Phase Control studies in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ Giant Magnetocaloric Compound

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Abstract

A systematic set of annealings on arc-melted synthesized $\text{Gd}_5\text{Si}_2\text{Ge}_2$ sample was performed. Through powder x-ray diffraction (XRD) and magnetometry measurements we monitored the effect of varying the annealing time with constant temperature ($T = 1473\text{K}$) on the formation of the Monoclinic (M) crystallographic phase fraction, which is the one responsible for the Giant Magnetocaloric Effect (GMCE) in this compound. The conversion of the Orthorhombic $O(I)$ crystallographic phase into M was achieved, resulting in a significant increase of the M mass fraction. Such conversion led to a change in the magnetic transition nature, evolving from a second to a first order transition for the as-cast and annealed samples, respectively. An optimal annealing time range for the M phase conversion was identified to be within 80 - 120 minutes at $T = 1473\text{ K}$ followed by a rapid quenching to liquid N_2 . Furthermore, an increase up to $\sim 50\%$ of the magnetocaloric effect was obtained for the sample annealed during 120 minutes.

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I. INTRODUCTION

Room temperature magnetic refrigeration has been a challenge for the material scientists community for several years. Recently, a major step was achieved with the discovery of the Giant Magnetocaloric Effect (GMCE) near room temperature (RT) on the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound [1]. Furthermore, in the last decade an intense effort has been developed into the fabrication of prototypes and the understanding of the physical mechanism behind this magnetic property in a wide set of different materials [2–7]. Thus, many $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds (where R stands for a Rare earth element) have been synthesized and studied [3, 4, 8, 9], leading to the conclusion that the GMCE is a consequence of a strong coupling between spin and lattice degrees of freedom [10–12]. In fact, at RT, an optimal $\text{Gd}_5\text{Si}_2\text{Ge}_2$ sample should crystallize in the Monoclinic structure (M) ($\text{P}112_1/a$ space group), being in the paramagnetic state (PM) [11]. On cooling (or by applying a strong magnetic field or high pressure), this compound should undergo a simultaneous structural and magnetic (magnetostructural) phase transition to an Orthorhombic structure [$O(I)$] (Pnma space group) and ferromagnetic (FM) state, $[M, \text{PM}] \rightarrow [O(I), \text{FM}]$, at $T_{MS}^M \sim 275$ K [10, 11, 13]. This magnetostructural phase transition is the physical mechanism responsible for the observed temperature variation of $\Delta T_{ad} \sim 15$ K when a magnetic field of 5 T is applied and in adiabatic conditions: the so-called giant magnetocaloric effect [1, 10].

Nevertheless, several difficulties have been found on the synthesis and phase control of both single crystals and polycrystalline $\text{Gd}_5\text{Si}_2\text{Ge}_2$ samples. Such problems were detected in the 1960s when the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ were first discovered [14]. Moreover, since 1997, when Pecharsky and Gschneidner discovered the GMCE [1], the understanding of the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ crystallographic phase relations and the optimization of its M structural phase have become aims of the community [15–18]. The undesired phases which tend to appear in this compound can be classified in two types: spurious [which have the atomic ratio $Gd : (\text{Si}, \text{Ge}) \neq 5:4$] [19, 20] and secondary [which have the intended $Gd : (\text{Si}, \text{Ge}) = 5:4$ ratio but the $\text{Si} : \text{Ge}$ ratio is different from 1:1] [16]. The former phases are the closest neighbors of the wanted $Gd : (\text{Si}, \text{Ge}) = 5 : 4$ on the Gd-Si-Ge phase diagrams [particularly the $\text{Gd}:(\text{Si}, \text{Ge}) = 5:3$ and 1:1 phase] [21, 22]. Their presence is due to a partial eutectic-like decomposition that occurs during the cooling to RT, after the high-temperature synthesis process [17, 20]. In the other hand the secondary phases occur because the $x \sim 0.5$ composition is just at the border

between the M and $M+O(I)$ (phase mixture) regions according to the x - T phase diagram of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ [23]. Thus, the naturally occurring inhomogeneities on the Si and Ge distribution in the total sample volume, result in different $\text{Si} : \text{Ge}$ ratios along the sample and the formation of phases with different atomic and magnetic structures. Additionally, the microstrain arising from the thin plates of the spurious phases (5 : 3 and 1 : 1) induces the formation of secondary phases with $\text{Si} : \text{Ge} \neq 1$ [24, 25]. A very common phenomenon is the formation of phases with Si excess ($x \geq 0.55$) which stabilize in the $O(I)$ structure and have Curie temperature (T_C) ranging from 300 (for $x = 0.55$) to 340 K (for $x = 1$) [11, 23]. The segregation of such undesired phases on these compounds both attenuates significantly the GMCE [11, 26, 27], which is critical for technological applications, and undermines the full comprehension of their rich magnetic properties. Therefore it is of extreme importance to optimize sample production and thermal treatments in order to minimize the content of undesired phases, thus enhancing the amount of M structural phase. In the past few years, several works dealing with the annealing of these compounds have been presented [17, 23, 26, 28–30]. It was found that low temperature (< 700 K) annealings do not promote the M phase conversion [26, 27, 30], but instead enhance the $O(I)$ fraction, due to a not completely understood $M \rightarrow O(I)$ phase transformation occurring in this temperature range [31]. On the other hand, higher temperature annealings (> 1000 K) have shown interesting results, leading to the M phase conversion, particularly for annealings at $T = 1570$ K [26, 27]. Nevertheless, concerning technological applications, the whole annealing process should be optimized and thus the lack of annealing time dependent studies should be suppressed. Another key point in this optimization process is the ability to quantify the different phase fractions with an easy method. Traditionally the phase fraction estimation on these compounds has been performed exclusively through the XRD refinement technique. Although, due to the similar set of reflection peaks between the two 5:4 phases, the quantification is a rather difficult and time consuming task. Herein we study the effects of varying the annealing time maintaining the same annealing temperature ($T = 1473$ K) on the M phase conversion. Furthermore an alternative and simple method to estimate the different crystallographic phase fractions through magnetic measurements is here introduced, complementing the standard Rietveld refinement of XRD. Additionally, an integrated investigation on the magnetic properties of these samples allowed to better understand the measured 50% increase of the magnetocaloric effect on a representative annealed sample. Based on these

analysis, an optimal annealing time range is proposed.

II. EXPERIMENTAL DETAILS

A $\text{Gd}_5\text{Si}_2\text{Ge}_2$ polycrystalline sample (~ 4 g) was prepared from 99.9 wt% pure Gd and 99.9999 wt% pure Si and Ge commercial elements purchased from Alfa Aesar. The sample was synthesized using the arc-melting technique and, after the initial melting, three remeltings were performed to improve homogenization. Furthermore, this sample was cut into several smaller fragments. Each of these smaller samples was placed in a vacuum pumped quartz tube ($\sim 3 \times 10^{-5}$ mbar) and heated at $T \sim 1473$ K, for different annealing times. The quenching was done by diving the quartz tube directly into a liquid nitrogen container. The heat treated samples are here identified by the duration of the annealing they were subjected to: A0 - 0 min (as-cast); A1 - 60 min; A2 - 80 min; A3 - 100 min; A4 - 120 min; A5 - 140 min; A6 - 160 min and A7 - 180 min. The microstructure and chemical composition of all samples was investigated by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The room temperature (RT) crystallographic structures were determined by Rietveld refinements of the X-Ray powder Diffraction (XRD) spectrum [with incident beam of $\lambda_1 = 1.540598$ Å], using the FULLPROF software package [32]. Such refinements were done in a systematic way by considering the presence of four different crystallographic phases, which were added into the refinement one at a time in order to minimize wrong peaks association. Magnetic characterizations of powder samples were performed in a commercial (MPMS Quantum Design) Superconducting Quantum Interference Device (SQUID) magnetometer by measuring the magnetization thermal dependence of powder samples from 5 to 370 K (on heating) after field cooling with $H = 50$ Oe. The nature of the magnetic transitions was investigated using Arrott plot representations of the isothermal $M(H)$ curves up to 5 T. The estimated error of these measurements is within the SQUID resolution limit ($\sim 10^{-7}$ emu, when using the reciprocating sample option). Finally, the MCE was quantified following the method described by Caron and co-workers in Ref. [33].

III. EXPERIMENTAL RESULTS

A. Structural Characterization

Figure 1 shows the XRD patterns of samples A0 (as-cast) [down] and A2 (80 min) [up] in the 2θ : 25.5° - 39.5° range. One immediately observes that this heat treatment significantly changes the sample crystallography. The specific peaks associated with each phase are identified in Fig. 1 with different symbols. The vanishing of the peak intensities at $2\theta \sim 30.0^\circ$ [(1 1 1); star symbol] and $\sim 35.7^\circ$ [(1 1 2); triangle] is associated with the decrease of the spurious 1:1 and 5:3 phases concentration, respectively. Concerning the 5:4 phases, the decrease of the peaks intensities at $2\theta \sim 31.5^\circ$ [(1 3 2); square] and $\sim 34.5^\circ$ [(1 5 1); square] and the increase of the peaks intensities at $2\theta \sim 28.4^\circ$ [(-1 4 1); arrow] and $\sim 33.1^\circ$ [(-2 1 2); arrow] is associated with the decrease of the $O(I)$ and increase of the M phase concentrations, respectively. Such evidences are corroborated by the phases concentration estimated with the final Rietveld refinements of XRD pattern considering the $M+O(I)+5:3+1:1$ phases (see Fig. 2) which are shown in Table I. The same analysis was performed for all samples and the results are summarized in Table I. It is important to remark that for the as-cast sample there was no need to include the M phase in the Rietveld refinement analysis.

To confirm the presence of the above mentioned spurious crystallographic phases the samples were observed by SEM/EDS. In Fig. 3 a) and b) micrographs of samples A0 and A4 are shown. The overall detected chemical compositions were close to the expected 5:4. For A4 sample, the stoichiometry of the darker linear features was found to be 5:3 by local EDS analysis, whereas for the A0 sample no significant contrast was observed. The lighter linear features shown for this sample are surface scratches created during the polishing.

B. Magnetic Characterization

The temperature dependencies of the magnetic susceptibility [$\chi(T)$] and its temperature derivative [$d\chi/dT(T)$] for selected samples are plotted in Fig. 4 a) and b), respectively. These data shows that above 310 K all samples (as-cast and annealed) are in the PM state. For the as-cast sample (A0), a single and sharp peak at $T \sim T_C^{O(I)} \sim 300$ K is noticed on the $d\chi/dT$ data [see Fig. 4 b)], signaling the [FM]→[PM] magnetic phase transition (on heating). Considering the transitions temperatures that both M and $O(I)$ structural

FIG. 1: (Color online) $\theta - 2\theta$ X-Ray Diffraction spectra, in the 2θ : 25.5° - 39.5° range, for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ samples A ϕ (bottom) and A2 (top). Diffraction peaks associated with each crystallographic phase present are signaled with different symbols.

phases undergo in this compound, respectively ~ 275 K (magnetostructural transition) and ~ 300 K (magnetic transition) [23], these data suggests that the as-cast sample presents a very high amount of $O(I)$ and a very small amount of M phase corroborating the XRD Rietveld refinement result. Regarding the annealed samples, one notes the appearance of a second magnetic phase transition approximately at T_{MS}^M , associated with the enhancement of the amount of M phase in these samples. This is specially remarkable for the A4 sample, which exhibits a much higher $d\chi/dT$ peak at $T \sim T_{MS}^M$ than at $T \sim T_C^{O(I)}$. The difference between the absolute values of the samples susceptibility most probably arises from the highly preferential texture usually present in the $\text{R}_5(\text{Si,Ge})_4$ materials.

To inspect the nature of the magnetic transitions undergone by the as-cast and A4 sample, we

FIG. 2: (Color online) $\theta - 2\theta$ Room temperature X-Ray Diffraction pattern and respective Rietveld refinements for $\text{Gd}_5\text{Si}_2\text{Ge}_2$ samples A0 [(as-cast); a)] and A2 [$t = 80\text{min}$; b)] in the 2θ range: 20° - 80° .

used Arrott plot representation [H/M versus M^2 curves [34]] of the magnetization isothermal data close to their respective transition temperatures (Fig. 5). From Fig. 5 a) one can observe that the Arrott plot of the as-cast sample displays a positive slope within the whole M^2 range and for all temperatures. Such behavior is characteristic of a second order magnetic phase transition as the one found previously for samples with similar chemical composition crystallized in the $O(I)$ structure [35]. Nevertheless, a small variation of the slope is observed for high fields, revealing the presence of a small amount of M phase, in accordance with what was observed in the respective $d\chi/dT$ (T), seen in Fig. 4 b). On the other hand, the annealed sample shows a very different behavior with an horizontal "S" shape for $T \geq 275$ K curves. This indicates a change from a negative to a positive slope with increasing M^2 , similarly to

FIG. 3: Backscattered electron SEM micrographs of samples A0 [as-cast; a)] and A4 [120 min; b)].

what has been recently observed using high magnetic fields [36]. This feature is characteristic of a first order magnetic phase transition. The change of order character of the magnetic transition from the as-cast to the annealed sample results directly from the higher amount of M structural phase in the annealed sample, as it undergoes a simultaneous structural and magnetic transition.

In order to extract a more quantitative information on the phase fractions present in these samples, we developed a simple method based on fitting the reciprocal magnetic susceptibility data in the temperature range [325, 370]K (PM region for all samples). The fits were performed in order to account with the four different crystallographic phases, considering the different magnetic ordering temperatures and Curie constants assumed by each different phase. It is known that the total magnetic moment of a sample (M_T) is simply given by the addition of the magnetic moments of its constituent phases. Consequently the total magnetic susceptibility is also given by the sum of susceptibilities of each constituent phases, which can be expressed as:

$$\begin{aligned}\chi_T &= \alpha\chi_M + \beta\chi_{O(I)} + \gamma\chi_{5:3} + \eta\chi_{1:1} = \\ &= \alpha\frac{C_M}{T - T_C^M} + \beta\frac{C_{O(I)}}{T - T_C^{O(I)}} + \gamma\frac{C_{5:3}}{T - T_N^{5:3}} + \eta\frac{C_{1:1}}{T - T_N^{1:1}},\end{aligned}\quad (1)$$

where α , β , γ and η are the fractions associated with the M , $O(I)$, $5:3$ and $1:1$ crystallographic phases, respectively. So, the total reciprocal magnetic susceptibility is written as in

FIG. 4: (Color online) Temperature dependence of [a)] the magnetic susceptibility (M/H on heating in the 240-350 K range) and [b)] of the magnetic susceptibility temperature derivative [b)] ($d\chi/dT$) of A0(as-cast), A1 , A3 and A4 samples.

[37]. Hence, considering the Curie constant as $\chi = \frac{\mu_0 \mu_B^2 g^2 N J(J+1)}{3k_B}$, it is possible to put in evidence the common quantities of the Curie constant (the vacuum magnetic permeability, μ_0 , the Bohr magneton, μ_B , the Landé factor, g , and the Boltzmann constant, k_B) and account for the different values of the phase dependent parameters (the individual spin number, J , and the number of magnetic atoms per unit volume, N). The J values were considered to be equal for all phases, $7/2$ (Gd intrinsic spin value), except for the $O(I)$ phase where it was considered to be 4.2, accounting with the 20 % increase found in Ref. [38]. The N values were calculated assuming the unit cell volume of each phase as estimated from the Rietveld refinements here reported. Furthermore the ordering temperatures considered were: 305K, 209K for M , $O(I)$ (extracted from Ref. [13]) and a linear extrapolation of the magnetic ordering temperatures from the silicides and germanides was performed for both $5:3$ and $1:1$ phases, giving 65K and 55K, respectively [39–41]. The α , β , γ and η values were constrained to be between 0 and 1 and their sum to be equal to 1. In this way, [37] allowed to estimate the phase fractions of each crystallographic phase present in the samples. An example is given in Fig. 6, where the fittings of the reciprocal magnetic susceptibilities in

FIG. 5: (Color online) H/M versus M^2 selected isothermal curves (Arrott plots) for applied fields up to 50 kOe in the temperature range [a)] 282-318 K for the as-cast and [b)] 257-287 K for the A4 samples. Shaded regions highlight the isothermal curves close to the respective magnetic transition temperatures.

the 325 - 370K temperature range (paramagnetic region) for samples A $\emptyset$ and A3 are plotted, presenting a fair accordance with the experimental $\chi_T^{-1}(T)$ data. The obtained mass fractions estimations for all samples are reported in Table I and will be further discussed in section D.

C. Magnetocaloric effect measurements

Considering the aim of the present work, Fig. 7 shows the temperature dependence of the magnetic entropy change, $\Delta S_m(T)$ of the as-cast and the A4 (120 min) samples at 50 kOe applied field change. The curve from the later sample reach its maximum at $T \sim T_{MS}^M \sim 275$ K, while the former at $T \sim T_C^{O(I)} \sim 300$ K. This result is coherent with the XRD and magnetic data since it confirms that the A4 sample clearly has a higher M phase content, as the maximum entropy change occurs at the magnetostructural transition temperature. Another feature favoring this reasoning is that the amplitude of the magnetic entropy change is substantially improved (up to 50% higher than the one exhibited by the as-cast sample). This enhancement signaled in Fig. 7 as $\Delta S_m^{M \rightarrow O(I)}$, is caused by the magnetostructural phase transition that occurs in the sample with higher amount of M phase. As was re-

FIG. 6: (Color online) Reciprocal magnetic susceptibility fit (red curves) based on Eq. 1 of samples A0 and A3 (black and green circles, respectively) in their paramagnetic region, [325, 370]K. The M , $O(I)$, $5:3$ and $1:1$ phase fractions were estimated through these fits.

cently shown [36], this enhancement depends critically on the competition between the two crystallographic structures with different T_{Cs} [13, 38], being maximized when T_{MS} occurs exactly at the lower Curie temperature. Contrarily, the as-cast sample just undergoes a simple second-order magnetic phase transition within the same $O(I)$ crystallographic structure, thus presenting a significantly lower ΔS_m amplitude.

D. Discussion

The comparison between the $5:4$ phase fractions obtained by fitting $\chi^{-1}(T)$ curves and the ones obtained by Rietveld refinements of XRD spectra [" $\chi^{-1}(T)$ " and "XRD" column in Table I, respectively] is illustrated in Fig. 8 as a function of the annealing time. As can be seen a good agreement is found for the results obtained through the two different methods. A similar time dependent trend of the M phase fraction for both methods is found: rapid increase till a saturation value ($\sim 67\%$ and 74% , by XRD and $\chi^{-1}(T)$ methods, respectively) is reached for annealings within the 60-120 min time interval (see shadowed regions in Fig.

FIG. 7: (Color online) Magnetic entropy change of the as-cast and A4 annealed sample under a magnetic field change of 50 KOe.

8 a) and b)). This result is in accordance with previous reports that have considered the $T_{ann} = 1570 \text{ K}$ for 1 hour annealing as the most efficient treatment to achieve the conversion into the M phase [23, 26]. Although, in the aforementioned reports the time dependence behavior is not presented.

According to our results, the M conversion can be very efficiently achieved by converting both the $O(I)$ and 5:3 phases (which have their concentration reduced on average by $\sim 50\%$ and 15% , respectively according to our XRD analysis) into the M phase (whose concentration maximum enhancement is close to $\sim 70\%$). Considering spurious phases contents, both methods suggest that there is an increase of segregation of these phases for longer annealings ($> 120 \text{ min}$). These results allow us to deduce that for an optimal $\text{Gd}_5\text{Si}_2\text{Ge}_2$ sample preparation the annealing time should be smaller than 120 minutes. Although there is not a full $O(I) \rightarrow M$ phase concentration conversion in this study, it is important to

FIG. 8: (Color online) M , $O(I)$, $5:3$ and $1:1$ phase fractions, as estimated by XRD refinements [a)] and by fitting of the $\chi^{-1}(T)$ curves [b)] as a function of annealing time. The dashed lines are just guides to the eyes.

remark that this process started with an as-cast sample which presented negligible M phase concentration.

Since M and $O(I)$ are complex and have similar crystallographic structures they present a largely coincidental set of indexed peaks, making it difficult and less accurate to quantitatively distinguish both phases through XRD analysis. Hence, the $\chi^{-1}(T)$ fitting method can be used as a complementary method to corroborate the phase fractions information extracted by XRD analysis.

IV. CONCLUSIONS

In summary, we studied the effects of different annealing times on the crystallographic phase fractions of arc-melted $Gd_5Si_2Ge_2$ sample through XRD Rietveld refinements and magnetization measurements. Particularly, a simple approach of fitting $\chi^{-1}(T)$ curves was used to estimate the crystallographic phase fractions present, providing a complementary tool to check samples quality. We were able to promote the conversion of the M phase in a $Gd_5Si_2Ge_2$ as-cast sample with a high $O(I)$ character and residual M phase amount,

TABLE I: Structural phase amounts of Gd₅Si₂Ge₂ as-cast and annealed samples extracted from Rietveld refinement of room temperature XRD spectra and the presented reciprocal magnetic susceptibility fitting method.

Sample	Gd/(Si,Ge)	Space Group	XRD (mass.%)	χ^{-1} (T) (mass %)
A0 (as-cast)	5:4	P112 ₁ /a [<i>M</i>]	0	29
Rp: 8.38% Rwp: 10.7%	5:4	Pnma [<i>O(I)</i>]	72	71
Rexp: 6.95% Chi2: 2.39%	5:3	P6 ₃ /mcm	25	0
	1:1	Cmcm	3	0
A1 (60 min)	5:4	P112 ₁ /a [<i>M</i>]	66	74
Rp: 6.11% Rwp: 7.94%	5:4	Pnma [<i>O(I)</i>]	27	7
Rexp: 7.09% Chi2: 1.25%	5:3	P6 ₃ /mcm	5	10
	1:1	Cmcm	2	9
A2 (80 min)	5:4	P112 ₁ /a [<i>M</i>]	62	
Rp: 8.14% Rwp: 10.3%	5:4	Pnma [<i>O(I)</i>]	30	
Rexp: 8.06% Chi2: 1.62%	5:3	P6 ₃ /mcm	3	
	1:1	Cmcm	5	
A3 (100 min)	5:4	P112 ₁ /a [<i>M</i>]	67	70
Rp: 9.26% Rwp: 11.7%	5:4	Pnma [<i>O(I)</i>]	26	6
Rexp: 7.04% Chi2: 2.78%	5:3	P6 ₃ /mcm	2	7
	1:1	Cmcm	5	17
A4 (120 min)	5:4	P112 ₁ /a [<i>M</i>]	66	77
Rp: 7.52% Rwp: 9.93%	5:4	Pnma [<i>O(I)</i>]	28	5
Rexp: 6.57% Chi2: 2.29%	5:3	P6 ₃ /mcm	3	18
	1:1	Cmcm	3	0
A5 (140 min)	5:4	P112 ₁ /a [<i>M</i>]	59	67
Rp: 7.59% Rwp: 9.65%	5:4	Pnma [<i>O(I)</i>]	29	3
Rexp: 4.55% Chi2: 4.5%	5:3	P6 ₃ /mcm	5	16
	1:1	Cmcm	7	14
A6 (160 min)	5:4	P112 ₁ /a [<i>M</i>]	56	66
Rp: 5.58% Rwp: 7.17%	5:4	Pnma [<i>O(I)</i>]	24	4
Rexp: 7.03% Chi2: 1.04%	5:3	P6 ₃ /mcm	9	22
	1:1	Cmcm	9	8
A7 (180 min)	5:4	P112 ₁ /a [<i>M</i>]	61	77
Rp: 8.56% Rwp: 11%	5:4	Pnma [<i>O(I)</i>]	26	9
Rexp: 6.98% Chi2: 2.48%	5:3	P6 ₃ /mcm	11	14
	1:1	Cmcm	2	0

through annealings at $T = 1473$ K during 60-120 minutes with quenching to liquid nitrogen. A successful conversion of both spurious (5:3) and $O(I)$ phases into M phase was obtained through annealing process. This is particularly important considering the $Gd_5Si_2Ge_2$ technological potential applications, since only samples with high contents of the M phase will display a GMC effect, as was here shown by the $\sim 50\%$ enhancement of the magnetic entropy variation.

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