

The Crystal Structure of RuB_2 , OsB_2 and $\text{IrB}_{1.35}$ and Some General Comments on the Crystal Chemistry of Borides in the Composition Range MeB-MeB_3

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The most boron-rich phase in the Ru-B Os-B and Ir-B systems as observed in arc-melted alloys has the approximate composition RuB_2 , OsB_2 and $\text{IrB}_{1.35}$ respectively. The crystal structure of these phases has been determined with X-ray single crystal techniques. The isomorphous phases RuB_2 and OsB_2 have an orthorhombic structure with the probable space-group $Pmmm$. The unit cell axes of RuB_2 are: $a = 4.645 \text{ \AA}$, $b = 2.865 \text{ \AA}$, and $c = 4.045 \text{ \AA}$. Two ruthenium atoms are situated in 2 (*a*) with $z = 0.1508$ while the boron atoms occupy a set of 4 (*f*) positions. The corresponding figures for OsB_2 are: $a = 4.684 \text{ \AA}$, $b = 2.872 \text{ \AA}$, $c = 4.076 \text{ \AA}$ and $z = 0.1535$. $\text{IrB}_{1.35}$ has a monoclinic structure, the dimensions of the unit cell being $a = 10.525 \text{ \AA}$, $b = 2.910 \text{ \AA}$, $c = 6.099 \text{ \AA}$, and $\beta = 91^\circ 4'$. The iridium atoms are situated at two sets of 4(*i*) positions: $x_{\text{I}} = 0.0994$, $z_{\text{I}} = 0.1387$, $x_{\text{II}} = 0.3575$, $z_{\text{II}} = 0.2885$ in space-group $C2/m$. The boron atoms are very probably situated at three or four sets of the same kind of positions.

The relation of the reported structures to those of other boron-rich borides is discussed.

In a previous communication¹ the results of a study of borides with the nominal composition $\text{RuB}_{2.1}$, $\text{OsB}_{2.2}$, and $\text{IrB}_{1.5}$ were given. These results will be more fully presented and discussed in this paper. Chemical analyses have shown that the real compositions are lower in boron than the nominal ones and correspond closely to the formulæ RuB_2 , OsB_2 , and $\text{IrB}_{1.35}$ which have been adopted.

In a recent independent investigation on RuB_2 and OsB_2 Roof and Kempter² have reported results very similar to those obtained at this Institute.

EXPERIMENTAL

Alloys were prepared by arc-melting mixtures of the elements on a water-cooled copper hearth. The following chemicals were used:

Ruthenium, from Heraeus, claimed purity 99.9 %.

Osmium, from Heraeus, claimed purity 99.9 %.

Iridium, from Johnson, Matthey & Co., claimed purity 99.8 %.

Boron, from Borax Consolidated, claimed purity better than 99.0 %.

Powder photographs were taken in a Guinier-type focussing camera using $\text{CuK}\alpha$ -radiation and silicon ($a = 5.4305$) as an internal standard for the determination of the lattice parameters. The latter are determined with an accuracy higher than ± 0.05 %.

Single crystals of suitable size were selected from alloys with the nominal composition RuB_3 , OsB_3 , and IrB_2 . The crystals all of which had an irregular shape were examined in a Weissenberg camera using niobium-filtered MoK -radiation. For the ruthenium and osmium borides only the $h0l$ zone was registered, for the iridium boride the $h0l$, $h1l$ as well as $hk0$ zones were recorded. The multiple film technique with thin iron foil between the films was employed and the exposure time was chosen so as to make a good visual intensity estimation of about 70 per cent of the reflexions with $\sin \theta/\lambda < 1.35$ possible. All computations were made on the digital computers BESK and FACIT EDB in Stockholm with programmes kindly put at the author's disposal by Liminga and by Åsbrink and Brändén. The least squares program is described in Ref.³ The atomic scattering factors were interpolated from tables by Thomas and Umeda⁴ (Ru, Os, Ir) and by Ibers⁵ (boron). The real part of the dispersion correction was taken from the paper by Dauben and Templeton.⁶ In the final stages of refinement, the F_o -values of a few strong low-angle reflexions were replaced by the corresponding F_c -values. No corrections were made for absorption but an isotropic temperature factor was applied.

For the chemical analyses the samples were dissolved in a mixture of HCl and HNO_3 or HCl and HClO_4 at 260–350°C. This operation took place in a thick-walled Pyrex tube and required at least 20 h. The boric acid was separated with an ion exchanger, Dowex-1, (samples of the osmium and iridium borides) or through distillation of methyl borate (samples of the ruthenium boride) and was subsequently titrated with NaOH in the presence of mannitol. The metal was determined gravimetrically as elementary metal after precipitation as hydrated oxide and reduction with hydrogen. The relative accuracy is estimated to ± 0.3 % for the metal analyses and ± 0.5 % for the boron analyses. For the iridium sample with the nominal composition $\text{IrB}_{1.5}$ a considerably lower iridium content (88.6 %) was obtained after the sample had been stored over P_2O_5 for six months. Because of this the iridium content of this sample is somewhat uncertain.

RESULTS

Composition of the phases. The results of the chemical analyses are summarised below:

Nominal comp.	Analysed composition	Phases observed on powder photograph
$\text{RuB}_{2.15}$	82.49 % Ru 17.32 % B = $\text{RuB}_{1.97}$	RuB_2 and $\text{RuB}_{1.5}$ (small amounts)
$\text{OsB}_{2.20}$	90.29 % Os 9.87 % B = $\text{OsB}_{1.92}$	OsB_2 and $\text{OsB}_{1.6}$ (small amounts)
$\text{IrB}_{1.3}$	93.00 % Ir 6.39 % B = $\text{IrB}_{1.23}$	$\text{IrB}_{1.35}$ and more metalrich phases
$\text{IrB}_{1.50}$	91.4 % Ir 7.20 % B = $\text{IrB}_{1.41}$	$\text{IrB}_{1.35}$

These results show that the composition of the ruthenium borides corresponds closely to the "ideal" structural formula, RuB_2 and OsB_2 , derived from the X-ray results by Roof and Kempter² as well as from those reported below. As will be shown later no definite "ideal" structural formula can be derived from the present X-ray results for the iridium boride and this phase will be referred to as $\text{IrB}_{1.35}$ in the following. $\text{IrB}_{1.35}$ is probably only stable at elevated temperatures since it was present only in very small amounts or not at all in samples prepared by sintering mixtures of the elements at 1100°C or 900°C.

Table 1. Powder photograph of an arc-melted alloy with the nominal composition RuB_3 . (CuK α radiation).

hkl	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	I_{obs}	I_{calc}	$p F _{\text{calc}}^2 \times 10^{-2}$
001	0.0362	0.0363	st—	63	25.6
101	0.0641	0.0639	vst	154	124.5
110	0.0999	0.0999	vst	157	209.7
011	0.1087	0.1087	st	62	87.9
200	0.1103	0.1102	st	49	71.3
111	0.1364	0.1363	st	58	101.4
002	0.1454	0.1453	vw	5	9.7
201	0.1465	0.1465	m	37	69.6
102	0.1730	0.1728	st	71	151.8
012 } 211 }	0.2184	0.2177 } 0.2189 }	vst	62 80	160.3 216.3
112	0.2452	0.2452	w	10	27.7
202	0.2555	0.2555	vw	4	11.4
301	0.2843	0.2842	m	32	97.2
020	0.2894	0.2896	w+	25	75.6
310	0.3199	0.3203	m—	28	86.9
021 } 003 } 212 }	0.3277	0.3259 } 0.3269 } 0.3279 }	st+	9 13 53	27.7 39.1 159.8
121 } 103 }	0.3536	0.3535 } 0.3544 }	m	43 3	126.7 7.7
311	0.3569	0.3566	m—	31	90.9
302	0.3932	0.3932	w+	22	68.6
013 } 220 }	0.3998	0.3993 } 0.3998 }	m—	2 30	5.2 79.6
113	0.4269	0.4268	st	64	156.3
022 } 221 } 203 }	0.4365	0.4349 } 0.4361 } 0.4371 }	st	4 33 43	10.8 76.9 99.6
400	0.4406	0.4407	w	20	46.9
122	0.4620	0.4624	st+	81	176.0
312	—	0.4656	—	7	15.7
401	0.4768	0.4770	vw	14	28.9

For none of the phases significant lattice parameter variations have been observed, which indicates that their homogeneity ranges are narrow.

Crystal structure of the phases. The powder photographs of the isomorphous phases RuB_2 and OsB_2 could be indexed with a small orthorhombic unit cell (Tables 1 and 2). From the size of the unit cell it is concluded that it contains two metal atoms.

The only systematic extinctions are observed for $hk0$ reflexions which appear only for $h + k = 2n$. This is characteristic for the two orthorhombic space-groups $Pm\bar{m}n$ and $Pm2_1n$. The arrangement of the metal atoms, located at 2 (*a*) will be similar in either space-group. This also applies to the boron atoms which, as some crude space considerations show, are situated at 4 (*f*), if the space-group is $Pm\bar{m}n$, and at 4 (*b*), if the space-group is $Pm2_1n$. In the more symmetrical space-group all atoms have a fixed *y*-coordinate (1/4 or 3/4) which implies that the intensities of $h0l$ and $h2l$ are the same apart from normal decrease. If the symmetry is lowered there is a free choice of this

Table 2. Powder photograph of an arc-melted alloy with the nominal composition OsB_{2.5} (CuK α radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> _{obs}	<i>I</i> _{calc}	$p F ^2_{\text{calc}} \times 10^{-2}$
001	0.0358	0.0358	st—	191	77.6
101	0.0631	0.0629	vst	463	367.1
110	0.0992	0.0991	vst	423	556.0
011 } 200 }	0.1081	0.1078 } 0.1083 }	vst	204 142	287.6 219.2
111	0.1349	0.1349	m+	168	284.2
002	0.1432	0.1431	vw	18	29.6
201	0.1441	0.1441	m	106	174.2
102	0.1703	0.1702	m+	170	405.6
012 } 211 }	0.2162	0.2152 } 0.2162 }	vst	159 230	408.0 590.3
112	0.2423	0.2423	w+	34	93.0
202	0.2517	0.2515	w	16	43.8
301	0.2797	0.2796	m	88	266.3
020	0.2884	0.2882	m—	66	200.0
310	0.3160	0.3158	m	91	284.3
003	0.3219	0.3219	w	43	133.8
212 } 021 }	0.3239	0.3236 } 0.3240 }	st—	165 28	500.5 86.5
103 } 121 }	0.3515	0.3490 } 0.3511 }	st	5 136	16.3 398.8
311 }		0.3516 }		80	235.0
302	0.3872	0.3869	m	80	221.4
013	—	0.3940	—	4	11.4
220	0.3969	0.3965	m	98	257.3
113	0.4211	0.4211	m+	201	501.8
203 } 022 }	0.4304	0.4304 } 0.4313 }	m+	116 14	284.3 35.3
221 } 400 }	0.4335	0.4323 } 0.4334 }	m+	86 59	204.0 139.8
122 } 312 }	0.4583	0.4584 } 0.4591 }	st—	222 28	494.2 63.2
401	0.4693	0.4692	w+	39	83.5

coordinate. In this investigation no significant differences were found between the intensities of $h0l$ and $h2l$ reflexions and therefore $Pm\bar{m}n$ has been adopted.

After the approximate metal positions had been derived from the intensities of the $00l$ reflexions, the structures were refined with successive $\rho_0(xz)$ and $\rho_0(xz) - \rho_c(xz)$ electron density projections. The results, together with those reported by Roof and Kempter,² are summarised below.

Because of possible systematic errors in the intensities obtained in this study, the accuracy of the atomic coordinates may be somewhat less than is indicated by the standard deviations.

(Because of a misprint in the manuscript the c -axis of OsB₂ was erroneously given as 4.096 Å in the previous communication).¹

The structure of RuB₂ is illustrated in Fig. 1 and interatomic distances are given in Table 3.

The structure of RuB₂ and OsB₂ contain holes (corresponding to 2 (b) with $z = 0.8$) which are large enough to accommodate additional boron atoms. The

Space-group $Pm\bar{m}n$ (nr 59), origin at $\bar{1}$.

2 Me at 2(a)

4 B at 4(f)

	RuB ₂	
This study		Roof and Kempter ²
$a = 4.645 \text{ \AA}$		4.6443 \AA
$b = 2.865 \text{ \AA}$		2.8668 \AA
$c = 4.045 \text{ \AA}$		4.0449 \AA
$z_{\text{Ru}} = 0.1508 \pm 0.0005$		0.1523 ± 0.0006
$x_{\text{B}} = 0.059$		0.063 ± 0.006
$z_{\text{B}} = 0.639$		0.631 ± 0.006
$R = 10.4 \%$ ($h0l$ -reflexions)		
	OsB ₂	
This study		Roof and Kempter ²
$a = 4.684 \text{ \AA}$		4.6832 \AA
$b = 2.872 \text{ \AA}$		2.8717 \AA
$c = 4.076 \text{ \AA}$		4.0761 \AA
$z_{\text{Os}} = 0.1535 \pm 0.0004$		
$x_{\text{B}} = 0.058$		
$z_{\text{B}} = 0.632$		
$R = 11.7 \%$ ($h0l$ -reflexions)		

difference syntheses did not reveal any significant maximum at this position which makes it seem improbable that it is occupied by boron atoms to any larger extent.

The monoclinic symmetry of IrB_{1.35} was established from single crystal Weissenberg photographs about the b - and c -axes. A powder photograph of an alloy with the nominal composition IrB₂ is given in Table 4. From the size of the unit cell it is concluded that it contains eight iridium atoms.

The only systematically absent reflexions are hkl with $h + k = 2n + 1$. This points to the space-groups $C2/m$, Cm and $C2$. No significant differences are observed between intensities of pairs of $hk0$ and $h, k + 2n, 0$ reflexions (apart from normal decrease) and therefore the most symmetrical space-group $C2/m$ has been adopted. All the peaks of the Patterson sections $P(x0z)$ and $P(x\frac{1}{2}z)$ could be satisfactorily accounted for by assuming the iridium atoms to occupy two sets of 4 (i) positions. The final parameters of the iridium atoms were obtained from successive $\rho_o(xz)$ and $\rho_o(xz) - \rho_c(xz)$ electron density projections as well as from least squares refinement. The difference synthesis where the contribution of the iridium atoms had been subtracted contained

Table 3. Interatomic distances in RuB₂ and OsB₂ (in \AA).

Ru—6 Ru	: 2.87(2), 2.99(4)
—8 B	: 2.17(2), 2.20(4), 2.25(2)
B —4 Ru	: 2.17, 2.20(2), 2.25
—3 B	: 1.77, 1.90(2)
Os—6Os	: 2.87(2), 3.02(4)
—8 B	: 2.15(2), 2.22(4), 2.31(2)
B —4Os	: 2.15, 2.22(2), 2.31
—3 B	: 1.80, 1.88(2)

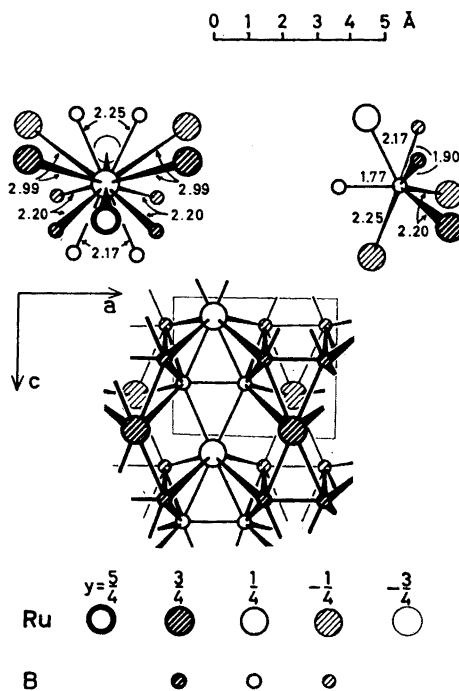


Fig. 1. The crystal structure of RuB_3 .

four positive regions that could correspond to boron atoms located at four sets of 4 (*i*) positions. The atomic coordinates of these positions as obtained after refinement are given below. Since the composition of the phase is $\text{IrB}_{1.35}$, only about 70 % of these possible boron positions are occupied. The experimental results are not accurate enough for any definite conclusions about the distribution of the boron atoms to be drawn, but some indications are given.

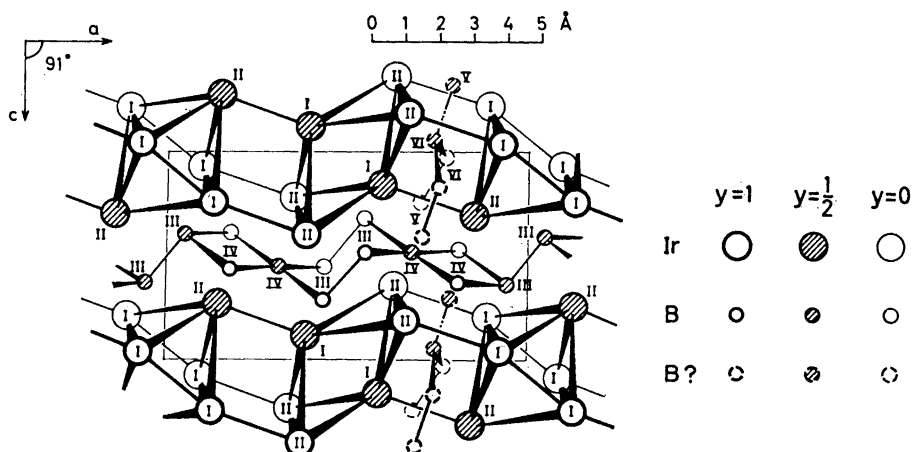


Fig. 2. The crystal structure of $\text{IrB}_{1.35}$.

Table 4. Powder photograph of an arc-melted alloy with the nominal composition IrB₂. CuK α -radiation.

hkl for IrB _{1.35}	$\sin^2\Theta_{\text{obs}}$	$\sin^2\Theta_{\text{calc}}$	I_{obs}	I_{calc}	$p F ^2_{\text{calc}} \times 10^{-3}$ *
001	0.0160	0.0160	w+	60	14.8 (17.8)
200	\sim 0.0214	0.0215	vvw	6	1.8 (0.0)
—	\sim 0.0234	—	vvw	—	—
$\bar{2}01$	—	0.367	—	1.5	0.6 (0.4)
201	0.0383	0.0382	w+	70	30.4 (25.2)
002	0.0640	0.0639	m	171	137.8
110	\sim 0.076	0.0756	vw	3	3.4 (3.2)
202	0.0840	0.0839	m+	240	275.6
400	0.0858	0.0859	st	320	370.2
202	0.0869	0.0869	m	164	193.2
$\bar{1}11$	—	0.0912	—	730	900.4
111	0.0914	0.0919	vst	54	67.2 (53.2)
$\bar{4}01$	0.1004	0.1004	w	32	43.4 (43.6)
401	0.1033	0.1033	m	120	173.2
310	0.1185	0.1185	w+	44	68.4 (73.2)
$\bar{3}11$	0.1335	0.1334	m—	81	137.6
311	0.1357	0.1356	st	290	498.0
$\bar{1}12$	0.1390	0.1388	w+	50	90.0 (91.2)
112	—	0.1402	—	6	10.0 (10.0)
003	—	0.1439	—	3	5.0 (2.8)
$\bar{4}02$	0.1467	0.1469	m	99	187.2
402	0.1528	0.1527	w—	18	34.6 (34.0)
$\bar{2}03$	\sim 0.163	0.1631	w—	39	78.8 (69.8)
203	0.1673	0.1675	m+	133	277.6
$\bar{3}12$	—	0.1802	—	0	0.0 (0.4)
312	0.1847	0.1846	st—	215	489.2
600	—	0.1932	—	2	3.8 (6.8)
510	0.2046	0.2044	w	41	103.6
$\bar{6}01$	—	0.2070	—	4	11.0 (10.6)
601	0.2114	0.2114	w+	41	106.2
$\bar{1}13$	—	0.2183	—	147	388.0
$\bar{5}11$	—	0.2185	—	205	543.2
113	0.2185	0.2205	st	54	142.0

* The $p|F|^2$ values have been calculated for complete occupation of the positions I—IV. Within parentheses are given some values for complete occupation of the positions I—VI.

Firstly, the peaks III and IV are higher than V and VI. Secondly, if all the positions III—VI are assumed to be completely occupied by boron atoms, the value of the temperature factor constant B is reasonable for atoms at the positions III and IV but seems improbably high for atoms at V and VI. These two observations indicate that boron atoms completely occupy the positions III and IV while the additional boron atoms of the unit cell are accommodated at a fraction of one or both of the positions V and VI. This tentatively suggested arrangement of boron atoms is further supported if distances to neighbouring atoms are considered (Table 5). Boron atoms at III and IV will have contacts of normal length while the occurrence of boron atoms at V or VI would imply that there are some very short Ir—B distances in the structure. This is particularly so for the position V and, therefore, one would guess that the boron atoms not located at III and IV mainly occupy position VI.

The final results for the structure of IrB_{1.35} are as follows:

Space-group: *C2/m* (No. 12).

8 Me in $2 \times 4(i)$ (positions I and II).

8 B in $2 \times 4(i)$ (positions III and IV).

ca. 3 additional B atoms distributed over both of the $4(i)$ positions V and VI.

$$a = 10.525 \text{ \AA}, \quad b = 2.910 \text{ \AA}, \quad c = 6.099 \text{ \AA}, \quad \beta = 91^\circ 4'.$$

		<i>B</i> (Å ²)
$x_I = 0.0993_6 \pm 0.00010$	$z_I = 0.1387_4 \pm 0.00016$	0.20
$x_{II} = 0.3574_9 \pm 0.00010$	$z_{II} = 0.2885_4 \pm 0.00016$	0.20
$x_{III} = 0.555 (\pm 0.004)$	$z_{III} = 0.388 (\pm 0.006)$	0.4
$x_{IV} = 0.183 \quad \gg$	$z_{IV} = 0.468 \quad \gg$	0.5
$x_V = 0.730 (\pm 0.02)$	$z_V = 0.320 (\pm 0.02)$	2.4
$x_{VI} = 0.745 \quad \gg$	$z_{VI} = 0.063 \quad \gg$	2.9
$R = 9.5 \%$, $h0l$ and $h1l$ reflexions.		

These values were obtained from the least squares refinement when the positions III—VI were assumed to be completely occupied by boron atoms. The atomic coordinates are insignificantly different from those obtained from refinement of the electron density projection and reported in the previous communication.¹

The structure is illustrated in Fig. 2. It can be described as built up of double layers of metal atoms and puckered layers of boron atoms. The layers alternate and are stacked in the *c*-direction. There are no close contacts ($< 3.8 \text{ \AA}$) between metal atoms in different layers. Interatomic distances are collected in Table 5 and Fig. 3.

Table 5. Interatomic distances in IrB_{1.35} (in Å).* (Me—Me $< 3.8 \text{ \AA}$, Me—B $< 3.5 \text{ \AA}$, B—B $< 2.6 \text{ \AA}$).

Ir _I —Ir _I : 2.66, 2.91(2)	
—Ir _{II} : 2.85, 3.03(2), 3.09(2)	
—B _{III} : 2.16(2)	
—B _{IV} : 2.18	
(—B _V (?) : 2.27(2)	
—B _{VI} (?) : 2.07, 2.17(2))	
Ir _{II} —Ir _I : 2.85, 3.03(2), 3.09(2)	
—Ir _{II} : 2.91(2)	
—B _{III} : 2.15, 2.16	
—B _{IV} : 2.13(2), 2.16	
(—B _V (?) : 1.99(2), 2.58)	
—B _{VI} (?) : 2.31(2), 2.38)	
B _{III} —Ir _I : 2.16(2)	B _V (?)—Ir _I : 2.27(2)
—Ir _{II} : 2.15, 2.16	—Ir _{II} : 1.99(2), 2.58
—B _{III} : 1.81	—B _{III} : 1.90
—B _{IV} : 2.04(2)	—B _{IV} : 1.57, 1.79(2)
(—B _V (?) : 1.90	—B _V : —
—B _{VI} (?) : —)	—B _{VI} : 1.58
B _{IV} —Ir _I : 2.18	B _{VI} (?)—Ir _I : 2.07, 2.17(2)
—Ir _{II} : 2.13(2), 2.16	—Ir _{II} : 2.31(2), 2.38
—B _{III} : 2.04(2)	—B _{III} : —
—B _{IV} : 2.06(2)	—B _{IV} : —
(—B _V (?) : 1.57, 1.79(2))	—B _V : 1.58
—B _{VI} (?) : —)	—B _{VI} : 1.65(2)

* The positions V and VI are not completely occupied by boron atoms (see text).

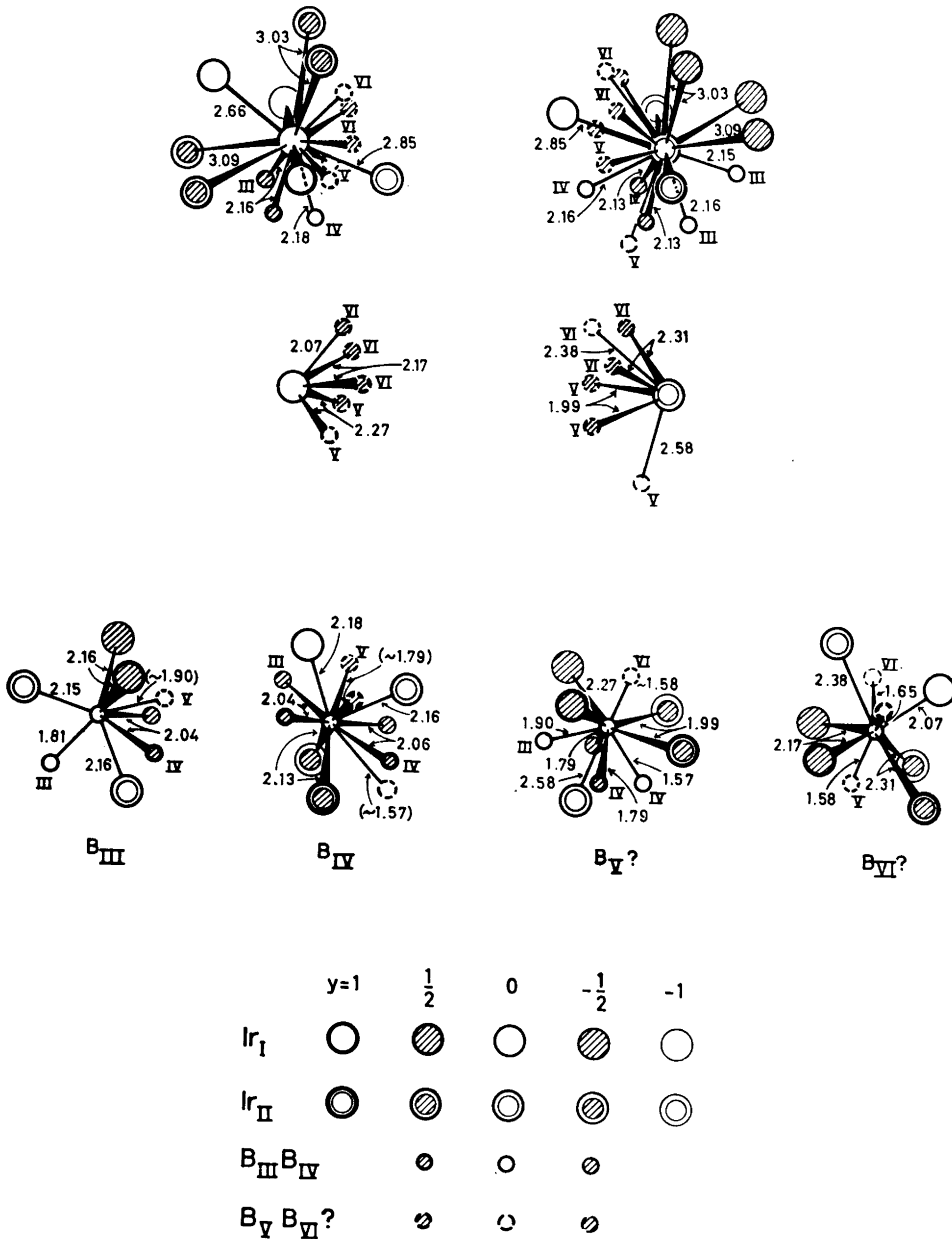


Fig. 3. Interatomic distances in IrB_{1.35}.

SOME COMMENTS ON THE CRYSTAL CHEMISTRY OF BORIDES CONTAINING 50–75 ATOMIC % BORON

The results presented in this paper have filled some gaps in our knowledge about non-metal-rich intermediate phases in systems of boron with the later group transition metals. It seems appropriate, at this stage, to summarise the available structural results on these phases and to give some general comments on their crystal chemistry.

As pointed out by Kiessling,⁷ several of the structures occurring among boron-rich borides of the later transition group metals are closely related and conveniently described as being built up of alternating layers of metal and boron atoms. These plane or slightly puckered layers are perpendicular to the unique (hexagonal or trigonal) axis of the various structure types. It is important to note that while the existence of closepacked metal layers is certainly established from the experimental results, this is generally not so with the boron layers. In deriving the latter it has been assumed that the space-group is characterised by the highest symmetry compatible with the metal arrangement and that the boron atoms completely occupy all positions in this space-group that do not imply the formation of unreasonably short interatomic distances. By this procedure one arrives at the boron layers *H* and *K* shown in Fig. 4. (This notation was suggested by Kiessling.⁷) As yet, there is no definite evidence that a space-group with a symmetry lower than that displayed by the metal arrangement alone should be chosen. However, there is definite experimental evidence to show that some of the phases, in which the layers of Fig. 4 have been believed to occur, have a boron content lower than

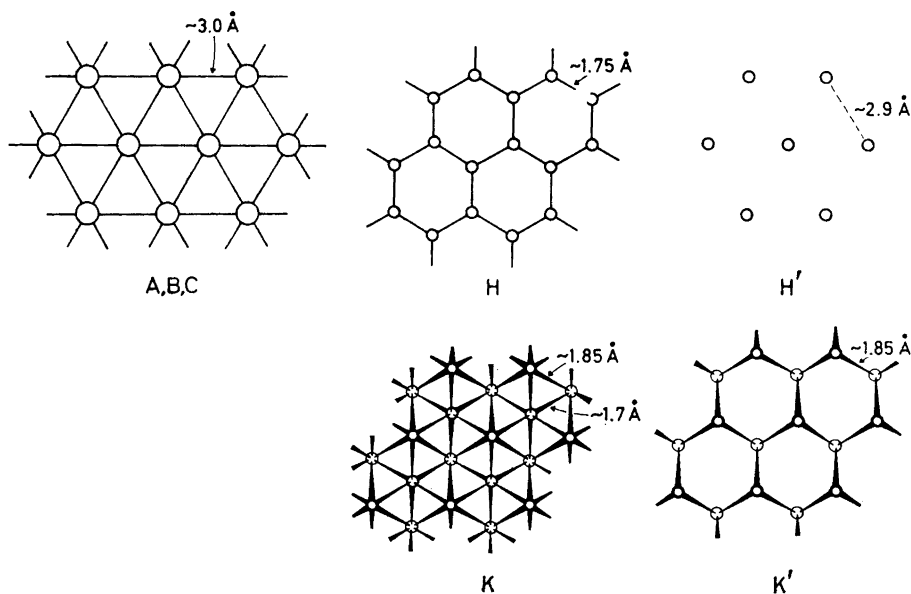


Fig. 4. Metal (*A, B, C*) and boron (*H, H', K, K'*) layers present in some boron-rich borides.

that expected for structures containing only completely occupied boron layers of the H and K types. The following question then arises: Are the boron atoms distributed statistically or in an ordered way over the possible positions? If the latter is the case, a more correct description of the boron arrangement may be achieved using the layers H' and K' rather than layers of the H and K types. Except for structures with the same metal skeleton as AlB_2 , the symmetry will remain the same whether the boron atoms form an H or an H' layer or whether they form a K or K' layer. If the H layer in the AlB_2 structure is replaced by an ordered H' layer stacked as in WC ⁸ the symmetry is lowered from $P6/mmm$ to $P6m2$.

Four different stacking sequences of close-packed metal layers (their orientation being denoted in the usual way) have been found in the borides under discussion and the corresponding "ideal" complete structures and their composition are given in Table 6. The last column contains known binary phases in which the mentioned arrangement of metal atoms has been established.

The approximate composition of $RuB_{1.1}$, $OsB_{1.2}$, $RuB_{1.5}$ and $OsB_{1.6}$ may be taken to indicate that these phases contain H' layers of boron atoms rather than H layers. A thorough study of these phases should be interesting. Me_2B_5 has since long been accepted as the "ideal formula" of the most boron-rich molybdenum and tungsten borides, and therefore it seemed natural⁹ to assign the analogously derived structural formula ReB_3 to the related rhenium boride. LaPlaca and Post¹⁰ have shown, however, that this latter phase, at least as

Table 6. Stacking sequences of layers illustrated in Fig. 4.

Stacking sequence of metal layers	Complete stacking sequence	"Ideal composition"	Known representatives among borides	Ref.
$AA\dots$	$AHAH\dots$ $AH'AH'\dots$	MeX_2 MeX	Appr. comp. * $RuB_{1.1}$ $OsB_{1.2}$	1
$ABAB\dots$	$AKBK\dots$ $AK'BK'\dots$	MeX_3 MeX_2	ReB_2	10
$AABB\dots$	$AHAKBHBK\dots$ $AHAK'BHBK'\dots$ $AH'AK BH'BK'\dots$ $AH'AK'BH'BK'\dots$	Me_2X_5 MeX_2 MeX_2 MeX_2	WB_2 ("W ₂ B ₅ ")	7,11
$AABBCC$	$AHAKBHBKCHCK\dots$ $AHAK'BHBK'CHCK'\dots$ etc.	Me_2X_3 Me_2X_5 MeX_2	$RuB_{1.5}$ $OsB_{1.6}$ $MoB_{2.3}$ ("Mo ₂ B ₅ ")	1 7

* TiB_2 , ZrB_2 , HfB_2 , UB_2 , NbB_2 , TaB_2 , CrB_2 , MoB_2 (stable at high temp. only), WB_2 (stable at high temp. only), MnB_2 have been reported to possess the AlB_2 -structure. For references see recent review article¹².

Note. In the table only such "ideal" structures are considered which fulfill the requirements that the symmetry and the unit cell dimensions are the same as those displayed by metal lattice alone. In addition, structures with H' layers between two metal layers with different orientation, are not included in the table. In structures of this type, e.g. the anti-NiAs structure $AH'BH'\dots$, there are close contacts between atoms in the two metal layers surrounding a H' layer, whereas in the structures of the Table the distance between atoms in metal layers with different orientation is about 4 Å or more.

present in a sintered 1:2 rhenium-boron sample, contains boron layers of the K' type and that consequently ReB_2 is a more appropriate formula for this phase. (In their discussion, in which these authors have kindly also repeated what the present author has published previously,⁹ they have preserved the earlier suggested notation $AKBK\dots$ for describing the rhenium boride structure. Since this notation is not consistent with their accurate X-ray results it seems inappropriate, however.) The results of a recent investigation of " W_2B_5 ", the homogeneity range of which is reported⁷ to extend from 66.7 to 68.0 atomic % boron (at 1200°C?) strongly indicate that the puckered boron layer in this phase is also best described as a K' layer.¹¹ According to Kiessling⁷ the composition of " Mo_2B_5 " is about $\text{MoB}_{2.3}$ and this gives no hint as to whether the boron arrangement in the puckered layers more closely corresponds to a K or a K' type.

Thus, the recently obtained results have shown that a structural description of the phases in Table 6, using H and K type layers only, is misleading. At present it seems very questionable if completely occupied K layers exist at all, and it would indeed be surprising if they did, since the environment of a boron

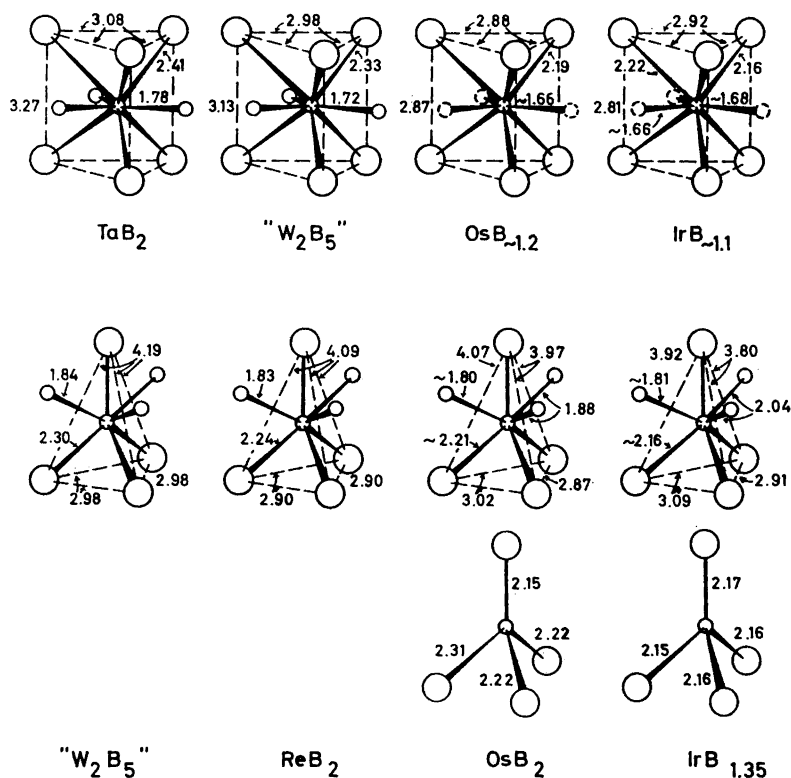


Fig. 5. Interatomic distances in boron-rich borides of tantalum, tungsten, rhenium, osmium and iridium.

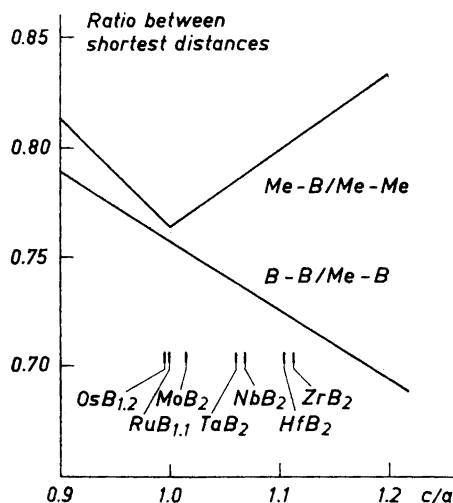


Fig. 6. The ratio between shortest distances in the AlB_2 -structure as function of c/a .

atom in such a layer would be a conspicuous exception to the general observation that boron atoms never have more than five boron neighbours within a distance less than 1.8 Å. The results of future thorough investigations will show whether the phases in Table 6 generally display only a narrow range of homogeneity and have atomic arrangement closely corresponding to the given idealised structures or whether they are characterised by a varying and more disordered arrangement of metal and boron atoms.

The structures of RuB_2 , OsB_2 and $IrB_{1.1}$ ($ThSi_2$ -type) are closely related to those discussed above but do not lend themselves to the same convenient description. The near environment of the boron atoms is very similar in RuB_2 , ReB_2 and " W_2B_5 " (the B_{IV} atom), and the same applies to $IrB_{1.1}$ and the AlB_2 -type borides, (see Fig. 5). However, in RuB_2 and in phases with the $ThSi_2$ -type structure neighbouring non-metals atoms do not form layers but are interconnected to a three-dimensional skeleton. The arrangements of the closest neighbours around the boron atoms in the complicated structure of $IrB_{1.35}$ are similar to those found in the more simple phases discussed in this paper.

The near environment of the boron atom in TaB_2 , " W_2B_5 ", ReB_2 , $OsB_{1.2}$, OsB_2 , $IrB_{1.1}$, and $IrB_{1.35}$ is illustrated in Fig. 5. As seen, the interatomic distances display some definite trends. The boron-metal contacts decrease in comparison with the radius sum as the atomic number of the metal increases. Simultaneously the boron-boron contacts become longer. This trend towards forming shorter contacts between unlike atoms and longer contacts between like atoms as the group number of the metal increases is quite general among borides, being clearly displayed also in more metal-rich phases as well as in borides of transition metals of the other long periods.¹² Associated with this trend is the appearance of different coordination numbers of boron, the smaller the ratio between the Me—B distances and the Me—Me distances, the more

favourable becomes the pyramidal or distorted octahedral arrangement of metal about the boron atoms. This arrangement gradually replaces the triangular prismatic boron environment as the atomic number of the metal increases. In the tungsten and iridium borides the average Me—B distance decreases by 0.03 Å as the coordination number drops from 6 to 4.

The observations about trends in interatomic distances (which at present cannot be given a satisfactory explanation in terms of fundamental electronic interactions) may be useful in attempts to systematise crystal chemical features of the borides. The occurrence of the various structure types, in particular those with high symmetry, can be regarded as largely depending on whether or not the requirements on the interatomic distances, imposed if the mentioned trends are to be followed, can be fulfilled. In the hexagonal AlB_2 -structure, for instance, where all atoms are situated in special positions, the ratio between any pair of distances is fixed when c/a is fixed (Fig. 6). Apparently the AlB_2 -type atomic arrangement is favourable for HfB_2 and TaB_2 , which are very stable phases. As is easily seen from Fig. 6, it becomes increasingly difficult to meet the simultaneous requirement of shorter Me—B and longer Me—Me and B—B distances, expected to arise as the atomic number of the metal increases, while retaining this structure. The ratio between the shortest Me—B and Me—Me distances is 0.72 in PtB, and the fact that this low value cannot be obtained in an AlB_2 -type arrangement could explain the non-existence of phase PtB_2 with this structure. It is also easily realised that in osmium and iridium borides with the AlB_2 , $ThSi_2$ and " W_2B_5 "-structures there would be considerably shorter boron-boron contacts than in the phases OsB_2 and $IrB_{1.35}$ described in previous sections. However, if the boron arrangement is made less dense, for instance by replacing H -type boron layers with H' -type layers, no such short distances between boron atoms would be obtained. The reluctance towards forming close boron-boron contacts may explain the fact that in $RuB_{1.1}$, $OsB_{1.2}$ (AlB_2 - or WC-structure) $RuB_{1.5}$, $OsB_{1.6}$ (" W_2B_5 "-structure) and $IrB_{1.1}$ ($ThSi_2$ -structure) the boron content is much lower than in borides of the earlier transition metals with the same metal skeleton. In the same way, some explanation is obtained for the suggested boron distribution in $IrB_{1.35}$. If the positions V and VI were completely occupied by non-metal atoms some very short boron-boron distances would be formed. If these positions are occupied to less than 50 % such close contacts between boron atoms would be entirely avoided.

Thus, on basis of the empirical assumption that the interatomic distances in any particular boride must be in general accordance with the observed trends, it is possible to give some explanation to the occurrence and composition of phases with a particular structure type. It should be emphasised again that the experimental results on which this discussion has been based are rather uncertain, particularly as regards the homogeneity ranges of the phases and the precise arrangement of boron atoms. Some modifications of the arguments advanced in the last paragraph are likely to be required when more accurate results accumulate, but it is thought that the general approach to the problem of systematising these results as given in this paper may still be useful.

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