Ce$_5$RuGe$_2$ with a Y$_2$HfS$_5$ anti-type structure, an ordered substitution variant of orthorhombic $\beta$-Yb$_5$Sb$_3$

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Ce₅RuGe₂ with a Y₂HfS₅ anti-Type Structure, an Ordered Substitution Variant of Orthorhombic β-Yb₅Sb₃

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Abstract. Pentacerium ruthenium digermanide, Mᵢ = 946.85, orthorhombic, op32, Pnma – d²c³ (No. 62), \( a = 12.255 (3), \ b = 8.898 (2), \ c = 8.008 (2) \) Å, \( V = 873.2 (4) Å³, \ Z = 4, \ Dₓ = 7.202 Mg m⁻³, \( \lambda(Mo \ Ka) = 0.71073 \) Å, \( \mu = 33.054 \) mm⁻¹, \( F(000) = 1592, T = 293 K, wR = 0.051 \) for 1160 contributing unique reflections. The CesRuGe₂ structure is an ordered ternary substitution variant of the β-Yb₅Sb₃ type and can be considered as an anti-type of the \( \beta \)-Yb₅Sb₃ structure. All these structures together with \( \text{U₃Se₅}, \text{U₂PbSe₅}, \text{Y₃Bi₃}, \text{Tm₃Ga₄}, \text{Pu₃Pd₅} \) and \( \text{La₂SnS₅} \) are related to the Rh₅Ge₃ type as particular site substitution and/or deformation variants.

Introduction. No systematic investigation of the rare-earth–Ru,Rh,Pd–Ge systems has ever been undertaken and no ternary diagrams have been published. There was only one compound known in the ternary system Ce–Ru–Ge, that is cubic Ce₃Ru₄Ge₁₃ (Segre, Braun & Yvon, 1981) with a Pr₃Rh₄Sn₁₃-type structure. Here we report on the structure determination of a new orthorhombic phase.

Experimental. The sample of nominal composition Ce₅RuGe₂ was prepared from the elements [Ce (99.9%), Ru (99.999%) and Ge (99.999%)] by arc melting under an argon atmosphere (the weight loss was 0.6%), annealing at 1073 K for two weeks in a silica tube under vacuum, and quenching in water. A single crystal with irregular shape (mean radius 0.033 mm) was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo Kα radiation with graphite monochromator. The unit-cell parameters were refined from 2θ values of 24 reflections (Mo Kα, \( \lambda = 0.71073 \) Å, \( 2θ < 2θ < 37° \)) using the program LATCON (Schwarzenbach, 1963). 2688 reflections were collected out to \( \sin(Sθ/λ) = 0.703 \) Å⁻¹ (0 ≤ h ≤ 17, 0 ≤ k ≤ 12, 0 ≤ l ≤ 11) and the anti-reflections) in the \( ω−2θ \)-scan mode, yielding 1344 unique reflections \( (R_{int} = 0.036) \). Two standard reflections, 401 and 122, were measured with maximum intensity variations 0.6 and 0.8% respectively. Absorption correction was made using the program LSABS (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0.2284 and 0.1425. The anomalous-dispersion coefficients were taken from International Tables for X-ray Crystallography (1974, Vol. IV). Systematic absences led to the following possible space groups: Pn2₁a (= Pna2₀ and Pnma (International Tables for Crystallography, 1983, Vol. A). The structure was solved in space group Pnma by the MULTAN87 program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and confirmed by the structure refinement, based on \( |F| \) values using the program CRYLSQ (Olthof-Hazekamp, 1990). 43 variables including anisotropic atomic displacement parameters were refined to \( R = 0.057 \) and \( wR = 0.051 \) \( [w = 1/o^{-2}(IF_{rel})], \ S = 3.897 \) considering 1160 contributing unique reflections with \( |F_{rel}| > 3σ(|F_{rel}|). \) The maximum shift/e.s.d. in the last cycle was 0.0002. Final residual electron density \( +3.65(-4.79) \) e Å⁻³. The programs used to refine the structure are all from the XTAL3.0 system (Hall & Stewart, 1990). The atomic positional parameters were standardized by using the STRUCTURE TIDY program (Gelato & Parthé, 1987). The atomic positional and displacement parameters are given in Table 1* and the interatomic distances in Table 2. One notes the very short Ce(1)−Ru distance of 2.72 Å. Attempts to refine occupancy factors and displacement parameters of the Ce(1) and the Ru positions did not improve the results. Short cerium–transition-metal distances in rare-earth-rich compounds have been reported before, as for example in \( \text{Ce₃Co₁₁} \) (2.61 Å) (Larson & Cromer, 1962).

Discussion. The structure of Ce₅RuGe₂ is shown in a projection along [010] in the top row of Fig. 1. It is a ternary ordered substitution variant of the β-Yb₅Sb₃ type.

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54568 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The equivalent isotropic atomic displacement factors are expressed as $U_{eq} = \frac{1}{3} \sum_i u_i a_i^* a_i^* a_i^* \cdot a_i^* a_i^* a_i^*$, where the e.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}(\AA^2 \times 100)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(1)</td>
<td>3.120 (3)</td>
<td>2.006 (3)</td>
<td>3.641 (3)</td>
<td>3.798 (3)</td>
</tr>
<tr>
<td>Ce(2)</td>
<td>3.469 (3)</td>
<td>3.823 (4)</td>
<td>3.898 (3)</td>
<td>3.575 (3)</td>
</tr>
<tr>
<td>Ce(3)</td>
<td>3.120 (3)</td>
<td>2.006 (3)</td>
<td>3.641 (3)</td>
<td>3.798 (3)</td>
</tr>
<tr>
<td>Ce(4)</td>
<td>2.006 (3)</td>
<td>3.641 (3)</td>
<td>3.798 (3)</td>
<td>3.575 (3)</td>
</tr>
</tbody>
</table>

The orthorhombic $Y_2HfS_5$ structure (Jeitschko & Donohue, 1975) and the monoclinic $U_2PbSe_5$ structure (Potel, Brochu & Padiou, 1975) have been interchanged.

The coordination polyhedra of the six different atom sites in $C_{6}RuGe_{2}$ are shown in Fig. 2. It can be seen from Table 2 that Ge has nine nearest Ce neighbours, which form a tricapped trigonal prism.

The family of deformation variants of the $R_{h}Ge_{3}$ type (Geller, 1955) and their ordered substitution derivatives, to which the above mentioned structures belong, has been studied by several authors (see, for example, Yatsenko, Gladyshevskii, Tchuntonov, Yarmolyuk & Grin', 1983). The basic feature of these structures is a framework of interconnected infinite columns of centred trigonal prisms, emphasized in the projections in Fig. 1.

The vertices of the trigonal prisms are occupied by atoms on sites to be called henceforth TPv and the sites at the centers (c) of the trigonal prisms will be labeled TPC. The prisms share triangular faces and edges with neighbouring prisms to form a threedimensional network with large deformed hexagonal channels. These channels may be considered as columns of face-sharing deformed hexagonal prisms. Inside (i) each hexagonal prism there are two atoms in the central plane (sites HPi) and one atom at the centre of each hexagonal base (b) plane of the prism (sites HPb). The occupation of these atomic sites in the different structures is summarized in Table 3. Note that $Rh_{3}Ge_{3}$ and $La_{2}SnS_{5}$ are the only two structures with 16 atoms/cell, all the others have a translation period twice as large in the direction perpendicular to the projection plane of Fig. 1.

The elongated hexagons which are the base planes of the hexagonal prisms in $Rh_{3}Ge_{3}$ and its ternary ordered variant $La_{2}SnS_{5}$ (Jaulmes, 1974) form, as shown in the bottom row of Fig. 1, a parquet-like patchwork which is also found, more or less distorted, in all the derivative structures. The distortion mechanism in the two deformation variants $\beta$-$Yb_{3}Sb_{5}$ and $Y_{2}Bi_{3}$ (Wang, Gabe, Calvert & Taylor, 1976) is very similar, i.e. the atoms on sites HPb are strongly displaced from the centres of the hexagons. Since the sense of these displacements is reversed for every second hexagonal base plane, a doubling of the translation unit parallel to the prism axes results. Instead of straight chains, zigzag chains of HPb atoms are now observed.
Fig. 1. Projections of $\beta$-Yb$_3$Sb$_3$, Ce$_5$RuGe$_2$, U$_3$S$_5$, Y$_2$HfS$_6$, Y$_3$Bi$_3$, and Tm$_3$Ga$_5$, along [010], U$_2$PbSe$_5$, along [100] and Pu$_3$Pd$_5$, Rh$_3$Ge$_3$, and La$_2$SnS$_5$, along [001]. For U$_2$PbSe$_5$, the small double circles stand for Pb at $x=\frac{1}{2}$, U at $x=0$. Stars in the drawings for Tm$_3$Ga$_5$ and Pu$_3$Pd$_5$ indicate that Ga and Pd atoms at $z=0$ and $z=\frac{1}{2}$ are hidden by the flagged Tm and Pu atoms.
Isopointal $\beta$-Yb$_5$Sb$_3$ and Y$_5$Bi$_3$ differ in the shifts along the column axis of the zigzag chains in neighbouring hexagonal channels and may be considered as stacking variants. Two ternary ordered derivative structure types are known for the first one, i.e. $\text{Y}_2\text{Hf}_5\text{S}_5$ with space group $\text{Pmma}$ and U$_3$PbSe$_5$ with an orthorhombic translation lattice but monoclinic symmetry corresponding to space group $\text{P2}_1/c$.† No substitution derivative of Y$_5$Bi$_3$ has been identified as yet.

The structure of Tm$_3$Ga$_5$ (Yatsenko, Gladyshevskii, Tschuntonov, Yarmolyuk & Grin’, 1983), shown in the third row of Fig. 1, is also isopointal with $\beta$-Yb$_5$Sb$_3$; however, the cell parameters and atom coordinates are sufficiently different to justify that this structure should be considered as a separate structure type. It can be seen from Fig. 1 that the trigonal prism skeleton is considerably distorted for this structure type, which is closely related to the Pu$_3$Pd$_5$ type (Cromer, 1976), also observed with rare-earth gallides but where all hexagons have the same orientation and the zigzag chains formed by atoms of the HPb sites have the same relative arrangement as in Y$_5$Bi$_3$.

From a chemical point of view the compounds crystallizing with one of these structure types can be divided into three main groups: iono-covalent compounds with stoichiometry $C_3A^{2+}S^{2-}$, $C_3^{2+}C^{4+}A^{2-}$ or $C_2^{2+}C^{2+}A^{2-}$, intermetallic ‘anti-types’ of these

* The $a$ and $c$ parameters of $\beta$-Yb$_5$Sb$_3$ and Y$_5$Bi$_3$ are interchanged in the conventional $\text{Pnma}$ setting. Representatives of both types are unfortunately considered as isotypic by Villars & Calvert (1985).

† In the book by Villars & Calvert (1985) the angle $\beta$ of U$_3$PbSe$_5$ is misprinted as 101° instead of 90° and the structure is erroneously considered together with the compounds crystallizing with the La$_2$GeS$_5$-type structure (Mazurier & Etienne, 1973).

![Fig. 2. The coordination polyhedra of the six different atom sites in Ce$_3$RuGe$_2$.](image)

<table>
<thead>
<tr>
<th>Type</th>
<th>Pearson Space group</th>
<th>Wyckoff sequence</th>
<th>TPv</th>
<th>TPc</th>
<th>HPI</th>
<th>HPe</th>
<th>HPe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_4$Ge$_7$</td>
<td>$\text{Pm}3m$ a</td>
<td>$\text{Rb}$</td>
<td>Ge</td>
<td>Ge</td>
<td>Ge</td>
<td>Ge</td>
<td>Ge</td>
</tr>
<tr>
<td>La$_3$Sn$_5$</td>
<td>$\text{Pm}3m$ a</td>
<td>$\text{Sn}$</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Pu$_3$Pd$_5$</td>
<td>$\text{Pm}3m$ a</td>
<td>$\text{Pd}$</td>
<td>Pu</td>
<td>Pu</td>
<td>Pu</td>
<td>Pu</td>
<td>Pu</td>
</tr>
<tr>
<td>$\beta$-Yb$_3$Sb$_3$</td>
<td>$\text{Pn}3m$ a</td>
<td>$\text{A}^{2+}$</td>
<td>Yb</td>
<td>Yb</td>
<td>Yb</td>
<td>Yb</td>
<td>Yb</td>
</tr>
<tr>
<td>Ce$_3$RuGe$_2$</td>
<td>$\text{Pn}3m$ a</td>
<td>$\text{Ce}$</td>
<td>Ce</td>
<td>Ce</td>
<td>Ce</td>
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<td>U$_3$S$_5$</td>
<td>$\text{Pn}3m$ a</td>
<td>$\text{S}$</td>
<td>S</td>
<td>S</td>
<td>S</td>
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</tr>
<tr>
<td>Y$_3$Bi$_3$</td>
<td>$\text{Pn}3m$ a</td>
<td>$\text{Bi}$</td>
<td>Bi</td>
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<tr>
<td>Y$_3$Ga$_3$</td>
<td>$\text{Pn}3m$ a</td>
<td>$\text{Ga}$</td>
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<tr>
<td>U$_3$PbSe$_5$</td>
<td>$\text{P2}_1/c$ e</td>
<td>$\text{Se}$</td>
<td>U</td>
<td>Pb</td>
<td>Se</td>
<td>U</td>
<td>Pb</td>
</tr>
</tbody>
</table>

Table 3. The occupation of the different crystallographic sites in Ce$_3$RuGe$_2$ and of corresponding sites in related structures

(Stoichiometry 5:3 or 5:1:2), and strongly distorted intermetallic derivatives with the same stoichiometry as the iono-covalent compounds.

The first group of compounds contains a series of sulfides and selenides, which may be considered as normal valence compounds. In the structure of highest symmetry, La$_3$SnS$_5$, the Sn site (HPb) is coordinated by an almost regular $S_4$ octahedron, whereas the La atoms centre the tricapped trigonal prisms (distances to the two capping atoms are slightly longer). The chalcogen atoms at the TPv sites centre square pyramids and squares, and those from the HPI site trigonal bipyramids.

It was shown by the authors of the structure refinement that the binary compound U$_3$S$_3$ is in fact a pseudo-ternary one, since U is present in two different oxidation states, the explicit chemical formula being $U^{3+}_{\text{III}}U^{4+}_{\text{II}}S^{2-}_{\text{II}}$. The three-valent U atoms occupy the trigonal prismatic sites (TPc) with two capping atoms at shorter distances and the third one at a longer distance. The four-valent U atoms occupy the HPb site with seven nearest neighbours and an additional atom caps one of the faces of the now strongly distorted octahedron. Owing to the distortions all S atoms at the TPv sites now centre U$_3$ square pyramids and those from the HPI sites U$_4$ tetrahedra. U$^{4+}$ may be replaced by other four-valent cations such as Th$^{4+}$, Zr$^{4+}$, Hf$^{4+}$ or Sn$^{4+}$, whereas U$^{3+}$ can be substituted either by other three-valent rare-earth metals, or by a mixture of two- and four-valent cations, as is the case for the representatives of the U$^{3+}_{\text{III}}$Pb$^{2+}_{\text{II}}$Se$^{2-}_{\text{II}}$ type.

Only minor changes of atomic coordinates are observed between the structures of these iono-covalent compounds and their ‘anti-types’, found with phosphides, antimonides and bismuthides. Slight variations occur in the coordination polyhedra and, in general, atom coordinations in $\beta$-Yb$_5$Sb$_3$ and
Y₃Bi₃ are higher than those of the corresponding sites in U₃S₅. Effectively, in both compounds all three atoms capping the trigonal prisms are at relatively short distances, two atoms now cap faces of the distorted octahedra. Some of the square pyramids are transformed into octahedra by the approach of a sixth atom and the tetrahedra change into trigonal bipyramids in a similar way. Atoms of the same atomic species should be included in the first coordination shell of the majority atoms for these compounds.

For all iono-covalent compounds and their metallic anti-types treated above, the majority atoms are larger than the minority atoms. This is not the case for the compounds belonging to the third group, i.e. the strongly distorted intermetallic compounds with the same stoichiometry as the iono-covalent compounds. The interchange in the size of the atoms explains the important distortions observed with respect to the structures of the first two groups of compounds. In Tm₃Ga₅ the homonuclear Ga—Ga distances are shorter than the heteronuclear distances and the Ga atoms of the TPv sites are displaced out of the square pyramids into Tm₃Ga₂ trigonal prisms. The numbers of heteronuclear contacts of the Tm compounds. In Tm₃Ga₅ the homonuclear Ga—Ga explains the important distortions observed with larger than the minority atoms. This is not the case for the compounds belonging to the third group, i.e. the strongly distorted intermetallic compounds with the same stoichiometry as the iono-covalent compounds. The interchange in the size of the atoms explains the important distortions observed with respect to the structures of the first two groups of compounds. In Tm₃Ga₅ the homonuclear Ga—Ga distances are shorter than the heteronuclear distances and the Ga atoms of the TPv sites are displaced out of the square pyramids into Tm₃Ga₂ trigonal prisms. The numbers of heteronuclear contacts of the Tm sites are, as expected, higher than for corresponding sites in the chalcogenides and pnictides, ten for the TPc site and nine for the HPb site, respectively.

We wish to acknowledge the help of Ms Birgitta Künzler for the preparation of the drawings. This study was supported by the Swiss National Science Foundation under contract 20-28490.90 and the Alfred and Hilde Freissler Fond.


**Monoclinic NdRuSi₂, a Distortion Derivative of Orthorhombic CeNiSi₂**

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**Abstract.** Neodymium ruthenium disilicide, \(M_6 = 301.48\), monoclinic, \(mP8\), \(P2_1/m - e^\parallel\) (No. 11), \(a = 4.4620(6)\), \(b = 4.0451(6)\), \(c = 8.242(2)\) Å, \(\beta = 102.23(1)^\circ\), \(V = 145.39(5)\) Å³, \(Z = 2\), \(D_x = 6.887\) Mg m⁻³, \(\lambda(Mo K\alpha) = 0.71073\) Å, \(\mu = 22.065\) mm⁻¹, \(F(000) = 264\), \(T = 293\) K, \(wR = 0.040\) for 459 contributing unique reflections. The structure is isopointal with TmLi₀.₅Ge₂ \((\alpha = 0.5)\), both being distortion variants of the orthorhombic CeNiSi₂-type structure. Opposite to what is observed for TmLi₀.₅Ge₂, the distortions in NdRuSi₂ are such that all non-metal atoms take part in infinite zigzag chains. Ru—Ru distances of 3.08 Å exist.

**Introduction.** No systematic investigations of the Nd—Ru—Si system have been reported. The only