

Inga Schellenberg, Theresa Block and Rainer Pöttgen*

Gd₅Rh₁₉Sb₁₂ – a metal-rich antimonide with a Sc₅Co₁₉P₁₂ related structure

<https://doi.org/10.1515/zkri-2025-0017>

Received April 16, 2025; accepted May 1, 2025;

published online May 23, 2025

Abstract: The metal-rich antimonide Gd₅Rh₁₉Sb₁₂ was synthesized by induction-melting of the elements in a sealed tantalum ampoule. The Gd₅Rh₁₉Sb₁₂ structure was refined from single crystal X-ray diffractometer data of a twinned crystal: $P31m$, $a = 1,349.3(3)$, $c = 417.99(12)$ pm, $wR2 = 0.0682$, 1545 F^2 values and 67 variables. Gd₅Rh₁₉Sb₁₂ is closely related to the Sc₅Co₁₉P₁₂-type. A split position of Rh5 is avoided by a *translationengleiche* symmetry reduction of index 2 from $P\bar{6}2m$ to $P31m$, leading to a fully ordered model. The crucial difference between Sc₅Co₁₉P₁₂ and Gd₅Rh₁₉Sb₁₂ concerns the position of the transition metal atoms on the c axis. The Co4 atoms show a split position around the origin in Sc₅Co₁₉P₁₂ (Co4@Sc₆ trigonal prisms) while the Rh5 atoms in Gd₅Rh₁₉Sb₁₂ are shifted by $c/2$ and then form Rh5@Sb₆ trigonal prisms. The remaining substructures of Sc₅Co₁₉P₁₂ and Gd₅Rh₁₉Sb₁₂ are comparable. The Rh–Sb and Rh–Rh distances within the [Rh₁₉Sb₁₂] substructure range from 255–290 and 292–336 pm, respectively.

Keywords: rare earth compound; antimonide; crystal structure; intermetallics

1 Introduction

The ternary systems $RE-T-P$ ¹ and $RE-T-Si$ ^{2,3} (RE = rare earth element, T = electron-rich transition metal) have intensively been studied and a manifold of ternary phosphides and silicides has been structurally characterized.⁴ The transition metal-rich parts of these phase diagrams are characterized by a large family of compounds with a metal-to-metalloid ratio of exactly or close to 2:1. The basic geometrical building units of all these structures are phosphorus or silicon centered trigonal prisms formed by the RE and/or T atoms.

Condensation of these prisms leads to a variety of extended geometrical motifs which spread from isolated prisms to *shamrock*-like trimeric units up to larger arrangements which are usually called propeller-shaped assemblies.^{5,6} This kind of modular principle is helpful to explain and classify the different, sometimes complex structure types.

Some of the structural families observed for the phosphides and silicides also occur with the higher homologues arsenic and germanium; however, to a lesser extent. While many of the $RE-T-Ge$ systems have thoroughly been studied,^{7,8} systematic phase analytical knowledge of the respective arsenic systems is poor. One of the largest series of isotopic representatives are the Zr₂Fe₁₂P₇-type phases $RE_2(\text{Co, Ni, Rh})_{12}P_7$ and $RE_2(\text{Co, Ni, Rh})_{12}As_7$.⁴ In going to antimony, only the metal-rich series $RE_3Pt_7Sb_4$ (RE = Ce, Pr, Nd, Sm)⁹ and $RE_6Rh_{30}Sb_{19}$ (RE = La–Nd, Sm, Eu)¹⁰ with antimony centered trigonal prisms are known.

During phase analytical studies in the $RE-T-Sb$ systems we have now obtained Gd₅Rh₁₉Sb₁₂, the first antimonide with a Sc₅Co₁₉P₁₂-related¹¹ structure. In the field of intermetallics, Sc₅Co₁₉P₁₂ type phases are known for the phosphides $A_5T_{19}P_{12}$ (A = Ca, Zr, Hf, rare earth metal; T = Fe, Co, Ni, Cu, Ru, Rh and Ir),^{12–27} the tetrelides (Sr, Ba, Eu, Yb)₅Mg₁₉(Si, Ge)₁₂^{28–32} and the recently reported silicides $RE_5Ir_{19}Si_{12}$ (RE = Y, Gd–Dy, Er, Tm, Lu).³³ Gd₅Rh₁₉Sb₁₂ is a remarkable compound since phosphorus was substituted by the much larger homologue antimony and still no arsenides with this structure type are known. The synthesis and structural chemistry of Gd₅Rh₁₉Sb₁₂ are reported herein.

2 Experimental

2.1 Synthesis

Starting materials for the synthesis of Gd₅Rh₁₉Sb₁₂ were gadolinium ingots (Johnson Matthey), rhodium powder (Degussa-Hüls) and antimony shots (Johnson Matthey), all with stated purities better than 99.9 %. The elements were weighed in the atomic ratio of Gd:Rh:Sb = 1:2:2 and arc-welded³⁴ in a tantalum ampoule. The latter was placed in a water-cooled sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 1.5/300),³⁵ heated to 1280 K and kept at that temperature for 10 min. The

*Corresponding author: Rainer Pöttgen, Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany, E-mail: pottgen@uni-muenster.de

Inga Schellenberg and Theresa Block, Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany

temperature was then lowered to 1080 K and the sample was annealed for another 3 h followed by rapid cooling (switching off the power supply). The temperature was controlled through a radiation pyrometer (Metis MS09, Sensortherm) with an accuracy of ± 50 K. The product sample was mechanically broken out of the ampoule. No reaction with the crucible material was evident. Gd₅Rh₁₉Sb₁₂ is stable in air. Single crystals exhibit silvery metallic luster.

2.2 X-ray diffraction

Pieces of the annealed sample were carefully crushed and small irregularly shaped single crystals were selected under an optical microscope. The crystals were glued to thin glass fibers using beeswax and their quality was first tested by Laue photographs on a Buerger camera (white molybdenum radiation, image plate technique, Fujifilm, BAS-1800). A complete data set of an appropriate crystal was collected at room-temperature on a STOE IPDS-II diffractometer (graphite-monochromatized MoK α radiation; oscillation mode). A numerical absorption correction

was applied to the data set. Details about the data collection and the structure refinement are summarized in Table 1.

2.3 EDX analysis

The Gd₅Rh₁₉Sb₁₂ single crystal studied on the image-plate diffractometer was semiquantitatively analyzed by EDX: Zeiss EVO[®] MA10 scanning electron microscope, LaB₆ cathode, variable pressure mode (60 Pa N₂) and an Oxford Instruments INCA[®] x-act detector. GdF₃, Rh and Sb were used as standards. The analyses on the irregular crystal surface resulted in the composition 12 ± 2 at.% Gd: 55 ± 2 at.% Rh: 33 ± 2 at.% Sb, in agreement with the ideal composition (13.9 : 52.8: 33.3). No impurity elements were detected.

3 Structure refinement

The diffractometer data set showed a hexagonal lattice and no further systematic extinctions. In agreement with our earlier studies on the RE₅Ir₁₉P₁₂ phosphides²⁷ and RE₅Ir₁₉Si₁₂ silicides,³³ the non-centrosymmetric space group $P\bar{6}2m$ was tested first. The starting atomic parameters were deduced with the charge-flipping algorithm³⁶ implemented in Superflip³⁷ and the structure was refined on F^2 with the Jana2020 software package,^{38,39} with anisotropic displacement parameters for all sites, except the 2e Rh5 split position which was refined with an isotropic displacement parameter. Separate refinements of the occupancy parameters gave no hint for deviations from the ideal composition. The Rh5 site is the decisive difference to the Sc₅Co₁₉P₁₂-type, since these rhodium atoms are shifted by $c/2$.

The split position called for a symmetry reduction. The simplest step is a *translationengleiche* symmetry reduction of index 2 to the trigonal space group $P31m$, where the 2e site splits into two one-fold sites 1a, of which only one needs to be occupied. The corresponding Bärnighausen tree^{40–43} is presented in Figure 1. We have thus transferred the coordinates of the subcell refinement to space group $P31m$ and refined the structure again, now with anisotropic displacement parameters for all sites. The loss of the $\bar{6}$ axis leads to twin formation. In the final refinement the twin matrices $(-1\ 0\ 0, -1\ 1\ 0, 0\ 0\ -1)$ and $(-1\ 0\ 0, 0\ -1\ 0, 0\ 0\ -1)$ were introduced and the refinement for the ordered model smoothly converged to the residuals listed in Table 1. The domain ratio of 0.44(14): 0.06(8): 0.44(8): 0.06(8) indicated, that the crystal essentially consisted of two equal domains only (no twinning by inversion; the small domains are in the order of the standard deviation). All atoms are located on sites $0\ 0\ z$, $1/3\ 2/3\ z$ and $x\ y\ z$. Due to the floating origin^{44,45} and to avoid large correlations we fixed the z

Table 1: Single crystal data and refinement parameters of Gd₅Rh₁₉Sb₁₂, $Z = 1$, space group $P31m$ and Pearson code $hP36$. The data set was collected on a Stoe IPDS II diffractometer with Mo-K α radiation ($\lambda = 71.073$ pm).

Formula	Gd ₅ Rh ₁₉ Sb ₁₂
Molar mass/g mol ⁻¹	4,202.5
Cell parameters/pm	$a = 1,349.3(3)$ $c = 417.99(12)$
Cell volume/nm ³	$V = 0.6591$
Calc. density/g cm ⁻³	10.59
Crystal size/ μm^3	$20 \times 20 \times 30$
Absorpt. corr.	Numerical
Absorpt. coeff./mm ⁻¹	35.9
Detector distance/mm	80
Irradiation time/min	5
ω range, increment/ $^\circ$	0–180; 1.0
Integr. param. (A; B; EMS)	13.2; 3.1; 0.022
$R(000)/e$	1,787
θ range/ $^\circ$	3.02–31.79
hkl range	$\pm 20; \pm 20; \pm 5$
No. Refl.	7,744
Indep. refl./ R_{int}	1,545/0.0613
Refl. with $I \geq 3\sigma(I)/R_o$	1,223/0.0480
Data/parameters	1,545/67
Goodness-of-fit	1.34
$R1/wR2$ ($I \geq 3\sigma(I)$)	0.0349/0.0666
$R1/wR2$ (all data)	0.0458/0.0682
Extinct. coeff.	71(9)
Flack parameter	0.12(12)
Largest diff. peak, hole/e $\text{\AA}^{-3}$	2.33/–2.25

parameter of the Sb1 position (the one with the highest total atomic form factor). This is similar to the structures of ScRh₆P₄⁴⁶ and YbMg_{0.75}In_{1.25}.⁴⁷ The final difference Fourier analyses was contourless. Further details on the refinement, the atomic coordinates, the displacement parameters and the interatomic distances are listed in Tables 1–3.

CCDC–2443530 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4 Crystal chemistry

Gd₅Rh₁₉Sb₁₂ is the first antimonide in the family of Sc₅Co₁₉P₁₂-related intermetallic compounds. The substitution of phosphorus by the larger antimony (110 vs. 141 pm covalent radius⁴⁸) leads to a drastic increase of the unit cell parameters

($a = 1,349.3(3)$, $c = 417.99(12)$ pm), when compared with the gadolinium-based phosphides Gd₅Co₁₉P₁₂ ($a = 1,210.04(3)$, $c = 370.0(1)$ pm)¹⁴ and Gd₅Ir₁₉P₁₂ ($a = 1,262.9(3)$, $c = 395.7(1)$ pm).²⁷ The increase is even stronger for the tetrelides (Sr, Ba, Eu, Yb)₅Mg₁₉(Si, Ge)₁₂,^{28–32} e. g., $a = 1,479.3(1)$, $c = 445.2(1)$ pm for Eu₅Mg₁₆Ge₁₂.³⁰ This leads to a small but important difference with respect to the prototype Sc₅Co₁₉P₁₂.¹¹ The crystal chemical differences are addressed in the following.

Before starting with the crystal chemical discussion, we first concentrate on the role of the Rh5 atoms, which manifest the difference to the Sc₅Co₁₉P₁₂ type. In the prototype structure, the corresponding cobalt atoms fill a trigonal Sc₆ prism at the unit cell origin, while in the case of Gd₅Rh₁₉Sb₁₂, the Rh5 atoms are shifted by $c/2$ to the Gd₁₃ triangles; however, refined with a split position in the prototype space group symmetry, $P\bar{6}2m$. A symmetry reduction then leads to a fully ordered model. The group-subgroup relation for the superstructure formation is

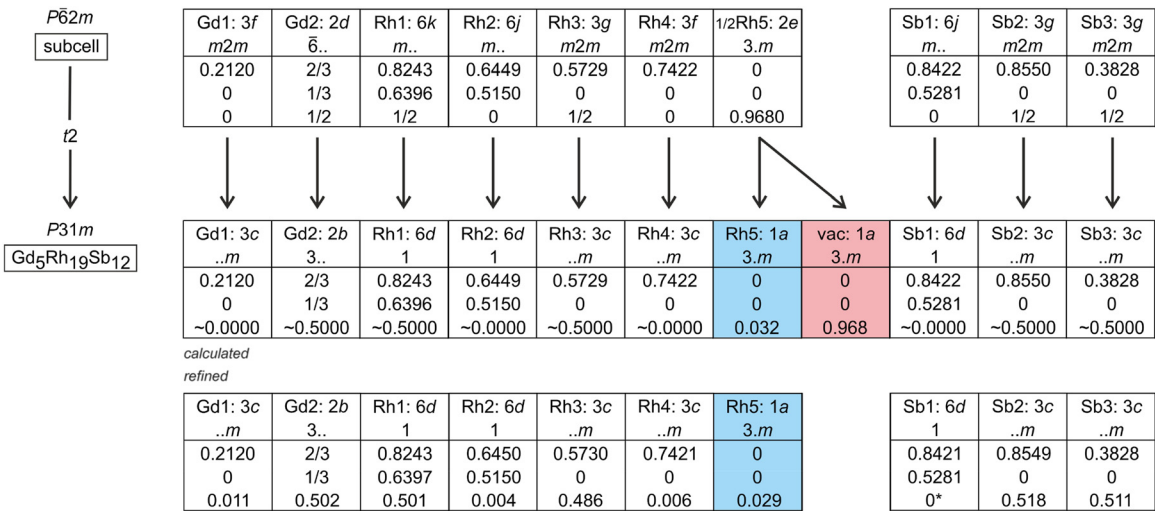


Figure 1: Group-subgroup scheme for the superstructure formation of Gd₅Rh₁₉Sb₁₂ in the Bärnighausen formalism.^{40–43} The index for the translationengleiche symmetry reduction and the evolution of the atomic parameters are given.

Table 2: Atomic coordinates and anisotropic displacement parameters (pm²) for Gd₅Rh₁₉Sb₁₂ at 300 K (space group $P31m$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}/U_{iso}
Gd1	3c	0.21196(9)	0	0.011(3)	97(3)	113(5)	108(8)	57(2)	−10(20)	0	104(4)
Gd2	2b	2/3	1/3	0.502(3)	134(4)	U_{11}	92(8)	67(2)	0	0	120(4)
Rh1	6d	0.82431(11)	0.63966(10)	0.501(2)	81(5)	92(5)	104(7)	40(5)	−10(20)	20(20)	94(5)
Rh2	6d	0.64496(10)	0.51504(9)	0.004(2)	95(5)	77(5)	123(8)	42(4)	−30(30)	10(20)	99(4)
Rh3	3c	0.57305(15)	0	0.486(4)	116(5)	193(9)	110(30)	97(5)	−14(18)	0	133(10)
Rh4	3c	0.74213(14)	0	0.006(3)	154(6)	101(8)	149(12)	50(4)	−30(30)	0	140(6)
Rh5	1a	0	0	0.029(7)	183(10)	U_{11}	270(70)	91(5)	0	0	210(30)
Sb1	6d	0.84212(9)	0.52809(9)	0*	99(4)	98(5)	93(8)	53(4)	0(2)	10(20)	95(4)
Sb2	3c	0.85493(13)	0	0.518(3)	168(6)	94(6)	102(15)	47(3)	−10(19)	0	130(6)
Sb3	3c	0.38275(11)	0	0.511(3)	97(5)	100(6)	97(10)	50(3)	−20(30)	0	97(5)

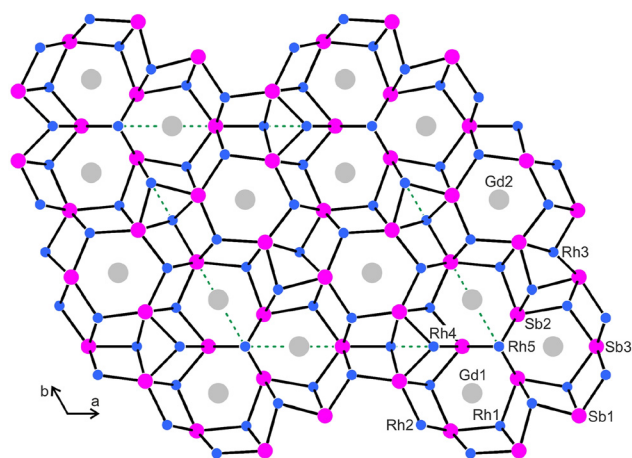
Table 3: Interatomic distances (pm) for $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$. All distances of the first coordination spheres are listed. Standard deviations are equal or smaller than 1.0 pm.

Gd1:	1	Rh5	286.1	Rh3:	1	Sb3	257.0
	2	Rh1	307.0		2	Sb1	278.2
	2	Sb3	311.1		2	Sb1	286.9
	2	Rh1	312.6		2	Rh1	292.6
	2	Rh2	319.2		1	Rh4	303.8
	2	Rh4	321.5		1	Rh4	315.1
	2	Sb2	326.5		2	Rh2	326.0
Gd2:	2	Sb2	330.2		2	Rh2	335.5
	1	Sb1	392.4	Rh4:	1	Sb2	254.5
	3	Sb1	325.9		2	Sb1	259.4
	3	Sb1	327.0		1	Sb2	262.6
	3	Rh2	333.9		2	Rh1	292.1
	3	Rh2	334.9		2	Rh1	295.1
	3	Rh1	358.0		1	Rh3	303.8
Rh1:	1	Sb1	265.3		1	Rh3	315.1
	1	Sb3	265.6	Rh5:	2	Gd1	321.5
	1	Sb1	265.9		3	Sb2	283.0
	1	Sb2	267.9		3	Gd1	286.1
	1	Rh4	292.1		3	Sb2	289.7
	1	Rh3	292.6	Sb1:	1	Rh2	254.5
	1	Rh4	295.1		1	Rh2	257.7
Rh2:	1	Rh2	298.8		1	Rh4	259.4
	1	Rh2	300.6		1	Rh1	265.3
	1	Gd1	307.0		1	Rh1	265.9
	1	Gd1	312.6		1	Rh3	278.2
	1	Gd2	358.0		1	Rh3	286.9
	1	Sb1	254.5		1	Gd2	325.9
	1	Sb1	257.7		1	Gd2	327.0
Rh3:	1	Sb3	260.8	Sb2:	1	Rh4	254.5
	1	Sb3	265.5		1	Rh4	262.6
	1	Rh1	298.8		2	Rh1	267.9
	1	Rh1	300.6		1	Rh5	283.0
	1	Rh2	303.6		1	Rh5	289.7
	1	Gd1	319.2		2	Gd1	326.5
	1	Rh3	326.0		2	Gd1	330.2
Rh4:	1	Gd2	333.9		2	Sb2	339.0
	1	Gd2	334.9	Sb3:	1	Rh3	257.0
					2	Rh2	260.8
					2	Rh2	265.5
					2	Rh1	265.6
					2	Gd1	311.1

presented in the Bärnighausen formalism in Figure 1. The *translationengleiche* symmetry reduction of index 2 ($P6_2/m \rightarrow P31m$) leads to free z parameters for all atoms and a splitting of the $2e$ site (split position in the subcell refinement) into two $1a$ sites, of which only one is occupied in the ordered model. This corresponds to a shift of the Rh5 atoms away from the Gd_{13} triangle (loss of the two-fold axis and of the mirror plane perpendicular to the c axis). Considering this peculiar detail, $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ crystallizes with its own structure type.

The $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structure contains five crystallographically independent rhodium sites. These rhodium atoms have between three and six nearest antimony neighbors with Rh–Sb distances ranging from 255–290 pm, comparable to the antimonides CeRhSb (268–287 pm Rh–Sb),⁴⁹ $\text{Ce}_2\text{Rh}_3\text{Sb}_4$ (259–270 pm Rh–Sb)⁵⁰ or $\text{Ce}_8\text{Rh}_{17}\text{Sb}_{14}$ (257–272 pm Rh–Sb).⁵¹ All these Rh–Sb distances are close to the sum of the covalent radii⁴⁸ of 266 pm for Rh + Sb. Together, the rhodium and antimony atoms build a covalently bonded $[\text{Rh}_{19}\text{Sb}_{12}]$ network (Figure 2). This network is additionally stabilized by weak Rh–Rh bonding. The Rh–Rh distances in the $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structure range from 292–336 pm, all slightly longer than in *fcc* rhodium (12×269 pm).⁵² The two crystallographically independent gadolinium atoms fill slightly distorted hexagonal prismatic cavities within the $[\text{Rh}_{19}\text{Sb}_{12}]$ network.

The structures of metal-rich phosphides can geometrically be described by a condensation pattern of phosphorus-centered trigonal prisms formed by the metal atoms.⁵ Often the condensation patterns resemble a *shamrock*-like arrangement.⁶ In analogy to the $\text{RE}_5\text{T}_{19}\text{P}_{12}$ phosphides^{11,14,27} and $\text{RE}_5\text{Ir}_{19}\text{Si}_{12}$ silicides,³³ we have drawn the $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structure with the trigonal prismatic arrangement around the antimony atoms (Figure 3). The *shamrock*-like motif that undulates through the middle of the unit cell looks quite regular with antimony atoms approximately within the centers of the trigonal prisms. This is different for the motif located around the origin of the unit cell. The three inner prisms that are directly condensed to form the Gd_6 prism have one strongly elongated edge and the antimony atoms are shifted towards the c axis. Also, the terminal prisms of this motif show a shift of the antimony atoms towards the outer Rh₄ faces. In Figure 4

**Figure 2:** View of the $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structure along the c axis. Gadolinium, rhodium and antimony atoms are drawn as medium grey, blue and magenta circles, respectively. The $[\text{Rh}_{19}\text{Sb}_{12}]$ network is emphasized. Atom designations are given at the lower right-hand part.

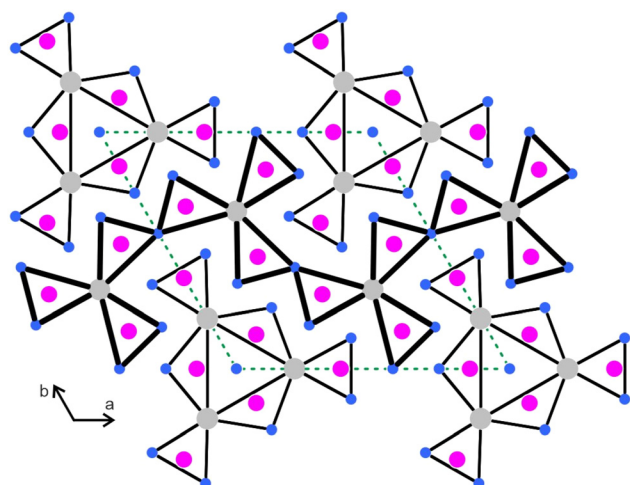


Figure 3: Projection of the $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structure along the c axis. Gadolinium, rhodium and antimony atoms are drawn as medium grey, blue and magenta circles, respectively. All atoms lie on mirror planes at $z = 0$ (thin lines) and $z = 1/2$ (thick lines). The trigonal prismatic coordination of the antimony atoms is emphasized.

we compare this arrangement with the one in the recently reported silicide $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$,³³ where all prisms are almost regular.

The main difference between the $\text{Sc}_5\text{Co}_{19}\text{P}_{12}$ -type phosphides and silicides with the comparatively small phosphorus and silicon atoms on one side and $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ on the other concerns the position of the rhodium atoms on the c axis. The local coordination in the gadolinium prisms in $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ is compared with that in $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$ in the lower part of Figure 4. The Rh5 atoms in $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ are shifted by $\sim c/2$ with respect to Ir4 in $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$ and the Sb2 atoms move towards the c axis, forming the trigonal prisms around Rh5. The Gd1 atoms are then capping the rectangular faces of these trigonal prisms. The Sb2–Sb2 contact of 339 pm, i. e., the edge of the triangles, is a weak one and corresponds to the secondary Sb–Sb interactions in elemental antimony (3×291 and 3×336 pm Sb–Sb).⁵² The distance of the Rh5 atoms to the Gd2 atoms of 286 pm is exactly the value of the sum of the

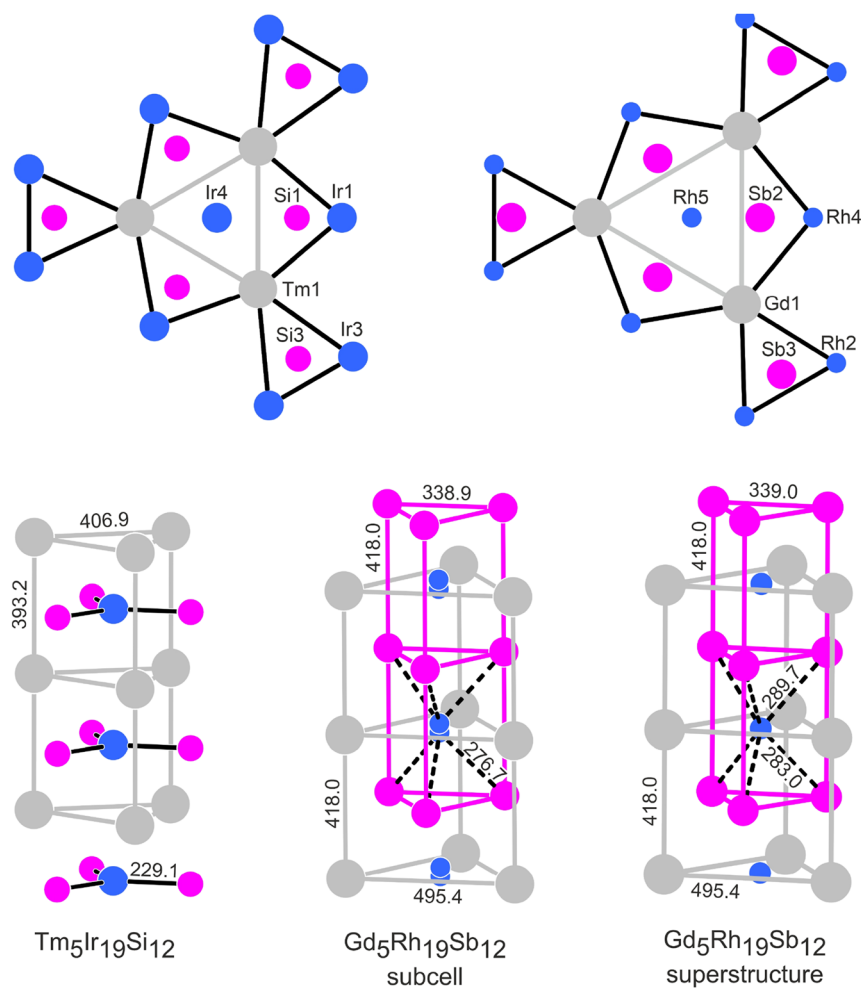


Figure 4: Comparison of the $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$ and $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ structures. Thulium (gadolinium), iridium (rhodium) and silicon (antimony) atoms are drawn as medium grey, blue and magenta circles, respectively. The trigonal prismatic building units around the origins of the unit cells are shown as projections onto the ab planes in the upper part. The lower part shows the local trigonal prismatic coordination in the strands that extend in c direction. Atom designations and relevant interatomic distances are given.

covalent radii for Gd + Rh.⁴⁸ Thus, the $\text{Rh}_{5@}\text{Gd}_{23}$ coordination is comparable to the $\text{Ir}_{4@}\text{Si}_{13}$ coordination in $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$.

Summing up, $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ adds a new structural motif to the family of the so-called 5-19-12 phases and can be considered as a proper structure type. The pnictides assigned to the $\text{Ho}_5\text{Ni}_{19}\text{P}_{12}$ type⁵³ are those phases that show no split position for the atom at the origin, while those related to the $\text{Sc}_5\text{Co}_{19}\text{P}_{12}$ type¹¹ show cobalt split positions as manifested by single crystal X-ray diffraction data also for $\text{Zr}_5\text{Co}_{19}\text{P}_{12}$ ¹³ and $\text{Ho}_5\text{Co}_{19}\text{P}_{12}$ ¹⁴ (these two branches are distinguished in the Pearson data base⁴). Important parameters that have an impact on the T5 subcell site are the size of the rare earth element (one can play with the lanthanide contraction, i.e., the size of the rare earth element) and also the crystal growth conditions (kind of flux and the temperature profile). Especially the thermal treatment of the samples influences a potential long-range order. Thus, it is difficult to predict the correct description of a 5-19-12 crystal. Furthermore, $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ is the first antimonide of this atomic arrangement with the much larger antimony atoms.

$\text{Th}_5\text{Fe}_{19}\text{P}_{12}$ ⁵⁴ and $\text{Yb}_5\text{Ni}_{19}\text{P}_{12}$,⁵⁵ on the other side, have the same atomic ratios as $\text{Tm}_5\text{Ir}_{19}\text{Si}_{12}$ and $\text{Gd}_5\text{Rh}_{19}\text{Sb}_{12}$ but a different condensation pattern of their phosphorus-centered trigonal prisms.

Future studies must now focus on $\text{RE}_5\text{Rh}_{19}\text{Sb}_{12}$ antimonides with rare earth elements larger and smaller than gadolinium, in order to check the existence range of this new type and further on antimony-arsenic substitution, since this is a gap with respect to the many $\text{RE}_5\text{T}_{19}\text{P}_{12}$ phosphides.

Acknowledgements: We thank Dipl.-Ing. U. Ch. Rodewald for the intensity data collection.

Research ethics: Not applicable.

Informed consent: Not applicable.

Author contributions: All authors have accepted responsibility for the entire content of this submitted manuscript and approved the submission.

Use of Large Language Models, AI and Machine Learning Tools: Not relevant. Our group is able to think and act independently.

Conflict of interest: The authors declare no conflicts of interest regarding this article.

Research funding: This research was funded by Universität Münster.

Data availability: Data is available from the corresponding author on well-founded request.

References

1. Kuz'ma, Yu.; Chykhrij, S. Phosphides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, Jr., K. A.; Eyring, L., Eds.; Elsevier Science: Amsterdam, Vol. 23, Chapter 156, 1996; pp. 285–433.
2. Parthé, E.; Chabot, B. Crystal Structures and Crystal Chemistry of Ternary Rare Earth-Transition Metal Borides, Silicides and Homologues. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, Jr., K. A.; Eyring, L., Eds.: North-Holland, Amsterdam, Vol. 6, Chapter 48, 1984; pp. 113–332.
3. Rogl, P. Phase Equilibria in Ternary and Higher Order Systems with Rare Earth Elements and Silicon. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, Jr., K. A.; Eyring, L., Eds.; North-Holland, Amsterdam, Vol. 7, Chapter 51, 1984; pp. 1–264.
4. Villars, P.; Cenzual, K., Eds. *Pearson's Crystal Data: Crystal Structure Database for Inorganic Compounds* (release 2023/24); ASM International®: Materials Park, Ohio (USA), 2023.
5. Gladyshevskii, E. I.; Grin', Yu. N. *Sov. Phys. Crystallogr.* **1981**, *26*, 683–689.
6. Zaremba, N.; Krnel, M.; Prots, Yu.; König, M.; Akselrud, L.; Grin, Yu.; Svanidze, E. *Inorg. Chem.* **2024**, *63*, 4566–4573.
7. Salamakha, P. S.; Sologub, O. L.; Bodak, O. I. Ternary Rare-Earth-Germanium Systems. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, Jr., K. A.; Eyring, L., Eds.; Elsevier Science B. V.: Amsterdam, Vol. 27, Chapter 173, 1999; pp. 1–223.
8. Salamakha, P. S. Crystal Structures and Crystal Chemistry of Ternary Rare-Earth Germanides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, Jr., K. A.; Eyring, L., Eds.; Elsevier Science B. V.: Amsterdam, Vol. 27, Chapter 174, 1999; pp. 225–338.
9. Schmidt, T.; Jeitschko, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 927–932.
10. Jeitschko, W.; Altmeyer, R. O.; Rodewald, U. Ch. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2440–2446.
11. Jeitschko, W.; Reinbold, E. J. *J. Naturforsch.* **1985**, *40b*, 900–905.
12. Jeitschko, W.; Meisen, U.; Reinbold, E. J. *Z. Anorg. Allg. Chem.* **2012**, *638*, 770–778.
13. Ghetta, V.; Chaudouet, P.; Madar, R.; Senateur, J. P.; Lambert-Andron, B. *J. Less-Common Met.* **1986**, *120*, 197–201.
14. Jakubowski-Ripke, U.; Jeitschko, W. *J. Less-Common Met.* **1988**, *136*, 261–270.
15. Chykhrij, S. I.; Kuz'ma, Y. B. *Russ. J. Inorg. Chem.* **1990**, *35*, 1821–1823.
16. Orishchin, S. V.; Zhak, O. V.; Koval'chuk, I. V.; Kuz'ma, Y. B. *Russ. J. Inorg. Chem.* **2001**, *46*, 1892–1895.
17. Budnyk, S. L.; Kuz'ma, Yu. B. *Pol. J. Chem.* **2002**, *76*, 1553–1558.
18. Babizhetskii, V. S.; Chykhrij, S. I.; Oryshchyn, S. V.; Kuz'ma, Y. B. *Ukr. Khim. Zh. Ukr. Ed.* **1993**, *59*, 240–242.
19. Stoyko, S. S.; Davydov, V. M.; Babizhetskii, V. S.; Oryshchyn, S. V. *Visn. Lviv Derzh. Univ., Ser. Khim.* **2003**, *43*, 40–44.
20. Oryshchyn, S. V.; Chykhrij, S. I.; Babizhetskii, V. S.; Kuz'ma, Yu. B. *Dopov. Akad. Nauk Ukr. RSR* **1991**, *6*, 133–136.
21. Cava, R. J.; Siegrist, T.; Carter, S. A.; Krajewski, J. J.; Peck, Jr., W. F.; Zandbergen, H. W. *J. Solid State Chem.* **1996**, *121*, 51–55.
22. Zandbergen, H. W.; Jansen, J. J. *Microsc.* **1998**, *190*, 222–237.
23. Jansen, J.; Tang, D.; Zandbergen, H. W.; Schenk, H. *Acta Crystallogr. A* **1998**, *54*, 91–101.
24. Demchyna, R. O.; Oryshchyn, S. V.; Kuz'ma, Y. B. *J. Alloys Compd.* **2001**, *322*, 176–183.

25. Dhahri, E.; Fourati, N. *J. Phys.: Condens. Matter* **1997**, *9*, 5517–5525.
26. Wurth, A.; Löhken, A.; Mewis, A. *Z. Anorg. Allg. Chem.* **2002**, *628*, 661–666.
27. Pfannenschmidt, U.; Rodewald, U.Ch.; Hoffmann, R.-D.; Pöttgen, R. *J. Solid State Chem.* **2011**, *184*, 2731–2737.
28. Steinwand, S. J.; Hurng, W.-M.; Corbett, J. D. *J. Solid State Chem.* **1991**, *94*, 36–44.
29. Nesper, R.; Wengert, S.; Zürcher, F.; Currao, A. *Chem. Eur. J.* **1999**, *5*, 3382–3389.
30. Slabon, A.; Cuervo-Reyes, E.; Kubata, C.; Mensing, C.; Nesper, R. *Z. Anorg. Allg. Chem.* **2012**, *638*, 2020–2028.
31. Vasquez, G.; Lattner, S. E. *Chem. Mater.* **2018**, *30*, 6478–6485.
32. Vasquez, G.; Wei, K.; Choi, E. S.; Baumbach, R.; Lattner, S. E. *Crystal Growth Des.* **2020**, *20*, 2632–2643.
33. Voßwinkel, D.; Block, T.; Pöttgen, R. *Z. Naturforsch.* **2025**, *80b*, 79–84.
34. Pöttgen, R.; Gulden, Th.; Simon, A. *GIT Labor-Fachzeitschrift* **1999**, *43*, 133–136.
35. Pöttgen, R.; Lang, A.; Hoffmann, R.-D.; Künnen, B.; Kotzyba, G.; Müllmann, R.; Mosel, B. D.; Rosenhahn, C. *Z. Kristallogr.* **1999**, *214*, 143–150.
36. Palatinus, L. *Acta Crystallogr.* **2013**, *B69*, 1–16.
37. Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.
38. Petříček, V.; Dušek, M.; Palatinus, L. *Z. Kristallogr.* **2014**, *229*, 345–352.
39. Petříček, V.; Palatinus, L.; Plášil, J.; Dušek, M. *Z. Kristallogr.* **2023**, *238*, 271–282.
40. Bärnighausen, H. *Commun. Math. Chem.* **1980**, *9*, 139–175.
41. Müller, U. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1519–1537.
42. Müller, U.; Wondratschek, H. *International Tables for Crystallography, Vol. A1, Symmetry Relations between Space Groups*; John Wiley & Sons: Chichester, United Kingdom, 2010.
43. Müller, U. *Symmetriebeziehungen zwischen verwandten Kristallstrukturen*, 2nd ed.; Springer Spektrum Berlin: Heidelberg, Germany, 2023.
44. Flack, H. D.; Schwarzenbach, D. *Acta Crystallogr.* **1988**, *A44*, 499–506.
45. Watkin, D. J. *Appl. Crystallogr.* **2008**, *41*, 491–522.
46. Pfannenschmidt, U.; Rodewald, U.Ch.; Pöttgen, R. *Monatsh. Chem.* **2011**, *142*, 219–224.
47. Reimann, M. K.; Pöttgen, R. *Z. Naturforsch.* **2024**, *79b*, 113–120.
48. Emsley, J. *The Elements*; Oxford University Press: Oxford, 1999.
49. Chevalier, B.; Decourt, R.; Heying, B.; Schappacher, F. M.; Rodewald, U.Ch.; Hoffmann, R.-D.; Pöttgen, R.; Eger, R.; Simon, A. *Chem. Mater.* **2007**, *19*, 28–25.
50. Cardoso-Gil, R.; Caroca-Canales, N.; Budnyk, S.; Schnelle, W. *Z. Kristallogr.* **2011**, *226*, 657–666.
51. Schellenberg, I.; Hoffmann, R.-D.; Schwickert, C.; Pöttgen, R. *Solid State Sci.* **2011**, *13*, 1740–1747.
52. Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974.
53. Pivan, J. Y.; Guérin, R.; Sergent, M. *Inorg. Chim. Acta* **1985**, *109*, 221–224.
54. Albering, J. H.; Jeitschko, W. *Z. Naturforsch.* **1992**, *47b*, 1521–1528.
55. Chikhrii, S. I.; Kuz'ma, Y. B.; Davydov, V. M.; Budnyk, S. L.; Orishchin, S. V. *Crystallogr. Rep.* **1998**, *43*, 548–552.