The Crystal Structures of Molybdenum and Tungsten Borides

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For the past two years binary systems, composed of a transition element and boron, have been studied at this institute. This report is concerned specifically with the borides of molybdenum and tungsten for which structure determinations have been carried out.

Chemical litterature is rather scanty concerning these compounds. In earlier experiments by Binet du Jassoneix [1], Tucker and Moody [2], and Wedekind [3] some intermediate phases, obtained at high temperatures by several methods, are reported. Varying compositions of these phases were recognized, which seem to depend on difficulties attending the isolation of the pure phases. Halla and Thury [4] isolated a compound of the composition WB_2 with a complicated X-ray pattern, prepared by aluminothermic methods. The purity of this compound, however, is questionable.

During the course of this study, Weiss [5] reported the existence of the phases Mo_2B, MoB, and WB, produced by electrolysing melts of borax together with the anhydrides of molybdenum and tungsten acids in the presence of sodium fluoride. The phases are well defined and some chemical and physical properties are described. These compounds are discussed below.

GENERAL METHODS

The borides were prepared in two ways. The general method was to heat weighed mixtures of boron and metal in evacuated quartz tubes for 48 hours at about 1200° C. After this time complete equilibrium seems to be established. The starting materials were molybdenum powder (Kahlbaum) which had been heated *in vacuo* at about 400° C, tungsten powder (Merck, puriss.) and boron. The initial studies were carried out with boron (amorph, Kahlbaum), purified

by chemical methods and with a boron content of 88 %. The results were later affirmed by using 98—99 % boron, prepared by thermic dissociation of BBr_3 in a heated quartz tube at about 700° C in the presence of hydrogen (Kiessling, unpublished). For control purposes mixtures of boron and metal were compressed to pastilles, placed in magnesia crucibles and heated for some minutes at a temperature of 1500—1600° C in a vacuum furnace.

In general, samples prepared by the first method were not analysed as there were no losses during the course of preparation. Some control analyses were made by the methods, given by Weiss [5], and samples prepared by the second method were also analysed in this way.

The preparations were examined under the microscope. The structure determinations were made by X-ray powder methods, since single crystals large enough for X-ray investigation by means of single crystal methods could not be prepared. The powder photographs were obtained with a set of focussing cameras (»A», »B», and »C»-cameras) which provided different glancing angles. The intensities of the reflections in the photographs were estimated visually, starting from 4 : 2 : 1 as relative values of the intensities of Cr-Ka_1, Cr-Ka_2, and Cr-$K\beta$ radiation. The lines in the three cameras were then coordinated to the same scale of intensity by means of lines common to the A—B and B—C cameras respectively. From the estimated intensities relative values of $p|F|^2$ were calculated by means of the expression, given by Hägg and Regnström.[6]

$$I = C \cdot \frac{\lambda^3}{\mu} \cdot \frac{1 + \cos^2 2\,\Theta}{\sin^2 \Theta \cdot \cos \Theta} \cdot \frac{1}{\sin (2\,\Theta - a) + \sin a} \cdot A_a \cdot A_p \cdot A_f \cdot p|F|^2$$

where the absorption factors of the cameras and the film have been taken into consideration. For a given wave length, camera, and preparation all factors preceeding p will be functions of Θ only.

Observed and calculated values of $p|F|^2$ are given in the tables. In these tables all intensity calculations are based on the metal atoms only; the scattering power of the boron atoms being too low compared with that of the molybdenum and tungsten atoms to give any variations great enough to be observed, even in the most boron rich phases. The positions of the boron atoms were determined using space considerations.

GENERAL SURVEY OF THE SYSTEMS

The phases of the two systems have been found to be isomorphous to a large extent and therefore will be described together.

The solubility of boron in the metallic lattices is apparently very low since the interferences in the powder photographs within the limits of error always occurred at fixed angles.

Three intermediary phases (γ,δ, and ε) were found in each system. The γ phases are isomorphous and have the composition Me_2B.

The δ phases are also isomorphous and exist in a slightly extended homogeneity range of about 48—51 atomic % boron.

The ε phases are not isomorphous but the two structures are very similar. Their »ideal» boron content is 71.4 atomic % but the real boron content is slightly lower.

THE γ PHASES

These phases were found to be homogeneous in samples, prepared at 1200° C, consisting of 33.3 atomic % boron. In each instance the lines in the powder photographs occurred at fixed angles, indicating that the homogeneity range of these phases is very narrow. Both phases were hard enough to scratch an agate mortar. Weiss [5] prepared Mo_2B and this phase seems to be identical with the γ phase in the Mo-B system. He gives a hardness of 8—9 according to Mohs, and describes some chemical properties all of which were found to be possessed by the γ phase.

The interpretation of the powder photographs (Cr-K and Cu-K radiation) showed the phases to be isomorphous and gave tetragonal cells with the dimensions:

$Mo_2B: a = 5.543$ Å, $c = 4.735$ Å, $c/a = 0.854$, $V = 145.5$ Å^3,
$W_2B: a = 5.564$ Å, $c = 4.740$ Å, $c/a = 0.852$, $V = 146.7$ Å^3.

With a cell content of 4 Me_2B the calculated densities are 9.31 for Mo_2B and 16.72 for W_2B, in good agreement with the observed values 9.1 and 16.0 respectively.

Fe_2B [7, 8], Co_2B, and Ni_2B [9], which are tetragonal have the following dimensions: *

$Fe_2B: \quad a = 5.109$ Å, $c = 4.249$ Å, $c/a = 0.842$,
$Co_2B: \quad a = 5.016$ Å, $c = 4.220$ Å, $c/a = 0.843$,
$Ni_2B: \quad a = 4.993$ Å, $c = 4.249$ Å, $c/a = 0.851$,

with 4 molecules of Me_2B in the cell. These borides are of the $CuAl_2$-type

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* All values, given in the litterature in Ångström units have been converted to true Ångström units = 10^{-8} cm by multiplying by the factor 1,00202.

Table 1. Mo_2B, Cr—K radiation.

$h\ k\ l$	R	$\sin^2\Theta$		I obs.	$p\lvert F\rvert^2$	
		obs.	calc.		obs.*	calc. $x = 1/6$
1 1 0	a	0.0857	0.0853	sv	0.4	1.5
2 0 0	a	1709	1706	m	5	6
0 0 2	a	2342	2338	st	9	12
2 1 1	a	2720	2717	st +	48	57
1 1 2	a	3191	3191	sv	1.6	3.7
2 2 0	a	3409	3412	sv	1.4	1.8
2 0 2	a	4049	4044	m	11	12
3 1 0	a	4268	4265	m	12	12
2 2 2	a_1	5742	5750	sv —	1.6	1.6
3 2 1	—	—	6129	—	0	0
3 1 2	a_1	6607	6603	m	18	14
4 0 0	a_1	6829	6824	sv —	2.0	2.6
2 1 3	a_1	7395	7392	st	38	35
3 3 0	a_1	7677	7677	sv	12	14
4 1 1	a_1	7832	7835	m	37	33
4 2 0	a_1	8533	8530	sv —	1.6	2.3
4 0 2	a_1	9160	9162	sv —	7	8
0 0 4	a_1	9351	9351	sv —	6	7

(C 16). The space group is D_{4h}^{18}—I $4/mcm$ with the metal atoms in an eightfold position.**

8 : (h) x, $1/2 + x$, 0; $\overline{x}$, $1/2$—x, 0; $1/2 + x$, $\overline{x}$, 0; $1/2$—x, x, 0; $1/2 + x$, x, $1/2$; $1/2$—x, $\overline{x}$, $1/2$; x, $1/2$—x, $1/2$; $\overline{x}$, $1/2 + x$, $1/2$.

The value of the parameter x is $1/6$.

The boron atoms are in a fourfold position:

4 : (a)   0, 0, 1/4; 1/2, 1/2, 3/4; 0, 0, 3/4; 1/2, 1/2, 1/4***.

Table 2. W_2B Cr-K radiation.

h k l	R	sin²Θ		I obs.	p|F|²	
		obs.	calc.		obs.*	calc. $x = 1/6$
1 1 0	a	0.0847	0.0847	sv +	2	7
2 0 0	a	1694	1693	st	12	25
0 0 2	a	2334	2334	st	34	46
2 1 1	a	2698	2700	st +	121	194
1 1 2	a	3179	3180	sv +	8	10
2 2 0	a	3384	3386	sv	6	5
2 0 2	a	4025	4027	st	63	38
3 1 0	a	4229	4233	m	58	37
2 2 2	a_1	5724	5720	sv	9	8
3 2 1	—	—	6086	—	0	0
3 1 2	a_1	6563	6567	st	66	62
4 0 0	a_1	6773	6773	sv —	12	15
2 1 3	a_1	7362	7367	st	176	132
3 3 0	a_1	7609	7619	st	64	57
4 1 1	a_1	7772	7779	st	109	127
4 2 0	a_1	8456	8466	sv —	8	7
4 0 2	a_1	9101	9106	sv	19	26
0 0 4	a_1	9330	9334	sv +	25	23

For Mo_2B and W_2B reflections $h\ k\ l$ were observed only for $h + k + l = 2n$, $h\ k\ 0$ for $h + k = 2n$, $h\ h\ l$ for $l = 2n$ and $0\ k\ l$ for $k = 2n$ and $l = 2n$, showing that the space group D_{4h}^{18} is possible. The further structure analysis showed, that the metal lattices of these borides have the symmetry of 8:(h) in D_{4h}^{18}. The agreement between observed and calculated $p|F|^2$ values was good for both borides with a value of the parameter $x = 1/6$ (Table 1 and 2).

The arrangement of the metal atoms is described by Hägg [7]. The metal atoms lie in the corners of slightly deformed tetrahedrons, packed in a regular manner. In this network of tetrahedrons, there are channels running parallel

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$v = 1/4$ the symmetry increases to D_{4h}^{18} and the correct position for the metal atoms in this group is 8:(h), given above. The boron atoms are said to be in a fourfold position in D_{4h}^{18}; 1/2, 0, 0; 1/2, 0, 1/2; 0, 1/2, 0; 0, 1/2, 1/2; this is, however, the correct position for the boron atoms in D_{2d}^{11}. In D_{4h}^{18}, because of the transformation of the coordinate system, the correct position for the boron atoms is 4 : (a), given above. This note is only a formal one, introduced to avoid mistakes, and does not alter the structure described by Hägg [7]. Compare the note of Hägg [8].

* Referred to a_1 for all lines.

3

to the c-axis, and these channels cut the ab plane in the points 0,0,0 and
1/2, 1/2,0. Each metal atom is surrounded by three other metal atoms at
about the same distance, which, for molybdenum is 2.61, 2.71, and 2.71 Å,
for tungsten 2.62, 2.71, and 2.71 Å. Four other metal atoms are situated at
distances of 2.92 Å for Mo and 2.93 Å for W and four others at distances of
3.00 Å for both Mo and W. With a slight variation of the parameter x from
1/6 (0.167) to 0.170 the distances to the three nearest neighbours become: for
Mo 2.66, 2.67 and 2.67 Å, for W 2.67, 2.68 and 2.68 Å. The rather small
number of interferences used for the determination of the parameter and the
rough estimation of their intensities renders an accurate determination of the
parameter difficult, but the latter value seems to be more correct. If the atoms
are assumed to be spherical and in contact with each other, the radius will be
1.33 Å for molybdenum and 1.34 Å for tungsten.

The boron atoms then must be placed in holes of the metal lattice. The
only holes large enough to be considered are in the channels. In D_{4h}^{18} there
are two positions where four boron atoms per cell may be placed in
the channels:

4 : (a) 0, 0, 1/4; 0, 0, 3/4; 1/2, 1/2, 3/4; 1/2, 1/2, 1/4,
or 4 : (c) 0, 0, 0; 0, 0, 1/2; 1/2, 1/2, 1/2; 1/2, 1/2, 0.

If the locations were those given in 4 : (c) the radius of the boron atom
would be 0.72 Å. In all earlier determinations the radius has been found to
have a value between that of carbon (0.77) and that of beryllium (1.12), and
in no case has a value less than 0.86 Å been found. For this reason the position
4 : (c) is excluded. The remaining position, 4 : (a) is the same as has been found
for boron in Fe_2B, Co_2B, and Ni_2B. It corresponds to the largest holes of the
lattice, the distance molybdenum-boron beeing 2.37 Å and tungsten-boron
2.38 Å, which gives a radius for the boron atom of 1.03 Å. For Fe_2B, Co_2B
and Ni_2B the values given for the boron radius are 0.97, 0.94, and 0.92 Å
respectively, whereas from the other phases of the molybdenum and tungsten
systems the value is about 0.87 Å. The reason for the varying values for Me_2B
may depend on the fact that the lattice is established by the metal atoms,
even if the holes have a slightly greater radius than the boron atom.

The γ phases, Mo_2B and W_2B, thus crystallize in space group D_{4h}^{18}, iso-
morphous with Fe_2B, Co_2B, and Ni_2B, with the metal atoms in:

8 : (h) x, 1/2 + x, 0; $\bar{x}$, 1/2—x, 0; 1/2 + x, $\bar{x}$, 0; 1/2—x, x, 0; 1/2 + x, x, 1/2;
1/2—x, $\bar{x}$, 1/2; x, 1/2—x, 1/2; $\bar{x}$, 1/2 + x, 1/2,

and the boron atoms in:

Table 3. Mo—B, δ phase, Cr-K radiation.

h k l	R	$\sin^2\Theta$		I obs.	$p|F|^2$	
		obs.	calc.		obs.*	calc. $z = 0.197$
0 0 4	a	0.0732	0.0728	sv	0.4	1.1
1 0 1	a	1406	1405	sv	1.3	3
1 0 3	a	1771	1769	st	9	20
1 0 5	a	2502	2497	st	21	25
1 1 2⎫ 0 0 8⎭	a	2910	⎰ 2900 ⎱ 2912	st +	46	⎰ 30 ⎱ 4
1 0 7	a	3595	3589	m	12	13
1 1 6	a	4361	4356	sv	8	7
1 0 9	a	5050	5045	sv —	1.2	0.5
2 0 0	a_1	5441	5436	m	19	18
2 0 2	—	—	5618	—	0	0
2 0 4	a_1	6165	6164	sv —	1.9	2.0
0 0 12	a_1	6561	6552	sv	4	4
2 1 1	a_1	6844	6841	sv	4	3
1 0 11	a_1	6874	6865	sv	4	4
2 0 6	—	—	7074	—	0	0
2 1 3	a_1	7209	7205	sv +	20	22
1 1 10	a_1	7276	7268	m	32	30
2 1 5	a_1	7934	7934	sv +	23	29
2 0 8	a_1	8352	8348	sv +	21	22
2 1 7	a_1	9026	9025	sv	11	15
1 0 13	a_1	9059	9049	sv	10	11

4 : (a) 0, 0, 1/4; 0, 0, 3/4; 1/2, 1/2, 3/4; 1/2, 1/2, 1/4.

The value of the parameter $x = 0.170$.

THE δ PHASES

At compositions of about 50 atomic % boron a pure phase occurred in each system. These phases were isomorphous and possessed a slightly extended homogeneity range. They were hard, had metallic properties and appeared to be identical with MoB and WB described by Weiss [5].

The interpretation of the powder photographs (Cr-K and Cu-K radiation) gave tetragonal cells with the following dimensions at the ideal composition, 50.0 atomic % boron:

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* Referred to a_1 for all lines.

Table 4. W—B, δ-phase, Cr-K radiation.

| h k l | R | sin²Θ | | I obs. | p|F|² | |
		obs.	calc.		obs.*	calc. z = 0.197
0 0 4	a	0.0725	0.0732	sv	1.2	5
1 0 1	a	1394	1397	sv	5	11
1 0 3	a	1768	1763	st	24	69
1 0 5	a	2497	2494	st	52	88
1 1 2	a	2880	2885	st +	92	105
0 0 8	a	2926	2927	sv	11	16
1 0 7	a	3592	3592	m	48	42
1 1 6	a	4345	4348	sv +	37	24
1 0 9	a	5057	5055	sv —	5	1.6
2 0 0	a_1	5409	5405	m	56	68
2 0 2	—	—	5588	—	0	0
2 0 4	a_1	6137	6137	sv —	9	8
0 0 12	a_1	6585	6585	sv	18	14
2 1 1	a_1	6801	6802	sv	18	13
1 0 11	a_1	6885	6884	sv	24	14
2 0 6	—	—	7051	—	0	0
2 1 3	a_1	7170	7168	sv +	61	84
1 1 10	a_1	7273	7275	m	97	113
2 1 5	a_1	7903	7899	m	68	111
2 0 8	a_1	8334	8332	m	63	85
2 1 7	a_1	8997	8997	m	48	59
1 0 13	a_1	9078	9079	sv	30	44

MoB: $a = 3.105$ Å, $c = 16.97$ Å, $V = 163.9$ Å³
WB: $a = 3.115$ Å, $c = 16.93$ Å, $V = 164.6$ Å³

With a cell content of 8 MeB the calculated densities will be 8.77 for MoB, and 16.0 for WB, in good agreement with the observed values 8.3 and 15.3 respectively.

Reflections $h\,k\,l$ were observed only for $h + k + l = 2n$, $h\,k\,0$ for $h = 2n$ and $k = 2n$, $h\,h\,l$ for $l = 2n$ and $2h + l = 4n$ and $0\,k\,l$ for $k + l = 2n$, which is characteristic of the space group D_{4h}^{19}—$I\,4/amd$. From space considerations all positions are excluded for eight metal atoms except 8:(e) having the coordinates:

8:(e) 0, 0, z; 0, 0, $\bar{z}$; 0,1/2, 1/4 + z; 0,1/2, 1/4—z; 1/2, 1/2, 1/2 + z; 1/2, 1/2, 1/2—z; 1/2, 0,3/4 + z; 1/2, 0, 3/4—z.

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* Referred to a_1 for all lines.

Table 5. Mo—B, and W—B, δ-phases.

| h k l | $p\|F\|^2$ (Mo) | | | | $p\|F\|^2$ (W) | | | |
| | obs. | calc. z = | | | obs. | calc. z = | | |
		0.194	0.197	0.200		0.194	0.197	0.200
2 0 4	18	10	20	31	64	38	75	116
0 0 12	37	21	37	54	125	77	139	204
2 1 1	37	38	34	31	128	143	128	116
1 0 11	37	67	38	15	171	250	143	58

The value of z was determined by means of systematic variations and calculations of $p\|F\|^2$, starting with values derived from space considerations. As will be seen from tables 3 and 4, the agreement is good for a value of $z = 0.197$.

The limits of z are $0.194 < z < 0.200$ (Table 5).

In Fig. 1 the structure is projected on (010) and (100). The distances, calculated for the W—B lattice are:

A—B = C—D = D—G = 2.89 Å,
A—C = A—D = A—F = 2.83 Å.

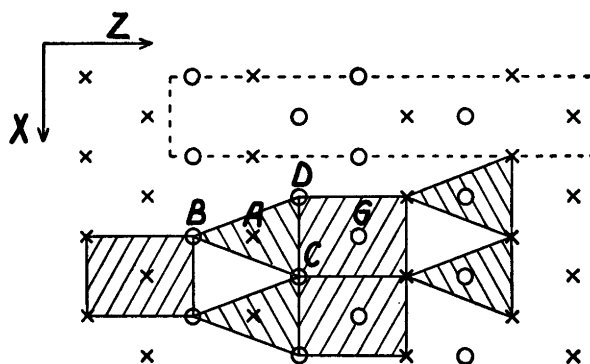If z is varied from 0.197 to 0.196 the distances become:

A—B = 2.86 Å
A—C = 2.86 Å.

Fig. 1a. The metal lattice of the δ phase, projected on (0 1 0). (The unit cell and the prisms of metal atoms are indicated.)
x = metal atoms in x 0 z
O = metal atoms in x ½ z

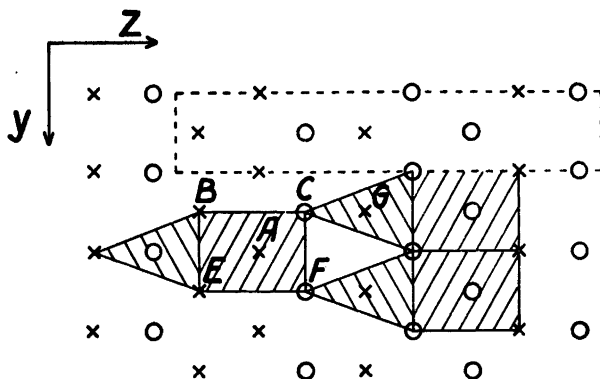*Fig. 1b. The same structure as in 1a projected on (1 0 0).*
x = metal atoms in 0 yz
O = metal atoms in ½ yz

This variation of z lies within the limits of error (Table 5) and gives a very regular arrangement of the metal atoms. Every metal atom, for instance A (Fig. 1), is surrounded by six neighbours at the same distance, 2.86 Å. The surrounding atoms lie in the corners of a trigonal prism with A in the centre (Fig. 2). The height of the prism, BE, is $= a = 3.115$ Å as is the base (CD) of the triangular face BCD. The height (BH) of this face is $= c/4 = 4.22$ Å. (a and c are the axes of the tetragonal cell.)

The metal lattice may be described as a packing of trigonal prisms in a manner indicated by Fig. 1.

The boron atoms must be situated in the holes of this lattice. As may be seen from Fig. 1 the lattice is crossed by a system of channels. These channels are of two kinds. Those parallel to the a axis have their centre at z coordinates 3/8 and 7/8. Those, running at right angles to the first, are parallel to the b axis and have z coordinates 1/8 and 5/8.
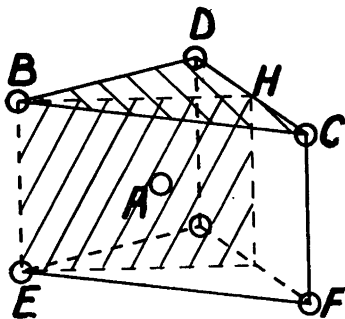

Fig. 2. Prism of metal atoms (compare fig. 1).

There are 8 boron atoms per cell and in D_{4h}^{19} they may be placed in the channels if they possess the same eightfold position, 8 : (e), as the metal atoms but with a value of $z = (5/12—z_{Me}/3) = 0.352$. This position corresponds to the largest holes in the lattice. Each boron atom lies in the center of a trigonal prism of six metal atoms, each at the distance 2.22 Å from the center of the boron atom. The boron atoms in each channel are connected to zig-zag-lines running through the channel, the distance boron-boron being 1.74 Å. Thus the radius of the boron atom will be 0.87 Å and the radius of the metal atom 1.35 Å. The chains of boron atoms are indicated in Fig. 3. The coordination of metal atoms around the boron atom is the same as has been found for FeB and CoB [9].

The δ phases in both the molybdenum and tungsten systems show an extended homogeneity range. The limits were determined from the variation of the a axis with the composition of the systems. For the molybdenum phase the limits were 48.8 atomic % boron $<\delta<$ 51.5 atomic % boron. The a and c axes for 48.8 atomic % boron are 3.105 Å and 16.97 Å respectively, while at 51.5 atomic % the a and c axes are 3.119 Å and 16.92 Å respectively.

For the tungsten phase the limits were 48.0 atomic % boron $<\delta<$ 50.5 atomic % boron, with the a and c axes varying from 3.096 Å and 16.96 Å to 3.120 Å and 16.92 Å respectively. The extended homogeneity ranges probably depend on possible variations in the number of boron atoms in the channels.

Thus the δ phases crystallize in space group D_{4h}^{19}—I 4/amd with the metal atoms in

8 : (e) . 0, 0, z; 0, 0, $\bar{z}$ 0, 1/2, 1/4 + z; 0, 1/2, 1/4—z; 1/2, 1/2, 1/2 + z; 1/2, 1/2, 1/2—z; 1/2, 0, 3/4 + z; 1/2, 0, 3/4—z.

The boron atoms are also in the position 8 : (e), the values of the parameters being $z_{Me} = 0.196$ and $z_B = 0.352$.

THE ε PHASES

In both the Mo—B and the W—B systems a third intermediate phase could be obtained by preparing the phases in evacuated quartz tubes at 1200° C. These phases seemed to be homogeneous at a composition of about 70 atomic % boron. Though not isomorphous, because of their similarity in structure they will be described together.

The physical properties were not thoroughly investigated, but the ε phases did not show the marked hardness of the γ and the δ phases.
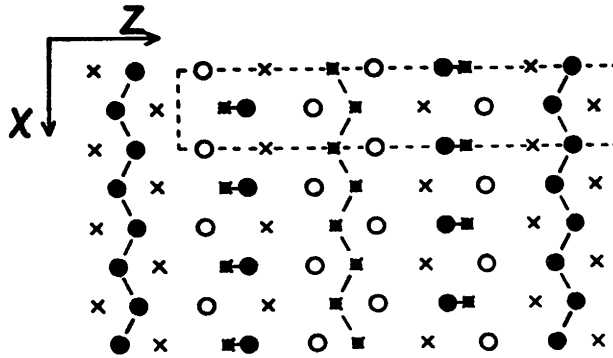
x = metal atoms in x0z
o = metal atoms in x½z
✖ = boron atoms in x0z
● = boron atoms in x½z
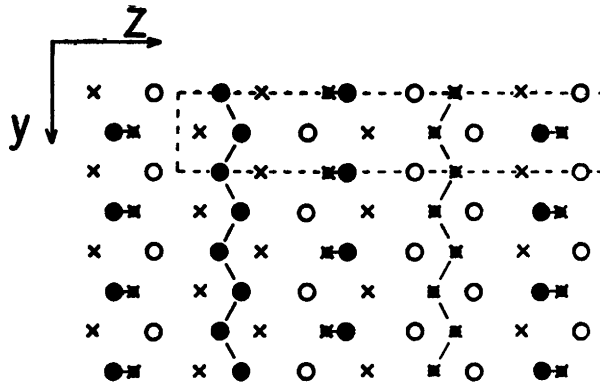
x = metal atoms in 0yz
o = metal atoms in ½yz
✖ = boron atoms in 0yz
● = boron atoms in ½yz

Fig. 3. *Chains of boron atoms in the δ phases.*
a/*Projection on (0 1 0).*
b/*Projection on (1 0 0).*

Table 6. Mo—B, ε-phase, Cr-K radiation.

Hexagonal h k i l	R	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.*	$p\|F\|^2$ calc. z = 0.075
0 0 0 6	a	0.1074	0.1077	st	3	8
0 1 $\bar{1}$ 1	a	1954	1957	st	14	19
1 0 $\bar{1}$ 2	a	2052	2047	sv	3	8
0 1 $\bar{1}$ 4			2406			2.1
0 0 0 9	a	2416	2423	sv	3	1.5
1 0 $\bar{1}$ 5	a	2679	2675	m +	8	11
0 1 $\bar{1}$ 7	a	3397	3393	st	26	19
1 0 $\bar{1}$ 8	a	3846	3842	m +	17	12
0 0 0 12	a	4311	4308	sv	7	4
0 1 $\bar{1}$ 10	—	—	4919	—	0	0
1 0 $\bar{1}$ 11	a_1	5553	5548	sv—	6	3
1 1 $\bar{2}$ 0	a_1	5784	5782	st	32	15
1 1 $\bar{2}$ 3	a_1	6060	6052	sv—	2	0.7
0 0 0 15	a_1	6733	6732	sv—	5	2
1 1 $\bar{2}$ 6	a_1	6861	6859	st	38	25
0 1 $\bar{1}$ 13	a_1	6984	6984	m	19	13
2 0 $\bar{2}$ 1	a_1	7738	7740	m	19	10
1 0 $\bar{1}$ 14	a_1	7783	7792	m	18	11
0 2 $\bar{2}$ 2	—	**	7830	—	**	4
2 0 $\bar{2}$ 4	—	—	8189	—	0	1.2
1 1 $\bar{2}$ 9	a_1	8198	8206	sv	9	5
0 2 $\bar{2}$ 5	a_1	8453	8458	sv +	10	6
2 0 $\bar{2}$ 7	a_1	9172	9176	m	14	11
0 1 $\bar{1}$ 16	—	—	9587	—	0	1.0
0 2 $\bar{2}$ 8	a_1	9621	9625	m	9	7
0 0 0 18	—	—	9694	—	0	1.2

The metal lattice of the Mo-B phase

The interpretation of the powder photographs (Cr-K and Cu-K radiation) gave for the Mo-B phase a rhombohedral lattice with the constants:

$$r = 7.190 \text{ Å}, \ a = 24° \ 10'$$

Because of the analogy with the hexagonal W—B phase, however, hexagonal axes will be used in the discussion of the structure. The dimensions of the hexagonal cell are:

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* Referred to a_1 for all lines.

** 0 2 $\bar{2}$ 2 is concealed by $K\alpha_2$ of 1 0 $\bar{1}$ 14.

Table 7. Mo—B, ε-phase.

h k i l	$p\lvert F\rvert^2$			
	obs.	calc. $z =$		
		0.072	0.075	0.078
0 1 $\bar{1}$ 7	125	191	186	176
1 0 $\bar{1}$ 8	82	141	118	94
0 0 0 12	34	26	37	48
0 1 $\bar{1}$ 10	0	5	0	5
1 0 $\bar{1}$ 11	31	12	32	57
1 1 $\bar{2}$ 0	150	150	150	150
1 1 $\bar{2}$ 3	11	13	7	3

$$a = 3.011 \text{ Å},\ c = 20.93 \text{ Å},\ V = 164.3 \text{ Å}^3$$

If the composition of the phase is assumed to be $MoB_{2.5}$ (71.4 atomic % boron) the observed density of 7.01 most closely corresponds to a cell content of 6 $MoB_{2.5}$ (calculated density 7.48).

Reflections $h\,k\,i\,l$ were observed only for $h-k+l = 3n$ and $h\,h\,2\bar{h}\,l$ for $l = 3n$. This is characteristic of the space groups D_{3d}^5—$R\,\bar{3}m$, D_3^7—$R\,32$ and C_{3v}^5—$R\,3m$.

The only possible positions for 6 Mo atoms are:

in D_{3d}^5 the sixfold position 6 : (c), one parameter,
in D_3^7 the sixfold position 6 : (c), one parameter,
in C_{3v}^5 two threefold positions 3 : (a), one parameter in each.

For all these positions the metal lattice will possess the symmetry of D_{3d}^5, the space group with the highest symmetry, and it will be enough to discuss 6 : (c) in D_{3d}^5 to discover the positions of the metal atoms. The coordinates are as follows:

6 : (c) 0, 0, z; 0, 0, $\bar{z}$; 1/3, 2/3, 1/3 + z; 1/3, 2/3, 1/3—z; 2/3, 1/3, 2/3 + z; 2/3, 1/3, 2/3—z.

Good agreement between observed and calculated $p\lvert F\rvert^2$ values is found for $z = 0.075$ (Table 6). The limits of z seem to be $0.072 < z < 0.078$ (Table 7).

The metal atoms (Fig. 4a) are situated in triangular closepacked planes. Two such planes with the same x and y coordinates are in near contact with each other, thus forming a double layer. Double layers of this kind are piled upon each other with a shift in the x and y coordinates similar to that in a
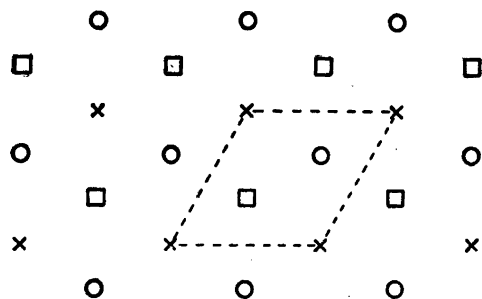
Fig. 4a. The metal lattice of the ε phase of the Mo-B system, projected on (0 0 1). (The unit cell is indicated.)

$$x = \text{Mo in } 00z, \, 00\bar{z}$$
$$\bigcirc = \text{Mo in } 1/3 \, 2/3 \, 1/3 + z, \, 1/3 \, 2/3 \, 1/3 - z$$
$$\square = \text{Mo in } 2/3 \, 1/3 \, 2/3 + z, \, 2/3 \, 1/3 \, 2/3 - z$$

cubic close packing. If in the ordinary cubic close packing the sequence of layers is described as A B C A B C A ... the sequence of layers of molybdenum atoms in the direction of the c axis in this structure will be AA BB CC AA BB CC AA ... The distance between the center of two adjacent Mo-atoms in the same A, B, or C layer will be $a = 3.01$ Å. The distance A—A, B—B or C—C will be $2zc = 3.13$ Å, and the distance A—B, B—C, or C—A will be $c(1/3 - 2z) = 3.82$ Å, where a and c are the lengths of the hexagonal axes.

The possibility of another value of z within the limits given above may, to a small extent, alter the distances between the atoms, but will interfere with neither the fundamental unit of structure nor the positions of the boron atoms, the arrangement of which is discussed below.
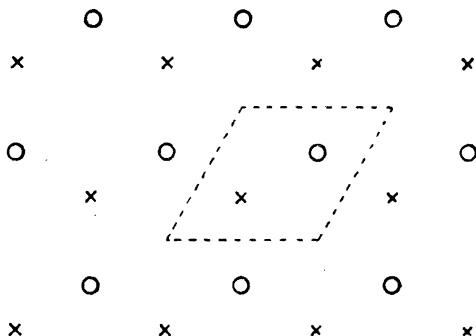

Fig. 4b. The metal lattice of the ε phase of the W-B system, projected on (0 0 1). (The unit cell is indicated).

$$\bigcirc = \text{W in } 1/3 \, 2/3 \, z, \, 1/3 \, 2/3 \, 1/2 - z$$
$$x = \text{W in } 2/3 \, 1/3 \, \bar{z}, \, 2/3 \, 1/3 \, 1/2 + z$$

Table 8. W—B, ε-phase, Cr-K radiation.

$h\,k\,i\,l$	R	sin²Θ		I obs.	$p\lvert F\rvert^2$	
		obs.	calc.		obs.*	calc. $z = 0.139$
0 0 0 4	a	0.1095	0.1090	st	7	12
1 0 $\bar{1}$ 0	a	1966	1965	sv +	4	9
1 0 $\bar{1}$ 1	a	2034	2033	st	10	31
1 0 $\bar{1}$ 2	—	—	2238	—	0	0.5
0 0 0 6	a	2456	2452	sv —	1.1	2.8
1 0 $\bar{1}$ 3	a	2582	2578	m	7	12
1 0 $\bar{1}$ 4	a	3053	3055	sv +	9	14
1 0 $\bar{1}$ 5	a	3670	3668	m +	26	37
0 0 0 8	a	4364	4358	sv	8	6
1 0 $\bar{1}$ 6	—	—	4417	—	0	3
1 0 $\bar{1}$ 7	—	—	5302	—	0	1.1
1 1 $\bar{2}$ 0	a_1	5895	5896	st	33	24
1 1 $\bar{2}$ 2	—	—	6168	—	0	1.4
1 0 $\bar{1}$ 8	a_1	6322	6324	sv —	2.4	7
0 0 0 10	a_1	6810	6810	sv —	4	5
1 1 $\bar{2}$ 4	a_1	6987	6985	st	49	40
1 0 $\bar{1}$ 9	a_1	7480	7481	sv +	24	33
2 0 $\bar{2}$ 0	a_1	7859	7861	sv	7	5
2 0 $\bar{2}$ 1	a_1	7926	7929	sv +	11	19
2 0 $\bar{2}$ 2	—	—	8133	—	0	0.3
1 1 $\bar{2}$ 6	a_1	8343	8347	sv	10	10
2 0 $\bar{2}$ 3	a_1	8476	8474	sv —	5	8
1 0 $\bar{1}$ 10	a_1	8770	8775	sv —	2	6
2 0 $\bar{2}$ 4	a_1	8952	8950	sv —	5	9
2 0 $\bar{2}$ 5	a_1	9559	9563	st	21	25

The metal lattice of the W—B phase

The interpretation of the powder photographs (Cr-*K* and Cu-*K* radiation) gave for the W—B phase a hexagonal cell:

$$a = 2.982 \text{ Å}, \ c = 13.87 \text{ Å and } V = 107.0 \text{ Å}^3$$

With an assumed composition of $WB_{2.5}$ the observed density of 11.0 corresponds to a cell content of 4 $WB_{2.5}$ (calculated density 13.1). The fact,

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* Referred to a_1 for all lines.

Table 9. W—B, ε-phase.

$h \; k \; i \; l$	$p|F|^2$				Resulting limits for z
	obs.	calc. $z =$			
		0.136	0.139	0.142	
0 0 0 8	76	67	55	42	$z<0.142$
1 0 $\bar{1}$ 6	0	8	34	47	
1 0 $\bar{1}$ 7	0	33	11	2	
1 1 $\bar{2}$ 6	104	65	102	140	$0.136<z<0.142$
2 0 $\bar{2}$ 3	51	88	75	63	
1 0 $\bar{1}$ 10	20	41	59	75	

that the c axis of the W—B phase is 2/3 of the c axis of the Mo-B phase is an additional indication of 4 W atoms per cell.

Reflections $h \; h \; 2\bar{h} \; l$ were observed only for $l = 2n$, which is characteristic of the space groups D_{3d}^2—$C \; \bar{3}1c$, C_{3v}^4—$C \; 31c$, D_{6h}^4—$C \; 6/mmc$, C_{6v}^4—$C \; 6mc$ and D_{3h}^4—$C \; \bar{6}2c$. From space considerations and from the fact that $h \; k \; i \; l$ were observed for both odd and even values of l the remaining possibilities of placing four tungsten atoms are:

in D_{3d}^2, the fourfold position 4 : (f),
in C_{3v}^4, two twofold positions 2 : (b),
in D_{6h}^4, the fourfold position 4 : (f),
in C_{6v}^4, two twofold positions 2 : (b).

For all these positions the metal lattice will obtain the symmetry of D_{6h}^4, the space group with the highest symmetry, and it will be sufficient to discuss 4 : (f) in D_{6h}^4 to learn the positions of the metal atoms. The coordinates of the position will be the following:

4 : (f) 1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, 1/2 + z; 1/3, 2/3, 1/2—z.

Good agreement between observed and calculated values is found for $z = 0.139$ (Table 8). The limits for the possible variations of z are $0.136<z<0.142$ (Table 9).

In this case the metal lattice (Fig. 4b) may be described as an arrangement similar to hexagonal close packing. If in the ordinary hexagonal close packing the sequence of layers is described as A B A B A B . . ., the sequence of tungsten atoms in the direction of the c axis will be . . .AA BB AA BB AA . . . The distance between the center of two adjacent tungsten atoms in the same A

or B layer will be $a = 2.98$ Å. The distance between two adjacent layers are. A—A or B—B $= c(\frac{1}{2}—2z) = 3.07$ Å and A—B or B—A $= 2zc = 3.85$ Å:

As was the case for the Mo-phase, the error in the determination of z has no influence on the fundamental unit of structure.

The boron positions

The boron atoms must be situated in holes of the metal lattices, and as these holes are of the same type in both the Mo- and the W-lattices, they may be considered together. In the structures there are three different types of holes.

1. The holes between the metal atoms of a doublesheet A—A, B—B or C—C.

In D_{3d}^5, the space group of the Mo-B phase, these holes correspond to the sixfold position:

6 : (c)   0, 0, z; 0, 0, $\bar{z}$; 1/3, 2/3, 1/3 + z; 1/3, 2/3, 1/3—z; 2/3, 1/3, 2/3 + z; 2/3, 1/3, 2/3—z,

where $z = 1/3$.

The distance center of boron-center of metal atoms for this position would be $\sqrt{a^2/3 + z_{M_0}^2 c^2} = 2.34$ Å.

In D_{6h}^4 (W—B phase) the corresponding positions are:

2 : (b)   0, 0, 1/4; 0, 0, 3/4, and
2 : (d)   1/3, 2/3, 3/4; 2/3, 1/3, 1/4,

and the distance boron-metal would equal 2.31 Å ($\sqrt{a^2/3 + (1/4 — z_W)^2\ c^2}$). The arrangement of metal atoms around the boron atom would be the same as was found for the δ phase; the boron lying in the center of a trigonal prism with six metal atoms at the corners. The boron atoms will then form a plane hexagonal network, similar to that of the carbon atoms in graphite (fig. 5a).

The distance boron-boron in the Mo-B phase is 1.74 Å and in the W—B phase 1.72 Å. If the boron atoms are assumed to be spherical and in contact their radius will be 0.86—0.87 Å in good agreement with the value given by Pauling and Weinbaum [17] for boron in CaB_6. Such plane hexagonal networks have been found for the boron atoms in AlB_2^{10} and $Zr\ B_2^{11}$.

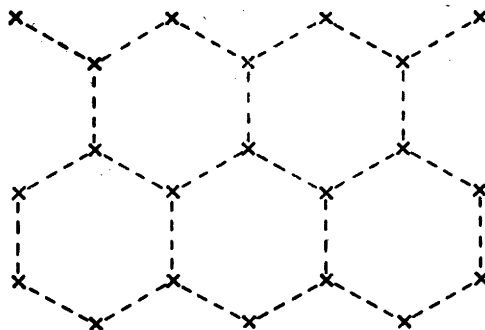In the interspaces between the double sheets there are two additional types of holes.

Fig. 5a. Network of boron atoms, occupying holes of type »1».

2. **Holes in the center of a tetrahedron of metal atoms.** In the Mo-B phase there are six such holes per unit cell with the center in

6 : (c) 0, 0, z; 0, 0. $\bar{z}$; 1/3, 2/3, 1/3 + z; 1/3, 2/3 1/3-z; 2/3, 1/3, 2/3 + z; 2/3, 1/3, 2/3—z (space group D_{3d}^5).

where $z = 1/6 + a^2/6\ c^2(1/3—2z_{Mo}) = 0.186$.

The distance center of boron-center of metal = 2.32 Å [$c\ (z_B—z_{Mo})$].
In the W—B phase there are four which are in

4 : (f) 1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, 1/2 + z; 1/3, 2/3, 1/2—z (space group D_{6h}^4).
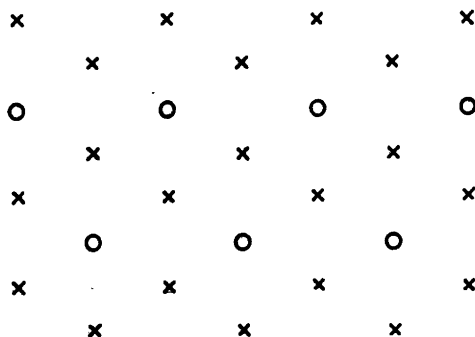
where $z = — a^2/12\ z_W^2\ c^2 = — 0.028$.

Fig. 5b. Sheet of boron atoms, occupying holes of type »2» and »3».
x = boron in hole of type »2».
O = boron in hole of type »3».

The distance boron-tungsten = 2.32 Å [c (z_W—z_B)].

3. Finally there is a third type of hole. The center for this type of hole have the position:

in D_{3d}^5 (Mo-B phase) 3 : (b) 0, 0, 1/2; 1/3, 2/3, 5/6; 2/3, 1/3, 1/6,
in D_{6h}^4 (W—B phase) 2 : (a) 0, 0, 0; 0, 0, 1/2.

A boron atom placed in such a hole would be surrounded by six metal atoms, all at a distance of 2.59 Å ($\sqrt{a^2/3 + c^2 z_W^2}$) from the center, and arranged at the corners of a deformed octahedron. If all the holes of type »2» were filled, a boron atom in »3» would not be in direct contact with any metal atom but with six other boron atoms, and the atoms of »2» and »3» would form a slightly puckered, close packed hexagonal sheet of boron atoms, lying in the interspaces between the doublesheets of metal atoms (Fig. 5b). The distances »2»—»3» = 1.76 Å and »2»—»2» = 1.92 Å.

Thus, from space considerations boron atoms may be placed in all the holes of the metal lattice described above. Such an »ideal» ε phase would have the formula Me_2B_5 corresponding to a boron content of 71.4 atomic %, and in these »ideal» phases, the arrangement of layers along the c axis would be ...

$$\overbrace{\hspace{3cm}}^{c}$$
Å H A K B H B K C H C K A H A K B ... for the Mo-B phase and

$$\overbrace{\hspace{2.5cm}}^{c}$$
Å H A K B H B K A H A K B H B K ... for the W—B phase. Here A, B, and C are the metal sheets described above, H are the hexagonal networks of boron atoms (holes of type »1») and K are the sheets of boron atoms (holes of types »2» and »3»).

The exact boron content of the phases was very difficult to determine because of the difficulties of isolating and analysing the pure phases. In both the systems, however, it seemed to be less than 71.4 atomic %. A study of the photographs of these phases, starting with different compositions Me-B indicated that for the Mo-B phase the reflections always occurred at fixed angles. The boron content of the phase was found to be about 70 atomic %. In the case of the W—B phase, however, there was a small variation of the $\sin^2 \Theta$ values (Table 10) which indicates an extended homogeneity range with the limits $66.7 < \varepsilon < 68.0$ atomic % boron.

The corresponding values of the axes are $a = 2.982$ Å, $c = 13.87$ Å and $a = 2.984$ and $c = 13.87$ Å respectively. The values of the limits, however, are rather uncertain because of the small variation and the possible errors of the composition. It is impossible to determine which holes of the metal lattices are occupied by boron atoms and which are not. The phases thus must be

Table 10. W—B, ε-phase.

$h\ k\ i\ l$	sin²Θ obs.					
	Boron content (atomic %)					
	64.0	66.7	67.3	67.9	71.5	82.3
1 1 $\bar{2}$ 0	5894	5896	5893	5887	5886	5884
1 1 $\bar{2}$ 4	6987	6987	6981	6974	6972	6972
1 0 $\bar{1}$ 9	—	7482	7479	7480	7475	7480
2 0 $\bar{2}$ 0	7865	7865	7858	—	7849	7849
2 0 $\bar{2}$ 1	7932	7926	7924	7918	7916	7912

described in relation to the ideal ε phase, described above. Of the boron positions in the ideal phase, 93 % are occupied in the Mo-B phase and 80—86 % in the W—B phase.

The ε phase in the Mo-B system thus crystallizes in D_{3d}^5—$R\ \bar{3}m$ with the metal atoms in the sixfold position

6 : (c) 0, 0, z; 0, 0, $\bar{z}$: 1/3, 2/3, 1/3 + z; 1/3, 2/3, 1/3—z; 2/3, 1/3, 2/3 + z; 2/3, 1/3, 2/3—z,

where $z = 0.075$.

Six boron atoms may be placed in 6 : (c) with $z = 1/3$, six in 6 : (c) with $z = 0.186$ and three in

3 : (b) 0, 0, 1/2; 1/3, 2/3, 5/6; 2/3, 1/3, 1/6.

About 93 % of these positions are occupied by boron atoms.

The ε phase in the W—B system crystallizes in D_{6h}^4—$C\ 6/mmc$ with the metal atoms in

4 : (f) 1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, 1/2 + z; 1/3, 2/3, 1/2—z,

where the parameter $z = 0.139$. Four boron atoms may be placed in 4 : (f) with $z = -0.028$, and two boron atoms in each of the following three positions

2 : (b) 0, 0, 1/4; 0, 0, 3/4,
2 : (d) 1/3, 2/3, 3/4; 2/3, 1/3, 1/4,
2 : (a) 0, 0, 0; 0, 0, 1/2.

About 80—86 % of these positions are occupied.

4

GENERAL CONCLUSIONS

The formation of interstitial compounds in the binary systems transition element-boron, carbon, nitrogen or hydrogen without serious distortion of the metal lattice, according to Hägg [12,13], is possible only when the ratio of boron radius: metal radius is less than 0.59. In discussing the radius of the boron atom the γ phases are excluded because of the variation of r_B in the isomorphous compounds Me_2B. From the distance boron-boron in the chains of boron atoms of the δ phases the value $r_B = 0.87$ Å is obtained, and from the hexagonal networks in the ε phases (holes of type »1») the values $r_B = 0.87$ Å (Mo-B) and $r_B = 0.86$ Å (W—B) are obtained. These values are in good agreement with the value 0.86 Å, reported by Pauling and Weinbaum [17] for boron in CaB_6, which seems to be the most accurate value from earlier experiments. Assuming 0.87 Å to be a correct value, the ratio $r_B : r_{Me}$ will be 0.62 for molybdenum and tungsten (1.40 and 1.41 Å beeing the value of r_{Mo} respectively r_W corresponding to 12-fold coordination). In fact, none of the intermediate phases in the systems Mo-B and W-B has the simple type of metal lattice which exists if $r_B : r_{Me}$ less than 0.59. The value 0.62, however, is close to the critical value and all the metal lattices are rather simple. The ε phase, for example, may be considered as consisting partly of a simple hexagonal lattice with the boron atoms in the interspaces.

The boron atoms seem to have a marked tendency to form first chains and then rings as the boron content of the system increases. Upon studying the arrangement of the boron, the following three cases may be distinguished:

1. In the γ phases, Me_2B, the boron atoms are present as isolated units in the lattice.

2. In the δ phases with 48—51 atomic % boron they form zig-zag shaped lines running through the channels of the lattice.

3. In the ε phases with 67—70 atomic % boron they form partly hexagonal networks and partly two-dimensional sheets.

All the metal borides previously recognized, may be classified in one of these groups, or in a fourth group with a three-dimensional network of boron atoms.

Fe_2B[7,8], Co_2B, and Ni_2B[9], having isolated boron atoms, belong to group 1.

In FeB and CoB[9] the boron atoms form zig-zag chains as in the δ phases above. The coordination around the boron is the same too, but the chains are all parallel. These borides belong to group 2.

AlB_2[10] and ZrB_2[11] belong to group 3, the boron atoms forming plane hexagonal networks, all of which are parallel.

The borides of type CaB_6 (D 2_1) belong to group 4 [14—17].

It is of interest to note that most of these stages can be distinguished in the configuration of the carbon atoms in the carbides. For example, in Fe_3C [18] and the carbides of manganese and nickel, the carbon atoms lie in isolated positions in the metal lattice, while in the chromium carbide Cr_3C_2 [19], the carbon atoms form zig-zag chains throughout the lattice. Potassium graphite compounds may be regarded as analogous to group 3, since they are compounds of potassium and infinitely extended hexagonal networks of carbon atoms. Carbides analogous to group 4 have not been observed.

It would be of great interest to learn whether or not this analogy may be extended to the formation of different boron hydrides, starting with borides from different groups above. Such an experiment, however, would be difficult to perform because of the problems involved in isolating the boron hydrides for study.

SUMMARY

The systems Mo-B and W—B have been studied by X-ray methods, and the following boride phases were found to exist:

γ phases Mo_2B and W_2B. Unit dimensions are given and the phases are shown to be isomorphous with Fe_2B, Co_2B, and Ni_2B.

δ phases, isomorphous and existing in a homogeneity range of about 48—51 atomic % boron. Unit dimensions are given and a complete structure determination has been made.

ε phases, whose ideal boron content is 71.4 atomic % boron, but which in reality exist at about 70.0 atomic % boron for Mo-B and whose range is 67—68 atomic % boron for W-B. Unit dimensions are given and a complete structure determination has been accomplished. The phases are not isomorphous but a close relationship exists between them. The ideal formula of both phases is Me_2B_5 but some of the boron atoms corresponding to this formula are missing.

A boron preparation with a purity of 98—99 % B, which was used in this investigation, was obtained by thermic dissociation of BBr_3 in a heated quartz tube at about 700° C in the presence of hydrogen.

The radius of the boron atom has been found to be 0.87 Å.

The structures are discussed according to the relation $r_B : r_{Me}$.

The boron atoms has a marked tendency to form first chains and then rings or sheets as the boron content of the system increases, and all the known borides of the metals may be classified according to the distribution of the boron atoms.

Similarity between the borides and some carbides is noted.

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