



# Structural and magnetic properties of the ternary compounds $Gd_2Sc_3X_4$ with $X = Si$ and $Ge$

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## ABSTRACT

X-ray diffraction on single crystal performed on  $Gd_2Sc_3Si_4$  reveals that this ternary silicide crystallizes as  $Gd_2Sc_3Ge_4$  in the orthorhombic  $Ce_2Sc_3Si_4$ -type with a small deficiency in gadolinium leading to the formula  $Gd_{1.88(1)}Sc_3Si_4$ . The structure is formed by  $[Gd_2Sc_3Si_4]$  slabs with Si–Si inter slab covalent bonds. The investigation of the  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  compounds by magnetization, electrical resistivity and specific heat measurements reveals their antiferromagnetic behaviors;  $Gd_2Sc_3Si_5$  having a Néel temperature (48–52 K) higher than that observed (22–23 K) for  $Gd_2Sc_3Ge_4$ .

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## 1. Introduction

The ternary compounds  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  have been prepared and characterized structurally for the first time by Morozkin et al. [1]. Using X-ray powder diffraction, these authors report that these intermetallics adopt the orthorhombic  $Ce_2Sc_3Si_4$ -type structure [2] an ordered ternary derivative of the  $Sm_5Ge_4$ -type (space group  $Pnma$ ) [3]. In  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$ , Gd atoms occupy one samarium  $8d$  site while Sc atoms are distributed on the two other  $8d$  and  $4c$  sites. More recently, using X-ray diffraction on single crystal, Misra and Miller [4] confirmed that  $Gd_2Sc_3Ge_4$  adopts the  $Ce_2Sc_3Si_4$ -type structure and it was observed a small exchange between gadolinium and scandium on the two  $8d$  sites with occupancy ratios Gd:Sc respectively of 0.967:0.033 and 0.031:0.969. Among the compounds adopting the  $Ce_2Sc_3Si_4$ -type structure, it was reported that  $Ce_{1.22}Sc_3Ge_4$  crystallizes with a defect derivative induced by a partial occupancy of the cerium site [5]. These two last studies show that the compounds crystallizing with the orthorhombic  $Ce_2Sc_3Si_4$ -type structure can exhibit defect or disordered structure. This is why a single-crystal X-ray diffraction investigation of  $Gd_2Sc_3Si_4$  was performed and will be presented for the first time in this paper.

It is also interesting to point out that in the series of compounds with structure deriving from the orthorhombic  $Sm_5Ge_4$ -type, the existence or not of inter slab covalent bonds between germanium or silicon atoms is of importance to understand their crystallographic

and physical properties [6,7]. These covalent bonds when they are observed increase the linking between the slabs formed by the rare-earth and the germanium or silicon atoms. For instance it was nicely shown in the  $Gd_5Si_4$ – $Gd_5Ge_4$  system that the making or breaking of these covalent bonds can be compared to the closing or opening of a nano-zipper [6,7].

Concerning, the magnetic properties of these compounds based on Gd, only the temperature dependence between 77 and 300 K of the susceptibility of  $Gd_2Sc_3Si_4$  was reported [8]. The ternary silicide exhibits a paramagnetic behavior in this temperature range with a positive ( $\theta_p = 43.6$  K) paramagnetic Curie temperature.

Considering that the intermetallics  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  coexist in the Gd–Sc–Si or Ge systems with the ferromagnetic compounds GdScSi and GdScGe showing an unusually high Curie temperatures ( $T_C = 318$  and 320–350 K respectively for GdScSi and GdScGe) [9–11], it is interesting to determine their magnetic properties. In this work, we present and discuss also our results obtained for the first time on the magnetic properties of  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  investigated by electrical resistivity, magnetization and specific heat measurements. These properties are compared to those reported previously on  $RE_2Ti_3Ge_4$  ( $RE = Gd, Tb, Dy, Ho$  and Er) [12] crystallizing as  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  in the orthorhombic  $Ce_2Sc_3Si_4$ -type.

## 2. Experimental

Starting materials for the preparation of the  $Gd_2Sc_3Si_4$  and  $Gd_2Sc_3Ge_4$  samples were ingots of gadolinium (smart-elements), scandium pieces (smart-elements), silicon and germanium pieces (Johnson–Mattey), all with stated purities better than 99.9%. The Gd ingots were then mixed with Sc and Si or Ge pieces in the ideal 2:3:4 atomic ratio and arc-melted under argon (1 atm) purified before with magnesium sponge (673 K). The product buttons were remelted three times to ensure homo-

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**Table 1**  
Crystal data and structure refinement<sup>a</sup> for Gd<sub>1.88(1)</sub>Sc<sub>3</sub>Si<sub>4</sub> at 293 K.

Chemical formula	Gd <sub>1.88(1)</sub> Sc <sub>3</sub> Si <sub>4</sub>
Cell setting, space group	Orthorhombic, <i>Pnma</i>
<i>a</i> (Å)	7.0728(11)
<i>b</i> (Å)	13.9710(11)
<i>c</i> (Å)	7.379(2)
<i>Z</i> , <i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	4, 4.943
Radiation type, $\mu$ (mm <sup>-1</sup> )	Mo K $\alpha$ , 20.06
Diffractometer	Nonius Kappa CCD
Absorption correction, shape	Gaussian, triangulare plate
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.734, 0.887
No. of measured, independent reflections, <i>R</i> <sub>int</sub>	7049, 1307, 0.059
No. of observed reflections ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	1082
$\theta$ <sub>max</sub> (°)	32.0
Refinement on	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.021, 0.050, 1.06
No. of reflections, of refined parameters	1307, 48
Weighting scheme	<i>w</i> = 1/( $\sigma^2(I)$ + 0.0004 $I^2$ )
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	0.75, -0.92

<sup>a</sup> Computer programs: *Jana2006* [14].

geneity. In the above procedure, the total weight loss (less than 0.2%) was negligible. Annealing was done for one month at 1073 K by enclosing the samples in evacuated quartz tubes. No reaction between the quartz tubes and the samples was observed.

X-ray powder diffraction with the use of a Philips 1050-diffractometer (Cu K $\alpha$  radiation) was done, before and after annealing, for the phase identification of the samples. The experimental patterns of the annealed samples matched a calculated one [13] indicating pure single phases on the level of X-ray powder diffraction. The orthorhombic parameters obtained through a least-squares routine *a* = 7.0700(10), *b* = 13.9675(13) and *c* = 7.3757(9) Å for Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub> and *a* = 7.2289(9), *b* = 14.0795(14) and *c* = 7.4783(8) Å for Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> are close to those reported previously [1,4].

The refinement of the crystal structure of Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub> was performed using single-crystal X-ray diffraction data. The single crystal was isolated from a crushed block of the annealed sample and selected by optical microscopy. Reflection data were collected at room temperature on an Enraf-Nonius Kappa charge coupled device (CCD) area-detector diffractometer using Mo K $\alpha$  radiation. A Gaussian-type absorption correction was applied, the shape of the single crystal being determined with the video microscope of the diffractometer. Data processing and all refinements were performed with the *Jana2006* program package [14]. The structure was refined with the space group *Pnma* (no. 62) and at the end of the refinement the reliability factors *R*/*R*<sub>w</sub> were equal to 2.10/4.99% with residual electron density in the range [−0.92, +0.75 eÅ<sup>-3</sup>]. Details of data collections, structure refinements and the atomic parameters are listed respectively in Tables 1 and 2. The interatomic distances are given in Table 3. Further information on the structure refinements may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. 422595.

Magnetization measurements were performed using a Superconducting QUantum Interference Device (SQUID) magnetometer in the temperature range 4.2–300 K and applied fields up to 4.6 T. For electrical resistivity measurements ( $\rho$ ), a bar of 1.5 mm × 1.5 mm × 5 mm was cut from the annealed buttons. The measurement was carried out above 4.2 K using the standard *dc* four-probe method with silver paint contacts and an intensity current of 10 mA. Because of the presence of microcracks into these bars, the absolute value of  $\rho$  could not be determined accurately; for this reason, a normalized representation  $\rho(T)/\rho(270\text{K})$  was given. Heat capacity measurements on the Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub> and Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> annealed samples were performed by a relaxation method with a Quantum Design PPMS system and using a two-tau model analysis. Data were taken in the 1.8–80 K temperature range. For the latter measurements, the sample was a plate (40–50 mg weight) obtained from the bar used for the electrical resistivity investigation.

### 3. Results and discussion

During refinement of the structure of Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> [4] a small disorder was observed between gadolinium and scandium atoms on

the Gd1 and Sc2 positions (see Table 2 for identifying atoms). In our study devoted to the determination of the crystal structure of Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub>, it appeared that the main deviation from the ideal Ce<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub>-type structure came from the occupancy factor of the Gd1 position. With the ideal model, the reliability factors *R*/*R*<sub>w</sub> were equal to 2.47/5.92% for 47 parameters. The use of the disordered model of Misra and Miller [4] for Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> led to a decrease of the reliability factors down to 2.08/4.92% for 49 parameters with occupancy of Sc2 position by Gd equal to 0.9(2)% and of Gd1 by Sc equal to 7.39(4)%. It was clear from these results that mixing of gadolinium and scandium on the Sc2 site is not significant whereas an excess of density is clearly evidenced on the Gd1 position. To reduce the electron density on the Gd1 position there are two possibilities that give the same reliability factors for the same number of parameters. With the first model a mixing of gadolinium and scandium is used on the Gd1 position and with the second only a refinement of the occupancy factor of the Gd1 position filled only by gadolinium is made. The calculated formulas are Gd<sub>1.828(7)</sub>Sc<sub>3.172(7)</sub>Si<sub>4</sub> and Gd<sub>1.875(5)</sub>Sc<sub>3</sub>Si<sub>4</sub>, respectively. The last model was chosen since it gave a chemical formula closer to the targeting one (Table 2). Moreover, such a defect was previously observed for the homologous compound Ce<sub>1.22</sub>Sc<sub>3</sub>Ge<sub>4</sub> [5]. With this final model the reliability factors were equal to 2.10/4.99% for 48 parameters.

In Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub>, the Gd1 and Sc2 atoms form as described for Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> [4] two-dimensional slabs stacked along the *c*-axis (Fig. 1a). In these slabs Sc3 atoms have a pseudo-cubic coordination [4Sc2, 4Gd1] and Si2 and Si3 atoms filled trigonal prismatic voids [4Sc2, 2Gd1] and [2Sc2, 4Gd1], respectively (Fig. 1b). These slabs are in close relationship with the tetragonal U<sub>3</sub>Si<sub>2</sub>-type structure. One can notice that Sc3 is also in an octahedral site of silicon atoms and the slabs are connected through the Si–Si interslab bonds. A first structural characteristic of this ternary silicide concerns the interatomic distances *d*<sub>Gd1–Gd1</sub> between Gd1 atoms (Table 3). Each Gd1 has only four next nearest neighbors at 3.707 (2 $\times$ ), 3.723 and 4.303 Å. This number of neighbors is small in comparison with that observed for the equiatomic compound GdScSi where each Gd atom has eight next nearest neighbors at 3.68 (4 $\times$ ) and 4.234 (4 $\times$ ) Å [15]. A second characteristic is the localization of gadolinium on only one site on contrary to what is observed for the homologous compound Gd<sub>2</sub>Y<sub>3</sub>Ge<sub>4</sub> [16]. This can be attributed to the significant difference in radius between scandium and gadolinium. In Gd<sub>2</sub>Y<sub>3</sub>Ge<sub>4</sub> gadolinium and yttrium atoms, which have almost the same metallic radius, are delocalized over the three RE (Rare-Earth) sites. Misra and Miller [16] showed that the RE3 site (corresponding to the Sc3 position in Gd<sub>1.875(5)</sub>Sc<sub>3</sub>Si<sub>4</sub>) is of great importance for the magnetic properties. Also in Gd<sub>2</sub>Y<sub>3</sub>Ge<sub>4</sub>, a magnetic dilution is obtained through the replacement of gadolinium by yttrium. This may explain why ferromagnetic ordering is still observed for Gd<sub>2</sub>Y<sub>3</sub>Ge<sub>4</sub> and not in Gd<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub> and Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> (see below). A third interesting point to be discussed is the interslab Si1–Si or Ge1–Ge1 contact (Fig. 1). For Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> [4], this Ge1–Ge1 distance is equal to 2.891 Å (Table 3) and is significantly higher than the sum of two covalent radii (2.40 Å) but significantly lower to the one observed in Gd<sub>5</sub>Ge<sub>4</sub> (3.621 Å) [6]. According to the analysis of these interslab distances made by Choe et al. [6,7] a strong covalent character of the Ge1–Ge1 bonding can be expected in Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub>. For Gd<sub>1.88</sub>Sc<sub>3</sub>Si<sub>4</sub>

**Table 2**  
Atomic positions and equivalent displacement parameters of Gd<sub>1.88(1)</sub>Sc<sub>3</sub>Si<sub>4</sub>. The identification of the atoms is similar to that used previously for Gd<sub>2</sub>Sc<sub>3</sub>Ge<sub>4</sub> [4].

Atom	Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Gd1	8d	0.938(3)	0.00953(2)	0.404016(12)	0.17476(2)	0.00624(6)
Sc2	8d	1	0.67061(9)	0.37520(5)	0.82418(8)	0.0056(2)
Sc3	4c	1	0.16234(11)	3/4	0.50389(12)	0.0062(2)
Ge1	8d	1	0.84184(13)	0.46108(7)	0.53566(13)	0.0076(2)
Ge2	4c	1	0.0327(2)	3/4	0.1175(2)	0.0070(3)
Ge3	4c	1	0.2870(2)	3/4	0.8729(2)	0.0069(3)

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