1. A stereoview in Fig. 2 shows that complex (1) possesses no symmetry element since the Co—C(13) axis is tilted 13·2° from the normal to the $\mathrm{Ru_3}$ plane, away from Ru(2). (1) may be viewed as constructed from the fragments '$\mathrm{Co(CO)_4}$' and '$\mathrm{Ru_3(\mu\text{-}H)(CO)_9}$' each of which possess idealized C_s symmetry. For the '$\mathrm{Co(CO)_4}$' fragment this mirror plane comprises Co, C(12), O(12), C(13), O(13), whilst for '$\mathrm{Ru_3(\mu\text{-}H)(CO)_9}$' the mirror plane contains Ru(1), H, C(3), O(3). Within complex (1), however, these fragment mirror planes are not coincident, but are rotated relative to each other by 57·8°. The bridging carbonyl ligands do not show the skewed C_3 arrangement found in the precursor anion $[\mathrm{CoRu_3(\mu\text{-}CO)_3(CO)_{10}}]^-$ (Steinhardt *et al.*, 1980), but approximately eclipse the Co—Ru vectors.

The hydride bridges the longest Ru—Ru bond [Ru(2)—Ru(3)] and the Ru—H distances compare favourably with the mean value of 1·79 (1) Å found over a range of structures containing the $\overline{\mathrm{Ru(\mu\text{-}H)Ru}}$ moiety (Teller & Bau, 1981). The μ_2 bonding mode found for the hydride ligand in (1) contrasts with the asymmetric μ_3 geometry of the $\mathrm{AuPPh_3}$ unit in $[\mathrm{CoRu_3(\mu_3\text{-}AuPPh_3)(\mu\text{-}CO)_3(CO)_{10}}]$ (Bruce & Nicholson, 1984), where this ligand bridges a $\mathrm{CoRu_2}$ face. These results thus provide further evidence that the isolobal relationship between H and $\mathrm{AuPPh_3}$ cannot reliably be used to infer hydride ligand positions from known stereochemistry in phosphineaurio derivatives.

Complex (1) appears to be isomorphous and isostructural to the osmium analogue $[\mathrm{CoOs_3(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_{10}}]$ (Raithby, personal communication).

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$\mathrm{ErRh_3Si_2}$ and Isotypes with an Orthorhombic Deformation Superstructure of the $\mathrm{CeCo_3B_2}$ Type

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Abstract. $M_r = 532\cdot1$, $oI24$, $Imma$, $a = 7\cdot098\ (8)$, $b = 9\cdot519\ (1)$, $c = 5\cdot500\ (1)$ Å, $V = 371\cdot6\ (5)$ Å^3, $Z = 4$, $D_x = 9\cdot51$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0\cdot71073$ Å, $\mu = 36\cdot3$ mm^{-1}, $F(000) = 924$, $T = 293$ K, $R = 0\cdot047$ for 291 independent reflections. $\mathrm{YRh_3Si_2}$, $\mathrm{LaRh_3Si_2}$ and $\mathrm{NdRh_3Si_2}$ are isotypic with $\mathrm{ErRh_3Si_2}$. The $\mathrm{ErRh_3Si_2}$ structure represents a new deformation superstructure of the hexagonal $\mathrm{CeCo_3B_2}$ (ternary $\mathrm{CaCu_5}$) structure where $a \simeq 2c[\mathrm{CeCo_3B_2}]$, $b \simeq 3^{1/2}a[\mathrm{CeCo_3B_2}]$ and $c \simeq a[\mathrm{CeCo_3B_2}]$. As compared with the parent type this deformation variant is characterized by zigzag chains of rare-earth atoms and by pairs of Si atoms. The structure of $\mathrm{ErRh_3Si_2}$ is further compared with four other deformation variants of the $\mathrm{CeCo_3B_2}$ type and a review of structure types related to $\mathrm{CaCu_5}$ is presented.

Introduction. $\mathrm{ErRh_3Si_2}$ and eight other $R\mathrm{Rh_3Si_2}$ compounds with R = Y, La, Nd, Sm, Gd, Tb, Dy and Ho were originally reported to crystallize with the $\mathrm{CeCo_3B_2}$-type structure by Chevalier, Cole, Lejay & Etourneau (1981) who also investigated their magnetic properties and superconducting behaviour. However, additional lines were present on all our powder X-ray diffraction films of samples containing $\mathrm{ErRh_3Si_2}$. We shall show here that $\mathrm{ErRh_3Si_2}$ and at least three other compounds reported by Chevalier *et al.* (and probably

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all) in fact crystallize with a new orthorhombic superstructure of the $CeCo_3B_2$ type with a unit cell four times as large.

Review of $CaCu_5$*-related structure types*

More than a hundred ternary borides, and a somewhat smaller number of aluminides, gallides and silicides (see Johnston & Braun, 1982; Parthé & Chabot, 1984) are known which crystallize with a great variety of structure types which can be derived from the hexagonal $CaCu_5$ type (*hP*6, *P*6/*mmm*). As a first approach they can conveniently be subdivided according to their compositions RT_xM_y, where R indicates a rare-earth element or alkaline-earth element (occasionally also Li, Sc, Zr, Hf, U or Th), T a transition element of the Fe, Co or Ni group and M a main-group element such as B, Al, Ga or Si. In the most common case $x+y=5$, however some structure types where $x+y>5$ or <5 can readily be related to the $CaCu_5$ type.

Substitution variants of the $CaCu_5$ *type.* Among the substitution variants of the $CaCu_5$ type with composition RT_xM_y where $x+y=5$ the most frequently encountered structure type is the hexagonal $CeCo_3B_2$ type [*hP*6, *P*6/*mmm*, $a \simeq A(CaCu_5)$, $c \simeq C(CaCu_5)$; Kuz'ma, Kripyakevich & Bilonizhko (1969)] where the M atoms occupy trigonal prismatic sites. A site-exchange variant of the $CeCo_3B_2$ type where T and M atoms have been interchanged occurs with $PrNi_2Al_3$ [*hP*6, *P*6/*mmm*; Rykhal, Zarechnyuk & Kuten (1978)].

Slabs of the $CeCo_3B_2$ type can also be intergrown with slabs of the binary $CaCu_5$ type (Kuz'ma & Bilonizhko, 1974; see also Parthé, Chabot & Cenzual, 1985). The chemical compositions of these structures, composed of m RT_5 slabs and n RT_3M_2 slabs, can be expressed by $R_{m+n}T_{5m+3n}M_{2n}$. Examples are:

$Nd_3Ni_{13}B_2$ [*hP*18, *P*6/*mmm*, $m=2$, $n=1$; Kuz'ma & Bilonizhko (1981)]
$CeCo_4B$ [*hP*12, *P*6/*mmm*, $m=1$, $n=1$; Kuz'ma & Bilonizhko (1981)]
$Lu_5Ni_{19}B_6$ [*hP*30, *P*6/*mmm*, $m=2$, $n=3$; Kuz'ma, Dub & Chaban (1985)]
$Ce_3Co_{11}B_4$ [*hP*18, *P*6/*mmm*, $m=1$, $n=2$; Kuz'ma & Bilonizhko (1981)]
$Ce_2Co_7B_3$ [*hP*24, *P*6/*mmm*, $m=1$, $n=3$; Kuz'ma & Bilonizhko (1981)]

Deformation variants of the $CeCo_3B_2$ *type.* There exist various deformation variants of the hexagonal $CeCo_3B_2$ structure, not all properly defined, which have larger cells and lower symmetry. Of the better defined variants can be mentioned:

$ErIr_3B_2$ [*mS*12, *C*2/*m*, $a \simeq A$, $b \simeq 3^{1/2}A$, $c \simeq C$; Ku & Meisner (1981)]
$LaRu_3Si_2$ [*hP*12, $P6_3/m$, $a \simeq A$, $c \simeq 2C$; Vandenberg & Barz (1980)]
$ZrCo_3B_2$ [*hR*54, $R\bar{3}$, $a \simeq 3^{1/2}A$, $c \simeq 3C$; Voroshilov, Kripyakevich & Kuz'ma (1971)]
URu_3B_2 [*hP*48, $P\bar{3}$, $a \simeq 2A$, $c \simeq 2C$; Rogl (1980)].

A series of Os-containing borides have further been reported to crystallize with an unknown structure type with an orthorhombic unit cell [*oI*72, $a \simeq A$, $b \simeq 3^{1/2}A$, $c \simeq 6C$; Ku (1980)].

R-deficient structures. Defect structure types with composition $R_{<1}T_3B_2$ have been observed with

$Ba_{1-x}Pt_3B_2$ [*hP*12-2*x*, $P6_3/mmc$, $a \simeq A$, $c \simeq 2C$; Shelton (1978)]
$Ba_2Ni_9B_6$ [*hR*102, $R\bar{3}c$, $a \simeq 3^{1/2}A$, $c \simeq 6C$; Jung & Quentmeier (1980)]
$La_{1-x}Rh_3B_2$ [*hP*18-3*x*, *P*6/*mmm*, $a \simeq A$, $c \simeq 3C$; Ku, Ma, Tai, Wang & Horng (1985)].

In $Ba_2Ni_9B_6$, $\frac{1}{3}$ of the R atoms are missing and the remaining R atoms form linear chains inside the hexagonal tunnels. In the case of $Ba_{1-x}Pt_3B_2$ ($x \simeq \frac{1}{3}$) and $La_{1-x}Rh_3B_2$ ($x \simeq 0{\cdot}19$) partially occupied R sites have been reported in addition to very small c parameters. A cell twice as large as that refined for $La_{1-x}Rh_3B_2$ has been proposed for YRh_6B_4 [*hP*33, $a \simeq A$, $c \simeq 6C$; Felner & Nowik (1980)].

Structures with mixed occupation. For some compounds a mixed population of R and T atoms has been proposed at those sites which in the $CeCo_3B_2$ type are occupied by T atoms (first example) or R atoms (second example) exclusively.

$Li_{1-x}(Ni_{1-y}Li_y)_3B_2$ [*hP*18-3*x*, $P6_222$, $a \simeq A$, $c \simeq 3C$; Jung (1977)]
$(Nd_{1-x}Rh_x)Rh_3B_2$ [*hP*6, $P\bar{6}2m$, $a \simeq A$, $c \simeq C$; Vlasse, Ohtani, Chevalier & Etourneau (1983)].

The former structure can also be considered as R deficient, in spite of the global formula which is $Li_{1.2}Ni_{2.5}B_2$, since about $\frac{1}{4}$ of the R sites are unoccupied.

Related structures where some R sites are shifted. A closely related structure type is known where $\frac{1}{3}$ of the R-atom sites in $CeCo_3B_2$ have been shifted by $00\frac{1}{2}$. The structure type was first observed at a composition implying mixed occupation of T and M atoms at some sites; however, later on two different ordered variants were reported in other systems.

$HoNi_{2.6}Ga_{2.4}$ [*hP*18, *P*6/*mmm*, $a \simeq 3^{1/2}A$, $c \simeq C$; Yarmolyuk & Grin' (1979)]
YNi_2Al_3 [*hP*18, *P*6/*mmm*, $a \simeq 3^{1/2}A$, $c \simeq C$; Zarechnyuk & Rykhal (1981)]
YCo_3Ga_2 [*hP*18, *P*6/*mmm*, $a \simeq 3^{1/2}A$, $c \simeq C$; Frémy, Gignoux, Moreau, Paccard & Paccard (1985)].

In YCo_3Ga_2 the arrangement of T and M atoms is the same as in the $CeCo_3B_2$ type, leading to the same stoichiometry; however, in YNi_2Al_3 the T atoms at one of the crystallographic sites have been replaced by M atoms.

Related $RT_{<3}M_2$ *structures.* The compounds belonging to the structural series with the general formula $R_{n+1}T_{3n+2}M_{2n+2}$ [Jung (1984); note that the formula given in the original paper was expressed in a different way] are often mentioned as $CeCo_3B_2$ defect structures with composition RT_xM_2 where $x<3$. In these structures n $CeCo_3B_2$-type slabs are intergrown with a slab of composition RT_2M_2, characteristic of $CaRh_2B_2$

Table 1. *Atom coordinates and isotropic displacement parameters for* $ErRh_3Si_2$ *with space group Imma and atom coordinates of* $CeCo_3B_2$, *referred to the conventional hexagonal cell, hP6, P6/mmm, and to an orthohexagonal cell with double height, similar to that of* $ErRh_3Si_2$

The temperature factor is expressed as $T = \exp\{-2\pi^2U[2(\sin\theta)/\lambda]^2\}$. E.s.d.'s are given in parentheses.

$ErRh_3Si_2$ *Imma*		x	y	z	$100U$(Å^2)
Er	4(*e*)	0	$\frac{1}{4}$	0·7101 (3)	0·62 (5)
Rh(1)	8(*f*)	0·2850 (2)	0	0	0·38 (5)
Rh(2)	4(*c*)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·62 (6)
Si	8(*h*)	0	0·0790 (8)	0·196 (3)	0·7 (1)

$CeCo_3B_2$		*P6/mmm*			*Imma*		
		x	y	z	x	y	z
Ce	1(*a*)	0	0	0	0	$\frac{1}{4}$	$\frac{3}{4}$
Co	3(*g*)	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{4}$ $\frac{1}{4}$	0 $\frac{1}{4}$	0 $\frac{1}{4}$
B	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	0	0	$\frac{1}{2}$	$\frac{1}{4}$

Table 2. *Cell parameters and measurement conditions of* YRh_3Si_2, $LaRh_3Si_2$, $NdRh_3Si_2$ *and* $ErRh_3Si_2$ *crystallizing with the* $ErRh_3Si_2$ *structure type*

	a (Å)	b (Å)	c (Å)	b/c	λ (Å)	Number of reflections	2θ range (°)
YRh_3Si_2	7·112 (2)	9·547 (3)	5·513 (2)	1·732	1·5418	13	$25 < 2\theta < 66$
$LaRh_3Si_2$	7·145 (2)	9·777 (4)	5·611 (2)	1·742	1·5418	14	$24 < 2\theta < 55$
$NdRh_3Si_2$	7·135 (2)	9·671 (3)	5·558 (2)	1·740	1·5418	12	$24 < 2\theta < 55$
$ErRh_3Si_2$	7·098 (8)	9·519 (1)	5·500 (1)	1·731	0·7093	12	$41 < 2\theta < 49$

(Schmidt & Jung, 1978) or of $ThCr_2Si_2$, ternary derivative of $BaAl_4$ (see Yarmolyuk, 1986). Examples are:

$Ca_2Rh_5B_4$ [*oF*44, *Fmmm*, $n = 1$; Jung (1984) for all compounds]
$Ca_3Rh_8B_6$ (*oF*68, *Fmmm*, $n = 2$)
$Sr_5Rh_{14}B_{10}$ (*oF*116, *Fmmm*, $n = 4$)
$Ca_7Rh_{20}B_{14}$ (*oF*164, *Fmmm*, $n = 6$).

However, if one single $CaRh_2B_2$- (or $ThCr_2Si_2$-) type layer can be directly derived from the $CeCo_3B_2$ type by removing T atoms from the Kagomé nets, the stacking of layers is accompanied by a shift of the successive RM_2 planes so that these structures cannot be considered as direct defect variants of the $CeCo_3B_2$ type.

Experimental.

Structure determination of $ErRh_3Si_2$

Plate-like triangular crystal (114 × 8 × 16 µm, cut along the longest face diagonal) isolated from a sample of nominal composition $Er_5Rh_{12}Si_7$ (Er 99·99, Rh 99·9, Si 99·999%), prepared in an arc furnace under purified Ar atmosphere. Philips PW 1100 four-circle diffractometer; graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined from 2θ values of 12 reflections (Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å; $41 \leq 2\theta \leq 49°$) using the program *FINAX* (Hovestreydt, 1983). Laue symmetry *mmm*; systematic absences $h + k + l \neq 2n$ and $hk0$ $h, k \neq 2n$, leading to possible space groups *Imma*, *Im*2*a* and *I*2*ma* (*Ima*2). 636 reflections collected out to $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1} ($0 \leq h \leq 9$, $0 \leq k \leq 13$, $0 \leq l \leq 7$ and all antireflections) in the ω–2θ scan mode, yielding 312 independent reflections ($R_{\rm int} = 0{\cdot}024$), of which 282 were considered significant [$|I| \geq 3\sigma(I)$]. Standard reflections 222 and $\bar{2}\bar{2}\bar{2}$ (max. intensity variation ±1·9%); absorption correction using indexed faces ($1{\cdot}33 \leq A^* \leq 1{\cdot}70$). Structure solved by direct methods, program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement in *Imma* using $|F|$ values of 291 independent reflections (including 9 less-thans calculated greater than observed). Four positional parameters and four isotropic displacement parameters, listed in Table 1, one scale factor, and one isotropic secondary-extinction parameter $g = 8{\cdot}3\,(5) \times 10^{-5}$ (mosaic spread, Gaussian distribution) refined to a final $R = 0{\cdot}047$ [$S = 3{\cdot}91$; shift/e.s.d. in the last cycle $\leq 0{\cdot}0008$; max. (min.) height in final residual electron density map = 6·5 (−5·2) e Å^{-3}].* Atomic scattering factors for neutral atoms, f' and f'' from *International Tables for X-ray Crystallography* (1974); programs used for data reduction and structure refinement from the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Isotypic compounds

Samples of YRh_3Si_2, $LaRh_3Si_2$ and $NdRh_3Si_2$ (Y, La, Nd 99·99%) were prepared at their nominal compositions in the arc furnace. The cell parameters, given in Table 2, were refined from the 2θ values measured on a Guinier film, internal standard Si ($a = 5{\cdot}4307$ Å), program *FINAX* (Hovestreydt, 1983). Superstructure lines, due to the doubling of the unit cell in the direction of the c axis of the $CeCo_3B_2$ type, can be seen on all films. For YRh_3Si_2 (as for $ErRh_3Si_2$) the b/c ratio is very close to $3^{1/2}$ and corresponding lines coincide on the film, only in the cases of $LaRh_3Si_2$ and $NdRh_3Si_2$ a slight line splitting was observed.

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* A list of structure factors arranged in a standard crystallographic data file (Brown, 1985) has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44462 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

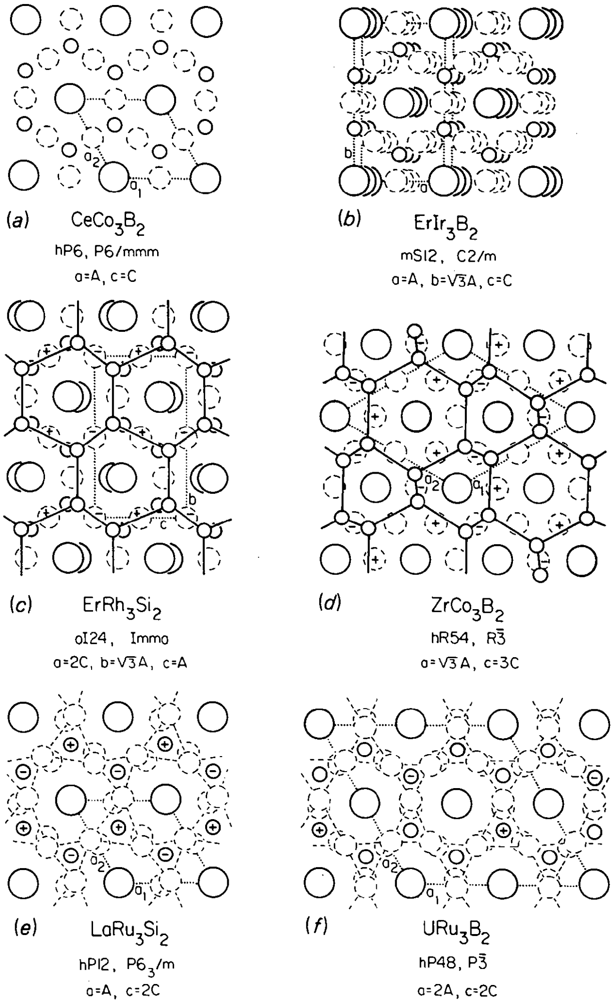
Discussion.

Description of the $ErRh_3Si_2$ *structure*

The $ErRh_3Si_2$ structure, *oI*24, *Imma*, is a deformation superstructure of the $CeCo_3B_2$ type, *hP*6, *P*6/*mmm*, which itself is a substitution variant of the $CaCu_5$ type, same Pearson symbol and space group. The coordinates of $ErRh_3Si_2$ are compared in Table 1 with those of $CeCo_3B_2$, referred to the conventional unit cell and to an orthohexagonal unit cell where $a_o = 2c_h$, $b_o = 3^{1/2}a_h$ and $c_o = a_h$. Significant deviations from the coordinates of the $CeCo_3B_2$ structure are observed in the z parameter of the sites occupied by Er and Si and in the x parameter of the Rh(1) site.

The parent structure, $CeCo_3B_2$, shown in Fig. 1(*a*), can be considered as built up of two kinds of alternate layers perpendicular to the hexagonal axis. One contains the rare-earth atoms (R) and the main-group element (M), the M atoms forming hexagons centred by the R atoms, and the other layer is a 3636-type (Kagomé) net of transition-metal atoms (T). In this way, each M atom in the structure is at the centre of a trigonal prism of T atoms. The larger R atoms have 6 M atoms and 12 T atoms at coordination distances, as well as 2 R atoms at a generally very short distance $= c/2$. The T atoms are surrounded by an icosahedron formed by a rectangle of T atoms in the xy plane, a rectangle of M atoms perpendicular to this one, and a rectangle of R atoms perpendicular to the former two. There are no short distances between M atoms; however, the R atoms form straight chains parallel to the c axis and the T atoms a two-dimensional network perpendicular to these. The strongest interactions seem to be between T and M atoms in the prisms and between the R atoms inside the chains.

The $ErRh_3Si_2$ structure is shown in Fig. 1(*c*) in a projection along [100] and a list of interatomic distances out to 4 Å and their relative contraction as compared with the sum of the atomic radii determined for 12-coordinated atoms (Teatum, Gschneidner & Waber, 1960) is presented in Table 3. On comparison of the projection of $ErRh_3Si_2$ with the non-distorted parent type in Fig. 1(*a*), it can be seen that the R and M atoms have been displaced from their positions in $CeCo_3B_2$ parallel to the unit-cell vector $\mathbf{a}_1$ which has become the c axis of the orthorhombic cell. The hexagonal network of M atoms (indicated with solid lines in the figure) is distorted so that Si-atom pairs are formed. The distance between the atoms of a pair [2·63 (1) Å] corresponds to twice the atomic radius of Si used in Table 3. The R atoms are moved towards the centre of the now distorted hexagons of M atoms. Directly over- or underlying atoms in the projection are displaced in opposite directions so that zigzag chains parallel to the former hexagonal axis, now the a axis in the orthorhombic structure, are observed. Owing to the zigzagging of the chain and to the relatively high value of the a parameter (as compared to twice the c parameter of the unit cell of the $CeCo_3B_2$ type), the distances between the R atoms inside these chains are considerably longer than those reported for other compounds crystallizing with distorted or undistorted $CeCo_3B_2$ structures. It can be seen from Table 3 that these distances (3·576 Å) exceed the sum of the atomic radii for 12-coordinated atoms whereas in other compounds with related structure types a strong contraction is



(*a*) $CeCo_3B_2$ hP6, P6/mmm a=A, c=C

(*b*) $ErIr_3B_2$ mS12, C2/m a=A, b=√3A, c=C

(*c*) $ErRh_3Si_2$ oI24, Imma a=2C, b=√3A, c=A

(*d*) $ZrCo_3B_2$ hR54, R$\bar{3}$ a=√3A, c=3C

(*e*) $LaRu_3Si_2$ hP12, P6$_3$/m a=A, c=2C

(*f*) URu_3B_2 hP48, P$\bar{3}$ a=2A, c=2C

Fig. 1. The hexagonal $CeCo_3B_2$ type in a projection along [001] and five of its deformation variants in similar projections: (*a*) $CeCo_3B_2$, (*b*) the monoclinic $ErIr_3B_2$ type, (*c*) the orthorhombic $ErRh_3Si_2$ type, (*d*) the rhombohedral $ZrCo_3B_2$ type, (*e*) the hexagonal $LaRu_3Si_2$ type and (*f*) the hexagonal URu_3B_2 type. Large circles represent R atoms, medium circles T atoms and small circles M atoms. In all structures, RM_2 layers (solid lines) alternate with T_3 layers (dashed lines). In the case of $ZrCo_3B_2$ only one third of the atoms in the triple hexagonal cell (layers at $z \simeq \frac{2}{3}$ and $\frac{1}{2}$) are shown, whereas for $ErIr_3B_2$ and URu_3B_2 the deformation has been exaggerated by a factor three in order to visualize the direction of the displacements. Strongly distorted networks in the plane of projection are emphasized by solid or dashed lines connecting the circles while plus and minus signs indicate displacements out of the plane of the layer immediately below the one containing the connected circles.

Table 3. *Interatomic distances* (d) *out to* 4 Å *and* $\Delta = (d - \sum r)/\sum r$ *for* $ErRh_3Si_2$

E.s.d.'s are given in parentheses. Atomic radii (r) used are 1·757 (Er), 1·345 (Rh) and 1·319 Å (Si) respectively (Teatum, Gschneidner & Waber, 1960).

		d (Å)	Δ (%)			d (Å)	Δ (%)
Er	–4 Rh(1)	3·054 (1)	–1·6	Rh(2)	–4 Si	2·426 (5)	–8·9
	2 Rh(2)	3·090 (2)	–0·4		4 Rh(1)	2·760 (1)	+2·6
	2 Si	3·130 (7)	+1·8		2 Er	3·090 (2)	–0·4
	2 Si	3·174 (7)	+3·2		2 Er	3·459 (2)	+11·5
	2 Si	3·261 (7)	+6·0		2 Rh(2)	3·549 (4)	+31·9
	2 Rh(2)	3·459 (2)	+11·5				
	4 Rh(1)	3·507 (2)	+13·1	Si	–2 Rh(1)	2·384 (6)	–10·5
	2 Er	3·576 (4)	+1·8		2 Rh(1)	2·413 (4)	–9·4
					2 Rh(2)	2·426 (5)	–8·9
Rh(1)	–2 Si	2·384 (6)	–10·5		Si	2·631 (10)	–0·3
	2 Si	2·413 (4)	–9·4		Er	3·130 (7)	+1·8
	2 Rh(2)	2·760 (1)	+2·6		Er	3·174 (7)	+3·2
	2 Rh(1)	2·795 (1)	+3·9		Si	3·255 (10)	+23·4
	Rh(1)	3·051 (4)	+13·4		Er	3·261 (7)	+6·0
	2 Er	3·054 (1)	–1·6		2 Si	3·598 (4)	+36·4
	2 Er	3·507 (2)	+13·1		Si	3·664 (10)	+38·9

generally observed. In opposition to the RM_2 layers the layers containing the T atoms are no longer planar as in the $CeCo_3B_2$ structure but puckered. Effectively, those T atoms which are now inside trapezia (instead of rectangles) of M atoms are displaced, parallel to the former hexagonal axis, towards the longest of the approximately parallel sides of the trapezium. Table 3 tells us that, as found in all related structure types, the most important contractions are observed in the distances between T and M atoms, *i.e.* inside the trapezia or rectangles from the point of view of the transition metal, or inside the trigonal prisms from the point of view of the Si atoms.

Comparison with other deformation variants of the $CeCo_3B_2$ *type*

In Fig. 1 are also shown four other deformation superstructures, mentioned above in our review of $CaCu_5$-related structure types and for which atom coordinates have been published.

Most of the known RIr_3B_2 compounds and those RRh_3B_2 compounds where R is one of the smaller rare-earth atoms (R = Tb–Lu or Y) crystallize with the slightly distorted monoclinic $ErIr_3B_2$ type ($\beta \simeq 91°$) shown in Fig. 1(*b*). The b/a ratios of all isotypic structures are very close to $3^{1/2}$ and no important deformations are suspected (the only possible deformation in space group $C2/m$ would be the displacement of B atoms towards or away from each other inside the RB_2 layers).

In the next two structures, $ErRh_3Si_2$ (Fig. 1*c*) and $ZrCo_3B_2$ (Fig. 1*d*), the M-atom nets are strongly distorted in the plane of projection. In both structures M_2 pairs are formed; the distance between the B atoms in the dumbbells in $ZrCo_3B_2$ is only 1·70 Å. However, while in $ErRh_3Si_2$ these pairs are arranged so that each Er atom is at the centre of a hexagon with two short sides, in $ZrCo_3B_2$ $\frac{1}{3}$ of the Zr atoms centre a regular hexagon with six long sides and the remaining $\frac{2}{3}$ strongly distorted hexagons with three short and three long sides. In both structures the layers of T atoms are puckered.

In the two structures shown at the bottom of Fig. 1, $LaRu_3Si_2$ (*e*) and URu_3B_2 (*f*), not the M- but the T-atom nets are distorted in the plane perpendicular to the hexagonal axis. As a result smaller and larger triangles are formed. The z coordinate of the site occupied by Si in $LaRu_3Si_2$ has not been refined but it is probable that these atoms are displaced towards the largest triangular face of the surrounding trigonal prisms and that the Si layers in this structure, as well as the B-atom layers in URu_3B_2, are puckered.

As shown in the introductory review, the family of structures of ternary derivatives of the $CaCu_5$ type contains a large number of members, many of which are still only partially known. Among the many borides belonging to the family only some RT_3B_2 borides containing Co, Rh or Ru seem to crystallize with the simple ordered substitution variant $CeCo_3B_2$. With other R or T elements a large number of more or less distorted variants occur, at or (and) around the stoichiometry 1–3–2. Aluminides and gallides (only known with T = Co, Ni) present other interesting structural features since if some aluminides crystallize with the simple $CeCo_3B_2$ type (where however T and M elements have been interchanged with respect to the structures of the borides), other closely related structure types appear where part of the rare-earth atoms have been moved into the Kagomé-net layers. Silicides are known only with Ru and Rh, each group of compounds crystallizing with a different deformation variant.

It is interesting to notice that M–M dumbbells are observed in several of the best-known deformation variants, however arranged differently in space. In addition to the $ErRh_3Si_2$ and the $ZrCo_3B_2$ structures, discussed above, B-atom pairs are also observed in $Ba_2Ni_9B_6$ (d = 1·75 Å). In this structure the dumbbells are parallel to the c axis which has 'collapsed' owing to the lower ratio of R atoms. It may be noticed that these three structure types all occur when an element with more valence electrons enters the structure, that is Si instead of B, Zr instead of a three-valent cation, Ni instead of an element from Group IX, respectively. Perhaps the results of the studies on some of the other apparently related structure types which are still unknown or only known in part will tell us more about the factors influencing stability and favouring the formation of one of the deformation variants of the $CeCo_3B_2$ type.

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Small Atomic Displacements in the Molybdenophosphates $AMo_2P_3O_{12}$ (A = K, Rb, Tl)

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Abstract. $KMo_2P_3O_{12}$, $M_r = 515{\cdot}90$, orthorhombic, *Pbnm*, $a = 17{\cdot}6398\,(14)$, $b = 9{\cdot}1761\,(4)$, $c = 12{\cdot}3000\,(8)$ Å, $V = 1990{\cdot}9\,(4)$ Å^3, $Z = 8$, $D_x = 3{\cdot}44$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}42$ mm^{-1}, $F(000) = 1952$, $T = 294$ K, $R = 0{\cdot}028$ for 2123 reflections. $RbMo_2P_3O_{12}$, $M_r = 562{\cdot}26$, orthorhombic, *Pbcm*, $a = 8{\cdot}8314\,(8)$, $b = 9{\cdot}2368\,(7)$, $c = 12{\cdot}3051\,(9)$ Å, $V = 1003{\cdot}8\,(4)$ Å^3, $Z = 4$, $D_x = 3{\cdot}72$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8{\cdot}08$ mm^{-1}, $F(000) = 1048$, $T = 294$ K, $R = 0{\cdot}044$ for 2073 reflections. The $Mo_2P_3O_{12}$ frameworks of the K, Rb and Tl compounds are almost the same. The main difference is in the position of the alkaline-earth ions in the tunnels, which induces, in the potassium compound, a superstructure along **a**. The alkaline-earth ions are slightly displaced as their size decreases in order that the A—O distances may agree with the sum of the ionic radii.

Introduction. Comparison of the behaviour of potassium, rubidium and thallium in different oxides with octahedral tunnel structures shows that these ions generally lead to the same structural type as shown, for instance, in the well known tungsten-bronze family A_xWO_3 (Magnéli, 1949*a*,*b*, 1952, 1953; Magnéli &