Michel, Provost & Raveau, 1981). [The content of the oxygen atoms can be artifically varied to keep the charge balance; this constrained refinement was also tried; it converged to almost the same, but slightly larger *R* value and to the occupancies Cu(1) 0·887 (5), O(1) 0·80 (1) and O(2) 0·39.]

The temperature factors of O(2) show the extreme anisotropy seen in Fig. 1; the amplitude of the thermal vibration is very large in the direction perpendicular to the Cu—O bond and in the (001) plane [U_{22} of O(2) is 0·063 (4) and 0·042 (10) Å^2 at 298 and 120 K, respectively]. The structure reported by Nakai *et al.* (1987), by contrast, showed that the thermal ellipsoid of this atom was elongated perpendicular to the (001) plane; this point as well as the occupancies of O(1) and O(2) differs from the present result. The bondings of O(2) to Cu and Ba might be very weak and easily removed; this bonding character would be reflected in the large values of the thermal parameters and in its low site occupancy.

The thermal parameters are reasonably lower at 120 K as mentioned above. The cell parameters and bond lengths at 120 K are all slightly shorter than those at 298 K. These facts and the experimental results at 90 K suggest no structural change from 298 down to 90 K.

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Zr_3Rh_5 with Pu_3Pd_5-Type Structure, a Structure Geometrically Related to the CsCl Type

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Abstract. $M_r = 788{\cdot}2$, orthorhombic, *Cmcm*, $a = 8{\cdot}6634$ (9), $b = 6{\cdot}9860$ (3), $c = 8{\cdot}6218$ (3) Å, $V = 521{\cdot}81$ (5) Å^3, $Z = 4$, $D_x = 10{\cdot}03$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 20{\cdot}3$ mm^{-1}, $F(000) = 1380$, $T = 293$ K, $R = 0{\cdot}052$ for 371 independent reflections. The structure of Zr_3Rh_5 can be derived from ZrRh with the

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Table 1. *Atomic coordinates for* Zr_3Rh_5 (*this work*) *and* Pu_3Pd_5 (*Cromer*, 1976) *with space group Cmcm*

The numbering of the sites in Pu_3Pd_5 corresponds to the original article; however, the coordinates have been transformed so that they can be directly compared.* The temperature factor is expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

		Zr_3Rh_5					Pu_3Pd_5		
		x	y	z	$100U$(Å^2)		x	y	z
Rh(1)	8(*g*)	0·2642 (2)	0·2411 (3)	$\frac{1}{4}$	0·75 (5)	Pd(3)	0·2781	0·2137	$\frac{1}{4}$
Rh(2)	8(*f*)	0	0·2878 (3)	0·5243 (2)	0·82 (5)	Pd(2)	0	0·3147	0·549
Zr(1)	8(*e*)	0·2090 (3)	0	0	0·69 (6)	Pu(2)	0·2018	0	0
Rh(3)	4(*c*)	0	0·0119 (4)	$\frac{1}{4}$	0·55 (6)	Pd(1)	0	−0·025	$\frac{1}{4}$
Zr(2)	4(*c*)	0	0·4403 (5)	$\frac{1}{4}$	0·88 (7)	Pu(1)	0	0·375	$\frac{1}{4}$

* In the original publication the z coordinate of Pd(3) was misprinted and should be $\frac{1}{4}$ instead of 0.

simple CsCl-type structure by replacing a quarter of the Zr atoms in the homoatomic layers perpendicular to the axis of the cubic cell by Rh atoms and making small adjustments, essentially in order to decrease the distances between the substituting Rh atoms and the surrounding Zr atoms. It is further shown that the Pu_3Pd_4 type can be derived from the CsCl type in a similar way by substituting a seventh of the larger atoms by those of the smaller atom kind and that the Rh_5Ge_3 type, found with Hf_3Rh_5, can be related to the same parent type by considering the stacking of alternatively rotated slabs.

Introduction. The Zr–Rh system has been the subject of some interest because of the exceptional stability of the compounds in the systems combining transition metals of the fourth group and platinoids (Brewer & Wengert, 1973), and because of the superconducting properties observed in the Zr-rich part of the system (Zegler, 1965). In a recent paper Küntzler & Waterstrat (1985) discuss the electronic properties, the stability and the occurrence of superconductivity in some Zr–Rh alloys.

A phase of approximate composition Zr_3Rh_5 was first observed by Raman & Schubert (1964) who reported it to be isotypic to 'NbRu' and proposed a face-centered orthorhombic cell with $a = 4{\cdot}40$, $b = 4{\cdot}33$ and $c = 3{\cdot}42$ Å. The structure of 'NbRu' has never been solved but the above-mentioned authors characterize it as an orthorhombic deformation superstructure of the Cu ($A1$) type. Giessen, Wang & Grant (1969) synthesized an alloy with composition Zr_3Rh_5 and excluded the existence of a phase isotypic with Ti_3Rh_5 and Hf_3Rh_5, which both crystallize with the Rh_5Ge_3 type, *oP*16 (Geller, 1955). Recent investigations of the Zr–Rh phase diagram (Eremenko, Semenova & Shtepa, 1980) include a peritectically forming compound of composition Zr_3Rh_5, whereas other authors (Waterstrat, 1984; Küntzler & Waterstrat, 1985) consider that it might be a metastable phase, a product of a martensitic transformation of the high-temperature modification of ZrRh with CsCl type.

The reinvestigation of the phase diagram (Jorda, Graf, Schellenberg, Müller, Cenzual, Gachon & Hertz, 1987) confirmed the existence of a peritectically forming compound with a narrow homogeneity range at 62·5 at.% Rh. We decided to study the structure of this phase by single-crystal X-ray diffraction and to look for geometrical relationships with other structure types.

Experimental. Melted sample of nominal composition Zr_3Rh_5 annealed at 1773 K for 24 h, at 1873 K for 10 min, and subsequently cooled slowly (6 K min^{-1}) to 773 K [for further information see Jorda *et al.* (1987)]. Single crystal of irregular shape (mean radius about 20 μm), Philips PW 1100 four-circle diffractometer; graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined from 2θ values of ten reflections (Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å; $51 \le 2\theta \le 60°$) using the program *FINAX* (Hovestreydt, 1983). Laue symmetry *mmm*; systematic absences hkl: $h + k \neq 2n$ and $h0l$: $h, l \neq 2n$, leading to possible space groups *Cmcm*, $Cmc2_1$ and *C2cm* (*Ama*2). The cell volume, axial ratios and possible space groups suggested isotypy with the Pu_3Pd_5 structure,† *oS*32, space group *Cmcm* (Cromer, 1976). Comparison between a Guinier film and the simulated powder diagram, calculated with the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977), supported this hypothesis. 850 reflections collected out to $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1} ($0 \le h, l \le 12, 0 \le k \le 9$ and all antireflections) in the ω–2θ scan mode, yielding 425 independent reflections ($R_{\rm int} = 0{\cdot}026$), of which 323 were considered significant [$|I| \ge 3\sigma(I)$]. Standard reflections $22\bar{2}$ and $\bar{2}\bar{2}2$ (max. intensity variation $\pm 2{\cdot}0\%$); spherical absorption correction ($\mu R = 0{\cdot}434$; $1{\cdot}861 \le A^* \le 1{\cdot}889$). Full-matrix refinement in *Cmcm*, from the coordinates of Pu_3Pd_5, using $|F|$ values of 371 independent reflections (including 48 'less-thans' calculated greater than observed). Seven positional parameters and five isotropic displacement parameters, listed in Table 1, one scale factor and one isotropic secondary-extinction parameter $G = 0{\cdot}74\,(5) \times 10^{-5}$° (mosaic spread, Gaussian distribution) refined to a final $R = 0{\cdot}052$ [$S = 2{\cdot}64$; (Δ/σ) in last cycle $\le 0{\cdot}0004$;

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† The same structure type is sometimes referred to as the Zr_3Ga_5 type (Pötzschke & Schubert, 1962) on the basis of the similarities between the compositions, the relative cell volumes, the axial ratios and the systematic absences. The structure of this compound has, however, to our knowledge never been solved, nor its isotypy proven.

$-4.5 \leq$ r.e.d. ≤ 5.0 e Å^{-3}].* Atomic scattering factors for neutral atoms, f' and f'' from *International Tables for X-ray Crystallography* (1974); programs for data reduction and structure refinement from the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. *The structure of* Zr_3Rh_5. In Table 1 the coordinates of the atom sites of Zr_3Rh_5 are compared with those of Pu_3Pd_5, which crystallizes with a unit cell of $a = 9.201$ (5), $b = 7.159$ (5), $c = 9.771$ (7) Å (Cromer, 1976). Zr_3Rh_5 is in fact the first isotypic compound observed where the c parameter is slightly shorter than the a parameter ($c/a = 0.995$), since for all known isotypic indides, thallides, stannides and plumbides (Villars & Calvert, 1985), c is longer than a [1·020 (Ba_3Pb_5) $\leq c/a \leq$ 1·062 (Pu_3Pd_5)]. It can be seen from Table 1 that the coordinates of the sites in Zr_3Rh_5 are in general closer to the particular values 0, $\frac{1}{4}$ and $\frac{1}{2}$ than those of the sites in Pu_3Pd_5.

The structure of Zr_3Rh_5 is shown in a projection along [010] in Fig. 1. Approximately square mesh layers appear which recall the CsCl structure type adopted by the stable phase at high temperature ($T \geq 943$ K) in the Zr–Rh system. In ZrRh with CsCl type square mesh layers of Zr atoms alternate with identical layers of Rh atoms, shifted by $(a_1 + a_2 + a_3)_{ZrRh}/2$. In Zr_3Rh_5 every second layer is formed exclusively by Rh atoms; however, as can be seen, for example, in the layer of atoms at $y \simeq \frac{1}{2}$ (shaded or filled in Fig. 1), the intermediate layers have the composition Zr_3Rh. In the corresponding layer at $y \simeq 0$ the sites occupied by Rh atoms are shifted by $a(Zr_3Rh_5)/2$. The Zr atoms surrounding the substituting Rh atoms in these layers are displaced parallel to the a axis, towards the rows of sites now occupied by Rh. In adjacent layers the under(over)lying Zr atoms are displaced in the opposite direction. The intermediate Rh atoms, centering now a trapezium instead of a square, move towards the longest of the parallel sides of the trapezium, *i.e.* perpendicular to the plane of projection on the drawing. Those Zr atoms which are situated between two substituting Rh atoms along the b axis are displaced towards one of these, alternately above and below the layers at $y \simeq \frac{1}{2}$ or 0, and the cubes of Rh atoms surrounding them are consequently distorted. Compared with ZrRh with CsCl-type structure, the a and c axes have contracted by about 6% and the b axis has elongated by about the same amount.

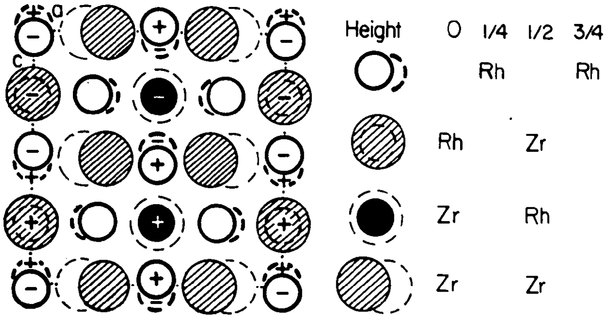

Fig. 1. Projection of the structure of Zr_3Rh_5 along [010]. Large circles Zr, small circles Rh. Plus and minus signs (signs inside double circles refer to the Zr atoms only) represent displacements of about 0·25 Å for Rh atoms and 0·4 Å for Zr atoms, out of the planes at the indicated heights. Shaded and filled atoms at $y \simeq \frac{1}{2}$.

Table 2. *Interatomic distances* (d) *up to* 3·8 Å *and* $\Delta = (d - \sum r)/\sum r$ *in* Zr_3Rh_5 *with* Pu_3Pd_5*-type structure*

E.s.d.'s are given in parentheses. Atomic radii (r) used are 1·602 (Zr) and 1·345 Å (Rh) respectively (Teatum, Gschneidner & Waber, 1960).

		d(Å)	Δ(%)
Zr(1)	2Rh(2)	2·714 (2)	−7·9
	2Rh(1)	2·777 (1)	−5·8
	2Rh(3)	2·816 (1)	−4·5
	2Rh(1)	2·823 (1)	−4·2
	2Rh(2)	2·932 (2)	−0·5
	2Zr(2)	3·343 (2)	+4·3
	2Zr(1)	3·565 (1)	+11·3
	Zr(1)	3·621 (3)	+13·0
Zr(2)	2Rh(2)	2·594 (2)	−12·0
	2Rh(1)	2·679 (3)	−9·1
	2Rh(2)	2·720 (3)	−7·7
	2Rh(1)	2·931 (3)	−0·5
	Rh(3)	2·992 (4)	+1·5
	4Zr(1)	3·343 (2)	+4·3
Rh(1)	Zr(2)	2·679 (3)	−9·1
	2Zr(1)	2·777 (1)	−5·8
	Rh(3)	2·784 (3)	+3·5
	Rh(3)	2·793 (2)	+3·8
	2Zr(1)	2·823 (1)	−4·2
	2Rh(2)	2·828 (2)	+5·1
	Zr(2)	2·931 (3)	−0·5
	2Rh(2)	3·308 (2)	+22·9
	2Rh(1)	3·502 (3)	+30·2
Rh(2)	Zr(2)	2·594 (2)	−12·0
	2Zr(1)	2·714 (2)	−7·9
	Zr(2)	2·720 (3)	−7·7
	2Rh(1)	2·828 (2)	+5·1
	Rh(3)	2·858 (3)	+6·2
	2Zr(1)	2·932 (2)	−0·5
	Rh(2)	2·995 (3)	+11·3
	Rh(3)	3·051 (3)	+13·4
	2Rh(1)	3·308 (2)	+22·9
Rh(3)	2Rh(1)	2·784 (3)	+3·5
	2Rh(1)	2·793 (2)	+3·8
	4Zr(1)	2·816 (1)	−4·5
	2Rh(2)	2·858 (3)	+6·2
	Zr(2)	2·992 (4)	+1·5
	2Rh(2)	3·051 (3)	+13·4

In Table 2 are listed the interatomic distances up to 3·8 Å in Zr_3Rh_5 and the relative contractions compared with the sum of the atomic radii of 12-coordinated Zr and Rh atoms (Teatum, Gschneidner & Waber, 1960). As a comparison it may be remembered that in the CsCl type each Cs atom is surrounded by eight Cl atoms at the vertices of a cube, and by six Cs atoms at a distance 1·155 times the former, forming an octahedron. In Zr_3Rh_5 the Zr(1) site has distances shorter than the sum of the atomic radii to the eight Rh atoms from the distorted cube, and to the two Rh(3) atoms which have substituted Zr atoms in the original octahedron. In the case of Zr(2) only one of these additional Rh atoms is at an approximate contact distance so that this site is coordinated by nine Rh atoms. The Rh(1) and Rh(2)

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* Lists of structure factors arranged in a standard crystallographic data file (Brown, 1985) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44208 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sites have, as expected $8-2=6$ Zr atoms at distances shorter than $r_{\rm Zr} + r_{\rm Rh}$ while Rh(3) (the site occupied by the substituting atoms), thanks to the deformations described above, has short relative distances to five of the six Zr atoms which in a structure of the CsCl type would form the second coordination polyhedron (the octahedron), but no distance shorter than $2r_{\rm Rh}$ to the eight surrounding Rh atoms.

Relationship between the Pu_3Pd_5 *and* Pu_3Pd_4 *types.* In a similar way to how the structure of the Pu_3Pd_5 type can be derived from the CsCl type, the other structure type identified at a stoichiometry near 1:1 in the Pu–Pd system, the Pu_3Pd_4 type (Cromer, Larson & Roof, 1973), can be derived from the same parent type by substituting this time one-seventh of the larger atoms by smaller atoms. As in the case of Zr_3Rh_5 quite important distortions are induced by this substitution. The Pu_3Pd_5 and Pu_3Pd_4 types, as well as the non-distorted CsCl derivative BiF_3 ($cF16$, $Fm\bar{3}m$, $a = 5{\cdot}85$ Å), may be considered as members of a family of structure types of compositions $L_{1-1/n}S_{1+1/n}$, obtained by replacing $1/n$ of the larger (L) atoms by smaller (S) atoms in the CsCl type, which is the end member with $n = \infty$. There are two kinds of alternating layers in these structures: layers fully occupied by S atoms and mixed layers of composition $L_{n-1}S$. Schematic drawings of these two layers for the types mentioned here, where $n = 2$, 4 and 7 respectively, are shown in Fig. 2. The small circles connected by thin lines represent the S-atom layers while the unconnected circles show the arrangement in the mixed layers. In the final structures these double layers are stacked upon each other and shifted so that the substituting atoms (filled small circles) occupy in sequence the stacking positions denoted by the numbers inscribed in the large circles.

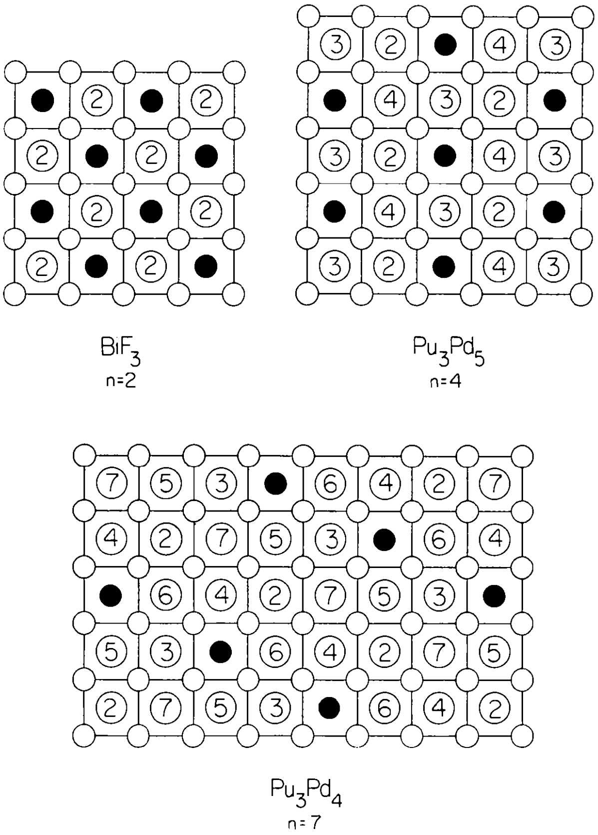
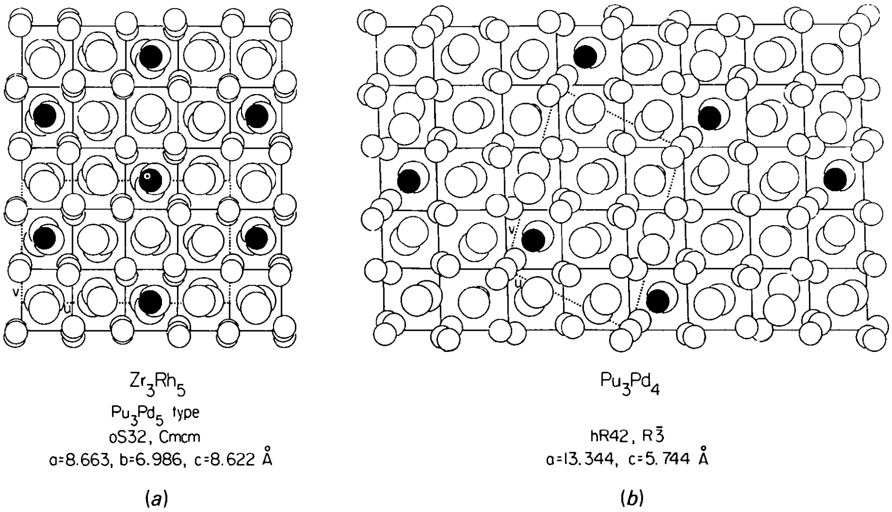


Fig. 2. Schematic drawings of some structure types that can be derived by substituting $1/n$ of the atoms with larger radius by atoms of smaller radius in the homoatomic layers perpendicular to the cell axes of the cubic CsCl type. Filled circles show the arrangement of the substituting atoms in one layer and numbers inside the large circles indicate the sites occupied by the atoms of small radius in subsequent mixed layers.



Zr_3Rh_5
Pu_3Pd_5 type
oS32, Cmcm
a=8.663, b=6.986, c=8.622 Å

(a)

Pu_3Pd_4
hR42, R$\bar{3}$
a=13.344, c=5.744 Å

(b)

Fig. 3. The structures of (*a*) Zr_3Rh_5 and (*b*) Pu_3Pd_4 in projections that can be directly compared with the schematic drawings in Fig. 2. For Zr_3Rh_5 the translation vectors of the cell in the plane of projection correspond to $\mathbf{u} = \mathbf{a}-\mathbf{c}$ and $\mathbf{v} = \mathbf{b}$, for Pu_3Pd_4 to $\mathbf{u} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{4}{3}\mathbf{c}$ and $\mathbf{v} = \frac{1}{3}\mathbf{a}_1 + \frac{2}{3}\mathbf{a}_2 - \frac{1}{3}\mathbf{c}$, referred to the triple hexagonal cell.

In Zr_3Rh_5 square mesh layers of composition Zr_3Rh are found not only perpendicular to [010] but also perpendicular to [101] and [10$\bar{1}$]. In the latter two families of parallel layers the substituting Rh atoms form a mesh of approximately equilaterial triangles. The schematic drawing of the Pu_3Pd_5 type in Fig. 2(*b*) can thus be compared with the projection of the structure of Zr_3Rh_5 along [101] shown in Fig. 3(*a*), whereas Fig. 2(*c*) can be directly compared with Fig. 3(*b*) where a slab of the real Pu_3Pd_4 structure is drawn in an unusual projection [the translation periods of the oblique mesh in the plane of projection, indicated with dotted lines, correspond to the vectors $\mathbf{u} = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{4}{3}\mathbf{c}$ and $\mathbf{v} = \frac{1}{3}\mathbf{a}_1 + \frac{2}{3}\mathbf{a}_2 - \frac{1}{3}\mathbf{c}$, referred to the triple hexagonal cell].

A compound of stoichiometry 3:4 has been reported also in the Zr–Rh system (Raman & Schubert, 1964) and the equilibrium phase diagram of the same system effectively shows the presence of a Zr_3Rh_4 phase, formed on cooling from ZrRh of CsCl-type structure by solid congruency (Jorda *et al.*, 1987). Unfortunately it has not been possible to identify the structure type of this phase.

Description of the Rh_5Ge_3 *type*. Despite the apparently similar chemical affinities of Zr and Hf, as stated above, Hf_3Rh_5 crystallizes with the Rh_5Ge_3 type (Geller, 1955). Giessen *et al.* (1969) pointed out that this structure type is geometrically related to the Cu (*A*1) type. We shall show that it can also be derived from the CsCl type by considering a different orientation of the parent type. A projection of Hf_3Rh_5 along [001] is shown in Fig. 4. The atom arrangement in the slabs delimited by thin zigzag lines is similar to the atom arrangement in the CsCl type, projected along [110]. The components of the interatomic distances in the plane of projection are similar to those calculated for HfRh with CsCl type (Raman & Schubert, 1964). However, the structure is somewhat compressed in the perpendicular direction as compared with HfRh [$c(Hf_3Rh_5) = 4{\cdot}25$ instead of $4{\cdot}56$ Å]. The slabs are alternately rotated by 180° around the twofold screw axis parallel to [010] and stacked upon each other along the **b** direction.

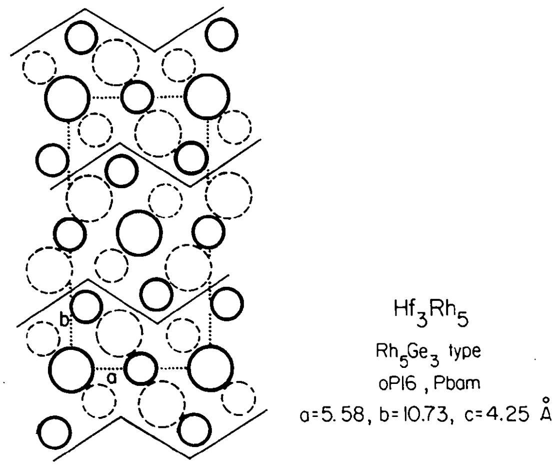


Fig. 4. The structure of Hf_3Rh_5 with Rh_5Ge_3 type in a projection along [001]. Large circles Hf, small circles Rh; circles drawn with full lines at $z = 0$, with dashed lines at $z = \frac{1}{2}$. Thin zigzag lines delimit the slabs in which the arrangement is similar to that of the CsCl type.

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