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The Crystal Structure of $LaIr_4B_4$, $ThOs_4B_4$, $ThIr_4B_4$ ($NdCo_4B_4$-Type) and URu_4B_4, UOs_4B_4 ($LuRu_4B_4$-Type)*

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The crystal structure of $LaIr_4B_4$ has been refined from single crystal counter data. $LaIr_4B_4$ is tetragonal, $P4_2/n$, $Z = 2$, isotypic with $NdCo_4B_4$, $\sum|\Delta F|/\sum|F_o| = 0.039$ for 312 independent reflections $[|F_o| > 2\sigma(F_o)]$. $ThIr_4B_4$ and $ThOs_4B_4$ also belong to the $NdCo_4B_4$-type structure. URu_4B_4 and UOs_4B_4 were found to crystallize with $LuRu_4B_4$-type structure. The crystal chemistry of $(RE)T_4B_4$-phases is discussed and simple geometric relations are shown to exist between them.

(Keywords: Crystal structure; Rare earth—noble metals—boron; Ternary metal borides)

Die Kristallstruktur von $LaIr_4B_4$, $ThOs_4B_4$, $ThIr_4B_4$ ($NdCo_4B_4$-*Typ*) *und* URu_4B_4, UOs_4B_4 ($LuRu_4B_4$-*Typ*)

Die Kristallstruktur von $LaIr_4B_4$ wurde an einem Einkristall bestimmt: tetragonal, $P4_2/n$, $Z = 2$, isotyp mit $NdCo_4B_4$, $\sum|\Delta F|/\sum|F_o| = 0{,}039$ für 312 unabhängige Reflexe $[|F_o| > 2\sigma(F_o)]$. $ThIr_4B_4$ und UOs_4B_4 gehören ebenfalls dem $NdCo_4B_4$-Typ an. URu_4B_4 und UOs_4B_4 kristallisieren im $LuRu_4B_4$-Typ. Die Kristallchemie der $(RE)T_4B_4$-Phasen wird diskutiert und einfache geometrische Beziehungen werden zwischen ihnen aufgezeigt.

Introduction

In a recent study of *RE* (Rare Earth)—{Os,Ir}—B systems[1], two series of isotypic compounds have been observed: {La,Ce,Pr,Nd,Sm}Os_4B_4 and {Y,La,Ce,Pr,Nd,Sm,Gd,Tb}Ir_4B_4. All compounds were found to crystallize with the $NdCo_4B_4$-type structure, whereas for combinations of smaller *RE* atoms (Y,Gd,Tb,Dy,Er,Ho,Tm,Yb) with osmium and boron a new structure

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* Dedicated to Prof. *B. T. Matthias* in celebration of his 60th birthday.

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type was observed, closely related to $NdCo_4B_4$ but corresponding to an approximate formula $(RE)_{\sim 1.25}Os_4B_4$ (Ref.[2]).

However, only little information could be found from literature about actinide (Th, U)—noble metal—boron systems.

A $CeCo_4B_4$-type structure was reported by *Vandenberg* et. al.[3] for $ThRh_4B_4$ while $ThRu_4B_4$ has been found to crystallize with the recently described crystal structure of $LuRu_4B_4$ (Ref.[4]).

In view of a better understanding of the various decisive influences of size, electrochemical, and energy band factors among $(RE)M_4B_4$-type structures, a study of the alloying behaviour of Th and U in combinations with noble metals and boron was carried out and is the subject of the present work.

Furthermore, single crystal counter data of $LaIr_4B_4$ have been analyzed in terms of precise atomic parameters, exact boron coordination, as well as boron—boron aggregation.

Arc melted alloys La—Ir—B confirmed the existence of $LaIr_4B_4$ (see Ref.[1]), samples however were poorly crystallized. To obtain single crystals, pellets of La(9)Ir(45)B(46) were heated at 1,600 °C for 10 minutes (well above melting) in a recrystallized alumina crucible sealed in a tantalum container. The mixture was then slowly cooled to 1,100 °C over a period of 20 minutes and finally radiation (argon) quenched. The crystal growth procedure was carried out in a purified argon atmosphere at a pressure of 1.1×10^5 Pa.

A small crystal suitable for structure determination was obtained by mechanical fragmentation of the melted button.

Table 1. *Crystallographic data for* $LaIr_4B_4$, $ThOs_4B_4$ *and* $ThIr_4B_4$. *Space group* $P4_2/n$ (C_{4h}^4; No. 86), $Z = 2$, $NdCo_4B_4$-type

$LaIr_4B_4$	$ThIr_4B_4$	$ThOs_4B_4$
$a = 0.76719(4)$ nm	$a = 0.7668(2)$	$a = 0.7579(2)$
$c = 0.39739(2)$ nm	$c = 0.3972(1)$	$c = 0.3999(1)$
$c/a = 0.518$	$c/a = 0.518$	$c/a = 0.528$
$D_x = 13.50$ kg/dm^3	$D_x = 14.84$	$D_x = 14.98$
$\mu(MoK\alpha) = 1{,}176$ cm^{-1}		

Weißenberg photographs of the crystal fragment ($\sim 30 \times 30 \times 50\,\mu m$; axis [001]) proved the crystal to be tetragonal with *Laue*-symmetry $4/m$. The extinctions (hkl) with $h + k \neq 2n$ and $(00l)$ with $l \neq 2n$* indicate $P4_2/n$ (No. 86) as the only possible space group. Lattice parameters and intensities were measured with graphite monochromated Mo-$K\alpha$ radiation on a PW-1100 computer controlled four circle diffractometer (Austrian Natural Science Research Council, Institute of Mineralogy, Technical University Vienna). Cell

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* From automatic diffractometer intensity recordings.

parameters were determined from least squares refinement of $2\,\theta$-values of ~ 30 reflections using the program PARAM (X-ray system[5]). The crystallographic data are given in Tab. 1.

A total number of 758 reflections were recorded to a limit of $\sin\theta/\lambda = 0.066\,\mathrm{nm}^{-1}$. A set of 312 symmetry independent intensities was obtained by averaging ("centered reflections" only). All observed intensities were used in the structure determination. An absorption correction was applied for an idealized spherical crystal ($\mu R = 2.0$; Ref.[6]).

Refinement of the Crystal Structure of $LaIr_4B_4$

Two formula units of $LaIr_4B_4$ were calculated from a comparison of the atomic volumes with the volume of the unit cell (assuming a space filling of 70%). Lattice parameters, composition and crystal symmetry confirm structural identity with the crystal structure of $NdCo_4B_4$ (Ref.[7]). Thus, with 2 La in 2b) and 8 Ir in 8g) the crystal structure refines satisfactorily with the full matrix least squares program CRYLSQ (X-ray system[5]). *Hartree-Fock* scattering factors[8] were used for La, Ir and B and anomalous dispersion correction[9] was considered for La and Ir. Unit weights were attributed to all observed reflections (there is no significant influence of different weighing schemes on the obtained R-value).

A difference *Fourier* map (F_o—$F_{\mathrm{La,Ir}}$; $R = 0.056$) clearly resolved 8 B-atoms in 8 g). Refinement of the occupancy of the La—as well as Ir-positions resulted in a merely insignificant change [$occ(\mathrm{La}) = 0.999$, $occ(\mathrm{Ir}) = 1.001$] with respect to full occupation of these atomic sites (R remained constant). The final R-value $R = \sum|\Delta F|/\sum|F_o|$ calculated with isotropic extinction and anisotropic thermal parameters was 0.039 for 312 observed reflections ($|F_o| > 2\,\sigma$). At this point a difference *Fourier* map was featureless. The final positional parameters and thermal factors are given in Table 2; the comparison of $|F_o|$ and $|F_c|$ in Table 3 and the atomic distances calculated up to a limit of 0.4 nm are shown in Table 4.

Isotypic $ThOs_4B_4$ and $ThIr_4B_4$ ($NdCo_4B_4$-Type)

Powder patterns of these new compounds were indexed completely on the basis of a primitive tetragonal cell (Table 1). Within the limits of error no changes of the lattice parameters were observed from multiphase alloys indicating a very narrow homogeneous range for $ThOs_4B_4$ and $ThIr_4B_4$ respectively. X-ray inspection of the powder diagrams revealed the same characteristic intensity differences as earlier encountered between the osmium and the iridium series of (RE)T_4B_4 compounds (see also Ref.[1]). These differences clearly explain from slightly different atomic parameters as well as from a small change

Table 2. *Atomic and thermal parameters for* $LaIr_4B_4$ ($P4_2/n$, *origin at* $\bar{1}$. Standard deviations are in parentheses. Isotropic temperature factors are expressed as $T = \exp\,[-2\pi^2 10^{-2} U\ (2\sin\theta/\lambda)^2$. Anisotropic thermal factors are of the form: $\exp\,[-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2} + 2\,U_{12} a^* b^* hk + 2\,U_{13} a^* c^* hl + 2\,U_{23} b^* c^* kl) \times 10^{-2}]$

	Site	x	y	z	occ.	U [10^{-2} (nm)^2]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La	2 (b)	1/4	1/4	3/4	1.00	0.89 (7)	U_{11}	1.56 (12)	0	0	0
Ir	8 (g)	0.5937 (1)	0.1397 (1)	0.1441 (2)	1.00	0.89 (4)	0.70 (4)	1.09 (5)	— 0.03	— 0.04	— 0.01
B	8 (g)	0.529 (2)	0.405 (4)	0.142 (6)	1.00	$U_{iso} = 1.7$ (5)					

Table 3. *Observed and calculated structure factors for* $\mathrm{LaIr_4B_4}$. Reading from left to right, the columns contain the value $h,k,l,|F_o|$, and $|F_c|$; L indicates unobserved reflections (less than 2σ)

h k l		$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l		$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l		$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l		$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l		$\lvert F_o\rvert$	$\lvert F_c\rvert$
0 2 0		25.19	24.79	1 10 1		116.73	108.87	10 1 1		148.49	150.90	7 2 2		167.24	176.42	6 5 3		47.82	48.79
0 4 0		232.16	230.23	2 1 1		278.52	278.76	10 2 1	L	9.08	4.07	7 3 2		76.91	80.84	6 6 3		67.88	64.45
0 6 0		123.75	126.88	2 2 1		207.84	208.57	0 0 2		161.01	164.41	7 4 2		37.23	39.09	7 1 3		107.57	111.04
0 8 0		146.88	149.81	2 3 1		171.60	164.87	0 1 2		230.17	230.10	7 5 2		27.55	26.34	7 2 3	L	5.74	6.78
0 10 0		30.02	26.83	2 4 1		108.14	102.68	0 2 2		59.84	58.37	7 6 2		52.07	53.74	7 3 3		56.03	56.72
1 1 0		124.83	118.64	2 5 1		167.92	158.80	0 3 2		232.89	241.24	8 1 2		95.27	101.26	7 4 3		98.54	105.15
1 3 0		313.27	300.02	2 6 1		128.92	119.86	0 4 2		14.80	12.06	8 2 2		19.88	18.05	7 5 3		147.45	148.92
1 5 0		203.63	194.27	2 7 1		35.17	32.82	0 5 2		115.97	118.17	8 3 2		182.89	189.59	8 1 3	L	15.95	14.82
1 7 0		232.63	224.53	2 8 1		56.59	52.57	0 6 2		65.79	66.45	8 4 2		26.57	28.28	8 2 3	L	7.31	6.78
1 9 0	L	8.96	5.46	2 9 1		111.33	104.01	0 7 2		123.17	127.91	8 5 2		109.42	118.44	8 3 3		33.89	30.64
2 2 0		59.46	59.13	2 10 1		23.45	21.36	0 8 2		63.05	63.13	9 1 2		46.45	48.27	0 0 4		192.93	197.28
2 4 0		92.02	89.74	3 1 1		163.82	168.44	0 9 2		23.35	24.23	9 2 2		113.43	119.14	0 1 4		87.89	85.52
2 6 0		179.41	174.92	3 2 1		151.32	154.08	1 1 2		31.15	29.58	9 3 2		60.37	61.00	0 2 4		75.04	70.04
2 8 0		219.88	214.29	3 3 1		44.37	45.16	1 2 2		85.31	84.02	0 1 3		77.07	72.87	0 3 4		97.65	91.04
2 10 0		130.84	120.60	3 4 1		217.24	211.35	1 3 2		135.04	135.03	0 2 3		93.68	90.32	0 4 4		200.66	204.57
3 1 0		171.81	170.27	3 5 1		207.77	196.62	1 4 2		256.02	264.27	0 3 3		84.42	84.14	0 5 4		41.86	38.94
3 3 0		130.14	131.86	3 6 1		220.98	213.53	1 5 2		83.98	84.47	0 4 3		41.31	39.87	0 6 4		15.83	6.28
3 5 0		54.37	52.37	3 7 1	L	8.34	6.55	1 6 2		119.26	123.66	0 5 3		26.90	23.42	0 7 4		47.57	44.69
3 7 0		31.13	28.74	3 8 1		119.56	109.78	1 7 2		21.02	19.39	0 6 3		163.41	164.05	1 1 4		147.20	142.53
3 9 0		61.11	59.43	3 9 1		140.40	130.36	1 8 2		189.34	193.27	0 7 3	L	0.00	7.49	1 2 4		25.30	27.32
4 2 0		261.11	262.33	4 1 1		55.72	53.56	1 9 2		31.77	28.48	0 8 3		79.76	77.25	1 3 4		142.65	141.89
4 4 0		251.23	252.02	4 2 1		22.89	23.82	2 1 2	L	4.84	1.67	1 1 3		160.78	152.39	1 4 4		103.87	102.33
4 6 0		127.65	127.30	4 3 1		68.60	70.33	2 2 2		61.54	61.41	1 2 3		121.13	118.08	1 5 4		46.25	45.14
4 8 0		51.37	48.77	4 4 1		58.39	60.47	2 3 2		99.20	100.00	1 3 3		59.32	56.56	1 6 4		44.31	45.12
5 1 0		56.48	59.21	4 5 1		77.15	76.19	2 4 2		27.42	26.87	1 4 3		43.80	42.96	2 1 4	L	7.06	.38
5 3 0		197.68	203.72	4 6 1		75.38	70.96	2 5 2		49.73	48.02	1 5 3		23.79	23.60	2 2 4		60.33	54.75
5 5 0		104.95	110.32	4 7 1		82.18	73.73	2 6 2		77.40	77.44	1 6 3		46.92	42.77	2 3 4		34.54	33.38
5 7 0		268.22	262.78	4 8 1		113.03	104.53	2 7 2		199.73	195.49	1 7 3	L	8.54	4.15	2 4 4		118.00	118.39
5 9 0		47.77	47.26	4 9 1		183.98	179.07	2 8 2		84.16	78.38	1 8 3		20.09	18.67	2 5 4	L	9.13	14.42
6 2 0		51.98	51.87	5 1 1		164.92	169.15	2 9 2	L	11.51	5.32	2 1 3		72.47	69.53	2 6 4		39.84	39.29
6 4 0		87.26	90.91	5 2 1		174.64	180.00	3 1 2		81.14	85.82	2 2 3		229.00	236.09	3 1 4		22.58	14.34
6 6 0		90.76	91.11	5 3 1		12.72	10.71	3 2 2		108.14	113.36	2 3 3		14.50	9.60	3 2 4		39.05	38.31
6 8 0	L	10.30	7.93	5 4 1		42.17	41.61	3 3 2		20.92	17.93	2 4 3		112.26	114.26	3 3 4		138.07	140.47
7 1 0		125.14	130.76	5 5 1		59.64	62.77	3 4 2		99.72	95.95	2 5 3		129.03	132.50	3 4 4		31.01	31.92
7 3 0		201.41	209.20	5 6 1		25.17	23.88	3 5 2		54.39	50.58	2 6 3		130.21	136.74	3 5 4		37.11	39.09
7 5 0	L	5.52	10.54	5 7 1	L	9.68	2.32	3 6 2	L	11.70	10.95	2 7 3		47.76	46.13	3 6 4	L	6.01	3.90
7 7 0		18.71	15.05	5 8 1		27.37	22.29	3 7 2		42.34	38.63	2 8 3		67.23	62.47	4 1 4	L	13.92	16.12
8 2 0		196.55	206.42	6 1 1		184.95	189.24	3 8 2		31.69	26.64	3 1 3		170.90	185.21	4 2 4		100.64	97.51
8 4 0	L	8.45	7.38	6 2 1		114.60	118.77	3 9 2		40.57	39.39	3 2 3		139.12	138.51	4 3 4		108.58	103.77
8 6 0		210.34	221.25	6 3 1		102.47	106.08	4 1 2		52.32	52.97	3 3 3		50.51	47.72	4 4 4		99.57	94.54
9 1 0		95.13	97.87	6 4 1		145.66	153.90	4 2 2		105.69	110.82	3 4 3		26.77	23.30	4 5 4	L	10.31	5.44
9 3 0		154.87	162.90	6 5 1		213.93	223.98	4 3 2		255.66	265.70	3 5 3		228.52	224.25	5 1 4		41.18	39.11
9 5 0		88.62	93.94	6 6 1		52.97	55.64	4 4 2		99.38	100.01	3 6 3		35.00	37.53	5 2 4		58.01	57.53
10 2 0		88.31	91.31	6 7 1		29.30	25.95	4 5 2	L	8.90	9.67	3 7 3		17.45	9.12	5 3 4		178.78	180.84
0 1 1		45.94	44.92	6 8 1		94.84	87.55	4 6 2	L	8.07	7.12	3 8 3		103.52	95.07	5 4 4		56.09	49.06
0 2 1		89.30	87.66	7 1 1		92.26	96.71	4 7 2		171.44	160.20	4 1 3		53.23	54.81	6 1 4	L	13.51	2.35
0 3 1		12.49	9.22	7 2 1		114.07	119.68	4 8 2		22.54	18.81	4 2 3		26.89	24.39	6 2 4		34.63	35.35
0 4 1		36.49	37.20	7 3 1		45.27	47.61	5 1 2		53.18	54.20	4 3 3		45.56	43.44	6 3 4	L	0.00	9.87
0 5 1		207.19	211.23	7 4 1		119.85	124.09	5 2 2		157.17	163.52	4 4 3		73.11	68.10	0 1 5		57.25	54.84
0 6 1		140.92	143.36	7 5 1		117.85	126.99	5 3 2		14.69	9.37	4 5 3		99.71	93.95	0 2 5	L	10.64	11.02
0 7 1		123.37	124.35	7 6 1	L	7.07	6.06	5 4 2		138.39	143.25	4 6 3		89.36	81.60	0 3 5		80.90	76.98
0 8 1		65.34	64.30	7 7 1		75.09	75.17	5 5 2		60.89	59.75	4 7 3		28.25	24.46	0 4 5	L	0.00	4.29
0 9 1		133.47	131.94	8 1 1		91.07	96.22	5 6 2		202.97	196.68	5 1 3		187.86	191.46	1 1 5		23.68	19.13
0 10 1		121.08	113.48	8 2 1	L	0.00	5.60	5 7 2		100.56	91.07	5 2 3		21.81	10.43	1 2 5		127.27	126.64
1 1 1		137.51	136.92	8 3 1		44.92	46.06	5 8 2		98.42	88.87	5 3 3	L	14.77	13.12	1 3 5	L	13.06	7.77
1 2 1		92.55	92.83	8 4 1		24.33	24.85	6 1 2		14.26	4.81	5 4 3		80.25	78.35	2 1 5		149.18	149.12
1 3 1		56.18	54.45	8 5 1		73.12	78.86	6 2 2		49.19	47.32	5 5 3		76.25	73.04	2 2 5		39.66	34.07
1 4 1		88.35	87.46	8 6 1	L	4.24	3.21	6 3 2		34.90	33.03	5 6 3		53.26	45.38	2 3 5		32.90	33.61
1 5 1		22.92	21.22	9 1 1		106.52	110.04	6 4 2		51.97	52.69	5 7 3	L	8.56	2.57	3 1 5		23.96	25.76
1 6 1		57.78	54.50	9 2 1		16.33	13.98	6 5 2		36.12	35.10	6 1 3		135.76	144.00	3 2 5		155.24	160.08
1 7 1	L	6.73	3.48	9 3 1		62.54	62.99	6 6 2	L	16.50	10.77	6 2 3		130.68	134.82				
1 8 1		88.54	85.68	9 4 1		136.87	142.12	6 7 2		133.26	125.22	6 3 3		20.21	19.71				
1 9 1		69.49	67.24	9 5 1		45.20	49.27	7 1 2		61.70	63.71	6 4 3		170.51	179.30				

Table 4. *Interatomic distances* (≤ 0.4 nm) *in* $\mathrm{LaIr_4B_4}$. The estimated standard deviations are less than 0.2 pm

La—2 La	0.3974	Ir—1 La	0.3249	B—1 La	0.2910
—4 Ir	0.3249	—1 La	0.3181	—1 Ir	0.2171
—4 Ir	0.3181	—4 Ir	0.2874	—1 Ir	0.2152
—4 B	0.2910	—1 Ir	0.2936	—1 Ir	0.2118
		—1 Ir	0.2824	—1 Ir	0.2103
		—1 B	0.2118	—1 B	0.1858
		—1 B	0.2152		
		—1 B	0.2171		
		—1 B	0.2103		

in c/a $[(c/a_{(RE)\mathrm{Os_4B_4}} \approx 0.53;\ c/a_{(RE)\mathrm{Ir_4B_4}} \approx 0.52]$. Thus using the atomic parameters earlier derived for $LaOs_4B_4$ from *Weißenberg* and powder photographs ($x_{\mathrm{Os}} = 0.605$, $y_{\mathrm{Os}} = 0.140$, $z_{\mathrm{Os}} = 0.140$; Ref.[1]) and $LaIr_4B_4$ (Table 2), observed and calculated intensities are in excellent agreement for both the thorium-compounds*. Intensity calculations can be obtained on request.

Table 5. *Crystallographic data for* URu_4B_4 *and* UOs_4B_4. Space group I $4_1/acd$ (D^{20}_{4h}, No. 142), $Z = 8$, $LuRu_4B_4$-type

URu_4B_4	UOs_4B_4
$a = 0.7459(2)$ nm	$a = 0.7512(2)$
$c = 1.4986(3)$ nm	$c = 1.5053(4)$
$c/a = 2.009$	$c/a = 2.004$

URu_4B_4 and UOs_4B_4 with $LuRu_4B_4$-Type Structure

X-ray analysis of the powder diagrams of the new compounds revealed striking similarity with the powder pattern of $ThRu_4B_4$ ($LuRu_4B_4$-type, Ref.[4]). In both cases indexing was complete on the basis of a body centered tetragonal cell (Table 5); a very narrow homogeneity region (1,400 °C) was derived from lattice parameter variation in multiphase alloys, thus confirming a formula $U\{Ru,Os\}_4B_4$. Lattice parameters, c/a-ratio, intensities as well as crystal symmetry prove structural identity with the crystal structure of $LuRu_4B_4$ (Ref.[4]). Using the Ru-parameter as derived by *Johnston*[4], observed and calculated powder intensities compare very well. Boron parameters however were recalculated. For the new derived parameters (see Table 6) boron—boron contacts of 0.176 nm are formed in good accordance with usual boron pair formation (0.175–0.182 nm). Ru—B distances range between 0.215–0.229 nm; U—B distances (0.294–0.317 nm) exceed the radii sum by more than 10% (weak or no interaction).

Discussion

In $NdCo_4B_4$ type phases, tetrahedral VIII-A metal clusters and *RE* atoms form a distorted NaCl-type array boron atoms accomodated within the voids of the metal framework (Fig. 1). Boron—boron

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* Meanwhile the crystal structure of $LaRu_4B_4$ ($NdCo_4B_4$) has been published by *Grüttner* and *Yvon*[13] with practically identical parameters as the ones obtained in Ref.[1].

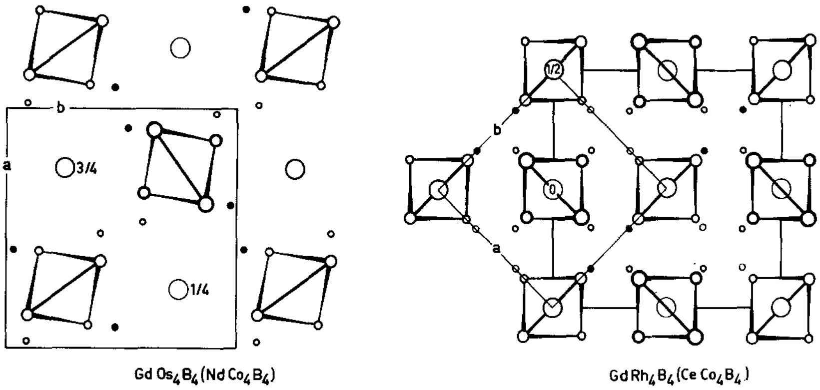
Table 6. *Powder diffraction data for* URu_4B_4 ($LuRu_4B_4$-type). Material: Alloy $U_{11}Ru_{44}B_{45}$, arc melted, 1,400 °C, 12 h. Method: Powder X-ray diffraction in a Siemens Diffractometer, Ni-filtered Cu$K\alpha$-radiation, Si-standard. $I = mF^2(1+\cos^2 2\theta)/\sin^2\theta\cdot\cos\theta$ is normalized to the strongest reflection having intensity 100. Space Group: $I4_1/acd$ (D_{4h}^{20}; No. 142, origin at 1)

8 U in 8b) 0, 1/4, 1/8
32 Ru in 32g) x, y, z ($x = 0.112$, $y = 0.100$, $z = 0.9375$)
32 B in 32g) x, y, z ($x = 0.826$, $y = 0.101$, $z = 0.955$)

	$10^4.\sin^2\theta$		Intensity	
(hkℓ)	obs.	calc.	obs.	calc.
112	319	318	10	14.2
004	420	421	33	13.9
200	426	425		21.2
202	532	531	3	3.8
211	557	558	2.5	3.3
213	768	769	38	41.3
204	847	847	37	29.6
220	850	851		11.8
116	1164	1161	150	45.9
312	1169	1169		100.0
215	1190	1190	26	25.3
224	1270	1272	18	15.4
206	1377	1374	1.5	1.3
321	1408	1409	11	9.4
314	1486	1485	4.5	3.3
323	1620	1620	6	6.0
008	1685	1686	2.5	1.7
400	1700	1702	3	1.9
217	1821	1822	2	1.2
411	1833	1834	4	2.8
316	2014	2012	3	1.5
332		2020		0.9
325	2040	2041	6	3.8
413		2045		0.2
208	2111	2111	27	9.6
404	2124	2123		7.7
420		2127		10.0
422	*	2232	*	0.7
415	*	2466	*	0.2
228	2536	2536	17	6.4
424	2548	2548		10.3
406	*	2650	*	0.0
219	*	2665	*	0.3
327	2673	2673	6	3.3
431	2687	2685		2.0
318	*	2749	*	0.0
11.10	2845	2846	41	10.6
336	2864	2862		12.8
512	2869	2870		15.6
433	*	2896	*	0.0
20.10	*	3059	*	0.3
426	*	3075	*	0.5
417	3100	3098	2	1.4
521	*	3111	*	0.0
514	3185	3187	2.5	1.5
435	*	3317	*	0.0
523	3321	3321	6	5.0
408	3388	3387	33	21.9
440	3403	3403		9.2

* not observed

distances in $LaIr_4B_4$ [0.185 (2) nm] are rather large compared to typical boron pair formation (0.176–0.182 nm). A similar result was earlier[1] obtained from $NdIr_4B_4$-powder diffraction data (0.182 nm). Despite the higher error figures (< 2 pm) for atomic distances of such low electron atoms derived from X-ray analysis, a calculation of the B—B distances (using the well established atomic parameters derived for $LaIr_4B_4$ and $LaOs_4B_4$ respectively) yielded values of ≥ 0.182 nm for all Ir and Os compounds with $NdCo_4B_4$ type[1]. On the other hand a strong VIII-A metal—boron interaction seems to be characteristic: B—T distances on average are shorter by ~5% than the sum of the metal radii. ($R_B = 0.088$, $R_{Ir} = 0.136$, $R_{Os} = 0.135$ nm). Similarly short Co—B distances were also observed from $NdCo_4B_4$ but the smaller radius ratio R_{Co}/R_B still enables short boron—boron contacts (~ 0.174 nm, see Ref.[7]). Boron coordination can be described as a very distorted triangular metal prism La (2) Ir (4). But with two rather large La—Ir distances (0.3669 nm) this coordination figure has to be regarded as a more "open" polyhedron inasfar as for each trigonal prisma corner atom is supposed to have at least three neighbouring corner atoms within bonding distance. A similar distorted, triangular prismatic metal



Gd Os$_4$B$_4$ (Nd Co$_4$B$_4$) Gd Rh$_4$B$_4$ (Ce Co$_4$B$_4$)

Fig. 1. Comparison of the crystal structures of $CeCo_4B_4$ and $NdCo_4B_4$ as seen in projection along [001]. For description of $CeCo_4B_4$ see Fig. 2. Similar principles are retained for description of $NdCo_4B_4$. Size of osmium atoms depending on hight: thin lined figures: $z = 0.144, 0.644$; heavy lined figures: 0.356 and 0.856. Boron atoms in 0.144 and black circles in $z = 0.641$. Boron coordination figures (very distorted trigonal prisms) are shown; distances, that considerably exceed the sum of radii are indicated by dashed lines

coordination figure RE_2T_{4+1} with two rather remote RE atoms, but one additional T-atom is already known from $CeCo_4B_4$- as well as $LuRu_4B_4$-type structures[3, 4]. At present little is known about the factors stabilizing a $(RE)T_4B_4$—compound in one of the mentioned structure types ($CeCo_4B_4$, $LuRu_4B_4$ and $NdCo_4B_4$). Furthermore a new structure type was reported for "$CeRe_4B_4$" by *Kuz'ma*[10]. Isotypic compounds were observed for {Y, La}—Re—B (Ref.[10]) but a complete characterization of its crystal structures is still lacking. As far as the size factor is concerned, the $NdCo_4B_4$-type structure is favoured for high ratios R_{RE}/R_T. The iridium and osmium series are found to be restricted to Tb and Gd respectively as the RE-member with the smallest radius to form a $NdCo_4B_4$-type structure.

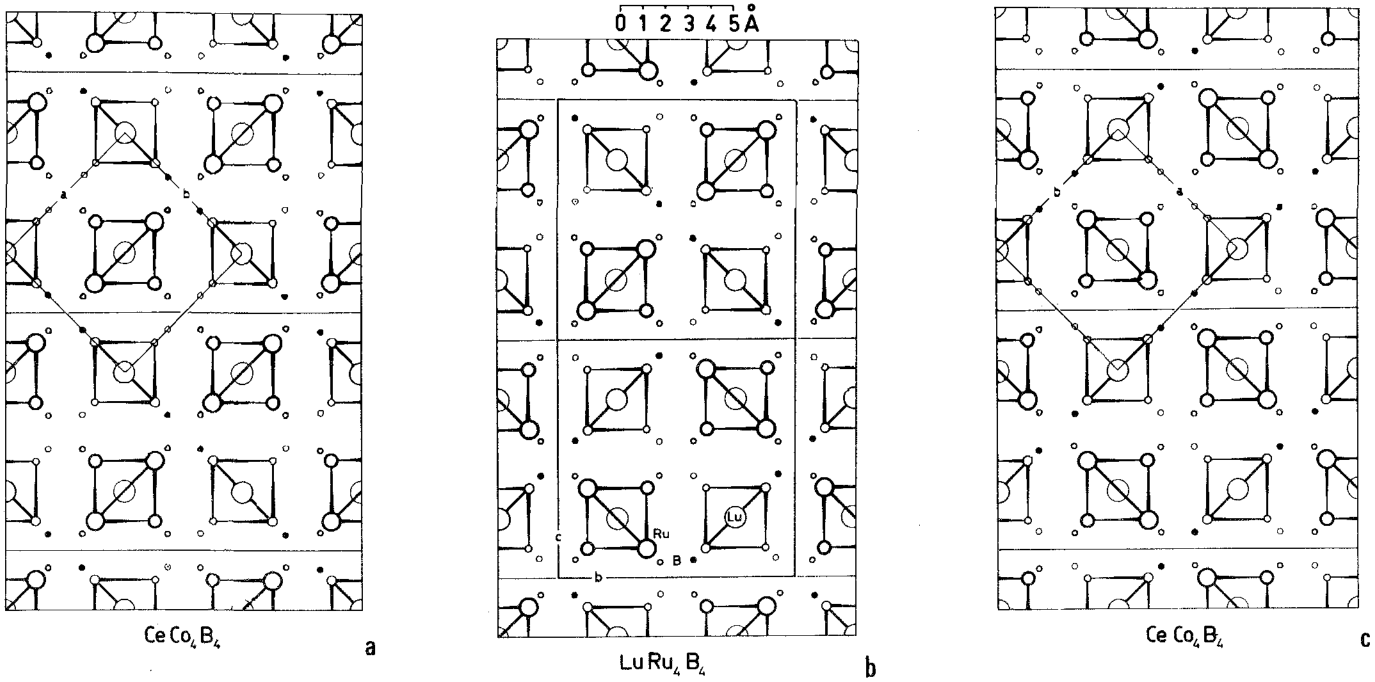


Fig. 2*a*,*b*,*c*. Projection of the crystal structures of $CeCo_4B_4$ (YRh_4B_4) along [001] (Fig. 2*a* and 2*c*), and of $LuRu_4B_4$ along [100] (Fig. 1*b*). Ce and Ru atoms form tetrahedra; thin heavy lined figures are generally displaced by hight of 1/2 perpendicular to plane of projection. Largest circles are *RE* atoms in 0 and 1/2, smallest circles are boron atoms ($z = 0.153$: thin circles, $z = 0.403$; 0.653 medium, black circles $z = 0.847$). Size of Co, Ru atoms depends on hight in projection (—0.137, 0.137, 0.363, 0.637; parameters for Rh in YRh_4B_4)

From the alloy chemistry of binary and ternary actinide—borides a thorium radius is observed comparable to one of the largest *RE* atoms. Thus it is not surprising that $ThIr_4B_4$ and $ThOs_4B_4$ crystallize with $NdCo_4B_4$-type structure. For comparison of lattice parameters and volume see Ref.[1]. Uranium on the other hand is a much smaller atom (to be grouped among smallest *RE* members) and thus from size factor it seems understandable that no $NdCo_4B_4$-type $U(Os,Ir)_4B_4$ compounds are formed. However differences in the electronic structure of almost equally sized noble metal atoms ($R_{Ru} \approx R_{Rh} = 0.134$, $R_{Os} = 0.135$, $R_{Ir} = 0.136$ nm) are strong enough to confine the decisive influence of the size factor within each isotypic series of compounds. URu_4B_4 and UOs_4B_4 are isotypic with the crystal structure of $LuRu_4B_4$ which seems to be favoured for the smaller Rare-Earths. A simple relationship between the crystal structures of $CeCo_4B_4$ and $LuRu_4B_4$ is obvious from Fig. 2. Thus the atomic arrangement of $LuRu_4B_4$ can be constructed by alternating slabs of $CeCo_4B_4$- and its mirrored counterpart (see Fig. 2) along [001] of $LuRu_4B_4$. This close relationship finds its expression in the lattice parameters: [$a(LuRu_4B_4\text{-type}) \approx \sqrt{2}.\ a(CeCo_4B_4)$; $c(LuRu_4B_4) \approx 2\sqrt{2}.\ a(CeCo_4B_4)$]. For the pair $NdCo_4B_4$-type and $CeCo_4B_4$-type (see Fig. 1) a similar relationship of the lattice parameters exists: $a(NdCo_4B_4) \approx \sqrt{2}.\ a(CeCo_4B_4)$; $c(NdCo_4B_4) \approx \frac{c}{2}(CeCo_4B_4)$—however the packing of tetrahedra differs. The rather rigid* three dimensionally linked VIII-metal framework in $NdCo_4B_4$-type phases (octogonal tubes with infinite linear chains of *RE*-atoms) depending on the ratio R_{RE}/R_T seems to be restricted to larger *RE* atoms. Thus for smaller *RE*-atoms the structure has to be adapted toward a higher *RE*/VIII metal ratio in order to maintain bonding within the *RE*-chains. This principle indeed seems to be maintained within the newly found series of *RE*—Os—B compounds (smaller *RE*-atoms Tb → Yb) which might be seen as an example of the so-called "infinite adaptable structures" of which only a few groups have been observed so far[11, 12].

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Single crystal intensity data collection was carried out on the PW-1100 four

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* A measure for the rigidity of the *T*-metal sublattice is found from the slope $\Delta L/\Delta R$ of the linear correlation between lattice parameters (*L*) and radius R^{3+}_{RE} (see also Ref.[1]).

circle diffractometer (Austrian Natural Science Research Council, Proj. Nr. 2178) of the Mineralogical Institute of the Technical University in Vienna. We gratefully acknowledge permission of Prof. Dr. *H. Preisinger* and kindly thank Dr. *H. Völlenkle* for technical assistance.

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