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Synthesis, structure, and magnetic behavior of a new gadolinium thiosilicate: $Gd_4[SiS_4]_3$

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Abstract

Single crystals of the title compound were prepared from the elements by a solid state reaction in an iodine atmosphere. Data collection were carried out using a STOE image plate detector at 293 K. The compound crystallizes in the space group $P2_1/n$ of the monoclinic system isotypically to $Tb_4[SiS_4]_3$ with four formular units in cells of dimensions: $a = 986.7(2)$ pm, $b = 1099.69(19)$ pm, $c = 1646.2(4)$ pm, $\beta = 102.67(3)°$. The corresponding residual (all data) for the refined structure is 3.09%.

The magnetic behavior of the compound was investigated on powdered samples in a temperature range between 1.7 and 300 K. The deviations from the Curie-behavior could be interpreted by the molecular field approach.

Keywords: X-ray diffraction; Crystal structure; Chemical synthesis; Chalcogénides; Inorganic compounds; Magnetic properties

1. Introduction

Compounds of lanthanides with silicon and chalcogen show a broad structural diversity. Whereas the research up to now mostly focused on oxosilicate systems [1], about the thiosilicates is by far less known. However, due to the stronger covalency of the lanthanide–sulfide bondings these structures promise for instance, a stronger magnetic exchange interaction than the comparable oxo homologs.

Up to now the reported lanthanide thiosilicate structures have all no oxo-analoga. The most often basic motif found is the tetrahedral coordination of silicon by four sulfide ions. In contrast, no simple *ortho*-oxo-silicate of the lanthanides has been published so far. The literature reports about Ln_2SiS_5 ($Ln = La-Nd$) with unknown structure [2], $Ln_6Si_{2.5}S_{14}$ ($Ln = Gd-Dy$, Y) [3,4], the trigonal crystallizing sulfides $Ln_4Si_3S_{12}$ (Ce–Gd) [4], and Eu_2SiS_4 [5].

Over the last years, we dedicated our work to the synthesis and characterization of compounds in the system of lanthanide, silicon, sulfur, and halogen [6–8]. Trying to prepare the heavier homologs of $Ln_3Br[SiS_4]_2$, we obtained instead single crystals of $Tb_4[SiS_4]_3$ [9], and $Dy_4[SiS_4]_3$ [10]. Crystals of the title compound could be prepared in an iodine atmosphere.

The magnetic behavior of $Gd_4[SiS_4]_3$ was investigated and compared to that of the homolog Tb compound. Here also antiferromagnetic interactions seem to be dominant and could be reproduced with the molecular field approach.

2. Experimental

Single crystals of $Gd_4[SiS_4]_3$ were obtained by reaction of the elements in an iodine atmosphere. Lanthanide metal chips (StremChem, 99.9%), sulfur powder (Aldrich, 99.98%), silicon powder (Merck, >99%), and iodine crystals (Merck, >99%) were loaded into fused-silica tubes in a glove box under argon atmosphere in a ratio of 1:2.26:0.53:0.8. The tube was sealed afterwards, placed into a furnace and exposed to a temperature gradient of 1000–850°C for 10 days. Then the ampoule was quenched in water. In the middle of the tube air-stable white crystals were obtained.

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3. X-ray structure determination

Well-grown crystals of the gadolinium thiosilicate were washed in ethanol and mounted on a STOE image plate detector. The structure was solved with direct method approaches using the SHELXS 97 [11] and SHELXL 97 [12] programs. Data analyses indicated the space group $P2_1/n$. Numerical absorption correction, using X-RED and X-SHAPE [13] was employed. The final refinement, performed with anisotropic atomic displacement parameters, yielded R1 (all data) = 3.09%. The crystal data and details of the acquisition and of the structural analyses are summarized in Table 1. Final values of the atomic and anisotropic displacement parameters can be found in Tables 2 and 3, selected bond distances in Table 4. Further details of the crystal structure investigation are available from the FACHINFORMATIONSZENTRUM KARLSRUHE, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-412620, the name of the authors, and citation of the paper.

Table 1
Crystallographic data and details of the structure determination of $Gd_4[SiS_4]_3$

Crystal system	Monoclinic
Space group, Z	$P2_1/n$ (14), 4
Lattice parameters (pm, deg) at 293 K	$a = 986.7(2)$ $b = 1099.69(19)$ $c = 1646.2(4)$ $\beta = 102.67(3)$
Volume of the cell (pm^3)	$1742.7(7) \times 10^6$
Density (g/cm^3)	4.185
Absorption coefficient μ (mm^{-1})	16.644
$F(000)$	1960
Crystal dimensions (mm^3)	$0.19 \times 0.19 \times 0.22\,mm^3$
Wavelength	Mo$K\alpha$ ($\lambda = 71.073$ pm)
θ min/max	2.54°/28.11°
h, k, l-range	± 13; ± 14; ± 21
No. of measured reflections	29,925
No. of independent reflections	4212
Observed reflections with $F > 2\sigma$	3468
Internal R-value	0.0995
Programs used	SHELXS-97 [11] and SHELXL-97 [12]
Absorption correction	Numerical with X-SHAPE [13]
Refinement method	Full matrix of F^2, least-squares fit
No. of refined parameters	173
GooF[a]	0.912
Residuals $[I > 2\sigma(I)]$[a]	$R_1 = 0.0221$; $wR_2 = 0.0484$
Residuals (all data)[a]	$R_1 = 0.0309$; $R_2 = 0.0498$
Extinction coefficient ε	0.0050(1)
$\Delta\rho$ min/max ($10^{-6}\,e\,pm^{-3}$)	$-1.820/1.260$

[a] Definitions according to [12].

Table 2
Atomic coordinates for $Gd_4[SiS_4]_3$

Atom	Lage	x/a	y/b	z/c
Gd1	4*e*	0.6113(1)	0.9831(1)	0.1251(1)
Gd2	4*e*	0.8775(1)	0.6526(1)	0.0600(1)
Gd3	4*e*	0.5329(1)	1.3770(1)	0.1298(1)
Gd4	4*e*	0.3237(1)	0.7595(1)	0.2890(1)
S1	4*e*	0.5059(1)	0.7756(1)	0.1882(1)
S2	4*e*	0.4189(1)	1.1529(1)	0.1830(1)
S3	4*e*	0.7499(1)	1.2130(1)	0.1360(1)
S4	4*e*	0.8478(1)	0.8357(1)	0.1888(1)
S5	4*e*	0.6131(1)	0.7617(1)	0.0134(1)
S6	4*e*	0.9093(1)	0.8482(1)	−0.0535(1)
S7	4*e*	1.0441(1)	0.4370(1)	0.0941(1)
S8	4*e*	0.3491(1)	1.4803(1)	0.2273(1)
S9	4*e*	0.6664(1)	0.4733(1)	−0.0222(1)
S10	4*e*	1.1525(1)	0.7311(1)	0.1263(1)
S11	4*e*	0.6582(1)	1.0591(1)	−0.0281(1)
S12	4*e*	0.7582(1)	1.5431(1)	0.1886(1)
Si1	4*e*	1.2218(2)	0.5540(1)	0.1167(1)
Si2	4*e*	0.7003(2)	0.8842(1)	−0.0608(1)
Si3	4*e*	0.7097(2)	0.7155(1)	0.2336(1)

Table 3
Anisotropic displacement parameters[a] U_{ij} (pm^2) for $Gd_4[SiS_4]_3$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd1	100(1)	67(1)	94(1)	6(1)	19(1)	10(1)
Gd2	79(1)	76(1)	93(1)	3(1)	15(1)	13(1)
Gd3	93(1)	79(1)	110(1)	−3(1)	−3(1)	7(1)
Gd4	119(1)	138(1)	94(1)	−15(1)	43(1)	−38(1)
S1	76(6)	150(7)	129(6)	43(5)	32(5)	20(5)
S2	83(6)	126(6)	87(6)	−14(5)	9(5)	6(5)
S3	135(6)	93(6)	92(6)	−13(5)	30(5)	−5(5)
S4	79(6)	83(6)	92(6)	−4(5)	16(5)	−2(5)
S5	97(6)	81(6)	94(6)	1(4)	20(5)	9(5)
S6	92(6)	124(6)	134(6)	10(5)	16(5)	15(5)
S7	100(6)	80(6)	126(6)	7(5)	11(5)	10(5)
S8	121(6)	131(6)	106(6)	9(5)	−7(5)	28(5)
S9	124(6)	110(6)	103(6)	−6(5)	32(5)	22(5)
S10	98(6)	79(6)	125(6)	−8(5)	9(5)	14(5)
S11	131(6)	61(6)	111(6)	−4(5)	23(5)	3(5)
S12	123(6)	69(6)	113(6)	−13(5)	34(5)	−12(5)
Si1	95(7)	72(7)	91(6)	−10(5)	18(5)	24(5)
Si2	95(7)	77(7)	81(6)	−11(5)	13(5)	12(5)
Si3	82(7)	69(7)	67(6)	5(5)	8(5)	4(5)

[a] Defined as temperature factor in the following way: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

4. Magnetic measurements

The magnetic behavior of finely grounded single crystals of $Gd_4[SiS_4]_3$ was measured in a temperature

Table 4
Selected interatomic distances (pm) in $Gd[SiS_4]_3$

Gd1–S11	279.0(1)	Gd2–S5	282.0(2)	Si1–S10	208.2(2)
Gd1–S1	280.1(1)	Gd2–S10	282.8(2)	Si1–S9[a]	211.7(2)
Gd1–S11[b]	282.3(2)	Gd2–S7	286.9(1)	Si1–S8[c]	213.2(2)
Gd1–S4	284.6(1)	Gd2–S12[d]	289.9(1)	Si1–S7	214.0(2)
Gd1–S3	286.1(1)	Gd2–S6	291.1(1)	Si2–S11	206.4(2)
Gd1–S2	296.6(1)	Gd2–S9	297.1(2)	Si2–S6	207.7(2)
Gd1–S5	305.4(1)	Gd2–S4	297.9(1)	Si2–S5	212.3(2)
Gd1–S12[e]	312.6(2)	Gd2–S7[f]	298.4(1)	Si2–S2[b]	213.5(2)
Gd3–S3	278.5(1)	Gd4–S1	270.6(1)	Si3–S1	209.3(2)
Gd3–S9[b]	286.1(2)	Gd4–S2[g]	279.3(1)	Si3–S3[e]	209.6(2)
Gd3–S12	287.6(1)	Gd4–S6[h]	280.7(2)	Si3–S12[c]	212.8(2)
Gd3–S8	290.3(2)	Gd4–S7[i]	284.8(1)	Si3–S4	214.2(2)
Gd3–S5[b]	291.0(2)	Gd4–S10[j]	285.3(2)		
Gd3–S2	292.1(1)	Gd4–S8[g]	294.4(2)		
Gd3–S4[i]	299.4(2)	Gd4–S8[d]	326.2(2)		
Gd3–S9[f]	325.1(1)				
Gd1–Gd1[b]	423.7(6)	Gd2–Gd2[f]	480.8(3)	Gd3–Gd3[k]	498.0(2)
Gd1–Gd2	474.2(2)	Gd2–Gd3[b]	455.2(8)	Gd3–Gd4[l]	423.0(3)
Gd1–Gd3[e]	440.4(1)	Gd2–Gd3[m]	487.8(2)		
Gd1–Gd3	487.3(8)	Gd2–Gd4[l]	448.1(2)		
Gd1–Gd4	497.4(4)			Gd4–Gd4[m]	576.0(6)

Symmetry operations:
[a] $-x+1, -y+2, -z$.
[b] $-x+1, -y+2, -z$.
[c] $x+1, y-1, z$.
[d] $x, y-1, z$.
[e] $-x+3/2, y-1/2, -z+1/2$.
[f] $x, y+1, z$.
[g] $-x+1/2, y-1/2, -z+1/2$.
[h] $x-1/2, -y+3/2, z+1/2$.
[i] $-x+3/2, y+1/2, -z+1/2$.
[j] $x-1, y, z$.
[k] $-x+1, -y+3, -z$.
[l] $-x+1/2, y+1/2, -z+1/2$.
[m] $x+1/2, -y+3/2, z-1/2$.

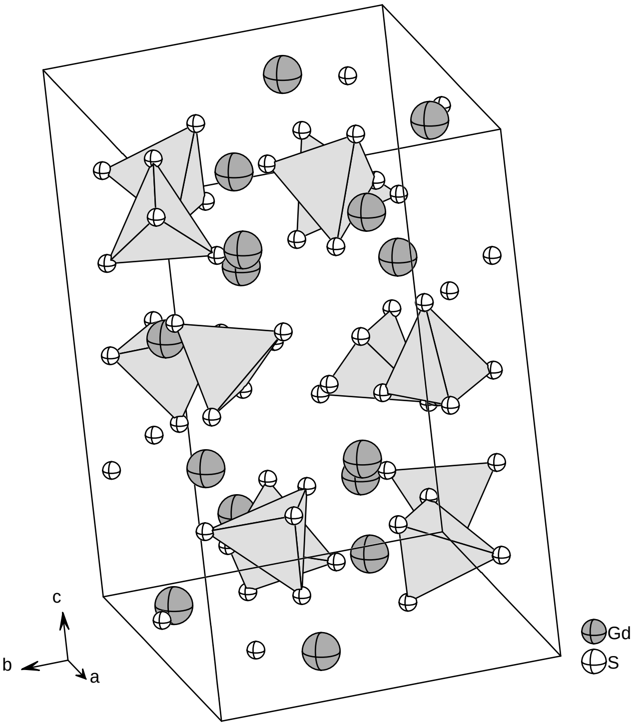

Fig. 1. View on the crystal structure of Gd4[SiS4]3. The $[SiS_4]$ tetrahedra are shown in gray.

range between 1.7 and 300 K in a magnetic field (H) of 5 kOe with a SQUID magnetometer (MPMS5, Quantum Design). The samples were placed in the lid of a gelatine capsule. To prevent orientation effects, the bottom of the capsule was pressed onto the sample to fix it. A second lid closed the sample holder which was sewed in a plastic straw. The magnetic raw data were corrected for diamagnetism of the carrier system as well as for the diamagnetic parts of the sample according to the correction by Selwood [14].

5. Structural results

The gadolinium thiosilicate $Gd_4[SiS_4]_3$ crystallizes isotypically to $Tb_4[SiS_4]_3$ [9] and $Dy_4[SiS_4]_3$ [10]. The crystal structure contains three different silicon sites and four crystallographically different gadolinium positions.

The silicon ions are surrounded by four sulfur ions, forming a slightly distorted tetrahedron. The resulting SiS_4 building blocks are isolated from each other in the structure (see Fig. 1). The Si–S distances range between 206.4(2) and 214.2(2) pm (cf. Table 4), the S–Si–S angles are between 102.2(1)° and 115.4(1)°.

The gadolinium position Gd1 forms with eight sulfides a twice-capped trigonal prism. It shares four of the eight sulfide ions with $Si2S_4$- and $Si3S_4$ building blocks, and two sulfide ions with another Gd1, thus resulting in a edge-shared dimer $Gd1_2S_{14}$ (see Fig. 2a). The distance between the two gadolinium atoms is 423.7(6) pm.

The coordination of Gd2 is similar: eight sulfide ions form a distorted quadratic antiprism. By connection via two $Si1S_4$ tetrahedra to a second Gd2 atom an edge-shared dimer results (see Fig. 2b). Here the Gd–Gd distance is 480.8(3) pm. The other sulfide ions are part of $Si2S_4$ and $Si3S_4$ tetrahedra.

Around Gd3 eight sulfide ions form a twice-capped trigonal prism. The polyhedron shares one sulfide ion each with one $Si1S_4$ and one $Si3S_4$ tetrahedron as well as two sulfide ions each with further $Si1S_4$, $Si2S_4$, and $Si3S_4$ tetrahedra. It also shares two S9 ligands with another Gd3, resulting in a $Gd3_2S_{14}$-dimer (see Fig. 2c). The observed distance between two gadoliniums in this building block is 498.0(2) pm.

The fourth Gd position, Gd4, is the only one to exhibit a coordination polyhedron of seven sulfide ions forming a single-capped trigonal prism. Gd4 shares one

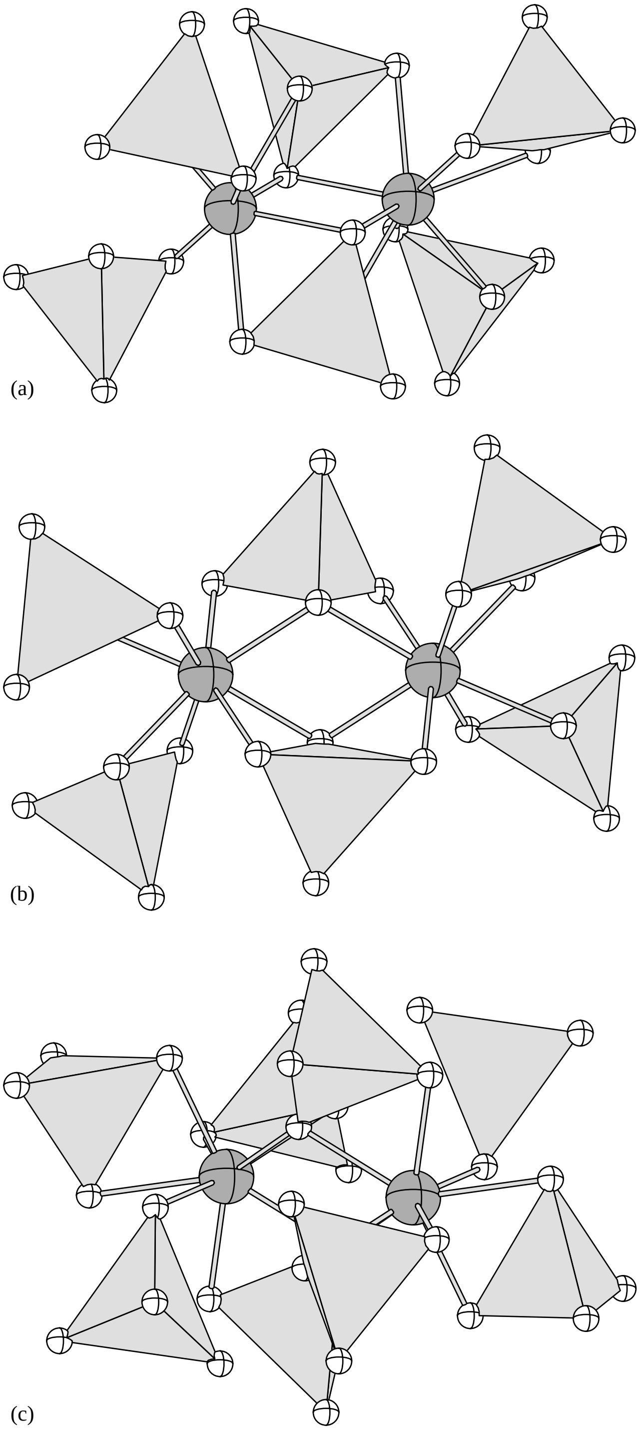

Fig. 2. View on the Gd1 (a), Gd2 (b), and Gd3 (c) dimers with surrounding [SiS_4] building blocks.

sulfide ion with two Si1 and one Si2 each. It shares an edge with an $Si3S_4$ tetrahedron. The Gd4 ions are connected via the sulfide ion of a $Si1S_4$ unit resulting in a corner-shared one-dimensional chain $^1_\infty[Gd4S_{5/1}S_{2/2}]$ along [010] (see Fig. 3). The distance between two Gd4 in this chain is 576.0(6) pm.

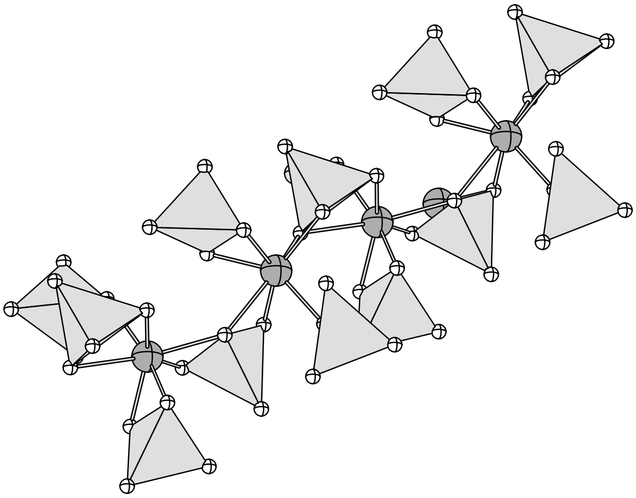

Fig. 3. View on the chain of $Gd4S_7$ polyhedra along [010].

The dimers of Gd1, Gd2, and Gd3 form a channel structure. Nearly parallel to the *c*-axis the $Gd1_2S_{14}$ and $Gd3_2S_{14}$ dimers build up strings by sharing edges. These strings are connected by $Gd2_2S_{14}$ dimers to a three-dimensional network structure forming channels along [010]. These channels are filled by the Gd4 chain (see Fig. 4).

6. Magnetic behavior

Fig. 5 shows the reciprocal magnetic susceptibility (χ_{mol}^{-1}), Fig. 6 the magnetic moment (μ), and Fig. 7 the magnetic susceptibility (χ_{mol}) for $Gd_4[SiS_4]_3$ in a magnetic field of 5 kOe in dependence of the temperature.

The Gd^{3+} ion with a $^8S_{7/2}$ ground state shows no crystal field effects, so the magnetic behavior in the high-temperature regime follows Hund's formula giving a temperature-independent magnetic moment of about $7.94\,\mu_B$. The deviation of the observed moment at low temperature can be due to saturation superimposed by antiferromagnetic interaction effects. The latter was also observed for the homolog Tb-compound [9]. A closer look on the magnetic susceptibility (cf. Fig. 7) also reveals a bend of the curve at 3 K which might be an indication for the existence of a Néel point.

The magnetic interactions between the gadolinium ions are taken into account by a molecular field approach as given by Eq. (1) [15–17]. Here $(\chi_{mol}^{I})^{-1}$ represents the calculated reciprocal magnetic susceptibility of the paramagnetic centers, where saturation effects are considered [15].

$$\chi_{mol}^{-1} = (\chi_{mol}^{I})^{-1} - \lambda. \tag{1}$$

In (1) the molecular field constant λ denotes the isotropic part of the magnetic exchange. The best fitting of the calculated to the observed values of χ_{mol}^{-1}

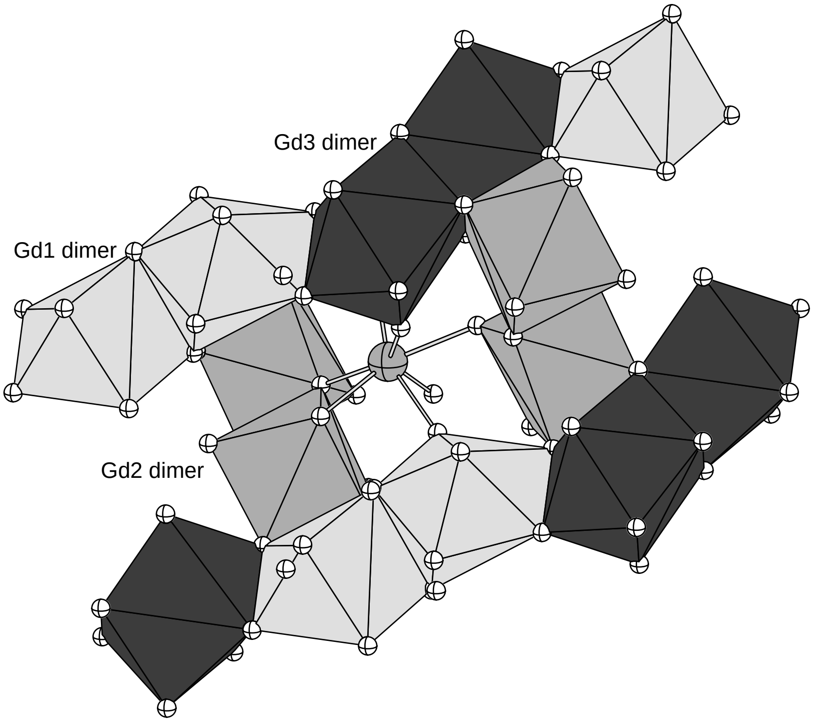

Fig. 4. Linkage of the Gd-dimers and the Gd4-chain.

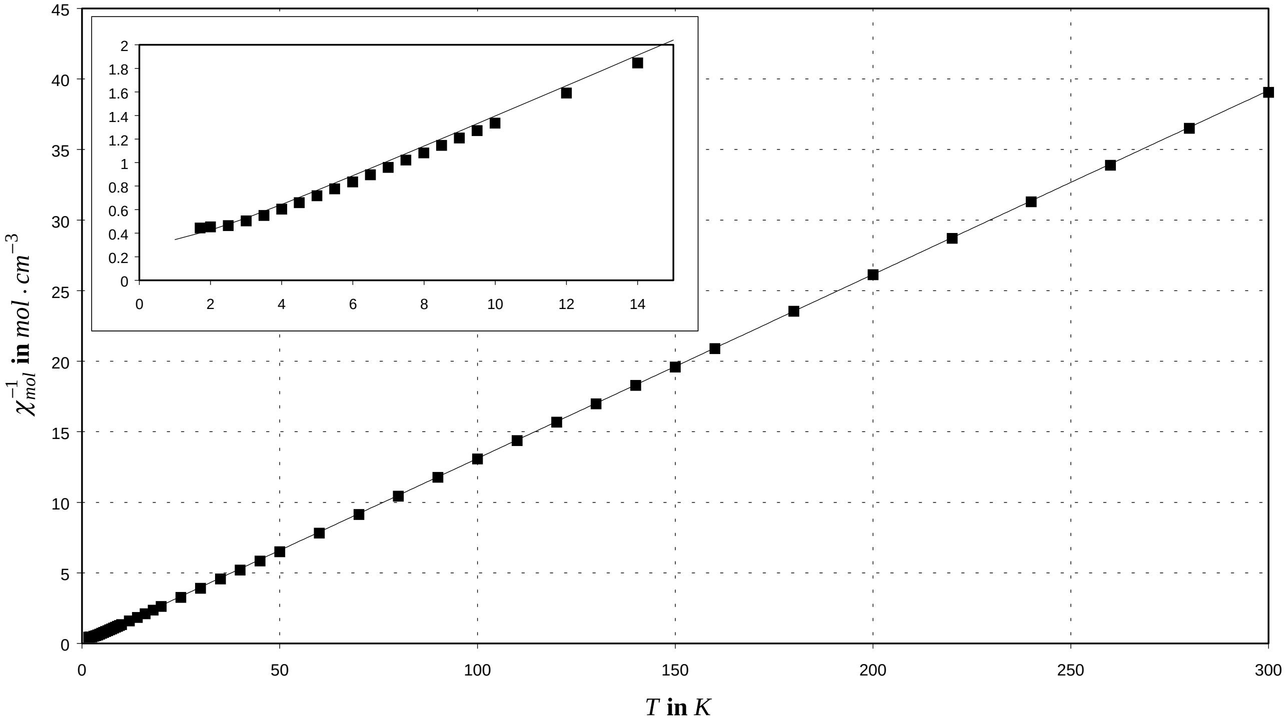

Fig. 5. Comparison of the observed and the calculated reciprocal magnetic susceptibility (—) for $Gd_4[SiS_4]_3$ ($H = 5$ kOe).

(cf. Fig. 5) was obtained with $\lambda = -0.07\,\text{mol}\,\text{cm}^{-3}$. The satisfactory fit of the magnetic moment can be seen in Fig. 6. The negative molecular field constant gives rise to the assumption of antiferromagnetic interactions between the gadolinium ions in good correspondence to the relatively short Gd–Gd distances (see Table 4).

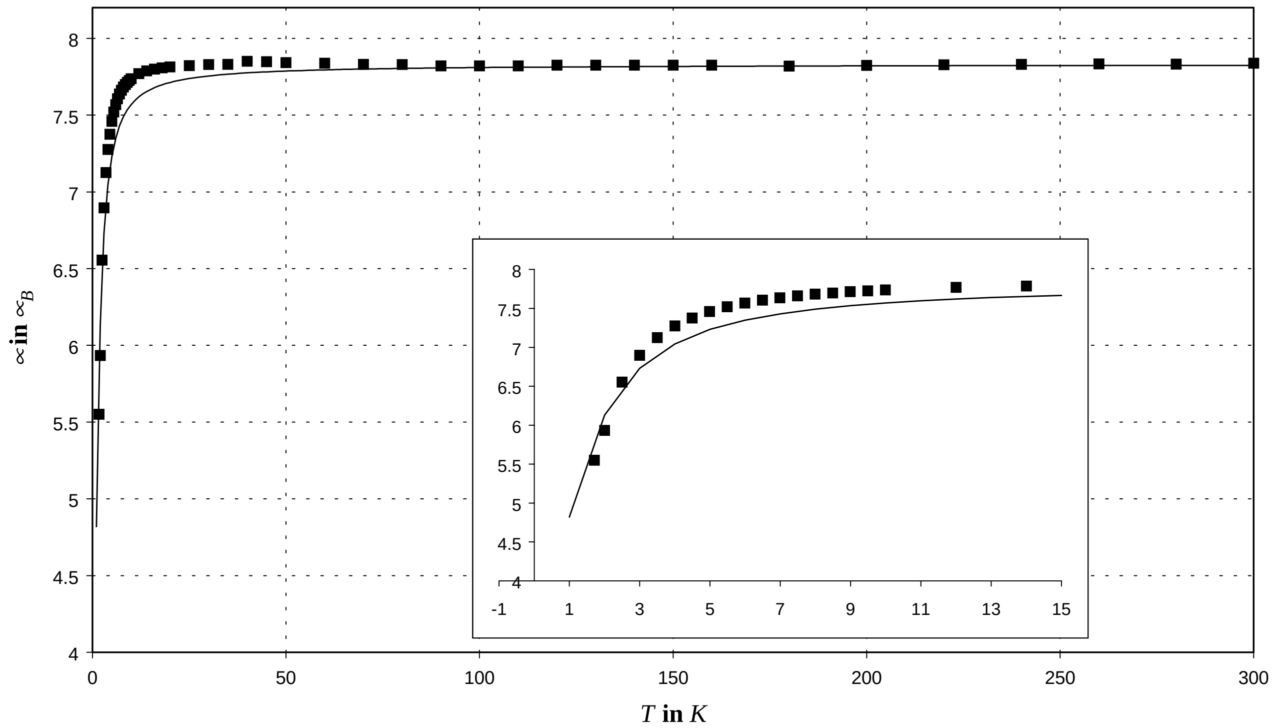

Fig. 6. Comparison of the observed and the calculated magnetic moment (—) for $Gd_4[SiS_4]_3$ ($H = 5\,kOe$).

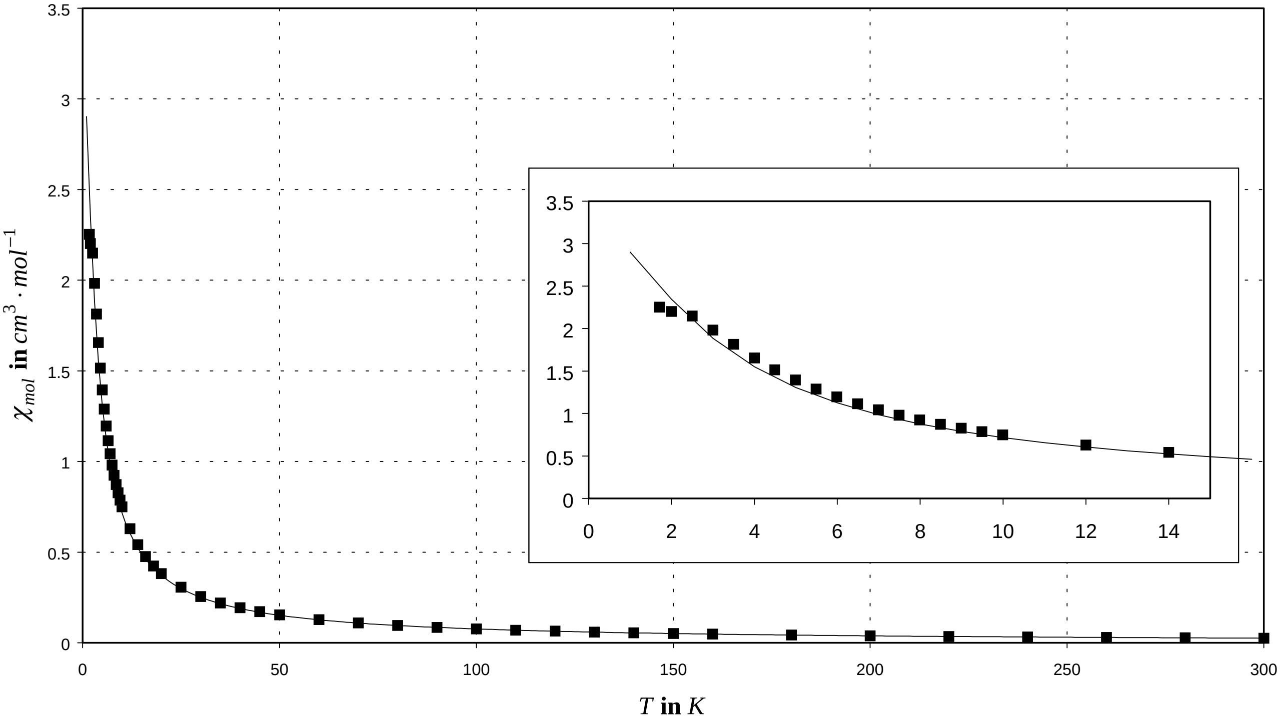

Fig. 7. Comparison of the observed and the calculated magnetic susceptibility (—) for $Gd_4[SiS_4]_3$ ($H = 5\,kOe$).

Compared to the terbium compound the molecular field constant is considerably smaller. There a λ of $-0.19\,mol\,cm^{-3}$ was found [9]. This is understandable considering the larger Gd–Gd distances in the title compound compared to those of the terbium one. The smallest distance between lanthanide ions (Ln3–Ln4) grows from 418.6 to 423.0 pm, and the next one (Ln1–Ln1) is increased from 421.0 to 423.7 pm.

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