

Orthorhombic LuRh_4B_4 – A New Polytype of $RT_4\text{B}_4$ Stoichiometry

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Abstract. LuRh_4B_4 , orthorhombic, *Ccca*, $a = 7.410$ (3), $b = 22.26$ (1), $c = 7.440$ (3) Å, $Z = 12$, $D_m = 10.19$ (2), $D_x = 10.22$ Mg m⁻³, single-crystal counter data. $\sum |\Delta F| / \sum |F_o| = 0.05$ for 388 reflexions with $|F_o| > 3\sigma(F_o)$. The structure is characterized by a NaCl-type arrangement of tetrahedral Rh_4 clusters [$d(\text{Rh}-\text{Rh}) = 2.662$ (5)– 3.110 (5) Å] and Lu atoms [$d(\text{Lu}-\text{Rh}) = 2.862$ (4)– 3.207 (4) Å], and by B atom pairs [$d(\text{B}-\text{B}) = 1.4$ (1) Å]. As for LuRu_4B_4 , the structure can be derived from the tetragonal CeCo_4B_4 structure by a shift of quasi two-dimensional infinite slabs along the cell diagonal. Isotypic compounds are found with the heavy lanthanides Ho, Er, Tm and Yb.

Introduction. Owing to their unusual low-temperature properties, ternary borides $RT_4\text{B}_4$ ($R = \text{Sc, Y, rare earth, Th, U}$; $T = \text{Rh, Ir, Ru, Os}$) are currently the subject of intensive research (Maple, 1981). So far, three different polytypes with closely related structures have been reported: the CeCo_4B_4 type (Kuzma & Bilonizhko, 1972), which is primitive tetragonal (*tP*18; $c/a \sim 1.4$), the LuRu_4B_4 type (Johnston, 1977), which is body-centred tetragonal (*tI*72, $c/a \sim 2$), and the NdCo_4B_4 type (Kuzma & Bilonizhko, 1978), which is primitive tetragonal (*tP*18, $c/a \sim 0.5$). While the two former structure types can be described by a slightly distorted NaCl-type arrangement of tetrahedral T_4 clusters ($T =$ transition element) and R atoms, the latter is characterized by quasi one-dimensional infinite columns of edge-sharing T_4 tetrahedra (Grüttner & Yvon, 1979; Rogl, 1980). In all polytypes the B atoms form pairs.

Recently, a fourth $RT_4\text{B}_4$ variant typified by LuRh_4B_4 has been discovered (Johnston & MacKay, 1979). As will be shown in this article, its structure is orthorhombic (*oC*108, $b/a \sim 3$, $c/a \sim 1$) and closely related to those of CeCo_4B_4 and LuRu_4B_4 .

Samples of composition $\text{RRh}_{4+\epsilon}\text{B}_4$ ($R = \text{Lu, Yb, Tm, Er, Ho}$), *i.e.* containing a slight excess of Rh ($\epsilon = 0.0$ – 0.3), were prepared by arc melting the high-purity elements in a Zr-gettered Ar atmosphere. X-ray powder diffraction analysis showed that the ingots

consisted mainly of the RRh_4B_4 phase with either the CeCo_4B_4 or the LuRu_4B_4 structure type. However, annealing at 1420–1520 K yielded different powder patterns which suggested the formation of a new phase. In particular, for an arc-melted ingot of composition $\text{LuRh}_{4.05}\text{B}_4$, which was annealed under Ar in a sealed Ta tube at 1470 K for 125 h then quenched into cold water, the powder data showed only the new phase, apart from a very weak impurity (RhB) reflection at $d = 2.36$ Å. This sample was crushed and a single crystal of irregular shape (average diameter ~ 80 μm) was isolated and analysed on a computer-controlled four-circle diffractometer. The Laue group was *mmm* and the space-group extinctions (*hkl* only with $h + k = 2n$; *0kl* and *h0l* only with $l = 2n$; *hk0* only with $h = 2n$) indicated the unique space group *Ccca* (No. 68). The cell volume ($V = 1227.2$ Å³) and measured density suggested 12 formula units per cell. Integrated intensities of 575 reflections were recorded with continuous θ – 2θ scans to a limit of $\sin \theta/\lambda = 0.6$ Å⁻¹. After applying an absorption correction for a spherical crystal [$\mu(\text{Mo K}\alpha) = 39$ mm⁻¹] and eliminating the space-group-absent reflexions a set of 490 unique observed data was retained.

In view of the simple relationship (see below also) between the lattice parameters of orthorhombic LuRh_4B_4 (see *Abstract*) and its tetragonal CeCo_4B_4 -type variant ($a_t = 5.294$, $c_t = 7.359$ Å; $a \sim c_t$, $b \sim 3a_t\sqrt{2}$, $c \sim a_t\sqrt{2}$) (Vandenberg & Matthias, 1977) the two modifications were assumed to be structurally related. The metal-atom positions of the orthorhombic polytype were obtained by trial and error assuming that Rh-atom tetrahedra and Lu atoms form a slightly distorted NaCl-type arrangement which satisfies the symmetry requirements of space group *Ccca*. The atomic and vibrational parameters were refined by the full-matrix least-squares program *CRYLSQ* of the XRAY program system (Stewart, 1976). Weights were given by the counting statistics and the atomic scattering factors and correction terms for anomalous dispersion were taken from *International Tables for*

Table 1. Fractional atomic coordinates and temperature factors of LuRh₄B₄, space group Ccca (No. 68, origin at centre of inversion)

The Debye-Waller factor is defined as $\exp[-2\pi^2 \times 10^{-2} \times U(2 \times \sin \theta/\lambda)^2]$. Standard deviations are given in parentheses

	Equipoint	x	y	z	U (Å ²)
Lu(1)	8(f)	0	0.5824 (1)	$\frac{1}{2}$	0.37 (7)
Lu(2)	4(a)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.35 (9)
Rh(1)	16(i)	0.1180 (5)	0.0417 (2)	0.0955 (5)	0.28 (8)
Rh(2)	16(i)	0.1530 (2)	0.1245 (2)	0.3670 (4)	0.26 (9)
Rh(3)	16(i)	0.3531 (5)	0.2065 (2)	0.1272 (5)	0.49 (9)
B(1)	16(i)	0.13 (1)	0.147 (4)	0.07 (1)	4 (2)
B(2)	16(i)	0.19 (1)	0.023 (3)	0.40 (1)	3 (2)
B(3)	16(i)	0.36 (1)	0.318 (4)	0.09 (1)	4 (2)

Table 2. Bond lengths (Å) in LuRh₄B₄

Standard deviations are in parentheses. Starred values indicate Rh₄ intra-cluster bonds, and double-starred values Rh₄ inter-cluster bonds. An *s* or *d* following the latter values indicates whether the two Rh₄ tetrahedra have the same (*s*) or different (*d*) orientations.

Lu(1)–Rh(1)	2 × 2.862 (4)	Rh(3)–Lu(1)	3.107 (5)
	2 × 3.117 (5)	Rh(3)–Lu(2)	2.936 (4)
	2 × 3.187 (4)		3.162 (4)
Lu(1)–Rh(2)	2 × 2.872 (4)		
	2 × 3.207 (4)	Rh(3)–Rh(2)	2.662 (5) ^{***}
Lu(1)–Rh(3)	2 × 3.107 (5)		2.951 (5) ^{***d}
Lu(1)–B(1)	2 × 2.95 (9)	Rh(3)–Rh(3)	2.663 (5)*
	2 × 3.37 (9)		2.843 (5)*
Lu(1)–B(2)	2 × 2.90 (8)		2.915 (6)*
	2 × 2.93 (8)		3.110 (5) ^{***d}
	2 × 3.24 (8)		
Lu(1)–B(3)	2 × 2.71 (9)	Rh(3)–B(1)	2.14 (9)
		Rh(3)–B(3)	2.16 (9)
Lu(2)–Rh(2)	4 × 3.138 (4)		2.20 (9)
Lu(2)–Rh(3)	4 × 2.936 (4)		2.34 (9)
	4 × 3.162 (4)		2.50 (9)
Lu(2)–B(1)	4 × 2.82 (9)	B(1)–Lu(1)	2.95 (9)
Lu(2)–B(3)	4 × 3.13 (9)		3.37 (9)
	4 × 3.29 (9)	B(1)–Lu(2)	2.83 (9)
Rh(1)–Lu(1)	2.862 (4)	B(1)–Rh(1)	2.37 (9)
	3.117 (5)	B(1)–Rh(2)	= Rh(2)–B(1)
	3.187 (4)	B(1)–Rh(3)	2.14 (9)
Rh(1)–Rh(1)	2.698 (5) ^{***s}	B(1)–B(3)	1.4 (1)
	2.888 (5)*		
	2.919 (5) ^{***d}	B(2)–Lu(1)	2.90 (8)
Rh(1)–Rh(2)	2.739 (5)*		2.93 (8)
	2.746 (5)*		3.24 (8)
	3.028 (5) ^{***d}		
Rh(1)–B(1)	2.37 (9)	B(2)–Rh(1)	= Rh(1)–B(2)
Rh(1)–B(2)	2.11 (8)	B(2)–Rh(2)	2.29 (8)
	2.12 (8)	B(2)–B(2)	1.4 (1)
	2.29 (9)		
	2.34 (8)	B(3)–Lu(1)	2.71 (9)
		B(3)–Lu(2)	3.13 (9)
Rh(2)–Lu(1)	2.872 (4)		3.29 (9)
	3.207 (4)		
Rh(2)–Lu(2)	3.138 (4)	B(3)–Rh(2)	2.03 (9)
		B(3)–Rh(3)	= Rh(3)–B(3)
Rh(2)–Rh(1)	2.739 (5)*	B(3)–B(1)	1.14 (1)
	2.746 (5)*		
	3.028 (5) ^{***d}		
Rh(2)–Rh(2)	2.858 (5)*		
Rh(2)–Rh(3)	2.662 (5) ^{***s}		
	2.951 (5) ^{***d}		
Rh(2)–B(1)	2.23 (9)		
	2.24 (9)		
	2.29 (9)		
Rh(2)–B(2)	2.29 (8)		
Rh(2)–B(3)	2.03 (9)		

Table 3. Lattice parameters of RRh₄B₄ compounds with orthorhombic LuRh₄B₄ structure type; data for two samples of the Tm and Er compounds are shown

R	a (Å)	b (Å)	c (Å)
Er	(±0.006)	(±0.02)	(±0.006)
	7.444	22.30	7.465
	7.439	22.30	7.460
Tm	7.432	22.28	7.455
	7.433	22.31	7.453
Yb	7.424	22.26	7.458
Lu	7.410	22.26	7.440

X-ray Crystallography (1974). The agreement index, *R*, was 0.07. After the B atoms had been located on an electron density difference map their positional parameters were refined in a final least-squares cycle.* The positional and thermal parameters are summarized in Table 1 and a list of bond lengths is given in Table 2. The lattice parameters of isostructural RRh₄B₄ compounds (*R* = Er, Tm and Yb) as refined from X-ray powder data are listed in Table 3; for *R* = Ho, the sample quality was insufficient for an accurate determination of the lattice parameters.

Discussion. The structural relationships between orthorhombic LuRh₄B₄ and the other known RT₄B₄ polytypes are illustrated in Fig. 1. As for the structure of tetragonal LuRu₄B₄, the structure of LuRh₄B₄ can be derived from the CeCo₄B₄ structure by a shift of quasi two-dimensional infinite slabs of T₄ tetrahedra with shift vector $\mathbf{v} = (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{c})/2$ (Fig. 1*b*). Whereas in LuRu₄B₄ the slabs consist of two sheets of T₄ tetrahedra, in LuRh₄B₄ they consist of three such sheets. Thus, the near-neighbour environments in all three structure types are practically identical. They differ, however, from those of the fourth known polytype, NdCo₄B₄, which is characterized by quasi one-dimensional columns of edge-sharing Co₄ tetrahedra parallel to the tetragonal *c* axis (Fig. 1*d*).

The structural chemistry and bonding of the CeCo₄B₄, LuRu₄B₄ and NdCo₄B-type borides have been investigated in detail by several authors (Kuzma & Bilonizhko, 1972, 1978; Johnston, 1977; Grüttner & Yvon, 1979; Rogl, 1980; Yvon, 1981). In this article only those aspects of the LuRh₄B₄ structure will be discussed which are novel with respect to the known features of the other RT₄B₄ polytypes. In contrast to the tetragonal polytypes CeCo₄B₄, LuRu₄B₄ and NdCo₄B₄, which contain only one kind of T₄ tetra-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36312 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

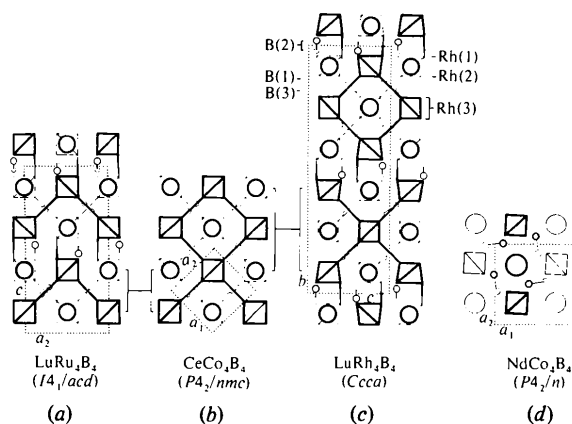


Fig. 1. The structure of orthorhombic LuRh₄B₄ (c) compared with those of the other known RT_4B_4 polytypes (for description, see text). The T_4 tetrahedra and M atoms outlined by thick lines and circles, and those outlined by thin lines and circles are centred on planes which are separated by half the lattice period perpendicular to the view direction. The boron atom pairs are shown by small circles. In LuRh₄B₄ the origin has been shifted by $0, \frac{1}{2}, \frac{1}{2}$ and only Rh–Rh bonds shorter than 2.919 Å are shown.

hedra and one kind of B-atom pair, orthorhombic LuRh₄B₄ contains two kinds of T_4 tetrahedra [one formed by Rh(3) and the other by Rh(1) and Rh(2); Fig. 1c], and also two kinds of B-atom pairs [one formed by B(2) and the other by B(1) and B(3)]. Whereas the point symmetry of the Rh(3) tetrahedra is 222, *i.e.* identical to that of the Ru₄ tetrahedra in LuRu₄B₄ and lower than those of the Co₄ tetrahedra in NdCo₄B₄ ($\bar{4}$) and CeCo₄B₄ (mm), that of the mixed Rh(1)/Rh(2) tetrahedra is 2. Thus the number of different T – T bond types in orthorhombic LuRh₄B₄ is higher and the distribution of T – T bond lengths more uniform than those in the tetragonal polytypes. Whereas the T_4 tetrahedra networks of NdCo₄B₄ (∞^1 Co₄ parallel to *c*), CeCo₄B₄ (∞^2 Co₄ perpendicular to *c*) and LuRu₄B₄ (∞^3 Ru₄) are characterized by respectively three, four and five types of T – T bonds which may be classified as either short [$2.6 < d(T-T) < 2.8$ Å] or long [$2.9 < d(T-T) < 3.2$ Å], that of LuRh₄B₄ (∞^3 Rh₄) is characterized by 13 types of Rh–Rh bonds, the lengths of which are uniformly distributed between 2.66 and 3.11 Å (Table 2). However, the uniformity of this distribution conceals important bonding characteristics of orthorhombic LuRh₄B₄. In particular, similar to the Rh₄ tetrahedra in CeCo₄B₄-type and LuRu₄B₄-type RRH_4B_4 compounds, in which the tetrahedra are not isolated from each other, the shortest *inter-cluster* bonds (2.66–2.70 Å, see Table 2) occur only to the adjacent four {for [Rh(3)]₄} or six {for [Rh(1), Rh(2)]₄} tetrahedra with the same orientation, whereas significantly longer bonds (2.92–3.11 Å) are found to the remaining eight or six adjacent tetrahedra, respectively, with the alternate orientation. Thus, orthorhombic LuRh₄B₄ contains two

distinct extended (three-dimensional) and *inter-penetrating* clusters, each of which is comprised of Rh₄ tetrahedra with the same orientation. Similar clustering occurs in the LuRu₄B₄-type materials to a lesser degree, but the extended clusters are different in the CeCo₄B₄-type compounds where the extended clusters are two-dimensional and do not interpenetrate.

The separation of the B atoms within the B-atom pairs of LuRh₄B₄ [1.4 (1) Å] is unusually short compared with the values found for most members of the other known RT_4B_4 structure classes (~ 1.8 Å). However, precedence for such a small separation has been set previously from single-crystal studies of LuRu₄B₄-type Y(Rh_{1-x}Ru_x)₄B₄ compounds, where the reported atomic positions (Yvon & Grüttner, 1980) yield $d(B-B) = 1.45$ (10) Å for $x = 0.5$. This large variability in $d(B-B)$ suggests that the B₂ dimers may be acting as electron sources or sinks under certain conditions, a situation which appears to be of great importance with regard to the superconducting properties of the RT_4B_4 compounds; this connexion will be described in more detail later.

In view of the simple structural relationship between orthorhombic LuRh₄B₄ and tetragonal LuRu₄B₄ and CeCo₄B₄, one expects that other shift variants of the CeCo₄B₄ structure exist. At the moment, however, the conditions for their formation and the criteria for the occurrence of a particular RT_4B_4 polytype are not yet known with certainty. Among the factors which appear to play a role in favouring one polytype over another are the radii ratio of the metal atoms (Rogl, 1979; Grüttner & Yvon, 1979) and the number of valence electrons on the T_4 clusters (Yvon, 1981) and/or perhaps on the B₂ dimers as noted above. However, the influence of the heat treatment and the stoichiometry cannot be neglected because some RRH_4B_4 compounds can be formed with at least two of the above structures, depending on the particular annealing conditions, and phase-diagram work (Johnston & Mackay, unpublished) has shown that the composition of orthorhombic LuRh₄B₄ is very close to LuRh_{4.00}B_{3.95}. The possibility that the latter structure is stabilized for instance by B defects is supported by its cell volume per formula unit ($V' = 102.3$ Å³), which is smaller than those of its tetragonal CeCo₄B₄-type and LuRu₄B₄-type modifications ($V' = 103.1$ Å³ and ~ 102.8 Å³, respectively).

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References

- GRÜTTNER, A. & YVON, K. (1979). *Acta Cryst.* **B35**, 451–453.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

- JOHNSTON, D. C. (1977). *Solid State Commun.* **24**, 699–702.
- JOHNSTON, D. C. & MACKEY, H. B. (1979). *Bull. Am. Phys. Soc.* **24**, 390.
- KUZMA, JU. B. & BILONIZHKO, N. S. (1972). *Sov. Phys. Crystallogr.* **16**, 897–898.
- KUZMA, JU. B. & BILONIZHKO, N. S. (1978). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, **3**, 275–277.
- MAPLE, M. B. (1981). *Proc. International Conference on Ternary Superconductors*, edited by G. SHENOY. New York: North-Holland.
- ROGL, P. (1979). *Monatsh. Chem.* **110**, 235–243.
- ROGL, P. (1980). *Monatsh. Chem.* **111**, 517–527.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- VANDEBERG, J. M. & MATTHIAS, B. T. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 1336–1337.
- YVON, K. (1981). *Superconductivity in Ternary Compounds*, Vol. I, edited by B. MAPLE & Ø. FISCHER, Ch. 2. Berlin: Springer Verlag.
- YVON, K. & GRÜTTNER, A. (1980). *Superconductivity in d- and f-Band Metals*, edited by H. SUHL & B. MAPLE, pp. 515–519. New York: Academic Press.

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Structure of Bis[dibromo(1,4-dioxane)gallium]

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Abstract. [Ga₂Br₄(C₄H₈O₂)₂], C₈H₁₆Br₄Ga₂O₄, triclinic *P*1̄, *a* = 9.039 (5), *b* = 11.24 (5), *c* = 9.018 (5) Å, α = 106.75 (2), β = 72.34 (2), γ = 97.52 (2)°, *Z* = 2, *D*_x = 2.527, *D*_m = 2.51 Mg m⁻³. The structure has been solved from 1195 diffractometer-measured intensities and refined by full-matrix least squares to *R* = 0.0827. The complex contains a Ga–Ga bond and is similar to the chloride complex.

Introduction. Although the metal–metal-bonded form of Ga₂Cl₄ is not known, stable complexes of the halide may be prepared, e.g. Ga₂Cl₄.2(dioxane) (Beamish, Small & Worrall, 1979), Ga₂Cl₆²⁻ (Brown & Hall, 1973), which contain Ga–Ga bonds. The Raman spectra of these two complexes contain very strong bands in similar positions (Beamish *et al.*, 1979) and it has been suggested that the presence of such intense bands may be used to identify Ga–Ga bonds (Tan & Taylor, 1974).

On the basis of a Raman spectroscopic investigation we have deduced that Ga₂Br₄.2(dioxane) has a structure similar to that of the chloride analogue and the aim of this work is to confirm this deduction.

Using a single crystal sealed in a Lindemann-glass tube, the crystal data were obtained from Weissenberg photographs taken with Cu *K*α radiation (λ = 1.542 Å). Intensity measurements were made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo *K*α radiation (λ =

0.7107 Å). On account of the unfavourable orientation of the Lindemann tube relative to the ω axis only layers *l* = 0–4 were measured. The crystals were irregular in shape and the crystal-face development complex so that crystal directions could not be recognized visually and therefore no correction was made for absorption (μ = 12.53 mm⁻¹). The size of the crystal used was 0.21 × 0.13 × 0.25 mm. Scaling of data was carried out with *SHELX* (Sheldrick, 1976); after elimination of those for which *I* < 3σ(*I*) there remained 1195 unique reflections. An *E* map obtained with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) revealed the positions of the Ga and Br atoms. These were used to phase (*F*_o – *F*_c) maps to give the positions of the remaining atoms (apart from H) using *SHELX*. Full-matrix least-squares refinement with unit weight of all atomic positions, anisotropic *U*_{ij} values for Ga and Br and isotropic *U* values for the remaining non-hydrogen atoms was carried out until convergence was reached at *R* = 0.0827. Atomic scattering factors were those of Cromer & Mann (1968) and Cromer & Liberman (1970). Final coordinates and equivalent values (*U*_{eq}) of the anisotropic temperature coefficients and isotropic (*U*) values are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, bond angles and distances not involving Ga, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36263 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.