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New Complex Borides with ReB_2- and Mo_2IrB_2-Type Structure*

P. ROGL AND E. RUDY

Oregon Graduate Center for Study and Research, 19500 NW Walker Rd., Beaverton, Oregon 97005

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The compound $V_{0.4}Os_{0.6}B_2$ was found to crystallize with ReB_2-type structure. V_2OsB_2, Mo_2OsB_2, and W_2OsB_2 are isotypic with the crystal structure of Mo_2IrB_2. The crystal chemistry of complex borides with ReB_2- and Mo_2IrB_2-type structure is discussed.

Introduction

In recent investigations of ternary boride systems of the type transition metal–noble metal–boron, a variety of new ternary compounds was observed, crystallizing with $Cr_{23}C_6$-, Fe_3C-, FeB-, CrB-, Ta_3B_4-, and ReB_2-type structures (*1*). New structure types of IrB_{1-x} (high and low), Mo_2IrB_2, and W_2IrB_{6-x} were determined by single-crystal techniques (*2*, *3*). A series of isotypic compounds having the Mo_2IrB_2-type structure were characterized (*4*), and recent superconducting property studies of these compounds (*5*) revealed critical temperatures ~3°K.

Up to now relatively few compounds with osmium metal have been prepared and characterized; therefore a closer inspection of the ternary systems {V, Cr, Mo, W}–Os–B was the subject of the present work.

Experimental

The samples were prepared in two stages. Pellets weighing 0.5–1 g were compacted from powders of the elements[1] (in steel dies without the use of binders or lubricants). The pellets were presintered under vacuum on a boron-nitride substrate (5.10^{-6} Torr, 1400°C, 12 hr). The presintered pellets were then arc melted on a water-cooled copper hearth under a purified He atmosphere. A low current input to the electrode (nonconsumable tungsten electrode) was used to effect gradual heating and negligible spattering. The buttons obtained were crushed and powdered to a grain size <20 μm, compacted again into pellets, and subjected to a final heat treatment for homogenization (1250°C, 24 hr; or 1400°C, 22 hr; or 1650°C, 12 hr; BN substrate, 5.10^{-6} Torr).

Alloys containing chromium were not arc melted, but prepared by repeated sintering under He atmosphere (1400°C for 22 hr). In almost all cases X-ray powder diffraction inspection proved the described preparation technique to be sufficient in obtaining homogeneous samples with sharp Debye–Scherrer patterns.

Lattice parameters of the different compounds were obtained from Debye–Scherrer photographs (filtered Cu*Kα* and Cr*Kα* radiation).

The Compound $V_{0.4}Os_{0.6}B_2$ with ReB_2-Type Structure

X-ray powder diffraction inspection of V–Os–B alloys with a boron concentration of 65–75 at.% B showed the existence of a new compound. This new phase is easily obtained

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* Dedicated to Prof. Dr. H. Nowotny on the occasion of his 65th birthday.

[1] Minimum purity 99.9%.

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with sharp powder patterns from arc melted samples as well as in pellets sintered at temperatures $\geqslant$1600°C. Homogeneous samples were prepared with a nominal composition (in at.%) V(13)Os(20)B(67). The new phase was not observed in sinteralloys (not arc melted, but heat treated at 1250°C, 24 hr) because reaction kinetics are very slow at temperatures below 1400°C and equilibrium was not obtained. However, X-ray powder diffraction and metallographic inspection of samples, arc melted and heat treated at 1250°C, 72 hr, proved the new compound to be stable also at lower temperatures ($\geqslant$1250°C).

Powder patterns of the new phase could be indexed completely with a hexagonal unit cell (a = 2.900 Å, c = 7.333 Å, Table I). No significant change of the lattice parameters was observed in two- and three-phase alloys, therefore the new phase probably has a very narrow homogeneity region, (1600°C) and can be represented by a formula $V_{0.4}Os_{0.6}B_2$.

Composition, lattice parameters as well as intensities indicate structural analogy with the ReB_2-type structure. Assuming statistical occupation of the Re sites in ReB_2 by osmium and vanadium atoms ($P6_3/mmc$, 0.8 V + 1.2 Os in $2c$, 4B in $4f$, z = 0.55) calculated and observed Debye–Scherrer intensities are in excellent agreement (Table II). The possibility of ordering among the metal atoms is supported by the fact that the observed metal ratio[2] $T/T^{VIII} \approx \frac{1}{2}$. However the intensity calculation for an ordered arrangement of the metal atoms according to a model earlier discussed (*6*) for $W_{0.3}Ru_{0.7}B_2$[3] is not compatible with the intensities observed.

The Compounds $\{V, Mo, W\}_2OsB_2$ with Mo_2IrB_2-Type Structure

Within the V–Os–B system a second new phase was observed in Debye–Scherrer photographs of alloys with ~40 at.% boron. Single-phase alloys (arc melted, 1600°C, 12 hr) were obtained from samples with a nominal composition (in at.%) V(40)Os(20)B(40). Similarly from Mo–Os–B and W–Os–B alloy samples

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[2] $T(T^{VIII})$ means transition metal (of group VIII in P.Ch.).

[3] $a' = a\sqrt{3}$, $c' = c$; 2 Os in $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$, $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$ and 4 Ru in $\frac{1}{3}\,0\,0$, $0\,\frac{1}{3}\,0$, $-\frac{1}{3}\,-\frac{1}{3}\,0$, $0\,0\,\frac{1}{2}$, $P\bar{6}2m$.

TABLE I

LATTICE PARAMETERS[a] AND RADII AND ELECTRON/ATOM RATIOS FOR BORIDES WITH ReB_2-TYPE STRUCTURE

Phase	a (Å)	c (Å)	c/a	$\bar{R}_T/R_B$[b]	e/a
$Mo_{0.3}Ru_{0.7}B_2$ (*6*)	2.90_1	7.39_5	2.55_0	1.55	4.4
$W_{0.3}Ru_{0.7}B_2$ (*6*)	2.90_6	7.45_2	2.56_5	1.54	4.4
$V_{0.4}Os_{0.6}B_2$	2.90_0	7.33_3	2.52_9	1.53	4.3
$Mo_{0.3}Os_{0.7}B_2$ (*6*)	$2{,}91_0$	7.44_2	2.55_7	1.55	4.4
$Wo_{0.3}Os_{0.7}B_2$ (*6*)	2.91_1	7.49_7	2.57_5	1.55	4.4
$Mo_{0.6}Ir_{0.4}B_2$[c]	2.92_8	7.48_8	2.55_7	1.56	4.4
$W_{0.56}Ir_{0.44}B_2$ (*6*)	2.92_6	7.55_9	2.58_3	1.57	4.4
ReB_2 (*8*)	2.90_0	7.47_8	2.57_9	1.55	4.3
TcB_2 (*9*)	2.89_2	7.45_3	2.57_8	1.55	4.3

[a] Lattice parameters were evaluated by a least-squares-fit-extrapolation method and in average are accurate to ±0.002 Å.

[b] Metallic radii R_T(CN12) were taken from Dickinson (*10*); $\bar{R}_T$ = weighted average of contributing metal atoms; R_B = 0.88 Å.

[c] Composition of homogeneous compound by a reinvestigation (P. Rogl, unpublished) of the phase equilibria within Mo–Ir–B at 1200°C. Composition given in Ref. (*6*) was nominal composition of a two-phase sample (1200°C) containing $IrB_{1.35}$.

TABLE II

POWDER DIFFRACTION DATA FOR $V_{0.4}Os_{0.6}B_2$; FILTERED Cu-Kα RADIATION

	$\sin^2\theta \cdot 10^4$			
$(h\ k\ i\ l)$	obs	calc	I_{obs}	I_{calc}
$(0\,0\,0\,2)$	441	442	*s*	59
$(1\,0\,\bar{1}\,0)$	937	942	*w*	27
$(1\,0\,\bar{1}\,1)$	1058	1053	*vs*	100
$(1\,0\,\bar{1}\,2)$	1383	1384	w^-	19
$(0\,0\,\bar{0}\,4)$	1771	1768	*vw*	12
$(1\,0\,\bar{1}\,3)$	1937	1937	*s*	51
$(1\,0\,\bar{1}\,4)$	2718	2710	vw^-	9
$(1\,1\,\bar{2}\,0)$	2832	2826	w^-	19
$(1\,1\,\bar{2}\,2)$	3274	3269	w^-	20
$(1\,0\,\bar{1}\,5)$	3711	3705	*vw*	12
$(2\,0\,\bar{2}\,0)$	3766	3769	*vvw*	3
$(2\,0\,\bar{2}\,1)$	3885	3879	*vw*	13
$(0\,0\,0\,6)$	3988	3979	*vvw*	3
$(2\,0\,\bar{2}\,2)$	4211	4211	*vvw*	3
$(1\,1\,\bar{2}\,4)$	4600	4595	w^-	16
$(2\,0\,\bar{2}\,3)$	4758	4763	*vw*	12
$(1\,0\,\bar{1}\,6)$	4925	4921	*vvw*	3
$(2\,0\,\bar{2}\,4)$	5535	5537	*vvw*	3
$(1\,0\,\bar{1}\,7)$	6361	6357	vw^-	10
$(2\,0\,\bar{2}\,5)$	6536	6532	vvw^+	7
$(2\,1\,\bar{3}\,0)$	6594	6595	*vvw*	3
$(2\,1\,\bar{3}\,1)$	6710	6706	vw^+	16
$(1\,1\,\bar{2}\,6)$	6805	6805	*vw*	12
$(2\,1\,\bar{3}\,2)$	7040	7037	*vvw*	5
$(0\,0\,0\,8)$	—	7073	—	2
$(2\,1\,\bar{3}\,3)$	7591	7590	w^-	21
$(2\,0\,\bar{2}\,6)$	7749	7747	*vvw*	3
$(1\,0\,\bar{1}\,8)$	8022	8015	*vvw*	3
$(2\,1\,\bar{3}\,4)$	8360	8363	vvw^+	8
$(3\,0\,\bar{3}\,0)$	8479	8479	vvw^+	9
$(3\,0\,\bar{3}\,2)$	8918	8922	vw^+	14
$(2\,0\,\bar{2}\,7)$	9180	9184	w^-	18
$(2\,1\,\bar{3}\,5)$	9354	9358	*w*	27
$(1\,0\,\bar{1}\,9)$	9891	9894	*m*	39

(composition 2 : 1 : 2) Debye–Scherrer photographs were obtained, which resembled the powder pattern of V_2OsB_2.

In all cases the powder patterns of the new compounds could be indexed completely with an orthorhombic unit cell. Their lattice parameter values are listed in Table III.

Composition, lattice parameters, and intensities revealed structural analogy with the crystal structure of Mo_2IrB_2 (*2*). Assuming an atomic arrangement with atom parameters as earlier derived in a single crystal study of Mo_2IrB_2, calculated and observed intensities are in excellent agreement, as is shown by the data for W_2OsB_2 given in Table IV. Calculated Debye–Scherrer intensities of V_2OsB_2 and Mo_2OsB_2 are not given because of their similarity to the calculations for V_2IrB_2 (*4*) and Mo_2IrB_2 (*2*), however, intensity calculations can be obtained on request.

A small homogeneity region was observed in W_2OsB_2 by changes in the lattice parameters with composition, indicating a small exchange on the metal sites ($W_{1.85}Os_{1.15}B_2$ to W_2OsB_2).

The crystal structure of Mo_2IrB_2 contains octahedral holes (in 2*b* sites) according to a formula $Mo_2IrB_2X_{0.5}$. The distances calculated for the center of the unsymmetric octahedral void (1.84 Å (2), 2.02 Å (4) for V_2OsB_2) are relatively small for an occupation by small nonmetal atoms like oxygen and nitrogen. To study the stabilizing influence of small amounts of oxygen and nitrogen on the formation of Mo_2IrB_2-type compounds, a part of each alloy was additionally heat treated for 12 hr at 1300°C under a gas stream (1 liter/hr) of an argon oxygen(nitrogen) mixture (0.25 vol% $O_2(N_2)$). However, neither an increase of Mo_2IrB_2-type phase in multiphase alloys nor a significant change of the degree of sharpness of the powder patterns could be observed after this treatment.

In the case of V_2OsB_2 the oxygen/nitrogen content was measured by a chemical analysis. The resulting oxygen/nitrogen content (350 ppm of O_2, 150 ppm of N_2) would allow for only a very incomplete occupation of the octahedral voids.

Investigation of superconducting properties for $\{V, Mo, W\}_2OsB_2$ revealed low transition temperatures: $T_K \approx 4°K$ for all three compounds.

Discussion

Table I is a representation of the compounds crystallizing with ReB_2-type structure.

TABLE III

LATTICE PARAMETERS,[a] RADII AND ELECTRON/ATOM RATIOS OF COMPLEX BORIDES WITH Mo_2IrB_2-TYPE STRUCTURE, OF Y_3Co_2 (Mo_2IrB_2-TYPE), AND OF THE RELATED CRYSTAL STRUCTURE OF Re_3B

Phase	a (Å)	b (Å)	c (Å)	c/a	V (Å^3)	$\bar{R}_T/R_B$[b]	e/a
V_2IrB_2 (*4*)	9.22_1	7.14_5	3.12_6	0.34	205.9	1.53	5.0
$V_{1.8}Ir_{1.2}B_2$ (*4*)	9.23_0	7.15_0	3.12_9	0.34	206.5		5.2
Cr_2IrB_2 (*4*)	9.23_0	7.11_7	2.99_8	0.33	196.9	1.49	5.4
Mo_2IrB_2 (*4*)	9.42_2	7.35_6	3.23_1	0.34	223.9	1.57	5.4
$Mo_{1.75}Ru_{1.25}B_2$ (*4, 5*)	9.59_9	7.48_0	3.09_4	0.32	222.2	1.56	5.3
$W_{1.75}Ru_{1.25}B_2$ (*4*)	9.57_9	7.45_9	3.07_2	0.32	219.5	1.57	5.3
$V_{\sim 1.8}Os_{\sim 1.2}B_2$	9.36_0	7.24_3	3.00_1	0.32	203.6	1.53	5.0
Mo_2OsB_2	9.61_8	7.51_7	3.08_8	0.32	223.3	1.57	5.2
$W_{1.85}Os_{1.15}B_2$	9.57_2	7.52_0	3.06_6	0.32	220.7	1.58	5.3
W_2OsB_2	9.61_2	7.52_0	3.07_4		222.2		5.2
Y_3Co_2 (*7*)	12.24_8	9.38_9	3.97_5	0.33	457.1	1.44	5.6
Re_3B (*11*)	9.31_3	7.25_8	2.89_0	0.31	195.3	1.56	6.0

[a] Lattice parameters were evaluated by a least-squares-fit-extrapolation method and in average are accurate to ± 0.002 Å.

[b] Metallic radii R_T(CN12) were taken from Dickinson (*10*); $\bar{R}_T$ = weighted average of contributing metal atoms, $R_B = 0.88$ Å.

No ternary ReB_2 phases have been found containing Rh, Pd, or Pt and besides ReB_2 and TcB_2 (*9*) no other binary ReB_2 borides were observed so far. Among the ternary representatives in Table I it is obvious that only combinations of one element to the left of the VII group with a partner element to the right of the VIIA group are able to yield ReB_2-type structures. Ru- and Os-containing phases were found with a ratio in composition $T/T^{VIII} = \frac{1}{2}$, whereas Ir-containing phases were observed at a higher ratio $T/T^{VIII} \approx 1$.[4] The different ratio can also be derived from a plot c versus c/a (Fig. 1). However the difference in composition seems to be regulated by a constant electron/atom ratio (Table I). Similar dominant electronic factors in the selection of different structure types were recently discussed for monoboride structures and Ti_3P- and Fe_3C-type borides, respectively (*13*). In all these cases modification of the electronic state of the metal atom seems to be decisive in the competition of different structure types. On the other hand the radius ratio $\bar{R}_T/R_B$ ($\bar{R}_T$ = radius of a VIIA-group pseudoelement) is for all combinations very close to the value 1.55 for ReB_2 (Table I). However the geometrical factor would not favor a statistical occupation of two kinds of metal atoms with high $R_T/R_{T^{VIII}}$ ratio (i.e., combination Ta–Ru).

The lattice parameter comparisons in relationship to the metal radii merely reflect the influence of a rigid boron net with strong boron–boron contacts, similar to AlB_2-type

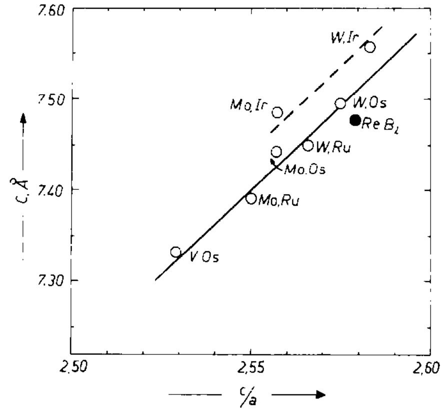

FIG. 1. Plot of c versus c/a for complex borides with ReB_2-type structure.

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[4] See footnote 2.

TABLE IV

POWDER DIFFRACTION DATA FOR W_2OsB_2; FILTERED CuKα RADIATION

(hkℓ)	$\sin^2\theta.10^4$ obs.	$\sin^2\theta.10^4$ calc.	I obs.	I calc.
(110)	373	374	vvw	5
(200)	-	568	-	0
(210)	-	800	-	1
(120)	1077	1070	vvw$^+$	6
(310)	-	1510	-	0
(101)	1530	1531	vvw	4
(011)	1623	1621	w	27
(111)	1769	1763	w$^-$	20
(320)	-	2206	-	0
(130)	2230	2230	w$^-$	20
(400)	2279	2272	m	45
(121)	-	2459	-	0
(410)	2514	2504	vvw	1
(230)	2666	2656	m	39
(301)		2667		13
(221)	2893	2885	vst	100
(311)		2899		16
(420)	-	3200	-	0
(330)	3356	3366	vw	10
(031)	3474	3477	vvw	2
(131)	3615	3619	vvw	4
(040)	3716	3712	vvw	5
(510)	3790	3782	vvw$^-$	2
(140)	-	3854	-	0
(411)	3895	3893	vw$^+$	15
(231)	-	4045	-	1
(240)	-	4280	-	0
(430)	-	4360	-	0
(520)	4480	4478	vvw	5
(421)	-	4589	-	0
(331)	-	4755	-	0
(501)	-	4939	-	0
(340)	-	4990	-	0
(600)	-	5112	-	0
(511)	5165	5171	vvw$^-$	3
(141)	5242	5243	vvw	4
(610)	-	5344	-	0
(002)	5547	5554	w$^-$	17
(530)	5635	5638	vvw	6
(241)	-	5669	-	0
(431)	5756	5749	vvw$^-$	2
(521)	-	5867	-	0
(112)	-	5928	-	0
(150)	-	5942	-	1
(440)	5979	5984	vvw	4
(620)	-	6040	-	0
(202)	-	6122	-	0
(212)	-	6354	-	0
(250)	-	6368	-	1
(341)	-	6379	-	1
(022)	-	6482	-	0
(122)	-	6624	-	1
(611)	-	6733	-	0
(531)	7029	7027	vvw$^+$	7
(222)	-	7050	-	0
(312)	-	7064	-	0
(350)	7084	7078	vvw$^-$	3
(051)	7188	7189	w$^+$	19
(710)		7191		1
(630)		7201		13
(540)	-	7263	-	0
(151)	7329	7331	vw	13
(441)	-	7373	-	0
(621)	7429	7429	w$^+$	34
(251)	-	7757	-	0
(322)	-	7760	-	0
(132)	7781	7784	vw	14
(402)	7817	7826	w$^+$	33
(720)	-	7887	-	2
(412)	-	8058	-	1
(450)	-	8073	-	2
(232)	8209	8210	m	39
(701)	8340	8347	vw$^+$	16
(060)	-	8353	-	0
(351)	8477	8467	vw^+_d	14
(160)		8495		13
(711)	8583	8579	vw$_d$	12
(631)		8589		6
(541)	8655	8651	vw$^-$	9
(422)	-	8754	-	0
(640)	-	8825	-	2
(332)	8920	8920	w$^-$	19
(260)	-	8921	-	0
(730)	9041	9047	vvw	8
(800)	9093	9089	w	18
(042)	9261	9266	vw	12
(721)	-	9275	-	0
(810)	9330	9321	vvw	3
(512)		9336		7
(550)	-	9351	-	0
(142)	-	9408	-	0
(451)	9460	9461	st	85
(360)	9626	9631	w	25

d = diffuse

TABLE V

COMPARISON OF ATOM PARAMETERS OF Mo_2IrB_2 AND Y_3Co_2 WITH IDEALIZED POINT POSITIONS[a]

	Mo_2IrB_2				Y_3Co_2[b]					
	x	y	z		x	y	z	Idealized point positions		
Ir	0.109	0.122	0	Y(2)	0.113	0.127	0	0.125	0.083	0
Mo(I)	0.368	0.312	0	Y(1)	0.372	0.307	0	0.375	0.250	0
Mo(II)	0.640	0.070	0	Y(3)	0.637	0.074	0	0.625	0.083	0
B(I)	0.035	0.616	0	Co(2)	0.038	0.617	0	0.042	0.583	0
B(II)	0.228	0.622	0	Co(1)	0.231	0.640	0	0.208	0.583	0

[a] The calculation (7) is based on trigonal prisms with equilateral triangles.

[b] The parameters are obtained by a shift (vector $\frac{1}{2}\frac{1}{2}0$) of the origin of the unit cell, derived by Parthé (7).

borides (*12*). Whereas in the crystal structure of AlB_2 all atoms are located in fixed-point positions, *M*B distances in ReB_2 are dependent on the free parameter z_B of B in 4*f*.[5]

Assuming direct boron–boron contacts ($R_B = 0.88$ Å) the calculated parameter z_B[6] is found to be 0.540 for all ReB_2 combinations of Table I. This value is in good accordance to the experimentally observed $z = 0.548$ (*8*). In using the derived *z*-parameter (0.540) the *M*B(II) distances reflect the sum of radii of metal and boron atom. The *M*B(I) distances in the direction of the *c*-axis are shorter ($MB(I) \sim 0.9\, MB(II)$) and compared to the metal–metal distances $MM = a/2$ in the direction of the *a*-axis yield a ratio $(MB(I) - R_B)/MM \sim 0.9$.

The ratio <1 indicates compression of the metal atoms in the direction of the *c*-axis (elliptical shape) in order to maintain strong boron–boron contacts within the puckered boron layers. Thus the atomic distances in ReB_2 phases reflect the same bonding principles as recently discussed for AlB_2 borides (*12*).

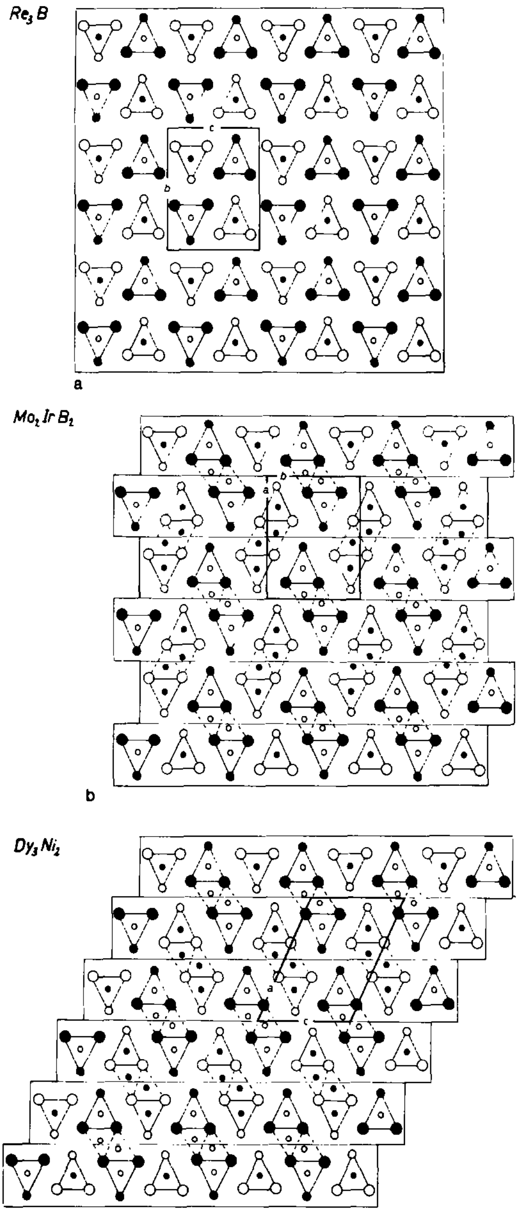

FIG. 2. Relationship among the crystal structures of Re_3B(a), Mo_2IrB_2(b), and Dy_3Ni_2(c). Shaded circles in $\frac{1}{2}$, open circles in 0; large circles: metal (Dy) atoms, smallest circles: boron (Ni) atoms. The two Re-sites in Re_3B (8*f* and 4*c*) are differentiated by larger and smaller circles.

Lattice parameters, radius ratio, and electron/atom ratio for complex borides with Mo_2IrB_2-type structure are presented in Table III. As in the case of the ReB_2-type borides, Mo_2IrB_2-type borides are observed for specific combinations of two kinds of metal atoms (ratio 2 : 1), one to the left and one to the right of the VIIA-group elements. Deviation from ordering (i.e., deviation from the ratio 2 : 1) among the metal atoms can be understood in the direction of a more favorable electron/atom ratio, which for all Mo_2IrB_2 compounds is observed within relatively narrow limits (Table III). The intermetallic compound Y_3Co_2, recently characterized by Moreau *et al.* (*7*) by single-crystal techniques, is found to be isotypic with the atomic arrangement of Mo_2IrB_2 (shift of the origin of Y_3Co_2 by a vector $\frac{1}{2}\, \frac{1}{2}\, 0$, Table V). The Co atoms occupy the boron sites. The analogy of the prismatic building element $RE_6\{Fe, Co, Ni\}$ on the one hand and T_6^{VIII} B[7] on the other hand was recently shown by Parthé (*14*) in a series of

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[5] 2 $\quad MB(I) = (z - \frac{1}{4})c$;
6 $MB(II) = \{(a/3^{1/2})^2 + [(\frac{3}{4} - z)c]^2\}^{1/2}$.

[6] $z = 0.5 + [((R_B)^2/c) - \frac{1}{12}(a/c)^2]^{1/2}$.

[7] See footnote 2.

corresponding structure types. It can be concluded from these considerations that the crystal structure of Dy_3Ni_2 (7) is very likely to be found among complex borides. Dy_3Ni_2 crystallizes in a slightly different arrangement of the same characteristic prismatic building blocks that were found in Y_3Co_2. It was also shown by Moreau (7) that the two crystal structures Y_3Co_2 and Dy_3Ni_2 are related by a simple geometrical shift.

The formation of VIIA pseudoelement in the observed combinations of Mo_2IrB_2-type borides is connected with a close relationship between the structure types of Re_3B and Mo_2IrB_2. The metal arrangement in Mo_2IrB_2 is easily obtained from the metal arrangement in Re_3B by a simple shift of every second prism row in Re_3B. Similarly the metal (Dy) arrangement in Dy_3Ni_2 can be generated by a shift of every subsequent prism row in Re_3B (Fig. 2). New T_6-prisms[8] are formed in this shift operations, which are occupied by additional boron/nickel atoms for a smaller T/B ratio[8]. The ordered metal arrangement in Mo_2IrB_2 implies also ordering in Re_3B, which in fact is indicated in VCr_2C_2 (Re_3B type).

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[8] See footnote 2.