Tailoring the magnetism of $\text{Tb}_5\text{Si}_2\text{Ge}_2$ compounds by La substitution

J. H. Belo, A. M. Pereira,^{*} and J. P. Araújo[†]*IFIMUP and IN-Institute of Nanoscience and Nanotechnology, Departamento de Física e Astronomia da Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal*

C. de la Cruz and A. M. dos Santos

Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6393, USA

J. N. Gonçalves and V. S. Amaral

Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

L. Morellon and M. R. Ibarra

Instituto de Nanociencia de Aragón, Universidad de Zaragoza, ES-50018 Zaragoza, Spain and Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain

P. A. Algarabel

Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, ES-50009 Zaragoza, Spain and Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain

C. Magen

Instituto de Nanociencia de Aragón, Universidad de Zaragoza, ES-50018 Zaragoza, Spain; Fundacion ARAID, ES-50004 Zaragoza, Spain and Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain

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In order to study the crystal structure, phase relationships, and magnetic properties of the system $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$, a series of polycrystalline samples with compositions ranging from $x = 0$ to $x = 5$ have been synthesized and characterized in detail. At room temperature, two structures have been detected: Compounds in the concentration range $0 \leq x < 1$ present a monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure, while for $x > 1$ a tetragonal Zr_5Si_4 -type structure is observed. The unit cell volume increases linearly with La concentration but with two different slopes: $\sim 18 \text{ \AA}^3/x$ and $\sim 33 \text{ \AA}^3/x$ for $0 \leq x < 1$ (monoclinic) and $x > 1$ (tetragonal), respectively. In the monoclinic region, an increase of T_C was observed, reaching a maximum value of $T_C \sim 154 \text{ K}$, at the $x = 0.75$ composition. This feature is explained based on specific La occupancy at the $R2$ site which was supported by density functional calculations for low La concentration. The samples that crystallized in the tetragonal structure exhibit a linear decrease of $T_C(x)$ with a slope of $\partial T_C/\partial x \sim -38 \text{ K/x}$, reaching 0 K for the $x = 5$ composition. A magnetic and structural x - T phase diagram of the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ system in the temperature range 4 – 300 K is proposed.

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I. INTRODUCTION

The $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ (R = rare earth) family has been the subject of intensive research due to its promising magnetoresponsive properties. The most notable of these phenomena are the giant magnetocaloric effect (GMCE) and the colossal magnetostriction effect.^{1–3} Recently it was found that such intense effects are a consequence of the close interplay between atomic structure and magnetic interactions.^{4–7} Therefore, a wide set of compounds of this ternary family have been synthesized and characterized, by changing both the Si:Ge ratio and the rare-earth element.^{1,3,8–11} These compounds stabilize into four main structures at room temperature: orthorhombic [O(I) and O(II)], monoclinic (M), and tetragonal (T or Zr_5Si_4) structures (for a review of the structural diversity see Refs. 2 and 3). The three former ones are associated with heavier rare-earth compounds (Sm, Gd, Tb, Dy, Ho, Er, and Lu), while the T structure occurs for the lighter rare-earth (La, Ce, and Pr) compounds.¹² These four structures share

similar building block units: two pseudocubes with the R atoms located at the vertices and the Si/Ge slightly displaced from the face centers [see cubes highlighted by squares in Fig. 1(b)]. The Si/Ge atoms bond in dimers that connect the pseudocubes, forming the rigid slabs in the ac plane (see T1,2 in Fig. 1) and allowing the packing of these slabs along the b direction [see T3,4 for M, O(I), and O(II) structures] or stripes in the bc plane [for the T structure, see Fig. 1(b)]. The three first structures are mainly distinguished by the distance which separates the interslab dimer formed by Si and Ge atoms in the T3,4 positions: larger, intermediate, and lower dimer distances are associated with O(II), M, and O(I) structures, respectively. In the tetragonal structure there are no defined slabs, as all the Si,Ge dimers have the same distance, and, consequently, there are no T3,4 atoms as can be seen in Fig. 1 and is described in more detail in Ref. 13. These crystal structures were found to be strongly correlated with their magnetic counterparts, enabling the construction of an universal structural and magnetic phase

FIG. 1. (Color online) Crystal structures of $\text{Tb}_5\text{Si}_2\text{Ge}_2$ (a) and $\text{La}_5\text{Si}_2\text{Ge}_2$ (b), corresponding to monoclinic ($P112_1/a$ space group) and tetragonal ($P4_12_12$ space group) structures, respectively.

diagram for the $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ (R = heavy rare earth) systems.¹⁴

In this context, chemical substitution can be a useful tool to stabilize atomic and magnetic structures and, consequently, tune and enhance the magnetoresponse properties of this system.^{15–17} Particularly for the substitution of Si and Ge, it was concluded that the valence electron concentration (VEC) plays an important role on the structure stabilization, for instance, by decreasing VEC (e.g., by substituting Ge for Ga)¹⁵ the O(I) structure is favored, while a VEC increase (e.g., substituting Si by P) leads to the formation of the O(II) structure.¹⁸ Less research has been devoted to the effects of substituting the rare-earth [$R_{1-x}R'_x(\text{Si},\text{Ge})_4$] systems. A notable result was obtained in a study on Tb substitution by Gd ($\text{Tb}_{5-x}\text{Gd}_x\text{Si}_4$), where it was shown that the Curie temperature increases linearly with the Gd concentration.¹⁹ In contrast, a similar study was performed on the $\text{Gd}_{5-x}\text{Y}_x\text{Ge}_4$ series, where a decrease on the magnetic ordering temperature with increasing Y was observed.¹⁶ Such effect was attributed to the dilution of the magnetic Gd sites by the nonmagnetic Y atoms. Intriguingly, an increase of the paramagnetic Curie temperature (θ_p) for $x = 1$ was detected experimentally and *ab initio* calculations showed a small polarization of the Y local magnetic moments. Recently, Mudryk and coworkers²⁰ have shown that, for small La concentrations, the La successfully substitutes Gd in Gd_5Ge_4 , which adopts the O(II) structure at room temperature (RT). Furthermore, they have shown that La occupies preferentially R2 sites (which are located at the slab edges as can be observed in Fig. 1). Despite the substitution of a magnetic (Gd) for a nonmagnetic ion (La), the magnetic behavior of the compound did not change significantly, because such low substitution did not interfere with the atomic chain responsible for the interslab ferromagnetic interactions ($R1\text{-}T3\text{-}T3\text{-}R1$). Inversely, in this same work, a similar amount of Lu substitution was shown to alter drastically the magnetic properties of the parent compound. Such behavior was explained by the Lu interference in the $R1\text{-}T3\text{-}T3\text{-}R1$ atomic chain, because it is proved that the R1 site is Lu preferential occupation site.²⁰ Therefore, after this study some important questions remained unanswered, namely what would be the role of higher La concentration on the

parent compounds exhibiting spontaneous magnetostructural transitions and how it would affect the magnetic exchange mechanisms.

Herein we report on the effects of substituting Tb magnetic ions by La (nonmagnetic) on the structural and magnetic properties of $\text{Tb}_5\text{Si}_2\text{Ge}_2$. The parent compound presents two distinct phase transitions (separated by approximately 10 K): one purely magnetic $[\text{PM},\text{M}] \rightarrow [\text{FM},\text{M}]$ followed (on cooling) by a structural change $[\text{FM},\text{M}] \rightarrow [\text{FM},\text{O(I)}]$.²¹ These features make $\text{Tb}_5\text{Si}_2\text{Ge}_2$ an ideal model system to study the effects of the dilution of nonmagnetic ions in systems with strong magnetostructural coupling, giving new insights to the important unanswered questions. To address this, a detailed magnetic and structural characterization of $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$, supported by density functional calculations, is presented and discussed in the following sections, resulting in a magnetic and structural x - T phase diagram.

II. EXPERIMENTAL DETAILS

Polycrystalline $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ samples with $x = 0, 0.075, 0.5, 0.75, 1, 2, 3, 4, 4.5$, and 5 were synthesized using an arc-melting furnace. The starting elements were 99.99 wt% pure Tb, 99.9 wt% pure La, and 99.9999 wt% pure Si and Ge (Alfa Aesar). Since there were no significant weight losses during the synthesis, the initial composition was assumed unchanged for all samples. The resulting structural phases and microstructure were checked by use of x-ray diffraction (XRD) [$\theta - 2\theta$ from 20° to 80° in steps of 0.03°] and scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS). The lattice parameters and unit cell volume of the predominant phases present in the samples were estimated using LeBail refinement with FULLPROF software.²² Density functional calculations using the WIEN2K code (L/APW + lo method) were performed. In these calculations the O(I) structure with a unit cell of composition $\text{Tb}_{19}\text{La}_1\text{Si}_8\text{Ge}_8$ was considered in order to calculate which Tb inequivalent site the La should occupy in order to minimize the system total energy. A superconducting quantum interference device (SQUID) was used to measure magnetization as a function of temperature in the range of 5–300 K and to measure $M(H)$ curves at 5 K, with applied fields up to $H = 50$ KOe. Neutron powder diffraction measurements were carried out at the HB-2A high resolution neutron powder diffractometer at the High Flux Isotope Reactor in the Oak Ridge National Laboratory with an incident-beam wavelength of $\lambda = 1.537660$ Å and in the temperature range of 4–300 K. Partial analysis of the neutron spectra was performed with SUPERCELL, a software included in the FULLPROF package,²² which correlates magnetic diffraction peaks with their corresponding propagation vectors.

III. EXPERIMENTAL RESULTS

A. Morphological and chemical characterization

In Fig. 2, representative SEM micrographs for samples with $x = 2$ and 0.5 [Figs. 2(a) and 2(b), respectively] are exhibited. The micrographs portray a dominant matrix associated with the main structural phase. Remnants of darker and lighter regions, related to lower and higher atomic mass,^{10,23} respectively, are highlighted in the insets. This observation was confirmed by

FIG. 2. (Color online) Backscattered electron SEM micrographs of samples with $x = 2$ (a) and 0.5 (b). Selected regions with secondary phases of these samples are highlighted in the respective insets.

the EDS spectra performed for each region, which revealed that the main phase has the $R:(\text{Si,Ge}) = 5:4$ stoichiometry ($R = \text{Tb} + \text{La}$), the darker regions correspond to the phase with 1:1 stoichiometry, and the lighter ones have the 5:3 composition (much less quantity). Such secondary phases commonly occur on these systems because, during the synthesis process, a eutectic-like decomposition occurs within a narrow region of the R -Si-Ge phase diagram.^{6,23,24} The overall stoichiometry of the sample detected by the micrographs and the EDS analysis demonstrates that all studied samples are macroscopically homogeneous with the 5:4 composition.

The XRD diffraction refinement analysis confirm the negligible amount of secondary phases, resulting in a volume fraction of less than 4% of the 1:1 phase for all samples. The addition of the 5:3 phase to the refinement did not improve the figure of merit and therefore was not included in the final refinement process. The main XRD analysis result revealed that, at room temperature (RT), the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ series presents two different crystallographic structures as a function of the La concentration. For $x < 1$, the typical monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure (P112₁/a space group) was found [see $x = 0.5$ sample refinement in Fig. 3(a)], whereas, for $x > 1$, the tetragonal Zr_5Si_4 -type (P4₁2₁2 space group) was obtained [see $x = 3$ sample refinement in Fig. 3(b)]. For the

FIG. 3. (Color online) $\theta - 2\theta$ X-ray diffraction patterns for $\text{Tb}_{4.5}\text{La}_{0.5}\text{Si}_2\text{Ge}_2$ (a) and $\text{Tb}_2\text{La}_3\text{Si}_2\text{Ge}_2$ (b) samples. The vertical ticks correspond to the peaks positions associated with the each phase used in the refinement [M and 1:1 for (a); T and 1:1 for (b)].

FIG. 4. (Color online) (a) Lattice parameters and (b) unit cell volume of $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ as a function of lanthanum concentration at RT, obtained from refinements of XRD data. For $x = 1$, the lattice parameters and volume of both monoclinic and tetragonal structural phases are represented. The inset at (b) is γ , the distorted angle of the M structure, as a function of x for $x < 1$ values at RT.

$x = 0$ and $x = 5$ samples (end members), our results are in accordance with the ones obtained from the literature.^{12,25} In the narrow region $x \sim 1$, both structures types were included in the refinement, resulting in a mixture of $\sim 30\%$ volume amount for the tetragonal phase and $\sim 60\%$ for the monoclinic one. The lattice parameters and volume dependence on the La concentration are displayed in Figs. 4(a) and 4(b), respectively, and summarized in Table I. From Fig. 4, it is clear that the lattice parameters increase with La content as expected, the major variation being in the longer axis, normal to the rigid slabs (b for M and c for T structures; see in Fig. 1). Consequently, the total unit cell volume follows the same trend, exhibiting a linear dependence with respect to the La content, although with two different slopes: $\partial V / \partial x \sim 18$ and $33 \text{ Å}^3/x$, for $x < 1$ and $x > 1$, respectively. The results show a continuous order parameter through the change of crystal structure, similarly to what has been previously shown in other rare-earth substitutions.^{16,26,27} The observed behavior arises mainly from the higher covalent radius of La ($r_{\text{La}} = 2.07 \text{ Å}$) when compared with the Tb one ($r_{\text{Tb}} = 1.94 \text{ Å}$).²⁸ The $\gamma(x)$ function (the distorted angle of the M structure), displayed in the inset of Fig. 4(b), decreases linearly with x , for the $x \leq 1$ region. This shows that with La substitution the structure symmetry elements increase and the unit cell becomes continuously orthorhombic.

B. Magnetic characterization

The temperature dependence of magnetic and structural characterization of the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ system are presented in this section through field-cooled magnetization curves $M(T)$ and $M(H)$ measured at $T = 5 \text{ K}$ and by neutron diffraction measurements.

1. For $x < 1$; monoclinic phase

The $M(T)$ and respective reciprocal magnetic susceptibility $[\chi^{-1}(T) = \frac{H}{M}(T)]$ curves measured with $H = 20 \text{ Oe}$, on heating, for the $x = 0.5$ composition are displayed in Fig. 5(a). Here it can be seen that a change of the magnetic state, from a PM to a FM state, occurs at $T = T_C \sim 140 \text{ K}$ [obtained by the minimum of the numerical derivative (dM/dT)]. This measurement is representative of the $M(T)$ data obtained for

TABLE I. Room-temperature crystalline structure, unit cell parameters, and volume for the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ compounds.

x	Structure	a (Å)	b (Å)	c (Å)	γ °	Vol. (Å) ³
0	P112 ₁ /a (M)	7.509(1)	14.658(9)	7.711(4)	93.010(4)	847.5(5)
0.075	P112 ₁ /a (M)	7.510(3)	14.660(7)	7.707(4)	93.000(3)	847.3(2)
0.5	P112 ₁ /a (M)	7.526(4)	14.711(8)	7.753(4)	92.523(3)	857.5(2)
0.75	P112 ₁ /a (M)	7.515(5)	14.742(1)	7.776(5)	92.109(4)	860.8(2)
1	P112 ₁ /a (M)	7.5445(4)	14.790(1)	7.7442(3)	91.794(7)	863.7(1)
1	P4 ₁ 2 ₁ 2 (T)	7.8664(6)	7.8664(6)	14.575(4)		901.9(3)
2	P4 ₁ 2 ₁ 2 (T)	7.898(4)	7.898(4)	14.594(7)		910.5(2)
3	P4 ₁ 2 ₁ 2 (T)	7.956(2)	7.956(2)	14.803(1)		937.1(2)
4	P4 ₁ 2 ₁ 2 (T)	8.043(4)	8.043(4)	14.973(9)		968.6(2)
4.5	P4 ₁ 2 ₁ 2 (T)	8.072(1)	8.072(1)	15.152(5)		987.2(6)
5	P4 ₁ 2 ₁ 2 (T)	8.100(2)	8.100(2)	15.382(7)		1009.2(5)

the compounds that crystallize in the M structure at RT. The most remarkable feature obtained for the other compounds with this structure was a surprising increase of the Curie temperature (T_C) with x , reaching a maximum of $T_C \sim 154$ K for the $x = 0.75$ compound (see Table II).

A second anomaly observed at $T \equiv T_{\text{SR}} \sim 52$ K on the $M(T)$ curve is assigned to a spin reorientation process similar to that observed for the parent compound.^{29,30} A decrease of T_{SR} with x is observed in this La concentration range, reaching a minimum of 48 K also for the $x = 0.75$ compound. Furthermore, the reciprocal susceptibility represented in the inset of Fig. 5(a) follows the typical Curie Weiss behavior, in the high-temperature region ($T > 200$ K); however, the existence of a deviation from this typical linear behavior starting at $T = T_G = 200$ K and ending at $T = T_C$ is clearly seen. Such behavior reveals the presence of short-range magnetic clusters in the PM matrix and was previously attributed to the so-called Griffiths-like phase.^{14,31–33} The effective paramagnetic moments obtained are generally lower than the one found for the parent compound of $\mu_{\text{eff}} = 9.8 \mu_B/\text{Tb}^{3+}$ and its theoretical value of $9.72 \mu_B/\text{Tb}^{3+}$.³¹ Such results indicate the presence of different local interactions that can decrease the effective magnetic moment, such as crystal field effects as recently found in the Ho system.³⁴

From the extrapolation of the high-temperature regime ($T > 200$ K), using the Curie Weiss law, the paramagnetic

Curie temperature (Θ_P) is extracted. Table II summarizes the μ_{eff} per Tb^{3+} ion and Θ_P values for all the studied compositions.

Neutron diffraction measurements were performed in order to obtain new information of simultaneously magnetic and atomic structure as a function of temperature, enabling the representation of neutron thermodiffractograms, which are shown in Fig. 5(c) and Figs. 7(a) and 7(b). The neutron thermodiffractogram [Fig. 5(c)] of $\text{Tb}_{4.5}\text{La}_{0.5}\text{Si}_2\text{Ge}_2$ collected in HB-2A in the temperature range 4–180 K on heating shows, at ~ 140 K, the appearance of the peaks resulting from diffraction of the atomic planes $[-1\ 3\ 2]$ (31.3°), $[0\ 1\ 3]$ (35.0°), and $[-1\ 1\ 3]$ (37.4°), characteristic of the M phase, and the disappearance of the peaks $[2\ 3\ 1]$ (32.2°), $[2\ 4\ 0]$ (34.5°), and $[2\ 2\ 2]$ (35.6°), characteristic of the O(I) phase, indicating the occurrence of the structural phase transition $[\text{O(I)}] \rightarrow [\text{M}]$, similarly to what was found in the parent compound. As for the magnetic structure, at ~ 140 K the total disappearance of the peaks with indices $[1\ 3\ 1]$ (24.3°), $[1\ 0\ 2]$ (25.8°) and $[2\ 3\ 0]$ (29.9°) can also be observed, revealing the magnetic order phase transition $[\text{FM}] \rightarrow [\text{PM}]$. This result is in complete accordance with the magnetization experiment, as can be observed in Fig. 5(b), where the experimental $M(T)$ curve is overlapped with the temperature dependence of the reflections: $[1\ 3\ 1]_{\text{mag}}$ (24.3°) and the structural ones $[2\ 3\ 1]_{\text{O}}$ (32.2°) and $[-1\ 1\ 3]_{\text{M}}$ (37.4°). From the contour plots it can

TABLE II. Relevant magnetic properties of the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ compounds.

x	T_C (K)	T_{SR} (K)	T_G (K)	Θ_P (K)	$\mu_{\text{eff}}/\text{Tb}^{3+}$ (μ_B)	$\mu_{\text{sat}}/\text{Tb}^{3+}$ (μ_B)
0	114	67	208	94.0	9.8	8.8 ^a
0.075	112	65	204	92.1	7.1	7.1
0.5	140	52	200	83.8	8.2	8.1
0.75	154	48	195	95.7	7.3	7.8
1	150	—	186	111.2	8.6	7.8
2	105	—	—	88.4	7.3	7.4
3	82	—	—	69.7	6.4	6.8
4	42	—	—	42.5	7.3	7.2
5	0	—	—	0	0	0

^aThis value is reported in Ref. 24.

FIG. 5. (Color online) (a) Field-cooled (FC) magnetization curve of $\text{Tb}_{4.5}\text{La}_{0.5}\text{Si}_2\text{Ge}_2$ measured with a $H = 20$ Oe. (Inset) Temperature dependence of the respective reciprocal magnetic susceptibility curve. (b) Comparison of $M(T)$ curve with integrated intensity of the magnetic neutron diffraction peak, $[1\ 3\ 1]_{\text{mag}}$ (24.3°), and nuclear structural peaks: $[2\ 3\ 1]_{\text{O}}$ (32.2°) and $[-1\ 1\ 3]_{\text{M}}$ (37.4°). (c) Contour plot of the neutron thermodiffraction of $\text{Tb}_{4.5}\text{La}_{0.5}\text{Si}_2\text{Ge}_2$ in the temperature range of 4–180 K. The circular and star symbols refer to diffraction peaks originated by atomic and magnetic structures, respectively.

be verified that the magnetic and structural transitions occur simultaneously: $\text{O}(\text{I}) \rightarrow \text{M}$ and $\text{FM} \rightarrow \text{PM}$, thus revealing a fully coupled magnetostructural transition at $T_{\text{MS}} \sim 140$ K, similarly to what was obtained in Refs. 35 and 36

For the $x = 0.5$ compound at $T = 4$ K, a refinement considering the magnetic and atomic structure was performed, leading to a result similar to the ones previously found,^{21,29} i.e., a commensurate magnetic structure with propagation vector $\vec{k} = (0, 0, 0)$.

2. For $x > 1$; tetragonal phase

Figure 6 presents $M(T)$ and $\chi^{-1}(T)$ (inset) curves for $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ and $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$. A decrease of ordering temperature with an increasing amount of La is observed (see Fig. 6), with $T_C \sim 105$ K and 42 K for $x = 2$ and 4, respectively. In the low-temperature region, no spin reorientation transition is detected.^{29,30} Likewise, there is also no evidence of the Griffiths-like phase on the reciprocal susceptibility data for these compounds [see insets of Figs. 6(a) and 6(b)].

The determined μ_{eff} values for both compounds are around $7.2 \mu_B/\text{Tb}^{+3}$, which, again, is lower than the one expected for a Tb ion. The value of Θ_P decreases with the amount of La, almost reaching $\Theta_P = T_C$ for $x = 4$. This reveals that the degree of competition between interactions (which yields spin canting) is reduced by the weakening of the magnetic moments interactions.

Neutron diffraction measurements in the temperature range 4–250 K were also performed in these compounds. The experimental results are displayed in Fig. 7(a) and 7(b) for $x = 2$ and 4, respectively. From these contour plots, no structural phase transition is observed, showing that the tetragonal phase remains stable at low temperatures, since the $[2\ 0\ 3]$ and $[2\ 1\ 3]$ (circles in Fig. 7) reflections suffer no significant change for these two compositions.

The major changes are observed at the low-scattering-angle region, related with the magnetic reflections corresponding to $[0\ 1\ 1]$ (12.7°), $[1\ 1\ 0]$ (15.8°), $[0\ 1\ 2]$ (16.39°), $[1\ 1\ 2]$ (20.0°), and $[1\ 2\ 1]$ (25.8°) for $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ and $[0\ 1\ 1]$ (12.4°), $[1\ 1\ 0]$ (15.5°), $[0\ 1\ 2]$ (16.2°), $[1\ 1\ 2]$ (19.6°), and $[0\ 2\ 2]$ (25.1°)

FIG. 6. (Color online) Field-cooled (FC) magnetization curves of (a) $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ and (b) $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$ measured with a 20-Oe applied magnetic field in SQUID. (Insets) The reciprocal susceptibilities for (a) $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ and (b) $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$.

FIG. 7. (Color online) Contour plot of the neutron thermodiffractograms of (a) $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ in temperature range 4–140 K and (b) $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$ in temperature range 4–80 K. The circular and star symbols refer to diffraction peaks originating from the atomic and magnetic structures, respectively.

for $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$, as is more clearly shown in Fig. 8. It should be noted that the small observed shift on the angles mentioned for the two compounds is related with volumetric effect ($x = 4$ has higher volume than $x = 2$ compound, as can be seen in Table I), rather than with different magnetic structures. For $x = 4$ a general decrease of the magnetic peaks intensities is observed in the contour plot of Fig. 7(b) when compared with the $x = 2$ diffraction results, as there are fewer magnetically active ions (reduction is more noticeable in Fig. 8). The neutron diffraction measurements are in agreement with the T_C values, ~ 105 and 42 K for $x = 2$ and 4 , respectively (see Table II).

In Fig. 8 the neutron diffraction spectra at $T = 4$ K for the $x = 2$ and $x = 4$ compositions are shown. In this figure, it is clear that magnetic structures are similar, although a significant

FIG. 8. (Color online) Neutron diffraction spectra in the 2θ range $[10,34]^\circ$ of $\text{Tb}_3\text{La}_2\text{Si}_2\text{Ge}_2$ (a) and $\text{Tb}_1\text{La}_4\text{Si}_2\text{Ge}_2$ (b) compounds in the FM region ($T = 4$ K). Each spectrum was normalized to maxima in order to allow a better comparison between spectra.

FIG. 9. (Color online) Magnetization isotherms for $x = 0.5, 0.75, 1, 2, 3, 4$, and 5 compounds measured at 5 K in magnetic fields up to 50 kOe.

reduction of magnetic scattering (low angles) is observed when comparing with the structural scattering (high angles), as previously mentioned. The major changes are observed in the intensities relation of the $[1\ 1\ 0]$ and $[0\ 1\ 2]$ peaks from the $x = 2$ to the $x = 4$ compositions and the absence of the $[1\ 2\ 1]$ reflection in the $x = 4$ spectrum. Such behavior may be explained by a reorientation of the Tb magnetic moments, from the ab plane for $x = 2$ toward the c direction for $x = 4$. By using the SUPERCELL software, it was found that the magnetic structure of both compounds is commensurate with the same propagation vector, $\vec{k} = (000)$, similarly with the monoclinic ones.

Measurements of the isothermal magnetization versus applied magnetic field (H) at 5 K were performed for all samples, in the range of 0 to 50 kOe (see Fig. 9). In Fig. 9, the expected lowering of saturation magnetization with La substitution can be observed. Nevertheless, the saturation magnetization moment per Tb^{3+} ion (see Table II) does not suffer significant changes with La substitution, averaging at $\sim 7.6 \mu_B$. Furthermore, the $M(H)$ curves present a FM character corroborating the magnetic state obtained from $M(T)$ curves.

IV. MAGNETIC-STRUCTURAL PHASE DIAGRAM AND DISCUSSION

Based on the presented results, we propose a magnetic and crystallographic composition-temperature (x - T) phase diagram of the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ system, which is displayed in Fig. 10. At RT, all compositions are PM and two distinct crystal structures are observed as a function of the composition (M and T structures).

The compounds with $0.25 < x < 1$, crystallize in the M structural phase at RT and, on cooling, undergo a fully magnetostructural transition from [M,PM] to [O(I),FM] similar to what is observed in $\text{Gd}_5\text{Si}_2\text{Ge}_2$. Nevertheless, for lower La doping levels ($x \leq 0.25$) no significant changes are observed in the magnetic and structural properties, being expected that the magnetic and structural transitions still occur separately, by a few degrees, as observed in the parent compound, $\text{Tb}_5\text{Si}_2\text{Ge}_2$.

FIG. 10. (Color online) Magnetic and crystallographic x - T phase diagram of $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ in the temperature range 5–250 K.

These results for low La concentration are in accordance with the previous result on Gd_5Ge_4 .²⁰

Surprisingly, for $0.25 \leq x < 1$ compositions, the magnetic phase transition temperature increases with La amount at a rate of $dT_C/dx \sim 57$ K/ x , reaching a maximum of 154 K. Mudryk and coworkers' report inferred that for higher La concentrations a loss of ferromagnetism should occur²⁰ and thus never predicting an increase of T_C as we observed experimentally for $0.075 < x < 1$ composition. A first possible explanation was to relate this behavior with the change of the unit cell volume caused by the La substitution. However, a previous work on a similar compound, $\text{Tb}_5(\text{Si}_{0.6}\text{Ge}_{0.4})_4$, showed that a 4-GPa external pressure (which promotes a reduction of the unit cell volume) causes the T_C to increase to 150 K.³⁷ Therefore, since in the present case a volume expansion of $\sim 2\%$ occurs (analogous to the application of a negative external pressure), this hypothesis was excluded. Hence, only an intrinsic mechanism can be associated with the increase of T_C 's, namely changes in the magnetic interactions of the parent compound induced by the La substitution. This T_C behavior has already been observed in binary compounds of Dy-La and Er-La, where it was attributed to a change in the magnetic structure, i.e., it was observed that La substitution favors effectively the collinear alignment of magnetic moments, destroying the helical structure observed in the elemental Dy and Er.^{38,39} Considering the θ_P obtained from $\chi^{-1}(T)$ (see Table II), an increase of the θ_P reaching maximum value at $x = 1$ is found. This observation reinforces the hypothesis that La substitution favors the collinearity of the Tb magnetic moments (similarly to what was observed in the binary compounds), thus probably reducing the antiferromagnetic (AFM) exchange which is responsible for the observed canting effect within the rigid slab in $\text{Tb}_5\text{Si}_2\text{Ge}_2$.^{29,30} As mentioned in the Introduction, since the ferromagnetism in these complex compounds stems from the $R1$ - $T3$ - $T3$ - $R1$ chain,²⁰ La is expected to occupy the $R2$ or $R3$ sites. Thus, in order to further investigate the preferential specific site of La substitution, density functional calculations were performed using the WIEN2K code (L/APW + lo method) considering the

FIG. 11. (Color online) In (a) the total energies difference of three simulated O(I) unit cells with $\text{Tb}_{19}\text{La}_1\text{Si}_8\text{Ge}_8$ composition and with La occupying one different Tb inequivalent site are presented. These results were obtained by density functional calculations using the WIEN2K code (L/APW + lo method) and the LDA (green circles) and LDA + U (red diamond-like symbols). In (b) the magnetization temperature dependence curve of $\text{Tb}_{4.5}\text{La}_{0.5}\text{Si}_2\text{Ge}_2$ after zero-field cooling measured on heating with $H = 20, 5000$, and 15000 Oe within the temperature range³⁰, 100] K.

intra-atomic Coulomb correlation term U (LDA + U), with U and J assuming the values 6.7 and 0.7 eV, respectively.⁴⁰ Three independent calculations were realized by substituting 1 of the 20 Tb atoms present in the unit cell of the O(I) structure by a La one, where for each calculation the La atom occupied a different inequivalent Tb site ($R1$, $R2$, and $R3$). These calculations assumed a ferromagnetic spin polarization of the Tb atoms and kept the structure fixed. As pictured in Fig. 11(a), according to LDA + U calculations, the resulting cell with composition $\text{Tb}_{19}\text{La}_1\text{Si}_8\text{Ge}_8$ has significantly lower energy when the La atom occupies the $R2$ site in the structure instead of the $R1$ or $R3$ sites [the $R2$ site in the O(I) structure is an identical site to the $R2$ site in the M structure, which is pictured in Fig. 1]. Comparing the lowest energy difference between the two considered sites, which is between the $R2$ and $R3$ sites ($\Delta_{R2-R3} \sim 555$ meV; see Fig. 11), with the energy arising from the spin-orbit interaction on the Tb^{3+} ion ($\Delta \sim 0.24$ meV, reported in Refs. 40 and 42), one realizes that Δ_{R2-R3} is more than 2 times higher than Δ . This observation suggests that the spin-orbit coupling interactions should not change the main results obtained in the LDA + U calculations. Furthermore, this outcome is in accordance with the proved La preferential occupation in the $R2$ site for the Gd_5Ge_4 .²⁰ Herein, we propose the following mechanism for low La concentration: The La is preferentially located at the $R2$ site, thus not interfering with the FM interaction at the $R1$ - $T3$ - $T3$ - $R1$ chain as stated in Ref. 20. Despite this fact, the $R2$ site is the one exhibiting higher spin canting in the parent compound ($x = 0$) and, thus, the La occupation of this site probably favors the magnetic moments collinearity (decrease of AFM interactions between Tb atoms).^{29,30}

For $x > 1$ at RT, these compounds crystallize on the tetragonal phase (Zr_5Si_4 structure), remaining unchanged down to 5 K. In this concentration region, a decrease of T_C is observed as generally expected,²⁰ with a rate of $dT_C/dx \sim -37.5$ K/ x

and extrapolating to zero for the concentration $x = 5$ (absence of Tb). We highlight that the percolation theory of diluted magnetic systems predicts a threshold for the non-magnetic ion concentration from which the long-range magnetic order is suppressed (absence of T_C). This was not observed in the present case, revealing that the main magnetic exchange mechanism is the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, as previously suggested.⁴¹ Since with this substitution the number of carriers is preserved, the decrease of T_C is only directly related with the increase of distance between the magnetically active ions, i.e., there is an increase on the RKKY coherence length. In this composition region it is expected that the $R2$ sites are already mostly occupied, and the La ions start populating the other R positions, therefore increasing the atomic distances between magnetically active ions, leading to a reduction of the exchange interactions and, consequently, to a decrease of T_C .⁴²

Concerning the spin reorientation transition observed at low temperatures, a decrease of T_{SR} with La concentration is observed for $x < 1$. For a higher La amount, where the tetragonal phase is observed, this transition is suppressed. In order to confirm the main mechanism playing in this transition, zero-field-cooled magnetization temperature dependence curves of the $x = 0.5$ composition for different applied magnetic fields ($H = 20, 5000$, and $15\,000$ Oe) were also performed and are represented in Fig. 11(b). According to these results, T_{SR} increases for increasing fields, until it becomes suppressed at a critical field (between 5000 and $15\,000$ Oe). This feature can be interpreted as evidence for the presence of crystal field interactions. Thus, it is expected that an enhancement of the Zeeman splitting effect, caused by increasing applied fields, promotes an increase of the crystal field gap between the ground state and the first excited state. For a certain field value, such an effect does not allow the crossover of levels responsible for the spin reorientation transition observed experimentally. Furthermore, due to the fact that the La^{3+} ion has all its s , p , and d levels occupied, but has a fully empty f band,⁴² a reduction of crystal field interactions is expected with an increasing La amount. This reasoning corroborates with our results, where a decrease (low La concentration) and even the suppression of this transition (higher La concentration) occurs. In fact, this f band is often responsible for the appearance of strong crystal field effects, promoting the appearance of spin reorientation transitions.⁴² Finally, the absence of a Griffiths-like regime was revealed for the tetragonal structure, proving that this exotic effect is inherent to structure symmetry, as previously suggested.¹⁴

V. CONCLUSIONS

This work presents a thorough study of the structural and magnetic properties of the $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ system which allowed us the construction of the respective x - T phase diagram in the temperature range 4 – 300 K. From this work the major outcomes are that for low La substitution a decrease on the distortion of the monoclinic structure occurs (γ decrease). Moreover, an increase of T_C is observed which is probably related to the favoring of the magnetic moments collinearity due to the preferential La substitution at the $R2$ sites. Furthermore, La substitution also influences the relation between atomic and magnetic structure by fully coupling the magnetic and structural transitions for $0.25 \leq x < 1$ compositions. For the $x > 1$ region, the stable atomic structure is tetragonal without any structural transition occurring down to 5 K. Magnetically, a decrease of T_C is observed due to the natural effect of nonmagnetic atoms dilution in the R sites, weakening/breaking the main magnetic atomic chain responsible for the interslab ferromagnetic interactions ($R1$ - $T3$ - $T3$ - $R1$). Additionally, the absence of T_{SR} unveils a decrease/annihilation of magnetocrystalline anisotropy competition within the rigid slabs. Finally, this ability to “manipulate” individually the atoms which tune the magnetic properties, previously identified by Mudryk and coworkers on Gd_5Ge_4 ²⁰ and here extended to the Tb system, constitutes an important tool in the study of the magnetism of the $R_5(\text{Si,Ge})_4$ compounds.

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*ampereira@fc.up.pt

†jearaujo@fc.up.pt

¹V. K. Pecharsky and K. A. Gschneidner Jr., *Pure Appl. Chem.* **79**, 1383 (2007).

²V. K. Pecharsky and K. A. Gschneidner Jr., *Adv. Mat.* **13**, 683 (2001).

³G. J. Miller, *Chem. Soc. Rev.* **35**, 799 (2006).

⁴L. Morellon, J. Blasco, P. A. Algarabel, and M. R. Ibarra, *Phys. Rev. B* **62**, 1022 (2000).

⁵V. K. Pecharsky, K. A. Gschneidner, Ya. Mudryk, and D. Paudyal, *J. Magn. Magn. Mater.* **321**, 3541 (2009).

⁶J. D. Moore, K. Morrison, G. K. Perkins, D. L. Schlagel, T. A. Lograsso, K. A. Gschneidner Jr., V. K. Pecharsky, and L. F. Cohen, *Adv. Mat.* **21**, 3780 (2009).

⁷C. Magen, Z. Arnold, L. Morellon, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, *Phys. Rev. Lett.* **91**, 207202 (2003).

⁸C. Ritter, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, *Phys. Rev. B* **65**, 094405 (2002).

- ⁹C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, C. Ritter, A. O. Pecharsky, K. A. Gschneidner Jr., and V. K. Pecharsky, *Phys. Rev. B* **70**, 224429 (2004).
- ¹⁰A. M. Pereira, J. B. Sousa, J. P. Araujo, C. Magen, P. A. Algarabel, L. Morellon, C. Marquina, and M. R. Ibarra, *Phys. Rev. B* **77**, 134404 (2008).
- ¹¹C. Ritter, C. Magen, L. Morellon, P. A. Algarabel, M. R. Ibarra, A. M. Pereira, J. P. Araujo, and J. B. Sousa, *Phys. Rev. B* **80**, 104427 (2009).
- ¹²K. A. Gschneidner, V. K. Pecharsky, A. O. Pecharsky, V. V. Ivchenko, and E. M. Levin, *J. Alloys Comp.* **303**, 214 (2000).
- ¹³J. Yao, P. Lyutyy, and Y. Mozharivskyj, *Dalton Trans.* **40**, 4275 (2011).
- ¹⁴A. M. Pereira, L. Morellon, C. Magen, J. Ventura, P. A. Algarabel, M. R. Ibarra, J. B. Sousa, and J. P. Araujo, *Phys. Rev. B* **82**, 172406 (2010).
- ¹⁵H. Wang, S. Misra, F. Wang, and G. J. Miller, *Inorg. Chem.* **49**, 4586 (2010).
- ¹⁶S. Misra and G. J. Miller, *J. Am. Chem. Soc.* **130**, 13900 (2008).
- ¹⁷V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature* **429**, 853 (2004).
- ¹⁸V. Svitlyk and Y. Mozharivskyj, *Solid State Sci.* **11**, 1941 (2009).
- ¹⁹Y. I. Spichkin, V. K. Pecharsky, and K. A. Gschneidner, *J. Appl. Phys.* **89**, 1738 (2001).
- ²⁰Y. Mudryk, D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, S. Misra, and G. J. Miller, *Phys. Rev. Lett.* **105**, 066401 (2010).
- ²¹L. Morellon, C. Ritter, C. Magen, P. A. Algarabel, and M. R. Ibarra, *Phys. Rev. B* **68**, 024417 (2003).
- ²²J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993).
- ²³J. S. Meyers, L. S. Chumbley, F. Laabs, and A. O. Pecharsky, *Scripta Mat.* **47**, 509 (2002).
- ²⁴F. C. Fernández, Ph.D. thesis, Barcelona University, 2003.
- ²⁵L. Morellon, C. Ritter, C. Magen, P. A. Algarabel, and M. R. Ibarra, *Phys. Rev. B* **68**, 024417 (2003).
- ²⁶K. Prabahar, D. M. Raj Kumar, M. Manivel Raja, and V. Chandrasekaran, *J. Magn. Magn. Mater.* **323**, 1755 (2011).
- ²⁷S. Misra, E. T. Poweleit, and G. J. Miller, *Z. Anorg. Allg. Chem.* **635**, 889 (2009).
- ²⁸B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, and S. Alvarez, *Dalton Trans.* **130**, 2832 (2008).
- ²⁹V. O. Garlea, J. L. Zarestky, C. Y. Jones, L.-L. Lin, D. L. Schlagel, T. A. Lograsso, A. O. Tsokol, V. K. Pecharsky, K. A. Gschneidner Jr., and C. Stassis, *Phys. Rev. B* **72**, 104431 (2005).
- ³⁰J. P. Araújo, A. M. Pereira, M. E. Braga, R. P. Pinto, J. M. Teixeira, F. C. Correia, J. B. Sousa, L. Morellon, P. A. Algarabel, C. Magen, and M. R. Ibarra, *J. Phys.: Condens. Matter* **17**, 4941 (2005).
- ³¹C. Magen, P. A. Algarabel, L. Morellon, J. P. Araujo, C. Ritter, M. R. Ibarra, A. M. Pereira, and J. B. Sousa, *Phys. Rev. Lett.* **96**, 167201 (2006).
- ³²Z. W. Ouyang, *J. Appl. Phys.* **108**, 03390 (2010).
- ³³W. Tian, A. Kreyssig, J. L. Zarestky, L. Tan, S. Nandi, A. I. Goldman, T. A. Lograsso, D. L. Schlagel, K. A. Gschneidner Jr., V. K. Pecharsky, and R. J. McQueeney, *Phys. Rev. B* **80**, 134422 (2009).
- ³⁴A. M. Pereira, J. P. Araujo, J. R. Peixoto, M. E. Braga, P. A. Algarabel, C. Magen, L. Morellon, M. R. Ibarra, and J. B. Sousa, *Phys. Rev. B* **83**, 144117 (2011).
- ³⁵L. 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).
- ³⁶A. M. Pereira, A. M. dos Santos, C. Magen, J. B. Sousa, P. A. Algarabel, Y. Ren, C. Ritter, L. Morellon, M. R. Ibarra, and J. P. Araújo, *Appl. Phys. Lett.* **98**, 122501 (2011).
- ³⁷Y. C. Tseng, H. J. Ma, C. Y. Yang, Y. Mudryk, V. K. Pecharsky, K. A. Gschneidner Jr., N. M. Souza-Neto, and D. Haskel, *Phys. Rev. B* **83**, 104419 (2011).
- ³⁸W. C. Koehler, *J. Appl. Phys.* **36**, 1078 (1965).
- ³⁹B. Coqblin, *The Electronic Structure of Rare-Earth Metals and Alloys: The Magnetic Heavy Rare-Earths* (Academic Press, New York, 1977).
- ⁴⁰D. Paudyal, Y. Mudryk, V. K. Pecharsky, and K. A. Gschneidner Jr., *Phys. Rev. B* **84**, 014421 (2011).
- ⁴¹W. 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).
- ⁴²J. Jensen and A. R. Mackintosh, *Rare Earth Magnetism* (Clarendon Press, Oxford, 1991).