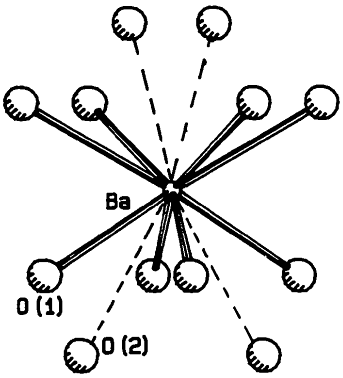

Fig. 2. View of the barium coordination by O atoms.

& Simonov, 1985). The bond angles O—Si—O and Si—O—Si in the ring are equal [107·6 (3)° and 162·4 (5)°, respectively]. Each barium and copper cation is coordinated by eight and four O(1) atoms, respectively, forming a three-dimensional network. The Cu^{2+} cation is located at site symmetry $4mm$, with four O(1) atoms (each from a different $[Si_4O_{12}]^{8-}$ group) forming a square coordination with Cu—O(1) = 1·925 (11) Å. This value is comparable to the Cu—O distances in other copper silicates (Pabst, 1959; Kawamura & Kawahara, 1976). The Ba^{2+} cation is surrounded by a regular square antiprism of O(1) atoms with Ba—O(1) = 2·940 (5) Å. There are four O(2) atoms outside this polyhedron at 3·263 (8) Å (Fig. 2.)

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$Ce_3Rh_2Ge_2$ and Isotypes with the Orthorhombic $La_3Ni_2Ga_2$ Type

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Abstract. $Ce_3Rh_2Ge_2$, $M_r = 771{\cdot}35$, orthorhombic, $La_3Ni_2Ga_2$ type, $oP28$, (57) $Pbcm - e^2d^2c$, $a = 5{\cdot}7001$ (9), $b = 8{\cdot}099$ (1), $c = 13{\cdot}461$ (3) Å, $V = 621{\cdot}4$ (1) Å^3, $Z = 4$, $D_x = 8{\cdot}244$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 35{\cdot}492$ mm^{-1}, $F(000) = 1312$, $T = 293$ K, $wR = 0{\cdot}022$ for 725 contributing unique reflections. Isotypes are found for $R_3Rh_2Ge_2$ with R = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu. The structure is characterized by infinite columns of trigonal-prism blocks along the c axis, each block being rotated with respect to its two neighbours by 180° around the column axis and shifted by $\frac{1}{2}\mathbf{c}$. Every block consists of three rectangular-face-linked trigonal prisms which are centred by Rh or Ge atoms. These columns are linked to neighbouring columns in a way similar to the linkage of the trigonal-prism columns in the FeB structure. Ignoring the difference in the site occupation of the prism centres the $La_3Ni_2Ga_2$ type can be considered a slab-stacking variant of the Y_3Co_3Ga type. The geometrical relation between these types corresponds to that already described for the FeB and CrB structure types, allowing the use of the same transformation equations for the cell parameters.

Introduction. In the system Ce–Rh–Ge only orthorhombic CeRhGe with TiNiSi type was known (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982), but a comparison with the large number of phases in the rare-earth–Fe group–Si systems led us to expect

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that more compounds should exist. We report here the crystal structure of newly found compounds of composition $R_3Rh_2Ge_2$ where R indicates Ce or another rare-earth element.

Experimental. $Ce_3Rh_2Ge_2$. Single crystals were found in a sample of nominal composition $Ce_4Rh_2Ge_3$. It was prepared from high-purity elements (Ce 99·9, Rh 99·999 and Ge 99·999%) by arc melting under argon atmosphere (the weight loss was 0·5%), annealed at 1073 K for 2 weeks in a silica tube under vacuum, and quenched in water. A needle-shaped single crystal [±(100): 0·012 mm, ±(010): 0·040 mm, ±(001): 0·012 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 2θ values of 23 reflections (Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $19 < 2\theta < 35°$) using the program *LATCON* (Schwarzenbach, 1966). 1880 reflections were collected out to $(\sin\theta/\lambda) = 0{\cdot}702$ Å^{-1} ($0 \leq h \leq 8$, $0 \leq k \leq 11$, $0 \leq l \leq 18$ and the anti-reflections) in the ω–2θ scan mode, yielding 940 unique reflections ($R_{\rm int} = 0{\cdot}044$). Two standard reflections ($\bar{1}\bar{1}\bar{4}$ and $0\bar{2}\bar{3}$) were measured with maximum intensity variations 1·1 and 1·0% respectively. Absorption correction was made using the program *LSABS* (Blanc, Schwarzenbach & Flack, 1991) with maximum and minimum transmission factors of 0·4756 and 0·4183. 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: $Pbc2_1$ (= $Pca2_1$) and $Pbcm$ (*International Tables for Crystallography*, 1983, Vol. A). According to the cell parameters and the possible space groups an isotype of the $La_3Ni_2Ga_2$ structure (Yarmolyuk, Grin', Gladyshevskii & Fundamenskii, 1984) was considered as the first possibility. This was confirmed by the structure refinement, based on $|F|$ values using the program *CRYLSQ* (Olthof-Hazekamp, 1990). 37 variables including anisotropic atomic displacement parameters were refined to $R = 0{\cdot}032$ and $wR = 0{\cdot}022$ [$w = 1/\sigma^2(|F_{\rm rel}|)$, $S = 1{\cdot}339$] considering 725 contributing unique reflections with $|F_{\rm rel}| > 3\sigma(|F_{\rm rel}|)$. Secondary-extinction correction parameter (Gaussian distribution of mosaic spread) was refined to $G = 0{\cdot}0092$ (2). The maximum shift/e.s.d. in the last cycle was 0·0002.[*] Final residual electron density +3·45 (−3·27) e Å^{-3}. The programs used to refined the structure are all from the *XTAL*3·0 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.

Table 1. *Atomic positional and displacement parameters for* $Ce_3Rh_2Ge_2$ *with space group Pbcm*

The equivalent atomic displacement factors are expressed as $U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. E.s.d.'s are given in parentheses.

	Wyckoff position	x	y	z	$U_{\rm eq}$(Å^2 × 100)
Ce(1)	8(*e*)	0·14707 (9)	0·39427 (6)	0·09815 (3)	1·00 (1)
Rh	8(*e*)	0·3787 (1)	0·03917 (9)	0·09112 (5)	1·06 (2)
Ge(1)	4(*d*)	0·1440 (3)	0·1052 (2)	$\frac{1}{4}$	0·95 (3)
Ce(2)	4(*d*)	0·6396 (1)	0·2534 (1)	$\frac{1}{4}$	1·01 (2)
Ge(2)	4(*c*)	0·6534 (3)	$\frac{1}{4}$	0	1·02 (3)

Table 2. *Interatomic distances* (Å) *in* $Ce_3Rh_2Ge_2$ (*up to* 4·0 Å *for* Ce *atoms and* 3·6 Å *for* Rh *and* Ge *atoms*)

E.s.d.'s are given in parentheses.

Ce(1)—Rh	2·920 (1)	Rh—Ge(1)	2·579 (1)
Rh	2·949 (1)	Ge(2)	2·621 (1)
Ge(1)	3·108 (1)	Ge(2)	2·6500 (8)
Ge(1)	3·138 (1)	Rh	2·887 (1)
Rh	3·1659 (9)	Ce(1)	2·920 (1)
Rh	3·220 (1)	Ce(1)	2·949 (1)
Ge(2)	3·321 (1)	Ce(2)	3·130 (1)
Ge(2)	3·3675 (8)	Ce(2)	3·153 (1)
Ge(2)	3·382 (1)	Ce(1)	3·1659 (9)
Ce(1)	3·5276 (8)	Ce(1)	3·220 (1)
Ce(1)	3·5674 (8)		
Ce(2)	3·655 (1)	Ge(1)—2Rh	2·579 (1)
Ce(2)	3·721 (1)	Ce(2)	3·070 (2)
Ce(2)	3·7573 (9)	Ce(2)	3·104 (2)
		2Ce(1)	3·108 (1)
Ce(2)—Ge(1)	3·070 (2)	Ce(2)	3·116 (2)
Ge(1)	3·104 (2)	2Ce(1)	3·138 (1)
Ge(1)	3·116 (2)		
2Rh	3·130 (1)	Ge(2)—2Rh	2·621 (1)
2Rh	3·153 (1)	2Rh	2·6500 (8)
2Ge(2)	3·3663 (8)	2Ce(1)	3·321 (1)
2Ce(1)	3·655 (1)	2Ce(2)	3·3663 (8)
2Ce(1)	3·721 (1)	2Ce(1)	3·3675 (8)
2Ce(1)	3·7573 (9)	2Ce(1)	3·382 (1)

Isotypic compounds. The twelve isotypic $R_3Rh_2Ge_2$ compounds listed in the *Abstract* and in Table 3 were also prepared by arc-melting method under Ar atmosphere. Our efforts to synthesize $R_3Rh_2Ge_2$ where R = Eu or Yb were not successful. The samples were annealed at 1073 K for 2 weeks in an Ar-filled silica tube. The observed powder patterns were compared with simulated powder diagrams, calculated using the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977). The unit-cell parameters for the $R_3Rh_2Ge_2$ phases isotypic with $Ce_3Rh_2Ge_2$ were refined from Guinier film data of the annealed samples. The films were measured with a film reader using an internal Si standard (a = 5·4308 Å). The program *LATCON* (Schwarzenbach, 1966) was used for the refinement.

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[*] Lists of anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54381 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Unit-cell parameters for* $Ce_3Rh_2Ge_2$ *and new isotypic germanides with* $La_3Ni_2Ga_2$ *type*

E.s.d.'s are given in parentheses.

	a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$Y_3Rh_2Ge_2$	5·563 (1)	7·775 (1)	13·225 (4)	572·1 (1)
$La_3Rh_2Ge_2$	5·7662 (7)	8·196 (1)	13·609 (2)	643·1 (1)
$Ce_3Rh_2Ge_2$	5·7001 (9)	8·099 (1)	13·461 (3)	621·4 (1)
$Pr_3Rh_2Ge_2$	5·674 (1)	8·059 (1)	13·445 (3)	614·8 (1)
$Nd_3Rh_2Ge_2$	5·6544 (9)	8·017 (1)	13·411 (2)	608·0 (1)
$Sm_3Rh_2Ge_2$	5·608 (1)	7·933 (1)	13·332 (3)	593·2 (1)
$Gd_3Rh_2Ge_2$	5·5898 (9)	7·856 (1)	13·289 (2)	583·6 (1)
$Tb_3Rh_2Ge_2$	5·5627 (8)	7·808 (1)	13·233 (2)	574·8 (1)
$Dy_3Rh_2Ge_2$	5·5475 (9)	7·767 (1)	13·196 (2)	568·61 (9)
$Ho_3Rh_2Ge_2$	5·5367 (7)	7·726 (1)	13·165 (2)	563·14 (9)
$Er_3Rh_2Ge_2$	5·5207 (8)	7·683 (1)	13·138 (2)	557·3 (1)
$Tm_3Rh_2Ge_2$	5·5097 (9)	7·654 (1)	13·097 (2)	552·3 (1)
$Lu_3Rh_2Ge_2$	5·4917 (8)	7·593 (1)	13·051 (2)	544·20 (9)

Discussion. A projection of $Ce_3Rh_2Ge_2$ along [001] is shown on the left-hand side of Fig. 1. This atom arrangement is known as the $La_3Ni_2Ga_2$ type (Yarmolyuk *et al.*, 1984) and has also been found independently with $Y_3Rh_2Si_2$ (Moreau, Paccard & Paccard, 1984).

In the $Ce_3Rh_2Ge_2$ structure the Rh atoms are at the centres of trigonal Ce_4Ge_2 prisms with four additional neighbours in the equitorial plane. The Ge atoms occupy sites at the centres of two different coordination polyhedra: they are for Ge(1) a tricapped trigonal Ce_6 prism and for Ge(2) an icosahedron of composition Ce_8Rh_4. Along the **c** direction there are blocks of three trigonal prisms which share rectangular faces with the prism axes parallel to the [120] (or to the [$\bar{1}$20]) direction. These blocks are linked by two outer edges to form an infinite zigzag prism-block column. One translation unit of this column is shown on the left-hand side of Fig. 2. These columns with their axes parallel to [001] are linked to each other in a way similar to the linkage of the simple infinite prism columns in the FeB type (column axes in FeB parallel to the *b* axis) (Hohnke & Parthé, 1966).

The same kind of infinite zigzag prism-block columns (but with a different site occupation) are found in the orthorhombic Y_3Co_3Ga structure (*oS*28, $Cmcm-f^2c^2a$) (Yarmolyuk, Grin' & Gladyshevskii, 1978), a site-exchange variant of the W_3CoB_3 type (Jedlicka, Benesovsky & Nowotny, 1969). A projection of the Y_3Co_3Ga structure along [001] is shown on the right-hand side of Fig. 1 and one translation unit of the infinite zigzag prism-block column in Fig. 2.

The $Ce_3Rh_2Ge_2$ structure is geometrically closely related to the Y_3Co_3Ga structure, one being a slab-stacking variant of the other (ignoring the different occupation of the centres of the rare-earth-metal trigonal prisms, which is the reason for the different stoichiometry). These two structures differ, as can be seen from their [001] projections given in Fig. 1, by the linkage of these zigzag prism-block columns. The interconnection of the prism columns in $Ce_3Rh_2Ge_2$ corresponds to the linkage in FeB, while those in Y_3Co_3Ga to the linkage of the simple prism columns in the CrB type. In particular, it is possible to formulate, as in the case of FeB and CrB, a set of

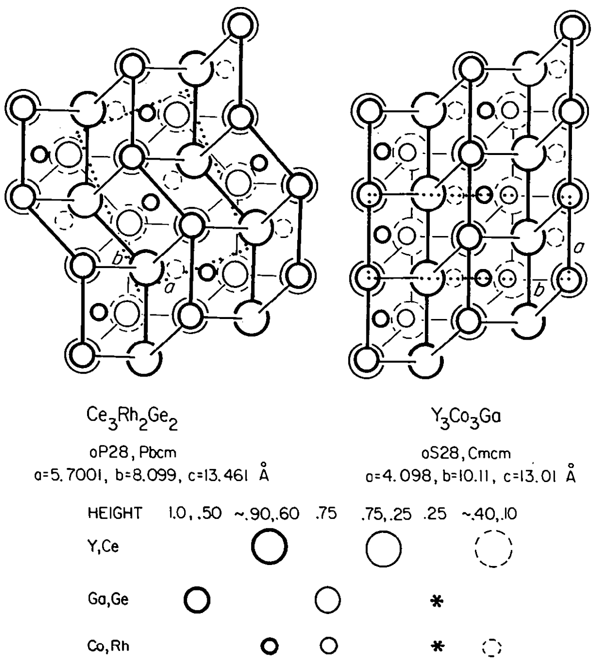

Fig. 1. Projections of the $Ce_3Rh_2Ge_2$ and Y_3Co_3Ga structures along [001]. The asterisks indicate Ge and Co atoms at height $z = 0·25$ which cannot be seen in the drawings, being hidden by overlying rare-earth atoms at $z = 0·60$ and 0·90.

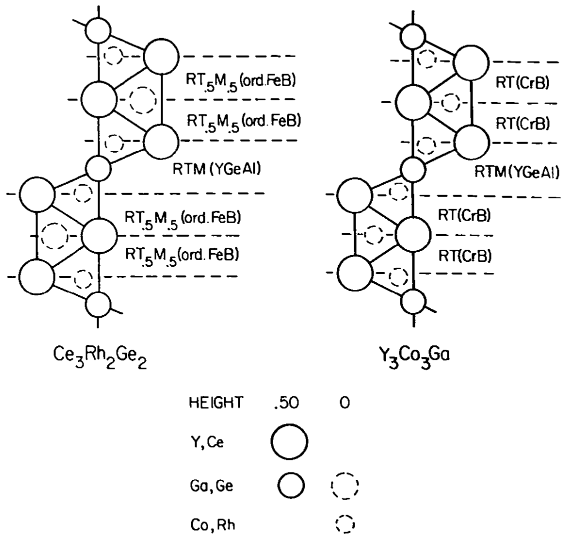

Fig. 2. The infinite zigzag prism-block columns found in the $Ce_3Rh_2Ge_2$ and Y_3Co_3Ga structures with their column axes parallel to [001]. The trigonal prism axes are parallel to [120] (or to [$\bar{1}$20]) in $Ce_3Rh_2Ge_2$ and to [100] in Y_3Co_3Ga.

trigonometric equations to correlate the unit-cell parameters of both crystal structures allowing one to use data of a known stacking variant to calculate unit-cell values of the other one. In analogy to the equations given for the FeB–CrB type transformation (Parthé, 1981) the following equations can be derived for the $La_3Ni_2Ga_2$ type–Y_3Co_3Ga type transformation:

$$a(La_3Ni_2Ga_2) \equiv a(Y_3Co_3Ga)/2\sin\psi \quad (1)$$

$$b(La_3Ni_2Ga_2) \equiv b(Y_3Co_3Ga)2\sin\psi \quad (2)$$

$$c(La_3Ni_2Ga_2) \equiv c(Y_3Co_3Ga) \quad (3)$$

$$V(La_3Ni_2Ga_2) \equiv V(Y_3Co_3Ga) \quad (4)$$

where ψ is defined by

$$\psi \equiv \arctan[a(Y_3Co_3Ga)/b(Y_3Co_3Ga)] \quad (5)$$

or

$$\psi \equiv (1/2)\arcsin[b(La_3Ni_2Ga_2)/2a(La_3Ni_2Ga_2)]. \quad (6)$$

A successful test of these equations was made for $Lu_3Rh_2Ge_2$ and Y_3Co_3Ga which is the only compound pair with approximately the same unit-cell volume and same ψ value.

The relationship between the two structures can also be expressed by the way the infinite zigzag prism-block columns are rotated with respect to each other. This point of view makes it possible to describe both structures as an intergrowth of two kinds of segments, one of composition RTM and built up as the YGeAl type (Zhao & Parthé, 1990) and a second one of composition $RT_{0\cdot5}M_{0\cdot5}$ or RT and constructed as the FeB (ternary ordered variant) or the CrB type, respectively. The combination of RTM with two segments of the latter gives the compositions $RTM + 2RT_{0\cdot5}M_{0\cdot5} = R_3T_2M_2$ and $RTM + 2RT = R_3T_3M$, respectively. As indicated by the composition of the segments in the Y_3Co_3Ga structure, all centres of the trigonal prisms are occupied by transition-metal atoms.

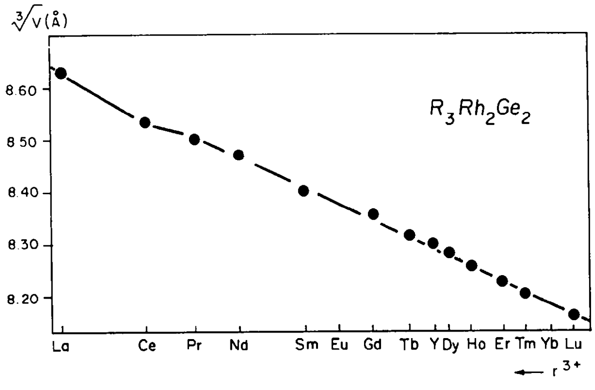

Fig. 3. The cube root of the unit-cell volumes of the $R_3Rh_2Ge_2$ phases with $La_3Ni_2Ga_2$ structure type plotted *versus* the trivalent ionic radii of the rare-earth elements.

The Y_3Co_3Ga structure is a member of a structure series of formula $R_{2m+2n}T_{2m+2n}M_{2n}$ (Grin', Gladyshevskii, Sobolev & Yarmolyuk, 1984) with $m = 2$ and $n = 1$. The series includes as other members the ternary structure types with composition 1:1:1 (YGeAl), 2:2:1 (Pr_2Ni_2Al, a site-exchange variant of the W_2CoB_2 type), 4:4:1 (Y_4Co_4Ga) and 5:5:1 (Y_5Co_5Ga). All these structures are built up of n segments from the YGeAl type intergrown with m segments taken from the CrB type. The $La_3Ni_2Ga_2$ type is the first member of a corresponding structure series based on YGeAl and (ordered or not ordered) FeB-type segments.

In Fig. 3 the cube roots of the unit-cell volumes of the $R_3Rh_2Ge_2$ phases are plotted *versus* the trivalent ionic rare-earth radii r^{3+}. The unit-cell volumes decrease smoothly with the increasing atomic number of the rare-earth metals as expected from the lanthanide contraction.

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