

## Entropy changes due to the first-order phase transition in the $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ system

G. J. Liu, J. R. Sun,<sup>a)</sup> J. Lin, Y. W. Xie, T. Y. Zhao, H. W. Zhang, and B. G. Shen  
*State Key Laboratory for Magnetism, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

(Received 13 December 2005; accepted 21 March 2006; published online 23 May 2006)

Entropy changes due to magnetostructural phase transition in  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  intermetallics have been studied based on a systematic analysis of experiment data and mean-field theory calculations. It is found that the magnetic and lattice entropy changes have the same sign. Further analysis indicates that the main entropy change ( $\sim 60\% - \sim 80\%$ ) comes from the field-induced change of the magnetic order, while the rest arise from the entropy difference of the two crystallographic modifications joined by the structural transition, probably due to the variation of the lattice vibration mode. The present work reveals the importance of lattice entropy for a system experiencing a first-order transition. © 2006 American Institute of Physics. [DOI: 10.1063/1.2201879]

Recently giant magnetocaloric effects have been observed in materials that experience a first-order phase transition, such as  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ ,<sup>1,2</sup>  $\text{La}(\text{Fe}, M)_{13}$  ( $M = \text{Si}, \text{Al}, \text{Co}$ ),<sup>3</sup>  $\text{MnAs}$ ,<sup>4</sup> and  $\text{MnFeP}_{1-x}\text{As}_x$ .<sup>5</sup> Since the first-order transition can cause a sharp drop of magnetization, the entropy change is usually quite large. It can be as high as  $\sim 20 - 30$  J/kg K for a magnetic field change of 0–5 T even near room temperature. These values are nearly double that of Gd ( $\sim 10$  J/kg K),<sup>6</sup> which has been regarded as the most promising material for room-temperature magnetic cooling.

A typical feature of a first-order phase transition is the simultaneous changes of crystal structure (or phase volume) and magnetic order of a material.<sup>1,2</sup> This actually implies possible changes in lattice and electronic entropies accompanying the phase transition. Indeed, signatures for the changes other than magnetic entropy have been experimentally observed. Recently, Gama *et al.* found that the entropy change of MnAs enhanced greatly under proper pressures, reaching the values far beyond the theoretical limit of magnetic entropy.<sup>7</sup> For  $\text{Gd}_5\text{Ge}_4$ , moreover, Pecharsky *et al.* suggested that the total entropy change should be the magnetic one plus the difference of the entropies of the two crystallographic modifications joined by the first-order transition,<sup>8</sup> and the latter is  $\sim 9.5$  J/kg K for  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ .<sup>9</sup> By comparing the entropy changes under different pressures, Morellon *et al.* ascertained that the magnetic and lattice entropy changes in  $\text{Tb}_5\text{Si}_2\text{Ge}_2$  are  $\sim 13.4$  and  $\sim 9$  J/kg K, respectively, under a field of 5 T.<sup>10</sup>

For a thorough understanding/controlling of the magnetocaloric effects, it is obviously important to distinguish the contributions from spin, lattice, and electrons. Unfortunately, work in this aspect is limited, and most of these studies have been based on an analysis of lateral evidence under the assumption that the magnetic entropy change remains constant when the magnetic transition evolves from second order to first order.<sup>10</sup> In this letter, we try to give a direct evidence for the entropy change due to structural transition for the  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  family by combining experimental data and theoretical analyses.

Most of the previous work focused on the temperature and magnetic-field dependence of the entropy change. Considering the fact that magnetic entropy change is a result of the variation of magnetic order, a unique correspondence between entropy and magnetization is expected. Based on this consideration, in the following we shall first establish a direct relation between entropy and magnetization for  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  using the published data in Refs. 1, 2, 11, and 12.

There are a number of reports on  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  with the Si content varying between 0 and 4, and it has been found that both the entropy change and Curie temperature ( $T_c$ ) are dependent on the content of Si.  $T_c$  is  $\sim 45$  K for  $\text{Gd}_5\text{Ge}_4$  under a magnetic field of 3 T,<sup>13</sup> and it grows monotonically with the increase of  $x$ , and reaches  $\sim 275$  K for  $x = 2$ .<sup>1,2</sup>  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  is a typical compound that has been intensely studied in the last few years because of its high Curie temperature and large entropy change, which suggests a possibility of this material as the refrigerant for room-temperature magnetic cooling. According to Pecharsky and Gscheidner, its entropy change is  $\sim 19$  J/mol K for a field change of 0–5 T (The units of J/mol K will be used hereafter to get a proper comparison of the entropy changes in different  $\text{GdSi}_x\text{Ge}_{4-x}$  compounds). In general, entropy change increases with the decrease of  $T_c$ . The maximum entropy change is  $\sim 72$  J/mol K, occurring in  $\text{Gd}_5\text{SiGe}_3$  ( $T_c \approx 140$  K).<sup>1,2</sup> This value is much greater than that observed in the  $\text{La}(\text{Fe}, M)_{13}$  alloys, for which the maximum entropy change is  $\sim 25$  J/mol K.<sup>3</sup>

Figure 1(a) shows the isothermal magnetization curves of  $\text{Gd}_5\text{SiGe}_3$  obtained by Pecharsky and Gscheidner (Ref. 2). In the low-temperature region, magnetization exhibits a sharp increase with applied field. This indicates a nearly collinear ferromagnetic order in this compound. A two-step variation of magnetization appears near and above  $T_c$ , which signifies the occurrence of a metamagnetic transition. Based on the Arrott plot in Fig. 1(b), spontaneous magnetization can be derived. Figure 1(c) shows the normalized spontaneous magnetization  $\sigma_0$  and the magnetization obtained under  $H = 5$  T ( $\sigma_{5T}$ ), where the saturation magnetization has been set to 200.18 emu/g assuming that only Gd contributes to magnetization and its magnetic moment is  $\sim 7.4\mu_B$ .<sup>14</sup> From

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: jrsun@g203.iphys.ac.cn

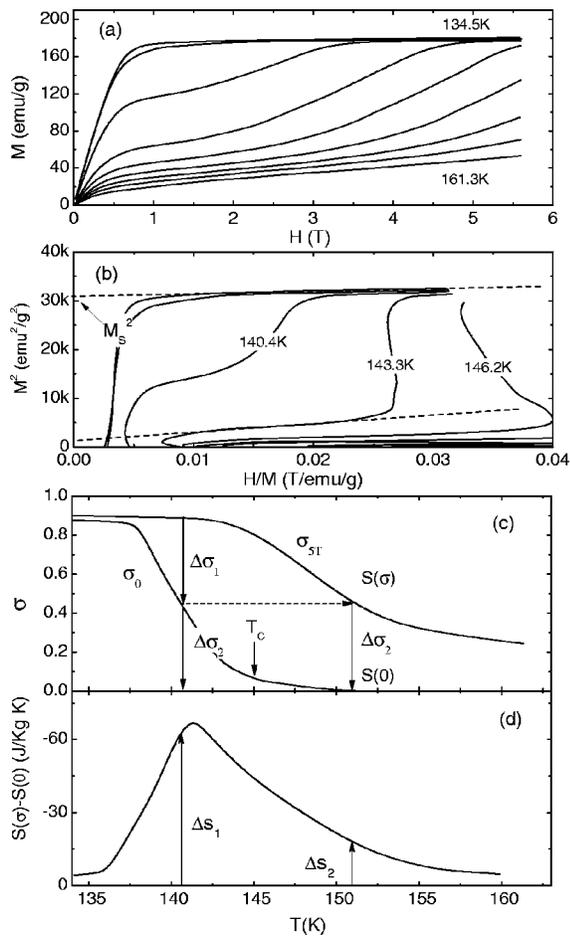


FIG. 1. (a) Isothermal magnetization curves measured near the Curie temperature of  $\text{Gd}_5\text{SiGe}_3$  by Percharsky and Gschneidner (Ref. 2). (b) An Arrott plot showing the derivation of spontaneous magnetization ( $M_s$ ). (c) Spontaneous magnetization and the magnetization obtained under 5 T as a function of temperature. (d) Entropy changes calculated by the Maxwell relation based on the data in (a). Dashed lines are guides for the eye.

Fig. 1(c), the magnetic transition begins at  $\sim 148$  K and ends at  $\sim 138$  K. External field drives the system from the paramagnetic state into the ferromagnetic state in the temperature just above  $T_c$ , producing significant magnetic entropy changes [ Fig. 1(d)].

Considering the fact that it is the variation of magnetization that affects magnetic entropy, an exclusive correspondence between  $\sigma$  and  $S(\sigma)$  (entropy) is expected. As shown in Figs. 1(c) and 1(d), the  $\sigma$  to  $S$  correlation is direct above  $T_c$  ( $\Delta\sigma_2$  vs  $\Delta S_2$ ). Entropy increases from  $S(\sigma)$  to  $S(0)$  as magnetization drops from  $\sigma$  to 0. Below  $T_c$ , the magnetization change  $\sigma_{5T} \rightarrow 0$  can be decomposed into  $\sigma_{5T} \rightarrow \sigma_0$  ( $\Delta\sigma_1$ ) and  $\sigma_0 \rightarrow 0$  ( $\Delta\sigma_2$ ). The entropy change corresponding to the first drop,  $\Delta S_1$ , can be directly extracted from Fig. 1(d), while approximated by  $\Delta S_2$  for the second drop. Therefore, the total entropy variation is  $\Delta S = \Delta S_1 + \Delta S_2$ . Similar analysis is applicable to other samples. As a representative, in Fig. 2 we show the spontaneous magnetization, the magnetization under  $H=7$  T, and the corresponding entropy change of  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  based on the work of Gigurè *et al.*<sup>11</sup>

It is obvious that for each temperature there is a  $(\sigma, \Delta S)$  pair, and all these points under different temperatures form a  $\Delta S$ - $\sigma$  curve. Figure 3 presents the  $\Delta S$ - $\sigma$  relation thus obtained. It is interesting that all the data of different samples collapse into a common curve, which reflects the universality

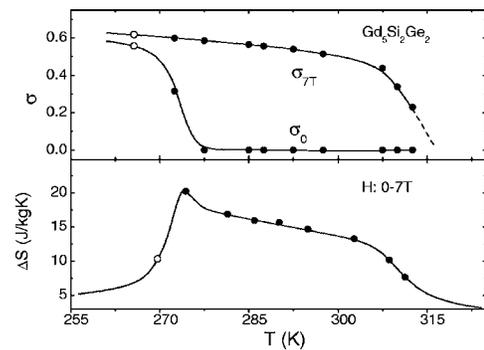


FIG. 2. (Top panel) Spontaneous magnetization for the  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  compound derived from the data in Ref. 11 and (bottom panel) corresponding entropy change.

of this relation. Deserving special attention is that  $\Delta S$  is not a simple magnetic entropy change, but a total one because of the simultaneous variation of magnetic order and crystal structure at the transition point.

The results in Fig. 3 indicate that the entropy change varies nonlinearly with magnetization. It is very sensitive to the change of magnetization when the system deviates from the fully spin-polarized state, as demonstrated by the rapid drop of  $\Delta S$  as  $\sigma$  reduces from 1, and relatively insensitive to  $\Delta\sigma$  when the system is at the nearly magnetically disordered state. This feature is also clear in Figs. 1(c) and 1(d) noticing that  $\Delta S_1 \gg \Delta S_2$  even if  $\Delta\sigma_1 \approx \Delta\sigma_2$ .

As mentioned above, a structural transition takes place accompanying the magnetic one in  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ . Extrapolating the  $\Delta S$ - $\sigma$  curve to  $\sigma=1$ , we obtained that the maximum  $\Delta S$  may significantly exceed theoretical limit  $Nk_B \ln(2J+1) \approx 90$  J/mol K, where  $k_B$  is the Boltzmann constant and  $N$  the number of spins. This suggests the presence of the contributions from lattice and electronic entropies, which, unfortunately, cannot be distinguished by the ordinary magnetic and calorimetric measurements. A theoretical calculation for the magnetic entropy change from a fully spin-polarized state to a magnetically disordered state is straightforward:  $\Delta S_M = Nk_B \ln(2J+1)$ . However, the same is difficult for a transition from a partially ordered to a partially disordered state. In the following we will estimate the magnetic entropy change based on the mean-field theory; its applicability is reasonable noting the localized magnetic moments of Gd in  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ .

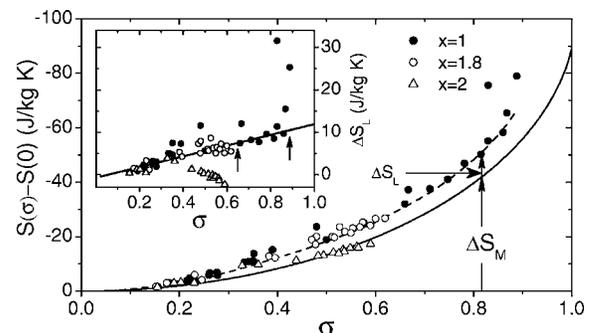


FIG. 3. Entropy changes against the reduced magnetization for the  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  family. Measured entropy changes are represented by symbols, while the theoretical results by a solid curve. Inset is a plot showing the difference between experimental and theoretical results. Solid and dashed lines are guides for the eye.

Based on the molecular field theory, the magnetic entropy change  $\Delta S_M$  will be

$$\Delta S_M = S_M(0) - S_M(\sigma) = Nk_B \left[ \ln(2J+1) - \ln \left( \frac{\sinh((2J+1)y/2J)}{\sinh(y/2J)} \right) + y\sigma \right], \quad (1)$$

where  $\sigma = B(y)$  is the Brillouin function with  $y = gJ\mu_B(H + \lambda\sigma)/k_B T$ ,  $\mu_B$ ,  $k_B$ , and  $g$  have the conventional meanings,  $J$  is the quantum number of spins, and  $N$  the number of Gd atoms in one mole of  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ . By fitting the saturation magnetization of  $\text{Gd}_5\text{Ge}_4$  to  $NgJ\mu_B$ ,  $J$  can be determined to be  $\sim 3.7$ .

Although Eq. (1) was obtained based on the molecular field assumption ( $H_{\text{eff}} \propto \sigma$ ), it is exactly true for any effective fields of the form  $H_{\text{eff}} \propto f(\sigma)$ , even for the case of a first-order transition, which can be realized by properly choosing  $f(\sigma)$ .<sup>15</sup>

From Fig. 3, it can be seen that the calculated  $\Delta S$ - $\sigma$  relation mimics the experimental one quite well in the whole  $\sigma$  range considered. The difference between the theoretical and experimental results is fairly small, and the typical difference is  $\sim 20\%$ , appearing at  $\sigma \approx 0.86$ . This result indicates that the main contributions to  $\Delta S$  come from the magnetic entropy.

However, differences between the two sets of data are also definite. The observed entropy change is larger than the magnetic one, and the deviation of the former from the latter increases nearly linearly with  $\sigma$  (inset in Fig. 3). This could be a signature for the entropy change in addition to the magnetic one noting the occurrence of structural transformation. It would be instructive to check to what extent the structure transition can affect the entropy of the compounds. As we know, for  $\text{Gd}_5\text{Ge}_4$  the latent heat of the field-induced structure transition at  $\sim 40$  K is  $\sim 646$  J/mol ( $\sim 600$  J/kg).<sup>16</sup> This implies that the lattice and/or electronic entropy changes will be  $\sim 16$  J/mol K considering the fact that the thermal effects due to the antiferromagnetic-ferromagnetic transition may be weak as follows from the work done for FeRh and  $\text{Eu}_{0.58}\text{Sr}_{0.42}\text{MnO}_3$ .<sup>17,18</sup> It is also known that volume change ( $\Delta V/V$ ) due to the structural transition is  $\sim 1.2\%$  for  $\text{Gd}_5\text{Ge}_4$  (Ref. 13 and  $\sim 0.6\%$  for  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ).<sup>19</sup>  $\Delta V/V$  could be  $\sim 0.9\%$  for  $\text{Gd}_5\text{SiGe}_3$  assuming a linear variation of it with  $x$ . As a result, the entropy change would be  $\sim 12$  J/mol K for  $x=1$  and  $\sim 8.8$  J/mol K for  $x=1.8$  when a simple linear variation of entropy change with volume change is adopted. (For  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ , a lattice entropy change of  $\sim 9.5$  J/mol K has been derived by Pecharsky *et al.*<sup>9</sup>) These values are in good agreement with the observed  $\sim 10.5$  and  $7.2$  J/mol K, which are the difference between the total and magnetic entropy changes near the Curie temperatures of  $\text{Gd}_5\text{SiGe}_3$  and  $\text{Gd}_5\text{Si}_{1.8}\text{Ge}_{2.2}$ , respectively (marked by arrows in the inset in Fig. 3).

To get the knowledge about the excessive entropy change, a further study on how it takes place may be helpful. If the phase transition merely modifies the density of free electrons, the change of electronic entropy will be  $2/3(\Delta V/V)\gamma T_C < 0.5$  J/mol K, where  $\gamma$  can be obtained by fitting the low-temperature heat capacity to  $\gamma T + \beta T^3$ . Its contribution is obviously unimportant because it is too small. Another effect of structural transition is the modification of

lattice vibration, and the resultant entropy change can be estimated based on the Debye approximation,

$$S_L(\Theta) = -3Nk_B \ln[1 - \exp(-\Theta/T)] + 12Nk_B \left( \frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^3 dx}{\exp(x) - 1}, \quad (2)$$

where  $N$  is the number of atoms per mole  $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$  and  $\Theta$  is the Debye temperature. We take  $\text{Gd}_5\text{SiGe}_3$  as an example since it gives the maximum entropy changes. According to Ref. 20, the Debye temperature is 121 K for  $\text{Gd}_5\text{Ge}_4$  and 241 K for  $\text{Gd}_5\text{Si}_4$ . It will be  $\sim 200$  K for  $\text{Gd}_5\text{SiGe}_3$  assuming a linear variation of  $\Theta$  with  $x$ . Variation of the Debye temperature due to the phase transition can be approximated by  $\Theta = \Theta_0(1 - \eta\Delta V/V)$ ,<sup>20</sup> where  $\eta$  is the Grüneisen parameter. Based on Eq. (2), it is easy to obtain that  $S_L(\Theta) - S_L(\Theta_0) \approx 8$  J/mol K if  $\eta=7$ ,  $\Delta V/V \approx 0.9\%$ , and  $T = T_c = 140$  K are adopted.  $\eta=7$  is somewhat large but still acceptable (generally  $\eta$  will take a value between 1 and 3 for solid materials<sup>21</sup>). This result indicates that modified lattice vibration can effectively cause an additional entropy change the same order as that observed.

This work has been supported by the National Natural Science Foundation of China and the National Basic Research of China.

<sup>1</sup>V. K. Pecharsky and K. A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997); V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

<sup>2</sup>V. K. Pecharsky and K. A. Gschneidner, Jr., *Advances in Cryogenic Engineering*, edited by P. Kittel (Plenum, New York, 1998), Vol. 43, p. 1729.

<sup>3</sup>F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Chen, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).

<sup>4</sup>H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).

<sup>5</sup>O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).

<sup>6</sup>S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).

<sup>7</sup>S. Gama, A. B. Coelho, A. de Campos, A. M. G. Carvalho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004).

<sup>8</sup>V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, Jr., and R. Rink, Phys. Rev. Lett. **91**, 197204 (2003).

<sup>9</sup>V. K. Pecharsky and K. A. Gschneidner, Jr., *Magnetism and Structure in Functional Materials*, edited by A. Planes, L. Mañosa, and A. Saxena (Springer, Heidelberg, 2005), Vol. 19, Chap. 11, p. 199.

<sup>10</sup>L. Morellon, Z. Arnold, C. Magen, C. Ritter, O. Prokhnenko, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, Phys. Rev. Lett. **93**, 137201 (2004).

<sup>11</sup>A. Gigurè, M. Foldeaki, B. Ravi Gopal, R. Chahine, T. K. Bose, A. Frydman, and J. A. Barclay, Phys. Rev. Lett. **83**, 2262 (1999).

<sup>12</sup>F. Casanova, X. Batlle, A. Labarta, J. Marcos, L. Mañosa, and A. Plaes, Phys. Rev. B **66**, 100401 (2002).

<sup>13</sup>Y. Mudryk, A. P. Holm, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **72**, 064442 (2005).

<sup>14</sup>Although the quantum number of the spins is  $J=3.5$  for Gd, the experimentally observed saturation magnetization is  $7.4-7.6\mu_B/\text{Gd}$ .

<sup>15</sup>C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962).

<sup>16</sup>F. Casanova, A. Labarta, and X. Batlle, Phys. Rev. B **72**, 172402 (2005).

<sup>17</sup>M. P. Annaorazov, S. A. Nikitin, A. L. Tyurin, K. A. Asatryan, and A. Kh. Dovletov, J. Appl. Phys. **79**, 1689 (1996).

<sup>18</sup>G. J. Liu, J. R. Sun, Y. W. Xie, D. J. Wang, C. M. Xiong, H. W. Zhang, T. Y. Zhao, and B. G. Shen, Appl. Phys. Lett. **87**, 182502 (2005).

<sup>19</sup>C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, Z. Arnold, J. Kamarad, T. A. Lograsso, D. L. Schlagel, V. K. Pecharsky, A. O. Tsokol, and K. A. Gschneidner, Jr., Phys. Rev. B **72**, 024416 (2005).

<sup>20</sup>P. J. von Ranke, N. A. de Oliveira, C. Mello, A. Magnus, G. Carvalho, and S. Gama, Phys. Rev. B **71**, 054410 (2005).

<sup>21</sup>C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).