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Gadolinium trisilicide – a paramagnetic representative of the YbSi₃ type series

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Abstract: Binary gadolinium trisilicide GdSi₃ was prepared by high-pressure high-temperature synthesis at typically 9.5(5) GPa and 870 K before quenching to ambient conditions. At ambient pressure, GdSi₃ exhibits an exothermic decomposition at 647(10) K into the thermodynamically stable phases GdSi₂₋ₓ and Si, indicating its metastable character. Powder X-ray diffraction data is consistent with the YbSi₃-type crystal structure comprising slabs of condensed Si₂ dumbbells, which enclose layered arrangements of gadolinium cations. Quantum chemical analysis of the chemical bonding shows, that the framework is formed by silicon dumbbells with homopolar bonds. The magnetic moment of 8.13(8) µB is consistent with Gd⁴⁺ (Gd³⁺ state) and antiferromagnetic ordering is observed below 64(1) K.

Keywords: chemical bonding; gadolinium; Gd⁴⁺ electronic state; high-pressure synthesis; silicon.

Dedicated to Professor Christian Näther on the occasion of his 60th birthday.

1 Introduction

Work carried out in recent years has shown that the already large number of covalent silicon frameworks can be significantly expanded by application of high-pressure synthesis. The prepared phases often show unique silicon arrangements with unusual coordination numbers and environments, e.g., the unique silicon framework in the new prototype MgSi₅ [1].

Often, the exotic coordination situations in the covalent partial structure give rise to novel bonding behaviour frequently beyond classical electron counting schemes.

Earlier studies revealed the presence of five-connected silicon atoms in layers of condensed Si₂ dumbbells realized in phases MSi₃ (M = Ca, Y, Lu [2]). The early studies focussed mainly on compounds with diamagnetic cations or late rare-earth metals like holmium or ytterbium [3, 4]. In the present concerted experimental and theoretical study, we report on the high-pressure, high-temperature synthesis of GdSi₃ and describe the bonding properties of the product as characterized by quantum-chemical methods operating in positional space.

2 Experimental

Preparation of the starting mixtures and subsequent handling of the product was performed in argon-filled glove boxes (MBraun, H₂O < 0.1 ppm; O₂ < 0.1 ppm) in order to avoid contamination. High-pressure, high-temperature syntheses proceeded in sealed boron nitride crucibles, which were transferred to the hydraulic press just before the experiment in order to minimize contamination.

Precursor samples were prepared by arc melting of the pure rare-earth element gadolinium (Chempur 99.9%), and pure silicon (Chempur 99.999%), in the ratio 1:3 with 0.5% excess of Si for compensation of evaporation losses during heating. The samples were melted 3–4 times to ensure homogeneity. The resulting material was thoroughly ground and put into BN crucibles, which were placed in MgO octahedra of 18 mm edge length. High temperatures were realized by resistive heating of graphite sleeves. Pressure and temperature calibration had been performed prior to the experiments by in-situ monitoring of the resistance changes of bismuth [5], and by performing calibration heating runs with a thermocouple, respectively.

High-pressure high-temperature syntheses were conducted using a multi anvil press equipped with a Walker-type module [6]. The purest samples of GdSi₃ were synthesized at a pressure of 9.5 GPa, a temperature of 870 K and a holding time of 180 min followed by quenching under load.

Phase identification was realized by powder X-ray diffraction techniques (Huber image plate Guinier camera G670 operated with CoKα radiation, λ = 1.7886 Å). Lattice parameters were refined using LaB₆ as an internal standard. For lattice parameter determination, crystal structure refinement and other crystallographic calculations, the program package WinCSD [7] was used.

The quality of the samples was examined by metallographic methods. Light microscopy images (Zeiss Axiosplan 2 with CCD Camera) were taken in bright-field, dark-field and polarized light at various magnifications. The phase investigation was realized with a scanning electron microscope SEM (Jeol JSM 7800F) with integrated energy-dispersive X-ray spectroscopy EDXS system (Quantax 600, Bruker, Silicon-Drift-Detector (SDD)), and wavelength dispersive...
X-ray spectroscopy (WDXS) analyses were performed with an electron microprobe (Cameca SX100, tungsten cathode).

Thermal analyses using the Differential Scanning Calorimetry (DSC) method were performed with a Netzsch DSC 404 C Pegasus-OTS-System apparatus in a temperature range from room temperature to 1273 K. Al₂O₃ crucibles were used in an argon atmosphere and the selected heating rate amounted to 10 K min⁻¹. For the observed effects, onset temperatures are given in text and figures.

Magnetic measurements were performed on a polycrystalline sample of GdSi₃ (m = 23.3 mg), and magnetic susceptibility (χ) was measured in the temperature range 1.85–300 K. Measurements were carried out with an SQUID magnetometer (MPMS3 Quantum Design) using a quartz sample holder at external fields between 0.01 and 0.1 T.

3 Quantum chemical calculations

Electronic structure calculations on GdSi₃ were performed using the all-electron, full-potential local orbital (FPLO) method [8]. The experimental values of lattice parameters and atomic coordinates were used for calculations with a semi-relativistic model for the electron density and ELI-D calculations. All results were obtained within the local density approximation (LDA) to the density functional theory through the Perdew-Wang parametrization for the exchange-correlation effects [9]. A mesh of 12 × 12 × 12 k points was used in the irreducible part of the Brillouin zone to ensure accurate DOS and band-structure information. For a correct description of the correlated 4f states of Gd, the explicit treatment of the strong Coulomb repulsion was modeled within the LSDA + U approximation using the atomic limit double-counting scheme [10]. A typical value for localized 4f electrons of U = 8 eV has been applied [11].

The analysis of the chemical bonding was performed using the electron localizability approach in position space [12, 13]. For this purpose, the electron localizability indicator (ELI) in its ELI-D representation [14, 15] and the electron density (ED) were calculated with a specialized module within the FPLO code [16]. The topologies of the calculated three-dimensional distributions of ELI-D and ED were evaluated by means of the DGrid program [17]. The atomic charges from ED and bond populations for bonding basins from ELI-D were obtained by integrating the ED within the basins (space regions), bounded by zero-flux surfaces in the corresponding gradient field. This procedure follows the Quantum Theory of Atoms in Molecules (QTAIM) [18].

4 Results and discussion

After high-pressure, high-temperature synthesis of the new compound GdSi₃, the similarity of the observed diffraction pattern reveals that this new compound adopts the YbSi₃-type [4] crystal structure. Metallographic investigation of a polished sample Gd₂5Si₇₅ indicated the composition Gd₂4.₉5Si₇₅.₀₅ after high-pressure synthesis in good agreement with the nominal value. Differential scanning calorimetry data of GdSi₃ at ambient pressure. With increasing temperature, the exothermal effect at T = 647(10) K (onset temperature) evidences a monotropic decomposition. The nature of the second, smaller exothermal effect at 737(10) K remains unsettled. Data measured in direction of increasing temperature are shown in red, the blue line indicates those taken upon temperature decrease.

Figure 2: Powder X-ray diffraction diagram of the decomposition products of GdSi₃ after heating the sample to T = 1273 K at ambient pressure and returning to room temperature (heating rate: 10 K min⁻¹). The decomposition yields GdSi₂₋ₓ (ofI2.74) and Si (cF8), which are the stable phases at ambient pressure according to the phase diagram. Thus, the disintegration at 647(10) K indicates that GdSi₃ is a metastable high-pressure phase.
calorimetry measurements at ambient pressure and temperatures up to 1273 K (Figure 1) gave an exothermic signal with onset at \( T = 647(10) \text{ K} \) upon heating indicating a monotropic decomposition of the compound. X-ray powder diffraction data of such a transformed sample (Figure 2) revealed a transformation of GdSi\(_3\) into GdSi\(_{2.9}\) (Pearson symbol d12.74) and Si (cF8). As these phases are stable at ambient pressure according to the phase diagram, GdSi\(_3\) is a quenchable high-pressure phase, which is metastable at ambient pressure.

Structure refinement of the atomic arrangement was performed with the tools implemented in the program package WinCSD. Refinement of the initial YbSi\(_3\)-type model for GdSi\(_3\) converged to \( R_1 = 0.040 \) (Tables 1–3 and Figure 3). The atomic arrangement is characterized by silicon slabs, which comprise condensed Si\(_2\) dumbbells. The two-dimensional building units embed double layers of gadolinium atoms (Figure 4).

In GdSi\(_3\), the Si–Si distances \( d(\text{Si1–Si1}) \) and \( d(\text{Si2–Si2}) \) of 2.53(2) and 2.452(9) Å (pink in Figure 4), respectively, within the dimeric units are similar to those of 2.443(3) and 2.452(5) Å, respectively, which have been determined on the basis of single crystal X-ray diffraction data of YbSi\(_3\) [4]. Longer distances \( d(\text{Si1–Si2}) \) of 2.581(5) Å and \( d(\text{Si2–Si2}) \) of 2.693(7) Å (grey in Figure 4) are observed between the diatomic units within layers orientated perpendicular to [001]. In YbSi\(_3\), these distances amount to \( d(\text{Si1–Si2}) \) of 2.556(2) Å and \( d(\text{Si2–Si2}) \) of 2.655(2) Å, respectively.

The magnetic susceptibility \( \chi(T) = M/H \) of GdSi\(_3\) is well described by a Curie–Weiss law at temperatures above \( 80 \) K (Figure 5). Fits to the data above yield the effective magnetic moment of \( \mu_{\text{eff}} = 8.13(8) \mu_B \) and the paramagnetic Weiss temperature of \( \theta_p = -6.7(5) \) K. The observed behaviour is consistent with the presence of...
trivalent Gd ions with $4f^7$ configuration ($^8S_{7/2}$ multiplet $\mu_{\text{tho}} = \mu_B = 7.94\,\mu_B$) and suggests antiferromagnetic ordering below $T_N = 64(1)\,K$. A broad cusp in $1/\chi(T)$ at approximately $11\,K$ is likely related to strongly anisotropic magnetic behaviour of the gadolinium moments as to be expected from the layer-type crystal structure.

GdSi$_3$ belongs to the group of trisilicides of the YbSi$_3$-type crystal structure, which previously have been described mainly for divalent cations or late rare-earth metals [2]. The crystal structure contains two symmetry-independent Gd positions. Therefore, the calculations of the band structure are performed for spin-polarized states in both the ferromagnetic ($fm$) and the antiferromagnetic ($afm$) configuration of the Gd atoms within the local density approximation (LDA) of the density functional theory. In this approximation, the total energy of the $fm$ system is lower, which disagrees with the findings of the magnetic measurements (see above). Only the correct description of the correlated $4f$ states of Gd by the explicit treatment of the strong Coulomb repulsion within the LSDA $+ U$ approximation yields a lower energy for the $afm$ configuration.

In the calculated DOS (Figure 6), the occupied Gd $f$ states are localized at approximately $-9\,eV$. Besides that, two broad regions in energy can be recognized. The first one ($E < -6\,eV$) is characterized by a dominance of the $s$ states of Si. This region is characteristic also for other trisilicides [2]. The second one ($-6\,eV < E < E_F$) is composed mainly of the Si $p$ states with minor admixture of Gd $d$ and $s$ states (the larger part of the latter remains unoccupied above the Fermi level). A similar structuring was also observed e.g., for LuSi$_3$ [2]. In the DOS of the corresponding alkaline-earth metal compounds, this region is dominated by $3p$ states of silicon. The similarity of the distribution of Si

![Figure 4: Projection of the crystal structure of GdSi$_3$ along [100]. Gd1 is shown in light blue, Gd2 in dark blue, Si1 in dark green and Si2 in light green. Short contacts within the dumbbells are shown in pink, grey lines indicate longer contacts.](image)

![Figure 5: Inverse molar magnetic susceptibility $1/\chi_{\text{mol}}$ versus temperature for a polycrystalline sample of GdSi$_3$ in an applied field of $\mu_H = 0.1\,T$.](image)

![Figure 6: Electronic density of states in GdSi$_3$ as computed by spin-polarized LDA $+ U$ calculations using $afm$ configurations of the two gadolinium atoms at different positions.](image)
Quantum chemical techniques in position space were applied for analyzing the chemical bonding. This procedure recently evolved to a powerful investigative tool, in particular for intermetallic compounds [19–21]. The effective charges of all atoms were determined from the calculated electron density. The zero-flux surfaces in the gradient vector field of the electron density form the boundaries of electron density basins, which represent atomic regions following the Quantum Theory of Atoms in Molecules (QTAIM [18], Figure 7). Although the shape of the QTAIM Gd species is close to spherical, it shows subtle differences to that of, e.g., cations in clathrates [22]. In the cage compounds, the QTAIM shape includes the inner shells, i.e., the electrons of the outer shells are transferred to the anionic part of the crystal structure. In case of the gadolinium atoms in GdSi₃, the deviations from the spherical shape for the QTAIM atoms point toward a more complex electron distribution between the inner and valence regions, which is in agreement with partially occupied d states in the calculated DOS (Figure 5). The shapes of both symmetry-independent silicon atoms have one flat face oriented toward the closest silicon neighbor, which is characteristic for covalent homoatomic bonding, while all other faces orientated towards the gadolinium neighbors are concave. The latter finding is an indication for strongly polar interactions, like it was recently found for the Mg–Ir bonding in Mg₃GaIr [23].

This result is in agreement with the QTAIM charges obtained by integration of the electron density in spatial regions, defined as atomic shapes, yielding the electronic population. Subtraction of the number of electrons of the neutral atoms (atomic number) yields the effective charge. At first glance unexpectedly, the observed effective charges of Gd between 1.1 and 1.2 are significantly smaller than those observed in the earth-alkaline metals trisilicides, e.g., the effective charges of +1.3 and +1.5 of calcium in CaSi₃ [2]. Despite the higher potential oxidation state of Gd in comparison with Ca, the effective charge transfer is smaller, which is in fact in agreement with the smaller electronegativity difference between Gd and Si in comparison to that between Ca and Si.

Further information on the bonding between atoms is obtained by analyzing the distribution of the electron localizability indicator ELI-D in position space. Non-interacting (isolated) atoms show a spherical distribution of ELI-D around the nuclei. If the atoms interact, the spherical distributions become distorted and ELI-D maxima (attractors) may appear in the regions of valence or penultimate shells signaling bonding and visualizing its geometrical location [12–15]. Similar to the atomic basins, a population for each bonding basin can be obtained by integration of the electron density. The determination of the contributions of the atomic to the bonding basins, evaluated by the basin intersection technique, allows to quantize the polarity of bonding, i.e., its covalency and ionicity [24, 25]. The bonding picture in GdSi₃ contains six types of attractors, visualized by their basins (Figure 8). Two out of these six show contributions from two neighboring silicon atoms, the basins of the remaining four have common surfaces with only one silicon core basin each. The first two types of basins visualize homoatomic Si–Si bonding. While the Si₂–Si₂ bonds (population of 1.64 e⁻, dark green in Figure 8) are completely two-atomic, i.e., only two silicon atoms contribute, the Si₁–Si₁ bonds (1.76 e⁻, light green in Figure 8) show minor contributions (0.06 e⁻) of two neighboring Gd atoms. All other four basins (blue, red, orange and yellow in Figure 8) have typically 90% of the population originating from one silicon atom each, and the remaining part is donated by two gadolinium atoms. According to published work [24, 25], the polarity of such three-atomic bonds is between 0.78 and 0.86 and,

![Figure 7: Computed QTAIM [18] atomic shapes and charges in GdSi₃.](image)
thus, close to the ionic limit as the scale ranges from 0 for covalent non-polar bonding to 1 for ionic bonding. In an isolated unit like \([\text{Si}–\text{Si}]_6\)^{−1}, such a basin would even represent a lone pair (‘mono-atomic bonding’), but for the compound GdSi₃ in the solid state, this basin represents multi-atomic strongly polar bonding.

The populations of both Si–Si bonds are close to 2, i.e., they may be considered as single bonds. Assuming Zintl-type Si–Si species, it would require 6 electrons in the lone-pair-like basins of each silicon. The real number of 3.76 e⁻ (0.92 e⁻ + 4 × 0.71 e⁻ for Si1 and 2 × 1.02 e⁻ + 2 × 0.86 e⁻ for Si2, see Figure 8) is much smaller. Thus, in the presence of cations the silicon dumbbells do not follow a Zintl electron count and the 8–N rule.

4.1 Summary

The new gadolinium trisilicide GdSi₃ is a representative of the YbSi₃ type series with a trivalent paramagnetic cation Gd³⁺ showing 4f⁷ configuration. The crystal structure contains layers of interconnected anionic Si–Si dumbbells separated by gadolinium cations. Despite the formally larger electron supply that can be provided by a gadolinium atom in comparison with atoms like the alkaline-earth metals, the charge transfer in GdSi₃ is essentially smaller owing to the smaller electronegativity difference between the metal and silicon atoms. From the population of the bonding Si–Si basins, the homopolar interaction within the dumbbells may be considered as a single bond. Due to the presence of cations in the neighborhood of the diatomic silicon units, the electron demand for their stabilization is markedly smaller than required by the Zintl concept.

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