Scaling of the entropy change at the magnetoelastic transition in $Gd_5(Si_xGe_{1-x})_4$

Fèlix Casanova, Xavier Batlle,* and Amílcar Labarta
Departament de Física Fonamental, Universitat de Barcelona, Av. Diagonal 647, 08028-Barcelona, Catalonia, Spain

Jordi Marcos, Lluís Mañosa, and Antoni Planes
Departament d'Estructura i Constituents de la Matèria, Universitat de Barcelona, Av. Diagonal 647, 08028-Barcelona, Catalonia, Spain

Differential scanning calorimetry under a magnetic field H has been used to measure the entropy change ΔS at the magnetoelastic transition in $Gd_5(Si_xGe_{1-x})_4$ alloys, for $x \leq 0.5$. We show that ΔS scales with the transition temperature, T_t, which is tuned by x and H, from 70 to 310 K. Such a scaling demonstrates that T_t is the relevant parameter in determining the giant magnetocaloric effect in these alloys, and proves that the magnetovolume effects due to H are of the same nature as the volume effects caused by substitution.

The magnetocaloric effect (MCE) has been studied for decades owing to its potential application to magnetic refrigerants.[1] The MCE is the isothermal entropy change or the adiabatic temperature change arising from the application or removal of a magnetic field H on a system with magnetic degrees of freedom. Many efforts have been devoted to the analysis of the MCE both in the vicinity of second-order magnetic phase transitions, where Gd is the element that shows the largest effect close to room temperature,[1,2] and in order-disorder blocking processes, e.g., in molecular magnets.[3] However, the MCE may be maximized in the vicinity of a first-order magnetoelastic phase transition, when the crystallographic transformation is field induced, resulting in an additional contribution to the entropy change[4,1]: a giant MCE has been discovered in the $Gd_5(Si_xGe_{1-x})_4$ compounds with $x \leq 0.5$,[5–7] and recently in MnAs-based materials.[8,9]

This paper is aimed at studying the entropy change ΔS associated with the first-order magnetoelastic phase transition in $Gd_5(Si_xGe_{1-x})_4$ alloys, which has lately aroused much discussion.[5,10–13] Two compositional ranges are of interest. For $0.24 \leq x \leq 0.5$, the giant MCE is related to a first-order magnetoelastic phase transition from a high-temperature paramagnetic (PM), monoclinic phase ($P112_1/a$) to a low-temperature ferromagnetic (FM), Gd_5Si_4-type orthorombic-I phase ($Pnma$), at temperatures ranging from 130 K ($x=0.24$) to 276 K ($x=0.5$).[6,14] The structural transition occurs by a shear mechanism[15] and yields a large volume contraction. The field-induced, reversible nature of the magnetostructural transition then results in strong magnetostriction[14] and giant (negative) magnetoresistance.[16] For $x \leq 0.2$, a second-order PM-to-antiferromagnetic (AFM) transition occurs at T_N (from $\sim$125 K for $x=0$ to $\sim$135 K for $x=0.2$).[6] Upon further cooling, a first-order AFM-FM transition takes place, whose temperature ranges linearly from about 20 K ($x=0$) to 120 K ($x=0.2$). MCE is related to such a first-order phase transition. The nature of the AFM phase is currently under discussion,[17] and the magnetic structure may correspond to that of either a canted ferrimagnet, as proposed for Nd_5Ge_4 (Ref. 18) or a canted antiferromagnet, as for the Ge-rich region of the $Tb_5(Si_xGe_{1-x})_4$ alloys.[19,20] The AFM-FM tran-

sition occurs simultaneously with a first-order structural transition from a high-temperature Gd_5Ge_4-type orthorombic-II phase to the low-temperature orthorombic-I phase, a large volume contraction also taking place. No structural anomalies are detected at the second-order PM-AFM transition.[17] In the intermediate range $0.2 < x < 0.24$, orthorombic-II and monoclinic structures coexist.[7]

Differential scanning calorimetry (DSC) is the most suitable method to obtain the latent heat and entropy change at a first-order phase transition.[21] In contrast, quasiadiabatic calorimetry, commonly used for the study of the MCE,[22] is designed to measure the heat capacity C_p. However, at a first-order phase transition, the experimental determination of C_p is intrinsically uncertain due to the release of latent heat.[23] DSC under H is thus expected to be the ideal technique for the study of ΔS at first-order magnetoelastic transitions. We have developed a high-sensitivity DSC with built-in H. In this paper, the calorimetric measurement of ΔS as a function of T and H is reported for $Gd_5(Si_xGe_{1-x})_4$ alloys. A ΔS scaling plot is obtained, where the scaling variable T_t is the temperature of the first-order magnetoelastic phase transition. As T_t is shifted with x and H, the scaling of ΔS thus summarizes the giant MCE in the $Gd_5(Si_xGe_{1-x})_4$ alloys. We also unambiguously show that calorimetric values of ΔS are in agreement with the indirect calculation obtained from the magnetization curves $M(H)$, using the Clausius-Clapeyron equation.[10,24]

$Gd_5(Si_xGe_{1-x})_4$ alloys with $x=0.1$, 0.18, 0.2, 0.25, 0.3, 0.365, and 0.45 were prepared by arc melting admixtures of the pure elements in the desired stoichiometry under an argon atmosphere. As-cast buttons were cut into slices, and some were thermally treated for four hours at 950 °C under a 10^{-5}-torr vacuum. The quality of the samples and their crystallographic structure were studied by room-temperature x-ray diffraction. ac susceptibility (77–300 K, $\nu = 111$–3330 Hz, $H_{ac} = 1.25$ Oe) was used to check that the temperatures of the first- and second-order phase transitions were in agreement with values in the literature.[6,7,17] $M(H)$ curves were recorded up to 230 kOe for $x=0.18$ and 0.45, both in increasing and decreasing H, from 4.2 to 310 K with a temperature step of 3 K. Calorimetric measurements were performed using two high-sensitivity differential scanning
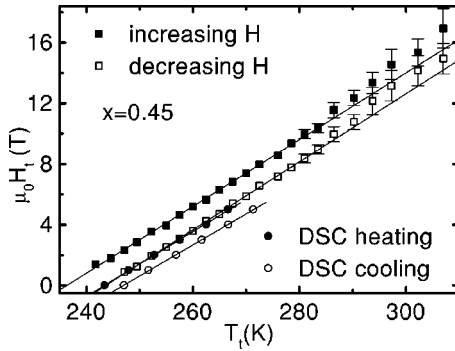
FIG. 1. Transition field H_t plotted as a function of the transition temperature T_t for $x=0.45$, obtained from $M(H)$ (increasing and decreasing H) and DSC data (cooling and heating). Solid lines are linear fits to experimental data.

calorimeters, specifically designed to study solid-solid phase transitions. Heating and cooling runs were performed within 77–350 K for $H=0$ in a LN$_2$ cryostat, and within 4.2–300 K under fields up to 50 kOe in a LHe cryostat. The calorimeter with built-in H furnishes a sensitivity ~ 10 times larger at room temperature than that for a conventional DSC, while a reasonably high value is obtained at low T. Neither the thermometry nor the heat flow sensors are affected by H. Data do not depend on the cooling/heating rate. The upper limit of the operating range is 5 K/min. A detailed description will be published elsewhere.[25]

The measured $M(H)$ isotherms for $x=0.45$ were similar to those previously reported[5,10] for $x=0.5$. The field-induced, first-order nature of the magnetoelastic PM-FM transition was evident from the data. It is worth noting that application of a field of 230 kOe shifts T_t by an amount of ~ 80 K. From the $M(H)$ curves a transition field H_t is defined at each T as the inflection point of the curve. The temperature dependence of H_t is shown in Fig. 1, for measurements under increasing and decreasing H. A linear relation between H_t and T_t is obtained, which yields $dT_t/d(\mu_0 H_t) = 4.5 \pm 0.2$ K/T.

DSC data for $x=0.18$ (Fig. 2) also reveal the first-order nature of the low-temperature AFM-FM transition and the second-order nature of the high-temperature PM-AFM transition. The first-order transition shows (i) a large peak in $\dot{Q}/\dot{T} \equiv dQ/dT$, where $\dot{Q}$ is the recorded heat flow and $\dot{T}$ is the heating/cooling rate; (ii) a hysteresis of 2–3 K between cooling and heating; and (iii) a significant field dependence of T_t, which is estimated as the temperature at the maximum of the peak. The calorimetric data enable us to confirm the linear relation between H_t and T_t, which is plotted in Fig. 1 for $x=0.45$, and yields $dT_t/d(\mu_0 H_t) = 4.8 \pm 0.1$ K/T. A slight difference (~ 5 K) in the determination of the zero-field transition temperature $T_t(H=0)$ from $M(H)$ and DSC curves is found, due to the use of different experimental devices. These values are in good agreement with those reported for $x=0.45$, $dT_t/d(\mu_0 H_t) = 4.5$ K/T (Ref. 14), and $x=0.43$, $dT_t/d(\mu_0 H_t) = 4.3$ K/T.[6] A linear $H_t(T_t)$ behavior is found for the other compositions, and the slopes are also
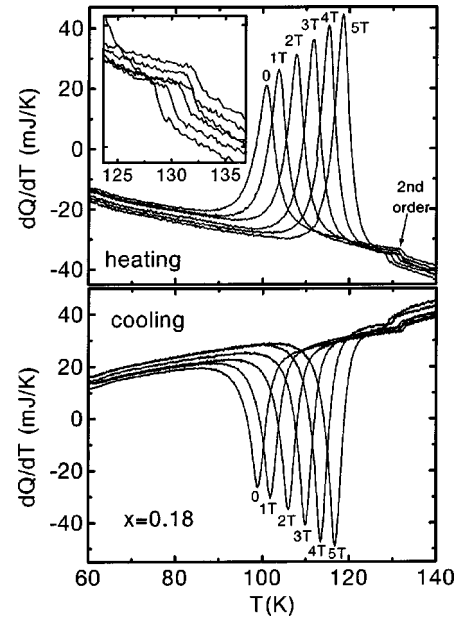

FIG. 2. DSC data for $x=0.18$ on heating and cooling the sample under H. Inset: details of the second-order transition on heating, from 0 (top) to 5 T (bottom).

consistent with published values.[26,17] The second-order transition is observed in DSC as a small λ-type jump in the dQ/dT baseline (Fig. 2, inset). Although DSC does not give the absolute value of C_p, the extrapolation at T_t of the baselines at temperatures above and below the first-order transition provides a good estimation of ΔC_p. It is found that ΔC_p is positive for the first-order AFM-FM transition for all compositions with $x \leqslant 0.2$ [see Fig. 3(a) for $x=0.1$], while a negative ΔC_p is obtained for the first-order PM-FM transition for $0.24 \leqslant x \leqslant 0.5$ [see Fig. 3(b) for $x=0.3$].

The absolute value of ΔS as a function of T_t is shown in Fig. 4. As T_t corresponds to the transition temperature of the first-order phase transition for each x and H, this allows us to sweep T_t from ~ 70 to ~ 310 K. ΔS was calculated as follows: (i) At $H=0$ (LN$_2$ cryostat) and up to 50 kOe (LHe cryostat), by numerical integration of $(dQ/dT)/T$ throughout the first-order calorimetric peaks[27]; and (ii) indirect ΔS evaluation from the $M(H)$ isotherms up to 230 kOe for $x=0.45$ and 0.18, using the Clausius-Clapeyron equation at a
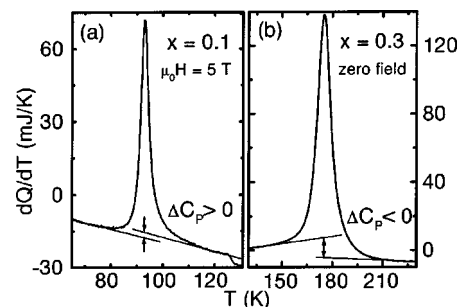

FIG. 3. DSC data for (a) $x=0.1$ on heating the sample with $\mu_0 H = 5$ T and (b) $x=0.3$ on heating the sample without applied field. The opposite sign of ΔC_p for the two compositions is shown.
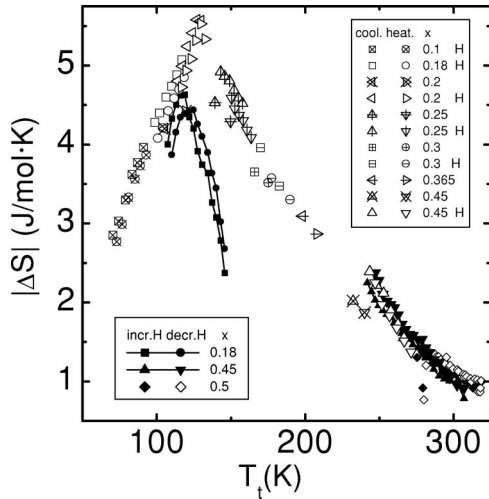
FIG. 4. Scaling of $|\Delta S|$ at the first-order transition for the Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ alloys. A variety of applied fields and compositions are represented. Connected symbols correspond to values obtained from $M(H)$. Solid and open diamonds are from Ref. 10. Symbols labeled/not labeled with an H correspond respectively to measurements with the LHe (under H)/$LN_2(H=0)$ DSC.

constant pressure, $\Delta S = -\Delta M(dH_t/dT_t)$.^{24,10} ΔM is determined from the magnetization jump at the transition. ΔS from the Clausius-Clapeyron equation reported by Giguère *et al.* for $x=0.5$, and obtained up to 70 kOe (see Fig. 2 in Ref. 10), is also displayed in Fig. 4. As T_t is tuned by both x and H, $|\Delta S|$ values scale with T_t. This enables us to derive a scaling of $|\Delta S|$ for all T_t, i.e., for all compositions with $x \leq 0.5$. The values given in Ref. 10 also collapse onto this scaling plot. This shows that the relevant parameter in determining $|\Delta S|$ is T_t. In addition, the scaling is not a trivial consequence of the scaling of both ΔM and dH_t/dT_t, i.e., neither ΔM nor dH_t/dT_t scale with T_t, which gives further relevance to the scaling of $|\Delta S|$. Notice also that $|\Delta S|$ extrapolates to zero at $T_t=0$, as expected from the third law of thermodynamics. The scaling is a consequence of the first-order nature of the transition: at a constant H, the Clausius-Clapeyron equation is written as $\Delta S = \Delta V(dP_t/dT_t)$, where ΔV stands for the volume jump and P_t for the transition pressure. Therefore, ΔV and ΔM are related as $\Delta V/\Delta M = -dH_t/dP_t$, and the scaling thus shows the equivalence of magnetovolume and substitution-related effects.

It is worth stressing that ΔS obtained from DSC measurements and from the Clausius-Clapeyron equation are coincident within the experimental error, for $x=0.45$ and 0.5, and for $x=0.18$ in the temperature range where the AFM-FM transformation takes place. This shows that ΔS obtained from the Clausius-Clapeyron equation provides an excellent evaluation of the total entropy change at the first-order magnetoelastic transition. A comparision of ΔS to the entropy change obtained through the Maxwell relation$^{10-13}$ was discussed elsewhere.^{28}

Two diferent trends are shown in Fig. 4. For $0.24 \leq x \leq 0.5$, $|\Delta S|$ associated with the PM-FM transition monotonically decreases with T_t, which is consistent with (i) $\Delta C_p < 0$ [Fig. 3 (b)], as expected from the thermodynamic rela-

tion $d(\Delta S)/dT = \Delta C_p/T$; and (ii) ΔM decreasing monotonically with T. Moreover, negative ΔC_p may also be estimated from Ref. 26. In contrast, for $x \leq 0.2$, $|\Delta S|$ either decreases or increases, depending on T_t. Due to the magnetoelastic coupling, the application of H shifts T_t, so that it is possible to observe both the AFM-FM transition at T_t and, at high enough H, a PM-FM transition, when $T_t(H) \geq T_N$. The latter transition is still first-order due to the crystallographic transformation and arises from the PM-AFM transition. For the AFM-FM transition, $|\Delta S|$ increases monotonically with T_t, in agreement with $\Delta C_p > 0$ [Fig. 3(a) and Ref. 26]. However, for the PM-FM transition, $|\Delta S|$ decreases with T_t for $x = 0.18$ and $x=0.2$, in agreement with (i) $\Delta C_p < 0$ [similar to Fig. 3(b)] and (ii) ΔM decreasing monotonically with T.

Consequently, $|\Delta S|$ is maximum for each composition at $T_t = T_N$, i.e., when, in the FM phase, the applied H is large enough to shift the first-order transition to overlap to the second-order transition at T_N. Therefore, the largest value $|\Delta S| = 5.58$ J/(mol K) occurs at $T_t \approx 131$ K [$\sim$ the highest value of T_N, which corresponds to $x=0.2$ (Ref. 6)]. All the foregoing suggests that $|\Delta S|$, and thus the MCE, will be maximum within the compositional range $0.2 < x < 0.24$, where the different crystallographic and magnetic phases coexist, and the two branches of $|\Delta S|$ join (Fig. 4). Finally, it seems that the slopes $d(|\Delta S|)/dT_t$ for the PM-FM transition for $x=0.18$ and that for $0.24 \leq x \leq 0.5$ are different. We argue that this is due to the high-temperature crystallographic phase being different (orthorombic-II and monoclinic phases, respectively, for $x=0.18$ and $0.24 \leq x \leq 0.5$).

In conclusion, DSC under H has been used successfully to measure the entropy change at the first-order magnetoelastic phase transition for Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$, $x \leq 0.5$. We have shown that the transition entropy change scales with T_t and it is in good agreement with the indirect measurements through the Clausius-Clapeyron equation. This is relevant for an understanding of the thermodynamics of first-order magnetoelastic transitions. The scaling of ΔS is a direct consequence of the fact that T_t is tuned by x and H and it is thus expected to be universal for any material showing strong magnetoelastic effects, yielding a field-induced nature of the transition. ΔS is expected to (i) go to zero at zero temperature, (ii) tend asymptotically to zero at high temperature since the latent heat is finite, and (iii) display a maximum at that temperature for which both ΔM is maximized and T_t shows the minimum field dependence. The specific shape of ΔS vs T_t will depend on the details of the phase diagram, $T_t(x)$. Finally, the scaling of ΔS proves that the magnetovolume effects due to H are of the same nature as the volume effects caused by substitution.

*Electronic address: xavier@ffn.ub.es

[1] V.K. Pecharsky and K.A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).

[2] S.Y. Dan'kov, A.M. Tishin, V.K. Pecharsky, and K.A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).

[3] F. Torres, J.M. Hernández, X. Bohigas, and J. Tejada, Appl. Phys. Lett. **77**, 3248 (2001).

[4] A. M. Tishin, in *Handbook of Magnetic Materials*, edited by K.H.J. Buschow (North-Holland, Amsterdam, 1999), vol. 12, pp. 395–524.

[5] V.K. Pecharsky and K.A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).

[6] V.K. Pecharsky and K.A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997).

[7] V.K. Pecharsky and K.A. Gschneidner, Jr., J. Alloys Compd. **260**, 98 (1997).

[8] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).

[9] O. Tegus, E. Brück, K.H.J. Buschow, and F.R. de Boer, Nature (London) **415**, 450 (2002).

[10] A. Giguère, M. Földeàki, B. Ravi Gopal, R. Chahine, T.K. Bose, A. Frydman, and J.A. Barclay, Phys. Rev. Lett. **83**, 2262 (1999).

[11] K.A. Gschneidner, Jr., V.K. Pecharsky, E. Brück, H.G.M. Duijn, and E. Levin, Phys. Rev. Lett. **85**, 4190 (2000).

[12] J.R. Sun, F.X. Hu, and B.G. Shen, Phys. Rev. Lett. **85**, 4191 (2000).

[13] M. Földeàki, R. Chahine, T.K. Bose, and J.A. Barclay, Phys. Rev. Lett. **85**, 4192 (2000).

[14] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. García-Landa, Z. Arnold, and F. Albertini, Phys. Rev. B **58**, R14 721 (1998).

[15] W. Choe, V.K. Pecharsky, A.O. Pecharsky, K.A. Gschneidner, Jr., V.G. Young, Jr., and G.J. Miller, Phys. Rev. Lett. **84**, 4617 (2000).

[16] L. Morellon, J. Stankiewicz, B. García-Landa, P.A. Algarabel, and M.R. Ibarra, Appl. Phys. Lett. **73**, 3462 (1998).

[17] L. Morellon, J. Blasco, P.A. Algarabel, and M.R. Ibarra, Phys. Rev. B **62**, 1022 (2000).

[18] P. Schobinger-Papamantellos and A. Niggli, J. Phys. Chem. Solids **42**, 583 (1981).

[19] P. Schobinger-Papamantellos, J. Phys. Chem. Solids **39**, 197 (1978).

[20] C. Ritter, L. Morellon, P.A. Algarabel, C. Magen, and M.R. Ibarra, Appl. Phys. Lett. **73**, 3462 (2002).

[21] W. Hemminger and G. Höhne, *Calorimetry. Fundamentals and Practice* (Verlag Chemie, Weinheim, 1984).

[22] V.K. Pecharsky, J.O. Moorman, and K.A. Gschneidner, Jr., Rev. Sci. Instrum. **68**, 4196 (1997).

[23] V.K. Pecharsky and K.A. Gschneidner, Jr., J. Appl. Phys. **86**, 6315 (1999).

[24] A.J.P. Meyer and P. Tanglang, J. Phys. Radium **14**, 82 (1953).

[25] J. Marcos, F. Casanova, X. Batlle, A. Labarta, A. Planes, and Ll. Mañosa (unpublished).

[26] V.K. Pecharsky and K.A. Gschneidner, Jr., Adv. Cryog. Eng. **43**, 1729 (1998).

[27] This procedure gives reliable values for ΔS in first-order phase transitions. See, for instance, J. Ortín and A. Planes, Acta Metall. **36**, 1873 (1988).

[28] F. Casanova, X. Batlle, A. Labarta, J. Marcos, Ll. Mañosa, and A. Planes, Phys. Rev. B **66**, 100401(R) (2002).