Lanthanum Ruthenium Boride, LaRu$_4$B$_4$

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Abstract. LaRu$_4$B$_4$, tetragonal, $P4_2/n$, $a = 7.541$ (3), $c = 4.012$ (1) Å, $Z = 2$, $D_x = 8.54$ Mg m^{-3}, single-crystal counter data. $\sum |\Delta F|/\sum |F_o| = 0.05$ for 446 reflexions with $|F_o| > 2\sigma(F_o)$. The Ru atoms form infinite chains of edge-sharing tetrahedra [d(Ru–Ru) = 2.705 (2), 4 × 2.772 (2) Å] which are separated by strings of La atoms [d(La–La) = 4.012 (1) Å] and by pairs of B atoms [d(B–B) = 1.83 (2) Å]. The compound is isostructural with NdCo$_4$B$_4$. A factor which favours this structure is the relative size of the rare-earth atoms with respect to the size of the transition-metal atoms.

Introduction. Recently a new series of ternary ruthenium borides containing isolated metal-atom tetrahedra and B atom pairs was reported (Johnston, 1977). The compounds were found to be body-centred tetragonal with composition MRu$_4$B$_4$, where M is either Y, Th or one of the lanthanides (Ln). The only rare-earth element which does not form this phase is lanthanum. This is surprising, and motivated the present study.

Alloys of the composition LaRu$_4$B$_4$ were prepared from the elements by arc melting under a protective argon atmosphere. A single crystal of size 50 µm was isolated from the crushed sample and was analysed on a computer-controlled four-circle diffractometer. The lattice showed the Laue symmetry $4/m$ and the space-group extinctions ($hk0$ only with $h + k = 2n$ and $00l$ only with $l = 2n$) indicated the unique space group $P4_2/n$ (No. 86). The cell volume of 228.2 Å^3 is about a quarter of that reported for the other LnRu$_4$B$_4$ phases, which suggests two formula units per cell. Integrated intensities of 629 reflexions were recorded with continuous θ–2θ scans to a limit of (sin θ)/$\lambda = 1.1$ Å^{-1}. After averaging equivalent reflexions and applying an absorption correction for a spherical crystal [μ(Mo $K\alpha$) = 21.75 mm^{-1}] a set of 505 unique observed data was retained. The structure was solved by trial and error, assuming that the Ru atoms form tetrahedral clusters which are arranged in a way similar to that in the b.c.t. LnRu$_4$B$_4$ phases. The B atoms were located on an electron density difference map. The atomic and vibra-

tional parameters were refined by the full-matrix least-squares program *CRYLSQ* of the XRAY program system (Stewart, 1976). The weighting scheme was $w = 1/\sigma^2$ and the atomic scattering factors and correction terms for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The final R calculated with isotropic extinction and anisotropic thermal parameters for 446 reflexions with $|F_o| > 2\sigma(F_o)$ is 0.05.† The positional and thermal parameters are summarized in Table 1 and a list of interatomic distances is given in Table 2.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34023 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and thermal parameters of* LaRu$_4$B$_4$ *with the* NdCo$_4$B$_4$ *structure type*

The Debye–Waller factor is defined as exp [$-2\pi^2 \times 10^{-2} \times U(2 \sin \theta/\lambda)^2$]. Space group $P4_2/n$, $\bar{1}$ at 0,0,0. The structural parameters of NdCo$_4$B$_4$ (Kuzma & Bilonizhko, 1978) have been included for comparison. Standard deviations are given in parentheses.

	Equipoint	x	y	z	U (Å^2)
La	2(b)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0.55 (5)
Ru	8(g)	0.6074 (1)	0.1413 (1)	0.1410 (3)	0.20 (4)
B	8(g)	0.543 (2)	0.417 (2)	0.144 (4)	0.6 (3)
Nd	2(b)	0.25	0.25	0.75	–
Co	8(g)	0.607	0.125	0.138	–
B	8(g)	0.525	0.400	0.125	–

Table 2. *Interatomic distances* (Å) *in* LaRu$_4$B$_4$

Ru–Ru	2.705 (2)	B–Ru	=	Ru–B
	4 × 2.772 (2)	B–La		2.99 (2)
	2.906 (2)			2.99 (2)
Ru–La	3.171 (1)			3.52 (2)
	3.225 (1)	B–B		1.83 (2)
	3.729 (1)	La–Ru	=	4 × (Ru–La)
Ru–B	2.13 (2)	La–La	=	2 × 4.012 (1)
	2.14 (2)	La–B	=	4 × (B–La)
	2.16 (2)			
	2.18 (2)			
	2.67 (2)			

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Discussion. Until recently there were only two different structure types known for ternary borides of the formula LnT_4B_4 (T = transition element). One is the $CeCo_4B_4$ type which is primitive tetragonal ($tP18$, c/a ~ 1·4) and occurs with Co (Kuzma & Bilonizhko, 1972) and with Rh (Vandenberg & Matthias, 1977). The other is the $LuRu_4B_4$ type which is body-centred tetragonal ($tI72$, c/a ~ 2) and is mainly observed in combinations with Ru, but also with Rh being partially replaced by Ru (Johnston, 1977). The two structure types are closely related and can be described by an arrangement of transition-metal tetrahedra, isolated rare-earth atoms and pairs of B atoms. In both types the rare-earth atoms and the centres of the T tetrahedra occupy the cation and anion sites, respectively, of a slightly distorted NaCl structure. The main difference between the two structure types concerns the orientation of the T tetrahedra with respect to each other. Interestingly enough neither one of the two structure types occurs with all rare-earth elements of a series containing a given transition element. Within the Co-based series for instance, the $CeCo_4B_4$ structure does not form with big rare-earth atoms, such as La, Pr, Nd, Sm, Eu and Yb (Kuzma & Bilonizhko, 1972). Within the Rh-based series the same structure type does not occur for a similar but more restricted group of Ln elements, *i.e.* for La, Ce, Pr and Yb (Vandenberg & Matthias, 1977). Finally, within the Ru-based series of alloys the $LuRu_4B_4$ structure does not form with the biggest rare-earth atom La, as already pointed out above.

The structure determined for $LaRu_4B_4$ in the present investigation is isotypic with a third structure type (see Table 1) first found for $NdCo_4B_4$ (Kuzma & Bilonizhko, 1978). This structure is again tetragonal and contains 18 atoms per cell ($tP18$, c/a ~ 0·5) with an axial ratio different from that of the $CeCo_4B_4$ type compounds ($tP18$, c/a ~ 1·4). It contains essentially the same building elements as those found in the other two structure types, *i.e.* transition-metal tetrahedra, rare-earth atoms and pairs of B atoms. Contrary to the $CeCo_4B_4$- and $LuRu_4B_4$-type phases, however, the transition-metal tetrahedra here are not isolated from each other but are fused together by sharing edges such that infinite chains are formed along the c direction (see Figs. 1 and 2). With respect to the environment of the rare-earth atoms, this structure type also differs substantially from the other two types. The Ln atoms in the $NdCo_4B_4$-type compounds can be considered to form infinite linear chains along the tetragonal axis, the Ln—Ln distances within the chain being equal to the c parameter of the cell $[d(La—La) = 3·81$ and $4·01$ Å, for $LaCo_4B_4$ and $LaRu_4B_4$, respectively]. In the $CeCo_4B_4$- and $LuRu_4B_4$-type compounds, however, the Ln atoms form a nearly cubic face-centred array and are well separated from one another $[d(Ln—Ln) > 5$ Å]. Thus from a topological point of view the

$NdCo_4B_4$-type structure is quite different from the $CeCo_4B_4$- and $LuRu_4B_4$-type structures. In contrast the latter two are closely related to one another. Fig. 3 shows a so-called 'L versus r^{3+} diagram' (Parthé, 1967), L being the cube root of the volume associated with the formula unit LnT_4B_4, and r^{3+} the effective ionic radius of the trivalent rare-earth atoms (Shannon, 1976). One can see that the Rh- and Ru-based compounds which crystallize with the $CeCo_4B_4$- and $LuRu_4B_4$-type structures, respectively, have practically the same average atomic volume. Since the Rh and Ru atoms are very similar in size, this demonstrates the close structural relationship between these two structure types. The formation of the $NdCo_4B_4$ structure, on the other hand, is associated with a rather strong and discontinuous volume expansion in both the Co- and Ru-based alloys. The switch-over to this less densely packed structure is only observed with big rare-earth atoms and occurs for both of the series of $LnCo_4B_4$ and

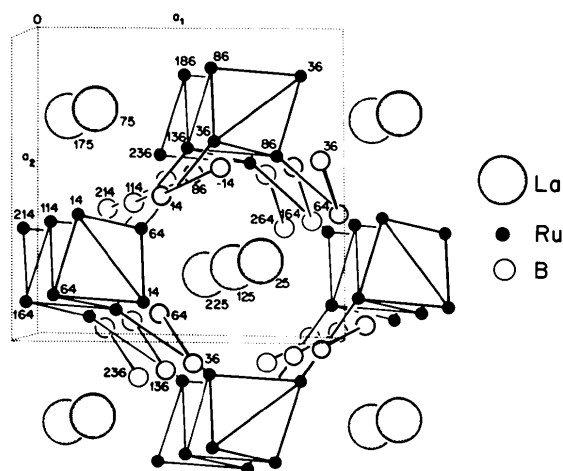Fig. 1. Structure of $LaRu_4B_4$, viewed approximately along the tetragonal axis. The numbers near the atoms indicate their z parameter, multiplied by 100.

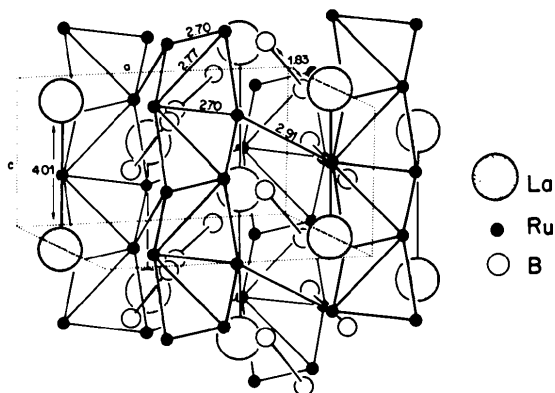Fig. 2. Structure of $LaRu_4B_4$, viewed approximately perpendicular to the tetragonal axis. The numbers indicate the Ru—Ru, La—La and B—B bond lengths.
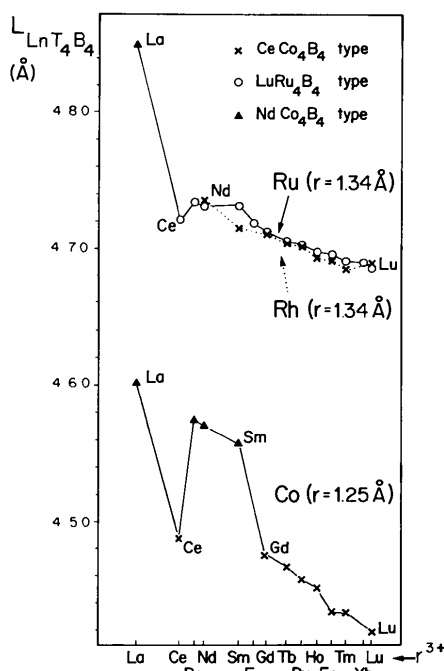
Fig. 3. L versus r^{3+} diagram for the LnT_4B_4 compounds containing Co, Rh and Ru. Full lines and dotted lines join compounds which contain the same transition element.

$LnRu_4B_4$ compounds. Particularly striking is the fact that it takes place with heavier, i.e. smaller, rare-earth atoms in the Co-based alloys than in the Ru-based alloys. Since the Co atoms are smaller than the Ru atoms one can conclude that the occurrence of the $NdCo_4B_4$-type structure depends primarily on geometrical factors such as the radius ratio between the rare-earth and the T atoms, whereas the occurrence and the relative stability of the $CeCo_4B_4^-$ and $LuRu_4B_4^-$ type compounds depends more on electronic factors such as the valence-electron concentration. The influence of the latter parameter can be seen in the Rh-based series of alloys. In fact these compounds normally crystallize with the $CeCo_4B_4$ structure but

form the $LuRu_4B_4$ structure if only 15% of Rh is substituted by Ru (Johnston, 1977). This indicates that the arrangement of the T-atom sublattice in these two structure types depends critically on the number of valence electrons of the T atoms (Rh: 9, Ru: 8 electrons).

To summarize, the present $LaRu_4B_4$ compound is the first known representative of the $NdCo_4B_4$ structure type which does not contain Co. Its structure differs from the other two LnT_4B_4 structure types mainly by the fact that the T-metal atom tetrahedra are fused together and form infinite linear chains. This leads to a pronounced directional character of both the T-metal and rare-earth sublattice and should give rise to rather anisotropic electronic and magnetic properties. On the other hand the occurrence of B atom pairs and T-metal tetrahedra in all three LnT_4B_4 structure types indicates that homonuclear bonding plays a most important role for the stability of this class of borides.

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