Chapter 6

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

6.1 Introduction

This chapter is aimed at studying the entropy change associated with the first-order magnetostructural phase transition, ΔS, in $Gd_5(Si_xGe_{1-x})_4$ alloys, as a function of both composition, x, and type of magnetic phase transition, *i.e.*, as a function of the phase diagram. The calorimetric measurements of ΔS as a function of T and H are analysed for $Gd_5(Si_xGe_{1-x})_4$ alloys, within the whole $0 \leq x \leq 0.5$ range. A ΔS scaling plot is obtained, where the scaling variable, T_t, is the temperature of the first-order magnetostructural phase transition. As T_t is shifted with x and H, the scaling of ΔS thus summarises the giant MCE in the $Gd_5(Si_xGe_{1-x})_4$ alloys.

6.2 Calorimetric measurements

As detailed in Chapter 4, DSC under H is the ideal technique for the study of ΔS at first-order magnetostructural transitions. Calorimetric measurements were performed using two high-sensitivity differential scanning 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 with the calorimeter described in section 3.2.3, and within 4.2-300 K under fields up to 5 T in a LHe cryostat with the calorimeter with built-in H described in Chapter 4.

				T_t (K)		ΔS (J/kgK)	
x	ID	Heat T.	$\mu_0 H$(T)	cool.	heat.	cooling	heating
0	#1	NO	0	-	-	-	-
			1	23.3	28.5	-6.55	7.12
			2	33.2	36.3	-15.06	14.74
			3	40.4	42.9	-21.20	21.26
			4	46.6	48.7	-24.59	23.94
			5	51.2	53.7	-28.81	28.89
0.05	#1	T4+Q	0	43.8	46.5	-14.57	14.29
			1	49.4	51.7	-18.11	17.95
			2	55.1	57.1	-23.04	22.00
			3	60.2	62.1	-25.92	24.59
			4	65.0	66.6	-27.86	26.77
			5	69.1	70.8	-28.32	26.76
0.1	#1	NO	0	70.4	73.1	-24.22	23.52
			1	74.2	76.7	-25.74	25.41
			2	78.9	81.1	-28.03	28.27
			3	83.2	85.4	-30.75	30.26
			4	86.9	89.0	-32.05	31.70
			5	91.0	92.9	-33.65	32.86
0.18	#1	T4	0	98.7	100.9	-36.87	35.12
			1	101.9	104.1	-37.89	36.23
			2	106.1	107.8	-39.62	38.11
			3	110.0	111.8	-40.81	39.47
			4	113.5	115.2	-42.06	40.44
			5	116.8	118.5	-43.70	41.75
0.2	#1	NO	0	113.9	116.6	-41.51	40.83
			1	117.1	119.6	-43.15	42.64
			2	120.6	123.3	-45.31	43.92
			3	124.0	126.4	-46.78	45.97
			4	127.1	129.7	-48.22	47.77
			5	129.6	132.5	-48.12	46.01

x	ID	Heat T.	$\mu_0 H$(T)	T_t (K) cool.	heat.	ΔS (J/kgK) cooling	heating
0.25	#2	NO	0	143.0	150.5	-42.88	39.98
			1	145.7	152.6	-42.38	38.82
			2	149.1	155.4	-41.90	38.09
			3	152.0	158.3	-40.86	37.53
			4	155.0	160.8	-39.42	35.64
			5	157.8	163.6	-39.42	35.64
0.3	#2	NO	0	169.7	177.5	-36.16	32.97
			1	172.2	179.2	-35.50	32.39
			2	175.2	182.4	-34.55	31.34
			3	177.8	185.4	-33.85	30.66
			4	180.4	188.6	-32.89	29.75
			5	182.4	189.9	-31.89	28.66
0.365	#3	NO	0	200.7	204.5	-29.90	28.78
			1	207.4	211.0	-29.38	28.35
			2	211.6	214.9	-28.61	27.64
			3	215.1	219.2	-27.27	26.04
			4	218.6	222.0	-26.51	25.00
			5	221.8	226.7	-25.93	24.48
0.45	#7	T4	0	243.5	247.1	-21.58	20.30
			1	248.0	251.7	-20.02	17.82
			2	252.8	256.9	-19.11	16.54
			3	257.6	261.7	-17.11	15.16
			4	262.5	266.7	-15.58	13.64
			5	266.6	271.4	-14.01	12.40

Table 6.1: Entropy change and T_t at the first-order transition obtained from DSC under magnetic field in all measured samples, on cooling and heating.

We measured $Gd_5(Si_xGe_{1-x})_4$ samples with x= 0, 0.05, 0.1, 0.18, 0.2, 0.25, 0.3, 0.365 and 0.45, using both calorimeters. For x=0, 0.05, 0.1 and 0.18, the DSC operating with LN_2 cannot reach their transition temperature. Calorimetric curves under magnetic field are described in section 5.3 and shown in Figs. 5.5, 5.6 and 5.7. ΔS was calculated by numerical integration of $(dQ/dT)/T$ throughout the first-order calorimetric peaks [1]. The results of ΔS and T_t (which is evaluated as the temperature at the maximum of the dQ/dT peak) are displayed in Table 6.1 as a function of x and H for the calorimeter with built-in H, and also in Table 3.4 (Chapter 3) for the calorimeter operating with LN_2.

Other relevant information can be obtained from the DSC curves, appart from the latent heat and transition entropy change: although DSC does not give the absolute value of C_p, the extrapolation to 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 $x \leq 0.2$ (see Fig. 6.1 (a) for x=0.1), while negative ΔC_p is obtained for the first-order PM-FM transition for $0.24 \leq x \leq 0.5$ (see Fig. 6.1 (b) for x=0.3). The case x=0.2 is very interesting (Fig. 6.1 (c)), since the first-order peak overlaps the second-order one for a high enough field (~3 T). For this reason, a change in the sign of ΔC_p is observed in this sample.

6.3 Scaling of the transition entropy change

The absolute value of ΔS as a function of T_t is shown in Fig. 6.2. 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 ~20 to ~310 K. ΔS from the Clausius-Clapeyron equation [$\Delta S = -\Delta M(dH_t/dT_t)$] reported by Giguère *et al.* for x=0.5, and obtained up to 7 T (see Fig. 2 in Ref. [2]), is also displayed in Fig. 6.2. 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. [2] also collapse onto this scaling plot. Values for x=0 are not included, since Gd_5Ge_4 alloy presents an irreversible transition which makes it different from the rest of $Gd_5(Si_xGe_{1-x})_4$ alloys (section 2.4.1 and Refs. [3, 4, 5]). This scaling shows that the relevant parameter in determining $|\Delta S|$ is T_t. Besides, 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[1], 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 proves that the magnetovolume effects due to H are of the same nature as the volume effects caused by substitution.

Two diferent trends are shown in Fig. 6.2. For $0.24 \leq x \leq 0.5$, $|\Delta S|$ associated with the PM/M-FM/$O(I)$ transition monotonically decreases with T_t, which is consistent with $\Delta C_p < 0$ (Fig. 6.1 (b)), as expected from the thermodynamic relation $d(\Delta S)/dT = \Delta C_p/T$. Moreover, negative ΔC_p may also be estimated from Ref. [6]. In contrast, for $x \leq 0.2$, $|\Delta S|$ either decreases or increases depending on

[1] ΔM always decreases with T_t and dH_t/dT_t presents a particular behaviour which is studied in detail in Chapter 7.

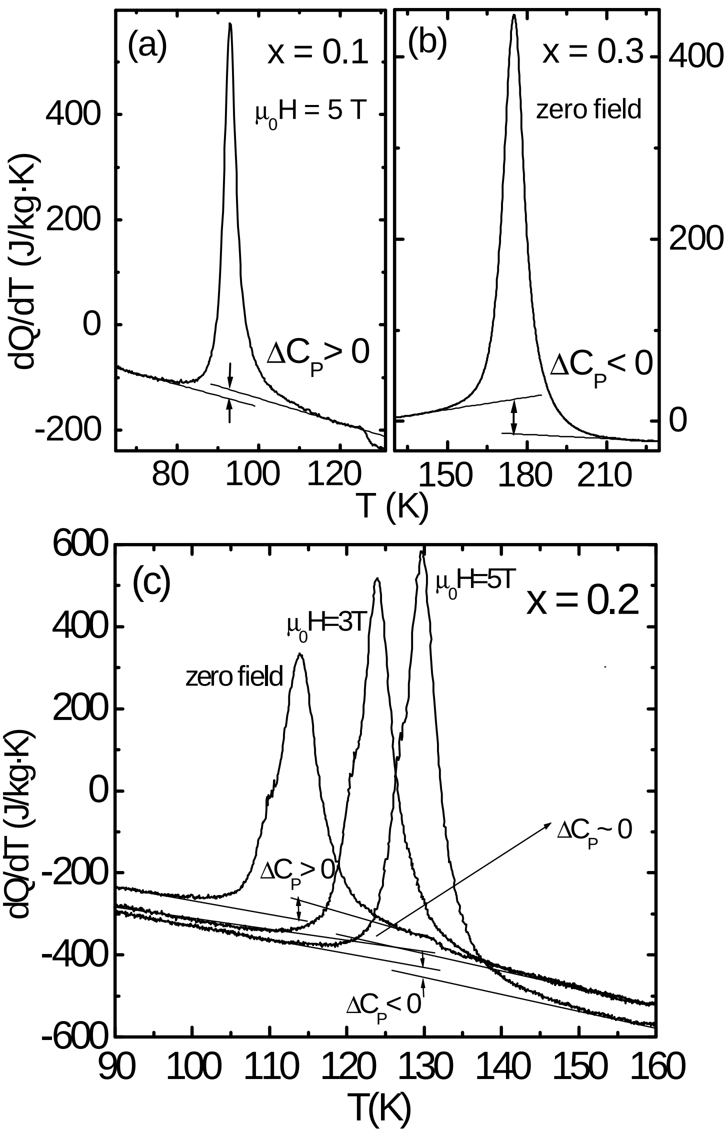

Figure 6.1: DSC data for (a) x=0.1 on heating the sample with $\mu_0 H$=5 T and (b) x=0.3 on heating the sample without applied field. The opposite sign of ΔC_p for the two compositions is shown. DSC data for x=0.2 at different applied fields on cooling is also shown in (c), where the change of the sign of ΔC_p is observed for a same sample. For the sake of clarity, the latter dQ/dT data have the opposite sign than the same data in Fig. 5.5, to enable a comparison with (a) and (b) heating runs.

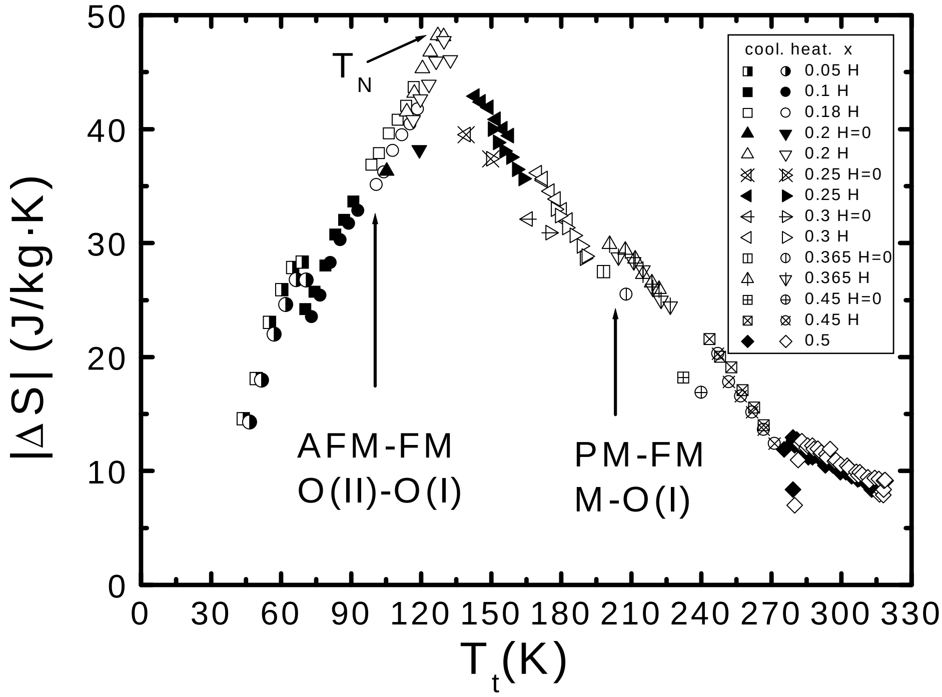

Figure 6.2: Scaling of $|\Delta S|$ at the first-order transition for the $Gd_5(Si_xGe_{1-x})_4$ alloys. A variety of applied fields and compositions are represented. Solid and open diamonds are from Ref. [2]. Symbols labeled with an H/H=0 correspond respectively to measurements with the LHe (under H)/LN_2(H=0) DSC.

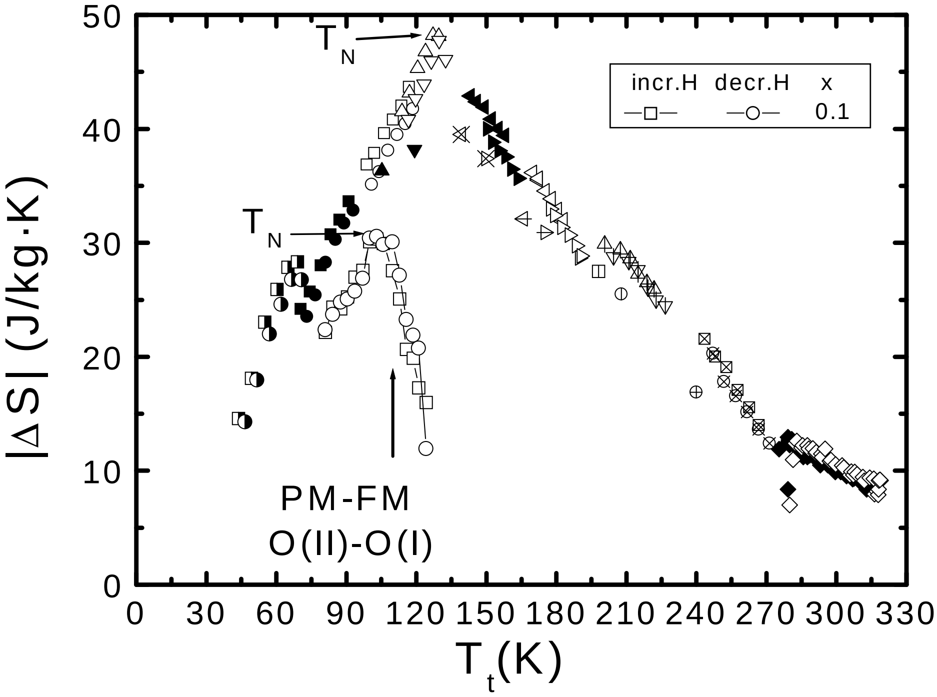

Figure 6.3: Scaling of $|\Delta S|$ at the first-order transition for the $Gd_5(Si_xGe_{1-x})_4$ alloys. Values obtained from $M(H)$ up to 23 T for x=0.1 have been added with respect to Fig. 6.2.

T_t. Due to the magnetoelastic coupling, the application of H shifts T_t, so that it is possible to observe both the AFM/$O(II)$-FM/$O(I)$ transition at T_t and, at high enough H, a PM/$O(II)$-FM/$O(I)$ 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/$O(II)$-FM/$O(I)$ transition, $|\Delta S|$ increases monotonically with T_t, in agreement with $\Delta C_p > 0$ (Figs. 6.1 (a), (c) and Ref. [6]). However, for the PM/$O(II)$-FM/$O(I)$ transition, $|\Delta S|$ decreases with T_t for x=0.2, in agreement with $\Delta C_p < 0$ (Fig. 6.1 (c)). Since in calorimetric ΔS measurements only a field of up to 5 T may be applied, ΔS values obtained from magnetisation up to 23 T by using the Clausius-Clapeyron equation have been added in Fig. 6.3. Then, the evolution of ΔS in the PM/$O(II)$-FM/$O(I)$ transition is clearly observed. The magnetisation measurements are detailed in section 5.2. For the sake of clarity, only values for x=0.1 are shown in Fig. 6.3, but all samples with $x \leq 0.2$ present the same behaviour. The slight difference between calorimetric and magnetic ΔS values in these samples, as also seen for x=0 and 0.05 in Fig. 5.9, may be related to the fact that the transition is induced in different directions of the phase diagram (see Chapter 9).

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 (labeled in Figs. 6.2 and 6.3). Therefore, the largest value $|\Delta S|$=48.22 J/(kgK) occurs at T_t ≈130 K (∼ the highest value of T_N, which corresponds to x=0.2 [7]). All the foregoing suggests that $|\Delta S|$, and thus 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 (Figs. 6.2 and 6.3).

6.4 Conclusions

DSC under H has been used successfully to measure the entropy change at the first-order magnetostructural phase transition for $Gd_5(Si_xGe_{1-x})_4$, $x \leq 0.5$. We have shown that the transition entropy change scales with T_t. 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 maximised 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 shows the equivalence of magnetovolume and substitution-related effects in $Gd_5(Si_xGe_{1-x})_4$ alloys.

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