spun $LaFe_{13-x}Si_x$ alloys. These are found to follow the same field dependence, despite the fact that for certain compositions ($x < 1.8$) they experience a phase transition of first, rather than second, order.

Near-room-temperature magnetic refrigeration is developing at a rapid pace, the prospects of a breakthrough into the domain of commercial use looking more realistic than ever.[1,2] Regrettably, designing magnetic cooling devices is still a slow and largely intuitive process, because few reliable mathematical expressions for the magnetocaloric effect (MCE) are known. Significant advances in this field are due to Romanov and Silin,[3] as well as Amaral *et al.*,[4] who used Landau's theory of second-order phase transitions. Another important contribution was made by Franco *et al.*[5] within the framework of the theory of critical phenomena. The aim of this paper is to advance matters further in this direction.

One of the key parameters for the evaluation of MCE is the magnetic entropy change, ΔS_M. In ferromagnets, $-\Delta S_M$, regarded as a function of temperature T, peaks near the Curie point T_C. The height of the peak, $(-\Delta S)_{max}$, grows with magnetic field H according to some complicated law. This law is the subject of our work.

When dealing with the matter it is essential to distinguish between the two paradigmatic cases in room-temperature refrigeration, namely, between refrigerants experiencing a first-order phase transition and those which undergo a phase transition of second order. In the former case the growth of $(-\Delta S)_{max}$ takes place in weak to moderate magnetic fields and is generally accompanied by hysteresis. Thereupon the field dependence of $(-\Delta S)_{max}$ should saturate; that is, for a stronger field the peak in $-\Delta S_M(T)$ should be broader but hardly any higher. In the materials undergoing a second-order transition $(-\Delta S)_{max}$ was predicted to grow as $H^{2/3}$ (Ref. [6]).

In reality, the situation is yet more complicated. In refrigerants with first-order transitions $(-\Delta S)_{max}$ continues to grow in strong magnetic fields, albeit rather more slowly. No quantitative description of $(-\Delta S)_{max}$ vs H has been found so far. Sometimes no hysteresis is observed in the temperature- and field-induced transitions: For instance, the hysteresis is almost absent in melt-spun and porous $LaFe_{13-x}Si_x$

($x < 1.6$), but the transitions in these materials remain clearly of first order.[7,8]

With respect to materials with second-order transitions, it turns out that no simple proportionality relation between $(-\Delta S)_{max}$ and $H^{2/3}$ holds. Rather, besides a term in $H^{2/3}$, $(-\Delta S)_{max}$ contains an extra term independent of H (Ref. [9]). This fact has been explained recently[10] on the basis of Landau's theory of second-order phase transitions[11] applied to spatially inhomogeneous ferromagnets. Earlier, Romanov and Silin used this approach to study the adiabatic temperature change.[3] The idea to apply the same technique to the magnetic entropy change was put forward by Amaral *et al.*[4] As a result, the following expression was obtained:[10]

$$(-\Delta S)_{max} = \alpha \left(\frac{H}{4b} \right)^{2/3} - \frac{\alpha^2}{18b} \Delta T_C, \qquad (1)$$

where ΔT_C is the width of the distribution of transition temperatures around the mean Curie point and α and b are positive quantities independent of T or H that enter in the standard Landau expansion,

$$\Phi = \Phi_0 + \alpha(T - T_C)M^2 + bM^4 - MH, \qquad (2)$$

where Φ is the thermodynamic potential and Φ_0 is a term of zeroth order in M, M being magnetization. It is rather obvious that the linear relation between $(-\Delta S)_{max}$ and $H^{2/3}$ [Eq. (1)] only holds over in a limited range of magnetic fields. It is bound to fail for small H, because it does not comply with an obvious requirement that $(-\Delta S)_{max}$ must vanish in the limit $H \to 0$. Equally unrealistic is the prediction of an unlimited growth as $H \to \infty$. In fact, the magnetic entropy change has an upper bound, which in the case of localized magnets equals $k \ln(2J + 1)$ per magnetic atom.[12] Estimates for Gd metal show that the trend to saturation for $(-\Delta S)_{max}$ vs $H^{2/3}$ should be clearly visible at $\mu_0 H \sim 10$ T (Ref. [13]).

So we set out to find an expression valid for a broader range of magnetic fields. We begin with the case $H \to 0$ and the

difference $T - T_C$ remaining finite. (This is to be distinguished from the case investigated in Ref. [10]: H finite, $T \to T_C$). Minimization of the potential (2) with respect to M yields

$$M^3 = \frac{\alpha}{2b}(T_C - T)M + \frac{H}{4b}. \tag{3}$$

Now the solution to Eq. (3), $M(H,T)$, is presented as an expansion in powers of H carried to linear terms:

$$M = \begin{cases} \sqrt{\frac{\alpha}{2b}(T_C - T)} + \frac{H}{4\alpha(T_C - T)}, & T < T_C, \\ \frac{H}{2\alpha(T - T_C)}, & T > T_C. \end{cases} \tag{4}$$

Taking the square of this expression and substituting it for M_{fin}^2 in Eq. (6) of Ref. [10] results in

$$-\Delta S_M = \begin{cases} \sqrt{\frac{\alpha}{8b}} \frac{H}{\sqrt{T_C - T}}, & T < T_C, \\ 0, & T > T_C, \end{cases} \tag{5}$$

where only terms in H are taken into account. Now Eq. (5) should be averaged over the distribution of local Curie points in the inhomogeneous sample. The exact form of the distribution—not known *a priori*—does not appear essential for the final result. Following Ref. [10], we make the simplest choice by adopting a rectangular distribution of width ΔT_C centered about T_{cntr}. The result of the averaging is as follows:

$$\langle -\Delta S_M \rangle = \begin{cases} \sqrt{\frac{\alpha}{2b}} \frac{H}{\Delta T_C} \left(\sqrt{T_{\text{cntr}} + \frac{1}{2}\Delta T_C - T} - \sqrt{T_{\text{cntr}} - \frac{1}{2}\Delta T_C - T} \right), & 0 < T < T_{\text{cntr}} - \frac{1}{2}\Delta T_C, \\ \sqrt{\frac{\alpha}{2b}} \frac{H}{\Delta T_C} \sqrt{T_{\text{cntr}} + \frac{1}{2}\Delta T_C - T}, & T_{\text{cntr}} - \frac{1}{2}\Delta T_C < T < T_{\text{cntr}} + \frac{1}{2}\Delta T_C, \\ 0, & T > T_{\text{cntr}} + \frac{1}{2}\Delta T_C. \end{cases} \tag{6}$$

According to this expression, $\langle -\Delta S_M \rangle$ is a growing function of temperature in the first interval, it decreases with temperature in the second interval (whose width equals ΔT_C), and is zero at higher temperatures. Therefore, the maximum of $\langle -\Delta S_M \rangle$ is reached at $T = T_{\text{cntr}} - \frac{1}{2}\Delta T_C$ and is equal to

$$(-\Delta S)_{\text{max}} = \sqrt{\frac{\alpha}{2b\Delta T_C}} H. \tag{7}$$

This result, valid for $H \to 0$, can be readily combined with Eq. (1) in a single expression,

$$(-\Delta S)_{\text{max}} = A(H + H_0)^{2/3} - A H_0^{2/3}, \tag{8}$$

where

$$A = \frac{\alpha}{(4b)^{2/3}} \quad \text{and} \quad H_0 = \frac{2^{1/2}(\alpha\Delta T_C)^{3/2}}{27 b^{1/2}}. \tag{9}$$

Equation (8) becomes Eq. (7) if $H \ll H_0$ and Eq. (1) if $H \gg H_0$. Therefore, Eq. (8) is suitable for fitting experimental data down to $H = 0$.

According to Eq. (1), the maximum entropy change grows without limit in a strong magnetic field, $\sim H^{2/3}$, which is not possible. The growth of $(-\Delta S)_{\text{max}}$ should slow down as a sign of approaching saturation. Full saturation is, of course, intractable within Landau's theory, but a trend to saturation can be allowed for by including a term in M^6 in the expansion (2). If the applied field is not too strong the arising implicit expression [Eq. (32) of Ref. [13]] can be solved by iterations,

$$(-\Delta S)_{\text{max}} = A H^{2/3} + B H^{4/3} + \cdots. \tag{10}$$

Combining this with Eq. (8), we finally get

$$(-\Delta S)_{\text{max}} = A(H + H_0)^{2/3} - A H_0^{2/3} + B H^{4/3}. \tag{11}$$

Thus, the applicability of the simple linear relation (1) between $(-\Delta S)_{\text{max}}$ and $H^{2/3}$ is limited to a finite range of magnetic fields, $k_B \Delta T_C \ll \mu_0 \mu_B H \ll k_B T_C$. In small fields, as the left inequality fails, the $(-\Delta S)_{\text{max}}$ vs $H^{2/3}$ dependence acquires an upward curvature. In very strong fields, the right inequality

becomes invalid, one then observes a downward curvature in the $(-\Delta S)_{\text{max}}$ vs $H^{2/3}$ plots, which is a sign of incipient saturation. In the latter case the last term in Eq. (11) may not be neglected.

By definition, the parameters A and B are intrinsic material constants, both being combinations of Landau's coefficients. As against that, H_0 is an extrinsic parameter proportional to the distribution width ΔT_C and, thus, represents the material's homogeneity and/or purity. To obtain an estimate of these parameters, the field dependence of the maximum entropy change of a Gd single crystal and two polycrystalline Gd samples of different purity were studied. The gadolinium (99.8 at.% pure) used to grow the single crystal was prepared by the Materials Preparation Center[14] at the Ames Laboratory. Single-crystal preparation was done using the recrystallization method.[15] The crystal was oriented using back reflection Laue and a 3.5-mm-diameter rod spark cut from it. Both ends of the rod were ground with SiC paper on a lathe to round over the edges and produce a spheroid shape with dimensions 3.5 and 4.5 mm. A small flat was left on the ends to identify this crystallographic direction. The other two orthogonal low-index crystallographic directions were found and their locations were marked. Polycrystalline cube samples with the edge length of about 2.5 mm were prepared from commercially available Gd metal (MaTecK GmbH) with a purity of 99.99 wt% (sample A) and 99.9 wt% (sample B) with respect to other rare-earth elements. The interstitial contents were determined at the Ames Laboratory and are as follows: Sample A contains 11 at. ppm (1 wt. ppm) of N and 2930 at. ppm (298 wt. pmm) of O; sample B contains 4780 at. ppm (365 wt. ppm) of C in addition to 2920 at. ppm (260 wt. ppm) nitrogen and 15 000 at. ppm (1530 wt. ppm) oxygen. As one can see, sample A at best is only 99.7 at.% pure, while sample B is less than 97.7 at.% pure. According to Rietveld refinement of x-ray data (Co Kα radiation, not shown), the two polycrystalline Gd samples are single phase (hcp). The lattice constants of Gd A [$a = 3.6373(3)$ Å and $c = 5.7841(5)$ Å] are slightly lower than that of Gd B [$a = 3.6410(9)$ Å and $c = 5.789(2)$ Å]. The trend
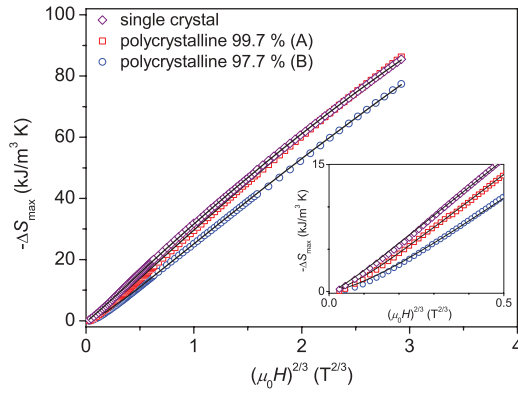
FIG. 1. (Color online) Magnetic field dependence of the maximum negative magnetic entropy change for single- and polycrystalline Gd metal of various purities. The lines are fits to Eq. (11) with the parameters listed in Table I.

FIG. 2. (Color online) Magnetic field dependence of the maximum negative magnetic entropy change for melt-spun (a) $LaFe_{13-x}Si_x$ and (b) $LaFe_{11.6}Si_{1.4}H_{1.6}$ and $LaFe_{11}Co_{0.8}Si_{1.2}$. The lines are fits to Eq. (11) with the parameters listed in Table I.

is consistent with the lattice parameters of high-purity Ames Laboratory Gd metal (99.8 at.% pure) [$a = 3.6336$ Å and $c = 5.7810$ Å].[15]

The magnetic entropy change has been calculated from the isothermal magnetization curves measured in a Superconducting Quantum Interference Device (SQUID) magnetometer in fields up to 5 T and a Physical Property Measurement System (PPMS) extraction magnetometer up to 14 T using the Maxwell relation. Magnetization measurements on the Gd single crystal were performed along the [0001] direction. Magnetization curves were corrected with an appropriate demagnetization factor N. Neglecting the demagnetization field leads to erroneous results: The height of ΔS_M curves is reduced and the peak temperature is shifted to higher temperatures (not shown). Furthermore, after the appropriate demagnetization correction the slopes of both sides of the ΔS_M peak differ by a factor close to 2, as expected in accordance with Ref. 10, whereas without the correction the shape of the peak is almost symmetrical.

Figure 1 shows the maximum entropy change $(-\Delta S)_{max}$ vs $H^{2/3}$ dependence for the single-crystal and polycrystalline Gd. The parameters A and B obtained from the fit of the plots using Eq. (11) are virtually the same for the polycrystalline Gd samples of different purities and for the single crystal
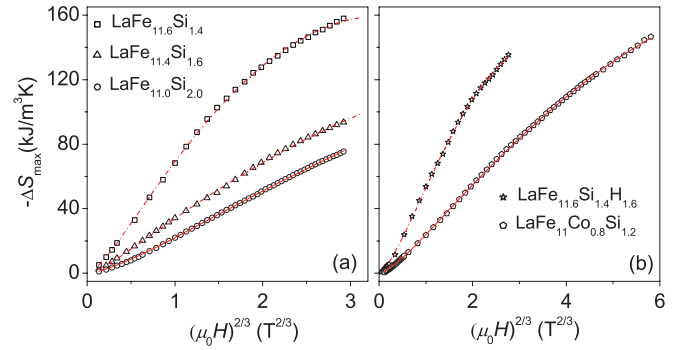
(Table I). As expected, the lowest H_0 is observed for the Gd single crystal, $\mu_0 H_0 = 0.011(1)$ T. As the purity of Gd is reduced from 99.7% to 97.7%, $\mu_0 H_0$ increases from 0.05(1) to 0.14(4) T, respectively. In order to estimate the Curie temperature distribution width ΔT_C, the left slope of the $\Delta S_M(T)$ peak, $\alpha^2/6b$, and the intercept from the linear fit of the data of Fig. 1 to Eq. (1), $\alpha^2 \Delta T_C/18b$, were determined for each sample. The procedure yields $\Delta T_C \approx 0.3$ K for the Gd single crystal. For the polycrystalline samples A and B the width of the distribution increases to $\Delta T_C \approx 4$ K and $\Delta T_C \approx 11$ K, respectively.

Now knowing ΔT_C, one can find the Curie point of Gd from the position of the $\Delta S_M(T)$ peak, T_{max}. It will be recalled that $T_{max} = T_C - \gamma \Delta T_C$, where γ is a numerical factor depending on the shape of the distribution (for a rectangular distribution $\gamma = 1/6$).[10] From our results, $\gamma \approx 1/3$ and $T_{max} \approx 294$ K and 291 K for 99.7% and 97.7% Gd, respectively. Thus, T_C of pure Gd is estimated to be approximately 295 K.

Independently, the Curie temperature of the Gd single crystal was determined by the thermodynamic method[16,17] and found to be 295(1) K. This is in excellent agreement with the T_C value for a high-purity single crystal reported in Ref. 18, presenting a comparative study of the adiabatic temperature change ΔT_{ad} for several Gd samples. Thus, depending on the purity and homogeneity, the position of the $\Delta S_M(T)$ peak, T_{max},

TABLE I. Parameters A, B, and H_0 obtained from a fit of data in Figs. 1 and 2 using Eq. (11) and the quality of the fits χ^2, the $\Delta S_M(T)$ peak position T_{max}, and the distribution width ΔT_C in single-crystal Gd (SC), in polycrystalline Gd with a purity of 99.7 at.% (A) and 97.7 at.% (B), and in $LaFe_{13-x}Si_x$-type alloys.

	$-A$ (m^{-1}K^{-1} T$^{2/3}$)	B (m^{-1}K^{-1} T$^{4/3}$)	$\mu_0 H_0$ (T)	χ^2	T_{max} (K)	ΔT_C (K)
Gd (SC)	35(1)	1.7(2)	0.011(1)	0.03	295	0.3
Gd (A)	34(1)	1.2(2)	0.05(1)	0.04	294	4
Gd (B)	32(2)	1.1(2)	0.14(4)	0.02	291	11
$LaFe_{11.0}Si_{2.0}$	43(2)	2.5(1)	1.1(4)	0.07	245	
$LaFe_{11.4}Si_{1.6}$	48(1)	3.9(3)	0.20(1)	0.22	211	
$LaFe_{11.6}Si_{1.4}$	118(4)	17.2(7)	0.33(5)	0.75	208	
$LaFe_{11.6}Si_{1.4}H_{1.6}$	124(13)	16(2)	1.2(4)	0.70	325	
$LaFe_{11}Co_{0.8}Si_{1.2}$	42.2(5)	2.14(5)	0.80(5)	0.15	280	

of polycrystalline Gd may lie as far as 4 K below the Curie temperature of a single crystal.

The applicability of Eq. (11) is further demonstrated on a series of melt-spun $LaFe_{13-x}Si_x$ alloys (preparation details can be found elsewhere[7]) with x varying from 1.4 to 2.0. The main phase in the melt-spun $LaFe_{13-x}Si_x$ is cubic La(Fe,Si)$_{13}$ (space group Fm-3c) with a minor amount of α-Fe (15 wt% in $LaFe_{11.0}Si_{2.0}$, 13 wt% in $LaFe_{11.4}Si_{1.6}$, and 5 wt% in $LaFe_{11.6}Si_{1.4}$). In this family of magnetic refrigerant materials, reducing Si content brings about a change in the magnetic phase transition from second to first order.[19] Importantly, the first-order transition in the melt-spun[7] and porous alloys with low Si concentration is not accompanied by hysteresis, which is ascribed to the removal of internal constraints hindering the volume expansion.[8] The absence of hysteresis is an essential practical advantage of $LaFe_{13-x}Si_x$: Hysteresis would have given rise to irreversible heat release during magnetic cycling—to the detriment of refrigeration. To us, the lack of hysteresis is important from a different prospective, it enables us to treat all $LaFe_{13-x}Si_x$ on the same footing, as if the phase transition were of second order in all of them. Figure 2(a) displays the $(-\Delta S)_{max}$ vs $H^{2/3}$ dependence for three samples of $LaFe_{13-x}Si_x$, with $x = 1.4$, 1.6, and 2.0. A first-order transition is manifest in the compounds with $x = 1.4$ and 1.6, as a strong bending of the curve is observed already in moderate fields. Yet Eq. (11) copes with all three data sets presented in Fig. 2(a). In all three cases the fits agree with the data. Figure 2(b) presents data for two further materials related to $LaFe_{13-x}Si_x$: a hydride $LaFe_{11.6}Si_{1.4}H_{1.6}$ and a cosubstituted alloy $LaFe_{11}Co_{0.8}Si_{1.2}$. The phase transition in the former is distinctly of first order, whereas in the latter it is thought to be

of second order. In both cases the data are fitted to Eq. (11) successfully.

This does not mean, of course, that Eq. (11) may be expected to apply to magnets with first-order transitions in general. Simply, it becomes inaccurate *gradually*, as x in $LaFe_{13-x}Si_x$ decreases beyond the tricritical point; see the square deviations in Table I. (In contrast, the order of the phase transition changes abruptly at the tricritical point.) The limitation does not detract from the usefulness of Eq. (11). Among materials with first-order transitions, only those close to a tricritical point (and therefore devoid of hysteresis) have a chance of finding use in magnetic cooling devices.

In summary, we have established the field dependence of the maximum magnetic entropy change $(-\Delta S)_{max}$ in materials with second-order magnetic phase transitions. The dependence of $(-\Delta S)_{max}$ on $H^{2/3}$ is linear in the field range of $k_B \Delta T_C \ll \mu_0 \mu_B H \ll k_B T_C$. The $(-\Delta S)_{max}$ vs $H^{2/3}$ dependence acquires an upward curvature in small fields, whereas a downward curvature is observed on approaching saturation. Regarding magnetic refrigerants with first-order phase transitions, at least some of them, for example, $LaFe_{11.6}Si_{1.4}$ and $LaFe_{11.6}Si_{1.4}H_{1.6}$, are found to follow the same field dependence, but the matter deserves a more thorough study. The established field dependence provides a tool for the evaluation of magnetic refrigerant performance in the entire field range, which is particularly important in calculations of cooling devices.

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