

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

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Abstract. Pentacerium ruthenium digermanide, $M_r = 946.85$, orthorhombic, $oP32$, $Pnma - d^2c^4$ (No. 62), $a = 12.255$ (3), $b = 8.898$ (2), $c = 8.008$ (2) Å, $V = 873.2$ (4) Å³, $Z = 4$, $D_x = 7.202$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 33.054$ mm⁻¹, $F(000) = 1592$, $T = 293$ K, $wR = 0.051$ for 1160 contributing unique reflections. The Ce₅RuGe₂ structure is an ordered ternary substitution variant of the β -Yb₅Sb₃ type and can be considered as an *anti*-type of the Y₂HfS₅ structure. All these structures together with U₃S₅, U₂PbSe₅, Y₅Bi₃, Tm₃Ga₅, Pu₃Pd₅ and 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 Ce₄RuGe 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 $K\alpha$ radiation with graphite monochromator. The unit-cell parameters were refined from 2 θ values of 24 reflections (Mo $K\alpha$, $\lambda = 0.71073$ Å, $24 < 2\theta < 37^\circ$) using the program *LATCON* (Schwarzenbach, 1966). 2688 reflections were collected out to $(\sin\theta/\lambda) = 0.703$ Å⁻¹ ($0 \leq h \leq 17$, $0 \leq k \leq 12$, $0 \leq l \leq 11$ and the anti-reflections) in the ω -2 θ -scan mode, yielding 1344 unique reflections ($R_{\text{int}} = 0.036$). 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: $Pn2_1a$ (= $Pna2_1$) 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 $wR = 0.051$ [$w = 1/\sigma^2(|F_{\text{rel}}|)$, $S = 3.897$] considering 1160 contributing unique reflections with $|F_{\text{rel}}| > 3\sigma(|F_{\text{rel}}|)$. 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 Ce₂₄Co₁₁ (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

* 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.

Table 1. Atomic positional and displacement parameters for Ce_5RuGe_2 with space group $Pnma$

The equivalent isotropic atomic displacement factors are expressed as $U_{eq} = \frac{1}{3} \sum_i U_{ij} a_i^* a_j^* a_i \cdot a_j$. E.s.d.'s are given in parentheses.

Wyckoff position	x	y	z	$U_{eq} (\text{\AA}^2 \times 100)$	
Ce(1)	8(d)	0.0703 (1)	0.5309 (1)	0.3156 (2)	1.01 (3)
Ge	8(d)	0.3287 (2)	0.5050 (3)	0.4331 (3)	0.83 (6)
Ce(2)	4(c)	0.0016 (2)		0.0343 (2)	0.91 (5)
Ru	4(c)	0.0188 (2)		0.4234 (4)	1.54 (8)
Ce(3)	4(c)	0.2051 (2)		0.6420 (2)	0.75 (5)
Ce(4)	4(c)	0.2866 (2)		0.1630 (2)	0.78 (5)

structure type (Brunton & Steinfink, 1971), where the Sb [4(c)] site is now occupied by transition-metal atoms. For the β - Yb_5Sb_3 type is known as *anti*-type U_3S_5 (Potel, Brochu, Padiou & Grandjean, 1972) which has two ternary ordered substitution variants: the orthorhombic Y_2HfS_5 structure (Jeitschko & Donohue, 1975) and the monoclinic U_2PbSe_5 structure (Potel, Brochu & Padiou, 1975). These three structures are presented in the second row of Fig. 1. It appears that the new Ce_5RuGe_2 structure can be considered as an *anti*-type of the Y_2HfS_5 structure where the rare-earth atoms and the main-group elements have been interchanged.

The coordination polyhedra of the six different atom sites in Ce_5RuGe_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. Ru is at the centre of a Ce_8 dodecahedron, one of the surrounding atoms is, however, at a considerably longer distance (3.89 Å) than the others. Two Ru and three Ge atoms form a trigonal bipyramid around the Ce(1) site, the first coordination sphere being completed by eight Ce atoms at increasing distances. The coordinations of Ce(2), Ce(3) and Ce(4) are characterized by four Ge and one Ru atoms at short distances and a larger number of Ce neighbours at longer distances [and one additional Ru atom in the case of Ce(4)].

The family of deformation variants of the Rh_5Ge_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 (v) 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 labelled TPc. The prisms share triangular faces and edges with neighbouring prisms to form a three-dimensional network with large deformed hexagonal

Table 2. Interatomic distances up to 4.1 Å in Ce_5RuGe_2

		E.s.d.'s are given in parentheses.	
Ce(1)—Ru	2.719 (2)	Ce(4)—Ru	2.929 (4)
Ru	3.059 (3)	2Ge	3.178 (3)
Ge	3.312 (3)	2Ge	3.184 (3)
Ge	3.319 (3)	Ce(2)	3.580 (3)
Ce(1)	3.463 (2)	Ce(2)	3.641 (3)
Ce(2)	3.469 (2)	2Ce(1)	3.823 (2)
Ce(2)	3.526 (2)	2Ce(1)	3.843 (2)
Ge	3.575 (3)	Ru	3.888 (4)
Ce(3)	3.648 (2)	Ce(3)	3.964 (3)
Ce(4)	3.823 (2)		
Ce(4)	3.843 (2)	Ru—2Ce(1)	2.719 (2)
Ce(1)	3.899 (2)	Ce(3)	2.877 (4)
Ce(3)	3.912 (3)	Ce(4)	2.929 (4)
Ce(3)	3.976 (2)	2Ce(1)	3.059 (3)
		Ce(2)	3.123 (4)
Ce(2)—2Ge	3.115 (3)	Ce(4)	3.888 (4)
2Ge	3.120 (3)		
Ru	3.123 (4)	Ge—Ce(2)	3.115 (3)
2Ce(1)	3.469 (2)	Ce(2)	3.120 (3)
2Ce(1)	3.526 (2)	Ce(4)	3.178 (3)
Ce(4)	3.580 (3)	Ce(4)	3.184 (3)
Ce(4)	3.641 (3)	Ce(3)	3.200 (3)
Ce(3)	3.898 (3)	Ce(3)	3.218 (3)
Ce(3)	4.012 (3)	Ce(1)	3.312 (3)
		Ce(1)	3.319 (3)
Ce(3)—Ru	2.877 (4)	Ce(1)	3.575 (3)
2Ge	3.200 (3)		
2Ge	3.218 (3)		
2Ce(1)	3.648 (2)		
Ce(2)	3.898 (3)		
2Ce(1)	3.912 (2)		
Ce(4)	3.964 (3)		
2Ce(1)	3.976 (2)		
Ce(2)	4.012 (3)		

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_5Ge_3 and La_2SnS_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_5Ge_3 and its ternary ordered variant La_2SnS_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 β - Yb_5Sb_3 and Y_5Bi_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.

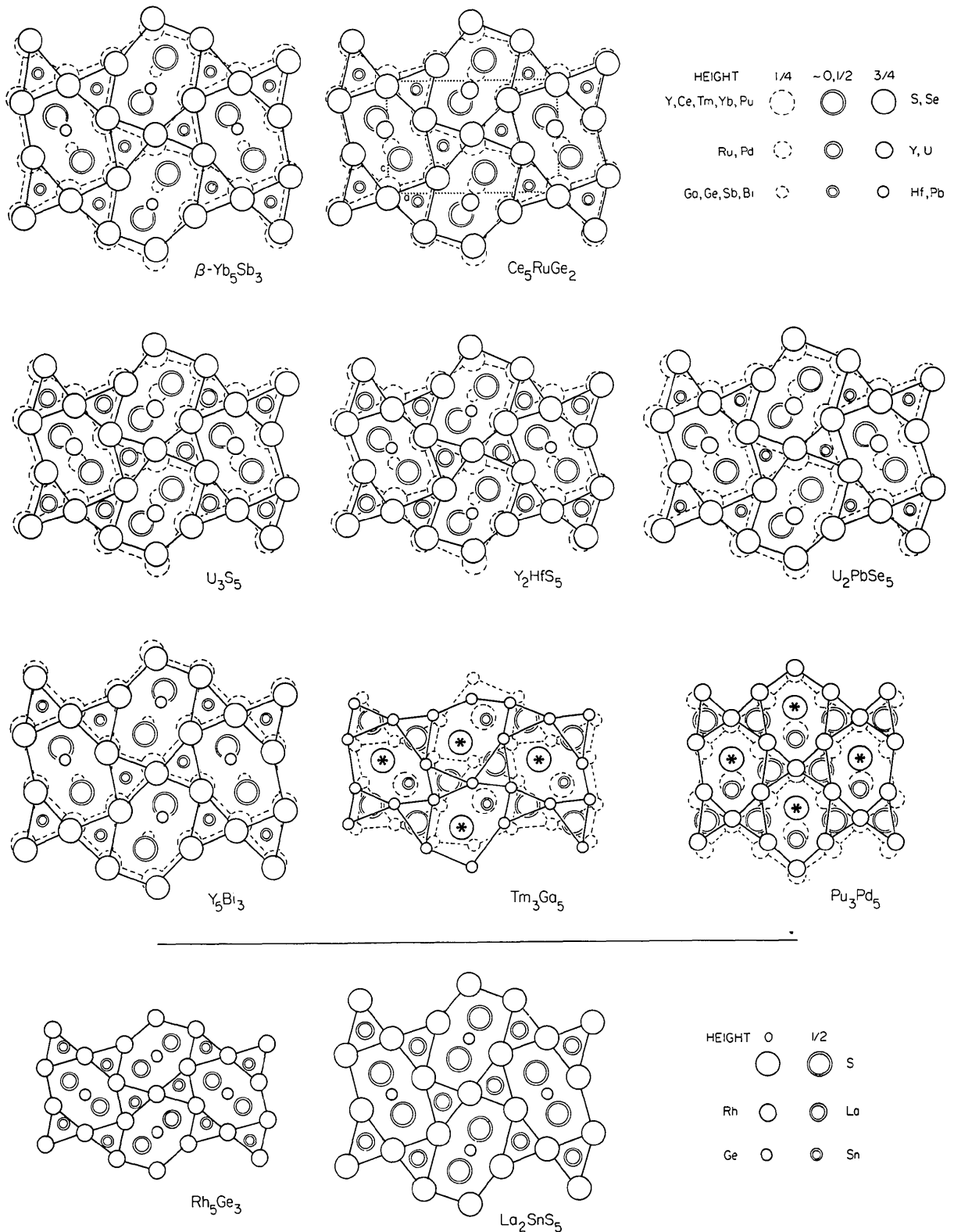


Fig. 1. Projections of β -Yb₅Sb₃, Ce₅RuGe₂, U₃S₅, Y₂HfS₅, Y₅Bi₃ and Tm₃Ga₅ along [010], U₂PbSe₅ along [100] and Pu₃Pd₅, Rh₅Ge₃ and La₂SnS₅ along [001]. For U₂PbSe₅, the small double circles stand for Pb at $x=\frac{1}{2}$, U at $x=0$. Stars in the drawings for Tm₃Ga₅ and Pu₃Pd₅ indicate that Ga and Pd atoms at $z=0$ and $z=\frac{1}{2}$ are hidden by the flagged Tm and Pu atoms.

Isopointal β - Yb_5Sb_3 and Y_5Bi_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.* Y_2HfS_5 with space group $Pnma$ and U_2PbSe_5 with an orthorhombic translation lattice but monoclinic symmetry corresponding to space group $P2_1/c$.† No substitution derivative of Y_5Bi_3 has been identified as yet.

The structure of Tm_3Ga_5 (Yatsenko, Gladyshevskii, Tchuntonov, Yarmolyuk & Grin', 1983), shown in the third row of Fig. 1, is also isopointal with β - Yb_5Sb_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_3Pd_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_5Bi_3 .

From a chemical point of view the compounds crystallizing with one of these structure types can be divided into three main groups: ionic-covalent compounds with stoichiometry $C_3A_5^{2-}$, $C_2^3+C^{4+}A_5^{2-}$ or $C_2^4+C^{2+}A_5^{2-}$, intermetallic 'anti-types' of these

* The a and c parameters of β - Yb_5Sb_3 and Y_5Bi_3 are interchanged in the conventional $Pnma$ setting. Representatives of both types are unfortunately considered as isotopic by Villars & Calvert (1985).

† In the book by Villars & Calvert (1985) the angle β of U_2PbSe_5 is misprinted as 101° instead of 90° and the structure is erroneously considered together with the compounds crystallizing with the La_2GeS_5 -type structure (Mazurier & Etienne, 1973).

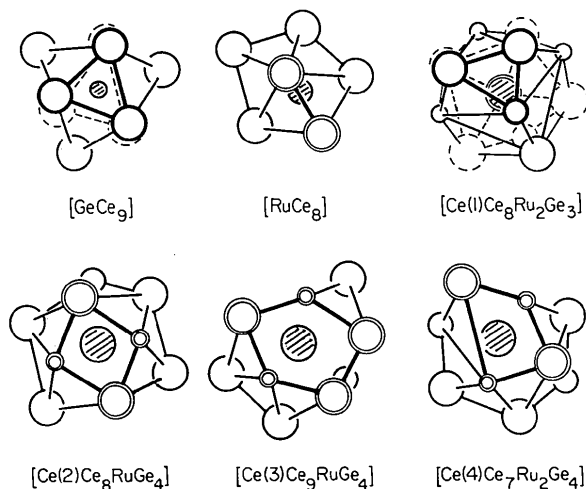


Fig. 2. The coordination polyhedra of the six different atom sites in Ce_5RuGe_2 .

Table 3. The occupation of the different crystallographic sites in Ce_5RuGe_2 and of corresponding sites in related structures

TPv: sites which constitute the vertices of the trigonal (and hexagonal) prisms, TPC: sites centring the trigonal prisms, HPI: sites inside the hexagonal prisms and HPb: sites in the base planes of the hexagonal prisms. In the case of Ce_5RuGe_2 the sites have been numbered in agreement with the numeration used in Table 1.

Type	Pearson code	Space group	Wyckoff sequence	TPv	TPc	HPI	HPb
Rh_5Ge_3	$oP16$	$Pham$	h^2gca	Rh	Ge	Rh	Ge
La_2SnS_5	$oP16$	$Pham$	h^2gca	S	La	S	Sn
Pu_3Pd_5	$oS32$	$Cmcm$	gfe^2	Pd	Pu	Pd	Pu
β - Yb_5Sb_3	$oP32$	$Pnma$	d^2c^4	Yb	Sb	Yb	Sb
Ce_5RuGe_2	$oP32$	$Pnma$	d^2c^4	Ce(2,3,4)	Ge	Ce(1)	Ru
U_3S_5	$oP32$	$Pnma$	d^2c^4	S	U	S	U
Y_2HfS_5	$oP32$	$Pnma$	d^2c^4	S	Y	S	Hf
Y_5Bi_3	$oP32$	$Pnma$	d^2c^4	Y	Bi	Y	Bi
Tm_3Ga_5	$oP32$	$Pnma$	d^2c^4	Ga	Tm	Ga	Tm
U_2PbSe_5	$mP32$	$P2_1/c$	e^8	Se	U,Pb	Se	U

(stoichiometry 5:3 or 5:1:2), and strongly distorted intermetallic derivatives with the same stoichiometry as the ionic-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_2SnS_5 , the Sn site (HPb) is coordinated by an almost regular S_6 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_3S_5 is in fact a pseudo-ternary one, since U is present in two different oxidation states, the explicit chemical formula being $U_2^{3+}U^{4+}S_5^{2-}$. 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_5 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 $U_2^{4+}Pb^{2+}Se_5^{2-}$ type.

Only minor changes of atomic coordinates are observed between the structures of these ionic-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 β - Yb_5Sb_3 and

Y_5Bi_3 are higher than those of the corresponding sites in U_3S_5 . 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 Tm_3Ga_5 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 Tm_4Ga_2 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.

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Monoclinic $NdRuSi_2$, a Distortion Derivative of Orthorhombic $CeNiSi_2$

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Abstract. Neodymium ruthenium disilicide, $M_r = 301.48$, monoclinic, $mP8$, $P2_1/m - e^4$ (No. 11), $a = 4.4620$ (6), $b = 4.0451$ (6), $c = 8.242$ (2) Å, $\beta = 102.23$ (1)°, $V = 145.39$ (5) Å³, $Z = 2$, $D_x = 6.887$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ 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 $TmLi_{1-x}Ge_2$ ($x = 0.5$), both being

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distortion variants of the orthorhombic $CeNiSi_2$ -type structure. Opposite to what is observed for $TmLi_{0.5}Ge_2$, the distortions in $NdRuSi_2$ 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

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