Magnetic structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{M}_{0.1}$ ($\text{M} = \text{Ga}, \text{Cu}$)

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Abstract. Powder X-ray diffraction patterns of the doped compounds, $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{M}_{0.1}$ ($\text{M} = \text{Ga}, \text{Cu}$), show the same crystal structure, orthorhombic Gd_5Si_4 -type in the ferromagnetic and paramagnetic phases. This is different to $\text{Gd}_5\text{Si}_2\text{Ge}_2$ whose paramagnetic phase is monoclinic. The magnetic structure at low temperature, solved from diffraction experiments with hot neutrons, is the same in all the three compounds, collinear ferromagnetic with moments along the crystal b -axis, or $F_y F_{By}$ according to Bertaut's notation. These results, combined with those of heat capacity and magnetocaloric effect indicate, similarly to Gd_5Si_4 , a second-order, purely magnetic, transition in the doped compounds explaining the absence of hysteresis.

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1. Introduction

Since the discovery of the “giant magnetocaloric effect” (GMCE) in 1997 by Pecharsky and Gschneidner [1] many families of compounds have been studied, regarding their potential technical application in magnetic refrigeration near room temperature. For studies until 2003 we refer the reader to the monograph by Tishin and Spichkin [2]. A review about the Mn based GMCE compounds has been published by Brück *et al.* [3]. The first family discovered, $Gd_5(Si_xGe_{1-x})_4$, ($0.2 < x < 0.5$) is by far the most studied one and remains among the most efficient GMCE materials. More than one hundred papers about it have been published in the last decade. In these compounds, the GMCE is due to the simultaneous magnetic and structural first-order transition from an orthorhombic ferromagnetic phase O(I) (Gd_5Si_4 type) to a monoclinic paramagnetic phase, M. Figure 1 shows a temperature/composition phase diagram at zero field. The transition temperature T_C can be tuned between 140 K and 270 K by selecting the Si/Ge ratio. At higher temperatures and zero field the O(I) structure is recovered, now in paramagnetic state [4]. Si-rich compositions (i.e. $x > 0.5$) have only a magnetic transition with T_C increasing slowly from 295 K for $x \rightarrow 0.5$ to 335 K, for $x = 1$. On the opposite end of the composition-temperature phase diagram, for $x < 0.2$ the ferromagnetic O(I) phase transforms first into an antiferromagnetic Sm_5Ge_4 type structure, O(II), and this one undergoes a magnetic transition to paramagnetic near 125 K. The O(I) and O(II) phases have the same space group, $Pnma$, and similar cell constants, but quite different atomic positions, so they are usually considered as different structure types. The main qualitative difference between phase O(I) and O(II) is the distance between Si or Ge atoms on sites $8d$, which changes from *ca.* 3.5 Å in O(II) to *ca.* 2.6 Å in O(I) [7], allowing the formation of dimers in this last phase. In the M phase, one half of the dimers is broken. These structural changes modify the exchange interactions and therefore determine the different magnetic structures and ordering temperatures.

In spite of the many works published on $Gd_5(Si,Ge)_4$, the magnetic structure has not been directly determined. Usually, considerations about it have been extrapolated from results in other rare earth compounds, like $Tb_5(Si,Ge)_4$ [8], or $Er_5(Si,Ge)_4$ [9]. However, the Gd atom has zero orbital angular momentum and the magnetic properties are not affected by the crystal field in the same way as in other rare earth atoms. The difficulty for a magnetic structure determination via neutron diffraction lies in the huge cross section, σ_a , of the natural Gd for the absorption of thermal neutrons. For a typical powder neutron diffraction experiment with wavelength $\lambda = 1.8$ Å, $\sigma_a = 48.8 \times 10^3$ barn [10], which gives a penetration depth $L = 8.2 \mu m$ in solid $Gd_5(Si,Ge)_4$. Using hot neutrons the absorption can be reduced to still high but tolerable values. Using by instance, $\lambda = 0.5$ Å, gives $\sigma_a = 760$ barn [11] and $L = 0.53$ mm. On the contrary, the resolution is not always enough to get single Bragg peaks in a powder neutron diffraction experiment with this short wavelength. Nevertheless, even complex magnetic structures in e.g. $GdNi_2Si_2$, $GdCu_2Si_2$ [12] and $GdCu$ [13] have been solved using hot neutrons

Figure 1. Temperature/composition phase diagram at zero field for $Gd_5(Si_xGe_{1-x})_4$, from [5] and [6]. Open circles: Transition to the ferromagnetic (FM) O(I) phase on cooling. Solid circles: Transition to paramagnetic (PM) M phase on heating. Triangles: Transition between antiferromagnetic (AFM) and paramagnetic phases. Lines, solid: First-order transitions. Dotted: Second-order transitions. Dashed: Borders of different crystal structures in the paramagnetic state. Between M and O(II) phases there is a narrow two-phase region.

powder diffraction.

Regarding applications in magnetic refrigeration, the main drawback of $Gd_5Si_2Ge_2$ is the large hysteresis, which imposes a minimum initial applied field near 2 T to achieve a complete isothermal ferromagnetic to paramagnetic transition, even at the most favorable temperature. Recently it has been reported that replacing (doping) a small amount of Ge by some other metal (Fe, Co, Cu, Ga, Mn, Al) reduces or even eliminates the hysteresis, keeping or increasing the net refrigeration capacity [14, 15]. We have chosen to study the effect of doping with the non magnetic Ga and Cu. The aim of this work is to study the crystal structures and the low temperature magnetic structures of the title compounds.

2. X-ray diffraction

The samples used in this study were the same used previously for SEM, magnetic [15] and thermal measurements [23]. These results suggest a second order transition at $T_C = 293.6$ K for the Ga-doped compound. For the Cu-doped compound our heat capacity experiments show a very similar behaviour with $T_C = 294$ K. In addition to previous experimental work, the samples were analysed by X-ray fluorescence and diffraction (XRD) between 200 K and 350 K. XRD patterns were collected in a rotating anode RU 300, operated at 80 mA. The data collection was performed every 0.03° using a goniometer Rigaku/Max System. Figure 2 (left) shows the XRD pattern of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ at 250 K and 350 K. In addition to the main phase there is 3.7% in mass of $Gd(Si,Ge)_1$ (1:1 alloy) and 14.4% of $Gd_5(Si,Ge)_3$ (5:3 alloy). The same phases were found in the Cu doped and in the non-doped compounds, with similar proportions. These proportions are consistent with the global analysis performed by

Figure 2. (Colour online) X ray diffraction patterns of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ at 250 K and at 350 K, and $Gd_5Si_2Ge_{1.9}Cu_{0.1}$ at 200 K and at 350 K. Symbols: Observed patterns. Black lines: Calculated for the O(I) structure. Green ticks: Position of the Bragg reflections for 3 phases: Main O(I) phase, $Gd(Si,Ge)_1$ and $Gd_5(Si,Ge)_3$. Green line: Calculated for the M phase, according to structural data given in [7]. Arrows indicate some characteristic reflections for the O(I) and M structures.

X ray fluorescence and with previous analysis. The structural data were taken from the literature for the nearest compositions [4, 17, 18, 19]. The $Gd_5Si_2Ge_2$ patterns were compatible with the M phase at room temperature and at 350 K. At 250 K the structure is O(I) type. For the doped compounds, a previous analysis of the structure at RT (i.e. some undetermined temperature between 290 K and 300 K) was not conclusive to assess if the paramagnetic phase is M or O(I) type, because of the proximity of the magnetic transition. Rietveld analysis was done for patterns at several temperatures, in ferromagnetic and paramagnetic phases (figure 2). The doped compounds have the O(I) structure for temperatures below 350 K. This is similar to the Si-rich alloys in $Gd_5(Si_xGe_{1-x})_4$ with $x > 0.5$. In the Cu-doped compound, the only difference between the 350 K pattern and the 200 K one is the appearance of two small peaks at $2\theta = 31.2^\circ$ and 32.6° . They correspond to the $(2\bar{3}1)$, $(1\bar{3}2)$ (very closely spaced) and (231) reflections, among the most intense for the M phase. That would indicate some inhomogeneity in composition, being the proportion of Cu too low to avoid the first order O(I)-M transition and/or being the Ge proportion higher than the nominal value in some small parts of the sample.

3. Neutron diffraction

The neutron diffraction (ND) experiment was carried out on the D4 diffractometer [16] at the Institut Laue-Langevin, Grenoble (France). This instrument uses a hot neutron source and a Cou-(220) monochromator providing neutrons of wavelength $\lambda = 0.4964 \text{ \AA}$. The scattered intensity is collected by a bank of 9 multi-detectors of $64 \text{ }^3\text{He}$ cells in steps of 0.125° , covering 8° each one, with gaps of 7° between two adjacent multi-detectors.

Every full pattern was collected by positioning the bank (position of the first cell of the first multi-detector) at 0° , 4° , 8° and 12° . The background radiation coming from parts of the cryostat lying out of the focusing center is shadowed by the collimators for some detector cells, depending on the position of the bank, which produces some jumps in the experimental diffraction pattern. To correct this effect, taking into account the absorption by the sample, a pattern was collected on an empty sample holder and another one with a sample of pure boron, considered as completely absorbent. The corrected intensity at a given angle 2θ is approximated by $y_{\text{corr}} = y_{\text{exp}} - \eta y_{\text{h}} + (1 - \eta)y_{\text{B}}$, where y_{exp} is the experimental intensity, properly weighted over the positions of the bank and efficiency of every cell. y_{h} and y_{B} are the intensities for the empty holder and for boron, respectively. η is a fitting parameter between 0 and 1. The geometry of the sample is not exactly the same as that of boron, therefore some jumps appear in the patterns (for instance at $2\theta = 4.625^\circ$) even with the best choice of η . These jumps are not related to any property of the sample but, as mentioned, to the different shadowing of the ambient neutron radiation by the collimators, for different detectors.

The sample was distributed over a hollow cylinder of 9 mm diameter and 0.5 mm thick, suitable for an average absorption length of $L = 0.53$ mm corresponding to a solid $Gd_5Si_2Ge_2$ sample. The resolution, *ca* 0.2° , does not allow to observe the individual reflections. Therefore the magnetic mode will be deduced by trial and error, comparing the observed pattern with the calculated one for every possible magnetic modes. The patterns (figure 3) were collected for all samples in the paramagnetic phase (above 300 K), few kelvin below the transition (240 K) and at 20 K. The scattering length of natural Gd for $\lambda = 0.4964$ Å was interpolated between the nearest values in table 1 of [11], giving $b = (1.067 - i0.042) \times 10^{-12}$ cm. For Si, Ge, Ga and Cu, usual values were taken, $(0.4149, 0.8185, 0.7288, 0.7718) \times 10^{-12}$ cm, as well as for the magnetic form factor of Gd.

The paramagnetic phase patterns are consistent with the structure derived from XRD, that is, M-type structure for $Gd_5Si_2Ge_2$ and O(I)-type for the doped alloys. In the non-doped sample the monoclinic distortion is not so evident as in the case of XRD because of the poorer resolution in the ND experiment, but in any case the Rietveld refinement gave acceptable reliability indexes only for the M-type structure ($R_p = 0.014$, $R_{wp} = 0.018$, $\chi^2 = 1.19$, $R_{Bragg} = 0.015$, over raw data, not corrected for background). The 20 K pattern clearly shows an increase of the already present nuclear reflections. The most evident cases are the (121) at $2\theta = 6.51^\circ$ (a rare case of a well separated reflection) and a group of 8 reflections between $2\theta = 8.20^\circ$ and 8.60° . The difference in the background is also evident and consistent with the incoherent paramagnetic scattering at 310 K. Two small bumps near 1.48° and 3.55° are supposed to correspond to the low temperature magnetic diffraction of the 5:3 phase, below 110 K [20]. From magnetic measurements the magnetic structure of the hexagonal Gd_5Ge_3 at low temperature was supposed to be helical [21]. Recent single crystal ND experiments [22] showed a modulated structure with wave vector $\mathbf{k} = (0, 0, 0.40)$, therefore we can expect a peak at $2\theta = 1.8^\circ$, but actually the 5:3 phase is composed of both Ge and Si

Figure 3. (Colour online) Left, symbols: observed neutron diffraction patterns of $Gd_5Si_2Ge_2$ at 310 K (green), 240 K (blue) and 20 K (red). Ticks: position of the Bragg peaks for the nuclear and magnetic scattering. Lines: calculated with structural parameters taken from XRD, for the ferromagnetic mode F_y (group $Pn'ma'$), with moments of $7 \mu_B$ (black). Arrows indicate the bumps ascribed to the possible modulated structure of the 5:3 phase. Right: Magnified portion of 20 K pattern, indicating some key reflections. Lines: calculated for the three ferromagnetic modes.

Table 1. Magnetic irreducible representations for the $4c$ and $8d$ positions of the space group $Pnma$ with $\mathbf{k} = 0$ [25, 26].

Irrep	x	y	z	x	y	z	group
Γ_1		C_y		C_{Bx}	G_{By}	A_{Bz}	$Pnma$
Γ_2	C_x		F_z	G_{Bx}	C_{By}	F_{Bz}	$Pn'm'a$
Γ_3	F_x		C_z	F_{Bx}	A_{By}	G_{Bz}	$Pnm'a'$
Γ_4		F_y		A_{Bx}	F_{By}	C_{Bz}	$Pn'ma'$
Γ_5	A_x		G_z	R_x	Q_y	L_z	$Pn'm'a'$
Γ_6		A_y		Q_x	R_y	P_z	$Pnma'$
Γ_7		G_y		P_x	L_y	Q_z	$Pn'ma$
Γ_8	G_x		A_z	L_x	P_y	R_z	$Pnm'a$

and the propagation vector is not necessarily the same as in Gd_5Ge_3 (if the magnetic structure were the same). As additional tips to ascribe these bumps to the 5:3 phase we can notice that: a) The bumps do not exist at 240 K, when the main phase is magnetically ordered (but not the 5:3 phase), and the heat capacity [23] does not reveal any other transition between 20 K and 240 K. b) The position of the bump at 1.48° does not correspond to any possible Bragg reflection with $\mathbf{k} = 0$, which could be ascribed to some kind of antiferromagnetic order. c) The magnetization data give a magnetic moment per atom of $7.52 \mu_B$ [24] for the very similar compound Gd_5Si_4 , slightly above the theoretical spin-only value of $7 \mu_B$. That is hardly compatible with a helical or sinusoidal antiferromagnetic structure, which would give a zero net moment. Some modulation around a non-zero moment cannot be completely ruled out but we keep the simplest hypothesis of a collinear structure with $\mathbf{k} = 0$ and constant moments. The

magnetic irreducible representations (table 1) for the nuclear space group $Pnma$ and $\mathbf{k} = 0$ were given in [25], based on Bertaut's theory [26] and corresponding to the 8 magnetic groups arising when the time inversion is combined with the space symmetry elements. In order to determine the magnetic group at 20 K we consider as a first approximation a fixed magnetic moment of $7 \mu_B$ in each Gd site. There are three Gd atoms in the asymmetric unit at Wyckoff sites $4c$, $8d$ and $8d$ of the crystallographic space group $Pnma$. Within a given magnetic group and for a collinear structure, we can choose the sign of one moment (for instance that of the $4c$ site) but two signs remain to be adjusted, what define the relative orientation (parallel or antiparallel) of two inequivalent moments at the $8d$ sites. That makes 32 possible magnetic modes, to be compared against the experimental pattern, one by one.

Let us consider first the non-doped compound at 20 K. The purely antiferromagnetic groups, corresponding to representations Γ_1 and $\Gamma_5 - \Gamma_8$ give strong peaks at low angles, near $2\theta = 3.63^\circ$ and $2\theta = 5.40^\circ$, or the peak (010) at $2\theta = 1.92^\circ$, which would be well separated but are not actually observed. Moreover, differently to the cases of Tb_5Ge_4 [25, 8] or Gd_5Ge_4 , antiferromagnetic order was not observed in magnetic measurements for $Gd_5Si_2Ge_2$. Therefore, let us assume as starting point one ferromagnetic collinear mode, Γ_2 as an example. The basis function of this representation is described by the symbol F_z , indicating a ferromagnetic configuration along the c -axis for the $4c$ moments. For the $8d$ sites, according to table 1, the possible moment configurations are the ones labelled as G_{Bx} , C_{By} , F_{Bz} , or several of them. We will shorten similarly the notation throughout the paper, i.e. $\Gamma_3 (F_x)$ or $\Gamma_4 (F_y)$. F_x gives a pattern similar to the observed one (figure 3, right), but produces a peak at $2\theta = 7.70^\circ$ (due to the reflections (040) and (131) with scattering vector $\mathbf{q}$ nearly parallel to the crystal b axis and perpendicular to the magnetic moments, for this mode) much more intense than the values observed in this range. On the contrary, there is not enough intensity in the range $2\theta = 8.20^\circ - 8.40^\circ$, produced by the reflections (102), (022), (201), (112) and (220), most of them with $\mathbf{q}$ nearly perpendicular to b axis. F_z explains the intensity of the region $2\theta = 8.20^\circ - 8.40^\circ$ but gives too much intensity in the range $2\theta \simeq 7.70^\circ$ of the reflections (040) and (131) and not enough in the range $2\theta \simeq 8.40^\circ - 8.80^\circ$ of the reflections (220) and (211). Finally the mode F_y (Γ_4 or $Pn'ma'$) gives a nice qualitative agreement with the experiment even with no refined structural parameters (figure 3, right).

The Rietveld refinement was made using the program FullProf [27] starting with the positional and cell parameters taken from XRD and the magnetic F_y mode with $7 \mu_B$ for all the moments. Due to the bumps at low angle and considering negligible the information at high angles, only the range $5^\circ < 2\theta < 40^\circ$ (1226 nuclear and 1401 magnetic reflections) was considered for the refinement. The results are displayed in table 2 and figure 4, left.

It is worthy to remark that the refined values of the magnetic moments have a large standard deviation and lie below the expected values from magnetization measurements at the same temperature. The group $Pn'ma'$ also allows components of the moments perpendicular to b (labeled as A_{Bx} and C_{Bz} in table 1) which would correspond to a

Figure 4. (Colour online) Left, symbols: Observed ND pattern of $Gd_5Si_2Ge_2$ at 20 K. Lines: Calculated after a Rietveld refinement with parameters given in table 2 (black), and difference (blue). Ticks: Position of the Bragg peaks for the nuclear and magnetic scattering. Right: Observed ND patterns at 20 K for $Gd_5Si_2Ge_2$ and the doped compounds.

canted structure, as observed in other $R_5(Si,Ge)_4$ compounds, for instance for $R = Tb$ [8] or Er [9]. In the present refinement, for $R = Gd$, the x or z components were included (refining the moments in spherical coordinates while maintaining the magnetic group) but the best fit corresponds to a non-canted structure, within the standard deviation. If there is some canting, it should be very small and well below the experimental sensitivity. Therefore, the magnetic structure corresponds simply to a collinear ferromagnet.

At 240 K the magnetic structure is the same, with smaller magnetic moments. The average microscopic magnetization can be determined from magnetic measurements by extrapolation of the isothermal magnetization curve to zero field. From figure 2 of [1], in $Gd_5Si_{1.72}Ge_{2.28}$ the magnetization value is about $130 \text{ Am}^2/\text{kg}$ at 242.2 K, which corresponds to an average moment of $4.6 \mu_B/\text{atom}$, in good agreement with the ND result of $4.0(3) \mu_B$ (table 2).

The doped compounds have the same magnetic structure as $Gd_5Si_2Ge_2$ with slightly different parameters. Figure 4, right, shows the patterns of the three compounds studied at 20 K and table 2 contains the final Rietveld fitting parameters. In some cases, refining individual magnetic moments in different sites led to divergence; therefore they were constrained to be equal. As in the non-doped compound, components perpendicular to the b axis are below $1 \mu_B$ and below the sensitivity of the experiment. In summary, the magnetic structure is quite similar to that of Er_5Si_4 at 3 K, that is, ferromagnetic with moments along b , but the crystal structure of the last compound is M-type [9]. The composition-temperature phase diagram of $Gd_5(Si,Ge)_4$ (figure 1) is similar to the one observed for $Tb_5(Si,Ge)_4$, but the magnetic structure is completely different, being the moments near the ac plane, non-collinear and undergoing a spin reorientation at low temperature for the Tb compound [8]. The monoclinic phase of $Pr_5Si_2Ge_2$ is also

Table 2. Parameters of the Rietveld refinement of the ND patterns of $Gd_5Si_2Ge_{1.9}M_{0.1}$ ($M = Ge$ means non-doped). Standard deviations in brackets, in units of the last digit. Tn = Si, Ge, Ga or Cu. Magnetic moments in Bohr magnetons. For $M = Cu$ the coordinates were not refined. N_{par} is the number of refined parameters.

M, T	Ge, 20 K	Ge, 240 K	Ga, 20K	Cu, 20K
Gd1(4c) x	0.355(3)	0.352(3)	0.380(3)	0.380
y	1/4	1/4	1/4	1/4
z	-0.018(2)	-0.017(2)	-0.002(4)	-0.002
Gd2(8d) x	0.0301(14)	0.0313(15)	0.024(2)	0.024
y	0.0920(6)	0.0921(7)	0.0963(10)	0.0963
z	0.8129(14)	0.8114(17)	0.809(2)	0.809
Gd3(8d) x	0.01781(16)	0.01808(19)	0.171(2)	0.171
y	0.1198(8)	0.1213(9)	0.1217(12)	0.1217
z	0.3231(13)	0.3211(15)	0.324(2)	0.324
T1(4c) x	0.983(5)	0.984(5)	0.991(7)	0.991
y	1/4	1/4	1/4	1/4
z	0.099(5)	0.100(5)	0.067(7)	0.067
T2(4c) x	0.265(5)	0.275(5)	0.269(9)	0.269
y	1/4	1/4	1/4	1/4
z	0.663(4)	0.663(4)	0.728(6)	0.728
T3(8d) x	0.185(2)	0.185(2)	0.228(5)	0.228
y	0.9487(12)	0.9488(12)	0.928(3)	0.928
z	0.537(3)	0.538(3)	0.544(5)	0.544
$\mu(\text{Gd1})$	5.8(4)	3.2(4)	6.4(2)	7.3(4)
$\mu(\text{Gd2})$	6.4(3)	5.1(3)	6.4(2)	7.3(4)
$\mu(\text{Gd3})$	6.9(2)	3.4(3)	6.4(2)	7.3(4)
$a(\text{\AA})$	7.586(6)	7.603(7)	7.572(9)	7.64(2)
$b(\text{\AA})$	14.873(14)	14.895(15)	14.822(20)	14.77(5)
$c(\text{\AA})$	7.874(6)	7.894(8)	7.839(10)	7.87(2)
$V(\text{\AA}^3)$	888.4(13)	894.0(15)	880.0(20)	887(4)
$R_p/R_{\text{wp}}(\%)$	1.7/2.1	1.4/1.8	3.2/4.1	2.2/2.9
$R_{\text{Bragg}}/R_{\text{mag}}(\%)$	2.2/3.2	2.1/3.2	4.9/5.4	11/8.7
χ^2	1.5	1.03	2.1	1.4
N_{par}	34	34	28	10

different since the moments lie along the a direction [28].

4. Conclusions

Previous heat capacity and direct magnetocaloric determinations [23] in $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ have shown a substantially different behaviour compared to that of $Gd_5Si_2Ge_2$. In the doped compound there is no first-order transition but a usual second-order magnetic transition with similar T_C to the one of Gd_5Si_4 . The heat capacity and the isothermal entropy increment are similar to the values for pure Gd, with a proper scaling due to the relative fraction of Gd atoms in the sample, and decreasing accordingly the MCE with respect to that of pure Gd. Now, the high and low temperature XRD patterns support

those results as they show the well known O(I) to M transition in $Gd_5Si_2Ge_2$ but not in the doped compounds, which remain in the O(I) phase across the magnetic transition. These conclusions agree with those given in [29] for $Gd_5Si_{2-y}Ge_{2-y}Ga_{2y}$ with $y \geq 0.05$ from DSC and magnetization data. The lower y value corresponds to the Ga amount of our compound, but in this case both Si and Ge are replaced by Ga.

The magnetic structure of $Gd_5Si_2Ge_2$ below T_C is the same as that of the doped compounds $Gd_5Si_2Ge_{1.9}M_{0.1}$ ($M = Ga, Cu$), collinear ferromagnetic $F_y F_{By}$, with the magnetic moments in the b direction of the $Pnma$ space group. This is different and much simpler than for compounds with other rare earths (Er, Tb, Yb) substituting Gd. At 20 K the average magnetic moment, $6.5(3) \mu_B/\text{atom}$, lies slightly below the value derived from magnetization measurements (between 7.2 and $7.5 \mu_B/\text{atom}$, taken from the literature) what can be due to the low precision of the ND experiment or to the magnetic polarization of the conduction electrons.

For $Gd_5Si_2Ge_2$ at 240 K, just below the magnetostructural transition, the magnetic moment is considerably lower than the saturation value of $7 \mu_B/\text{atom}$. This is not surprising, although it has strong consequences for the MCE since the magnetic entropy in the ferromagnetic phase is already quite high at this temperature. Therefore the magnetic entropy jump per atom at the transition is well below the theoretical limit of $k_B \ln(2S + 1)$. This imposes severe limitations for applications of these compounds in magnetic refrigeration. Mn or Fe compounds with a strong electronic contribution to the entropy jump at the transition have higher MCE than $Gd_5Si_2Ge_2$ in spite of their lower magnetic moments.

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