METAL BORIDES

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1. Introduction

METALS form binary compounds with elements from each of the Main Groups of the Periodic Table. The structures of the majority of the metal halides, oxides, and chalcogenides are well understood, and their chemistry has been intensively investigated. The structures of binary compounds with the elements of Group V, IV, and III are also well established, but less is known of their chemistry. The picture is one of increasing complexity the further away one moves from the halogens towards the left of the Periodic Table. Boron forms binary compounds with most of the elements, present exceptions being the rare gases and elements of the zinc, gallium, and germanium sub-groups. Metal borides provide the only systems, apart from the boron hydrides and their derivatives, in which extensive clustering and catenation of boron atoms occurs. The bonding in such systems has presented some interesting problems and in some instances may be tentatively explained by analogy with the hydride systems. Borides are also arousing considerable technological interest, since they are refractory and often chemically inert. In addition, many have useful physical properties; for example some lanthanide hexaborides are excellent thermionic emitters.

Studies of metal borides have been mainly concerned with their preparation, characterisation, structure, and physical properties; bonding has received some attention, but comparatively little is known of their chemistry. Previous reviews have dealt in some detail with specific aspects of metal borides such as structure,[1-8] preparation,[4,5,9] and physical properties,[1a,3,4,8,9] while discussions of bonding have either been restricted to a

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[1] B. Aronsson, *Arkiv Kemi*, 1960, **16**, 379.

[1a] B. Aronsson, T. Lundström, and S. Rundqvist, "Borides, Silicides, and Phosphides", Methuen, London, 1965.

[2] R. Kiessling, *Acta Chem. Scand.*, 1950, **4**, 209.

[3] B. Post, in "Boron, Metallo-Boron Compounds and Boranes", ed. R. M. Adams, Interscience, New York, 1964, p. 301.

[4] G. V. Samsonov, *Uspekhi Khim.*, 1959, **28**, 189 (available in translation as U.K.A.E.A. report AERE, Trans 849).

[5] G. V. Samsonov and L. Ya. Markovskii, *Uspekhi Khim.*, 1956, **25**, 190 (translation by Associated Technical Services, RJ-631).

[6] W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys", Pergamon, London, 1958.

[7] M. Hansen, "Constitution of Binary Alloys", McGraw Hill, New York, 1958.

[8] K. A. Gschneider, "Rare Earth Alloys", Van Nostrand, New York, 1961.

[9] P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals", MacMillan, New York, 1953.

few boride types[1,2,10] or have been rather uncritical.[3] The chemistry of metal borides has not recently been reviewed. This Review seeks to provide a concise, balanced, and critical account of those aspects of metal borides which are of primary interest to chemists, *viz.*, preparation, structure, bonding, and chemical properties.

Metal borides provide a rich variety of structures and compositions, the latter ranging from M_5B to MB_{12} or even, possibly, to MB_{70}. Although no one metal has yet been observed to span the whole range several metals form as many as six or seven distinct borides. The known borides are listed in Table 1, in which the formulae used represent ideal rather than

TABLE 1. *Known metal borides*

M	M_3B	M_7B_3	M_2B	M_3B_2	MB	M_3B_4	MB_2	M_2B_5	MB_4	MB_6	MB_{12}	Other
Na										+		
Be			+				+			+	+	Be_5B
Mg							+		+	+		
Ca									+	+		
Sr										+		
Ba										+		
Al							+		+		+	
Sc							+		+	+	+	
Y							+		+	+	+	YB_{70} ?
La									+	+		
Ce									+	+		
Pr									+	+		
Nd									+	+		
Pm									+	+		
Sm									+	+		
Eu									+	+		
Gd							+		+	+		
Tb							+		+	+	+	TbB_{70} ?
Dy							+		+	+	+	
Ho							+		+	+	+	HoB_{70} ?
Er							+		+	+	+	
Tm									+	+	+	
Yb									+	+	+	YbB_{70} ?
Lu							+		+	+	+	
Th									+	+		
U							+		+		+	
Pu					+		+		+	+		

R. Kiessling, *Metallurgical Reviews*, 1957, **2**, 77.

TABLE 1—*continued*

M	M_3B	M_7B_3	M_2B	M_3B_2	MB	M_3B_4	MB_2	M_2B_5	MB_4	MB_6	MB_{12}	Other
Ti					+		+	+				
Zr					+		+				+	
Hf					+		+					
V				+	+	+	+					
Nb			+	+	+	+	+					
Ta			+	+	+	+	+					
Cr			+		+	+	+			+		Cr_5B_3, Cr_4B
Mo			+		+		+	+	+		?	
W			+		+			+	+		?	
Mn			+		+	+	+		+		?	Mn_4B
Tc	+	+			+	+	+					
Re	+	+			+	+	+					
Fe			+		+							
Ru		+	+		+		+	+				$Ru_{11}B_8$
Os					+		+	+				
Co	+		+		+							
Rh		+			+		+					
Ir					+		+					
Ni	+		+		+							Ni_4B_3 (two forms)
Pd	+											Pd_5B_2
Pt					+							Pt_2B_3
Ag							+					
Au							+					

actual compositions of the various phases. The occurrence of non-stoicheiometry is discussed in Section 4.

It will be seen that only the diborides (MB_2) appear to be common to all classes of metal. As a general rule main-group and *f*-block elements form higher borides while transition elements form lower borides. Such generalisations should not however, be applied too rigidly as the examples Be_5B, ZrB_{12}, and CrB_6 indicate. The readiness with which transition metals form lower borides may be connected with their high heats of vaporisation, high ionisation potentials, and the availability of partially empty *d*-orbitals (see Section 5).

2. Preparation

Because of the high temperatures involved, metal borides are not easy to prepare pure and subsequent purification is often difficult. The six major preparative methods and typical examples are outlined below.[4,5,9,11]

(a) Direct Combination of the Elements.—This is probably the most widely used technique. The purity of the product depends mostly on that of the parent metal since the impurities in boron are often relatively volatile. Contamination by the crucible material must be guarded against; the best material seems to be boron nitride which has been heated in hydrogen to remove oxygen. Exact stoicheiometry is difficult to achieve by this method, especially when the metal is very volatile.

$$\mathrm{Cr} + n\mathrm{B} \xrightarrow{1150^\circ} \mathrm{CrB}_n$$

Small quantities of very pure borides can be obtained by preparing the boron (and sometimes the metal also) by pyrolysis of a halide on a hot metal filament in a hydrogen atmosphere:

$$2\,\mathrm{TiCl_3} + 4\mathrm{BCl_3} + 9\mathrm{H_2} \rightarrow 2\mathrm{TiB_2} + 18\mathrm{HCl}$$

(b) Reduction of the Metal Oxide with Boron.—This is also very convenient for a wide range of metals. The oxygen is eliminated as volatile oxides of boron. The method is therefore less efficient in its use of boron than is the preceding method:

$$\mathrm{Sc_2O_3} + 7\mathrm{B} \xrightarrow{1800^\circ} 2\mathrm{ScB_2} + 3\mathrm{BO}$$

(c) Reactions with Boron Carbide.—Boron carbide is a most useful source of boron, and will react with most metals or their oxides. Carbon or boric oxide may be added to ensure complete removal of oxygen or carbon as carbon monoxide.

$$\mathrm{Eu_2O_3} + 3\mathrm{B_4C} \xrightarrow{1600^\circ} 2\mathrm{EuB_6} + 3\mathrm{CO}$$

$$7\mathrm{Ti} + 3\mathrm{B_4C} + \mathrm{B_2O_3} \xrightarrow{2000^\circ} 7\mathrm{TiB_2} + 3\mathrm{CO}$$

(d) Electrolysis.—With suitable systems (*e.g.*, lanthanides, alkaline-earth metals) electrolysis can give pure products. The metal oxide and boric oxide or borax are fused together with a flux of alkali or alkaline-earth halides or fluoroborates. Frequently, however, the products consist of mixtures of several phases and are contaminated with elemental boron and electrode graphite. Separation of boron from borides is difficult although partial decontamination can be achieved by flotation.

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[11] P. Thornton, M.Sc., Dissertation, Durham, 1962.

(e) Carbon Reduction.—The reduction of mixtures of metal oxides and boric oxide with carbon is not generally satisfactory owing to heavy losses of boric oxide by volatilisation, and contamination of the product with boron, carbon, and boron carbide:

$$V_2O_5 + B_2O_3 + 8C \xrightarrow{1500^\circ} 2VB + 8CO$$

(f) Reduction of Boric Oxide with a Metal.—This method is even less satisfactory as the product must necessarily contain large quantities of the metal oxide.

(g) Other Methods.—It has been claimed[12] that a nickel boride can be obtained by the reaction of aqueous solutions of nickel salts with sodium borohydride. The precise composition of the product is not known, but it appears to contain about 10% of water. It is initially amorphous but after the product has been heated the *X*-ray diffraction patterns of elemental nickel and Ni_3B can be detected.[13]

3. Crystal Structure

The structures of metal borides are concisely and conveniently discussed in terms of the disposition and environment of the boron atoms. The treatment given here will be relatively condensed since detailed discussions of individual structures are readily available elsewhere.[1–8] In the majority of structure determinations only the metal atoms have been placed; the positions of the boron atoms have usually then been inferred from the known composition and density and the occurrence of suitable gaps in the metal lattice.

Despite the wide range of stoicheiometry found in boride systems the observed structures can be divided into two major classes: (*a*) those in which boron atoms are at the centres of trigonal prisms of metal atoms (M_3B to MB_2); and (*b*) those in which the boron atoms form infinite, rigid lattices (MB_2 to MB_{12}). The various structural types of boride and the corresponding environments of the boron atoms are summarised in Table 2.

(a) Trigonal Prismatic Borides (M_3B to MB_2).—Borides at the metal-rich end of the composition range have structures which are determined essentially by the metal lattice though it is misleading[1] to describe these compounds as interstitial phases. The metal atoms usually approximate to a hexagonal arrangement. Such quasi-hexagonal metal lattices can be built up in several ways from arrangements of more or less distorted trigonal prisms, some of which contain boron atoms. For many metals very similar

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[12] R. Paul, P. Buisson, and N. Joseph, *Compt. rend.*, 1951, **232**, 627; C. A. Brown and H. C. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 1005.

[13] P. Thonnart, P. Lenfant, and C. Legras, *Compt. rend.*, 1964, **258**, 5207; L. J. E. Hofer, J. F. Schultz, R. D. Pauson, and R. B. Anderson, *Inorg. Chem.*, 1964, **3**, 1783.

TABLE 2. *Structural types and boron environments in metal borides*

Ideal compn.	B network	B environment	Min d_{B-B} (Å)	Obsd. systems
M_4B	Isolated atoms	Square antiprism		Cr, Mn.
M_3B	„	Trigonal prism	*ca.* 2·1	Late *d*-block
M_5B_2	„	„		Pd
M_7B_3	„	„		Re, Ru, Rh
M_2B	„	Square antiprism	2·1	*d*-Block, Be
M_3B_2	Pairs	Trigonal prisms	*ca.* 1·75	V, Nb, Ta
M_4B_3	Isolated atoms and chains	„	„	Ni
$M_{11}B_8$	Branched chains	„	„	Ru
MB	Chains	„	„	*d*-Block
M_3B_4	Double chains	„	„	V—Ta, Cr, Mn—Re
MB_2	Hexagonal nets	„	„	All types
M_2B_5	Puckered hexagonal nets	„	„	Ti, Mo, W, Ru, Os
MB_4	Planes + octahedra		„	Mg, Ca, *f*-block Mo, W, Mn
MB_6	Octahedra		„	Be—Ba, Sc—La, *f*-block
MB_{12}	Cubo-octahedra		„	Sc, Y, Tb—Lu, U, Zr

structures are also found for carbides, silicides, nitrides, and phosphides.[1,1a] Thus, the most metal-rich borides, M_3B, M_5B_2, and M_7B_3, have structures isomorphous with, or closely related to, the cementite structure. In this structure trigonal prisms are so arranged that there is a metal atom (also part of a trigonal prism) beyond each rectangular face, so that the boron atom is co-ordinated to nine metal atoms in a "3:3:3" arrangement as shown in Fig. 1a. This effectively isolates the boron atoms from each other, the minimum boron–boron distance being 2·1 Å.

As the boron content increases up to MB_2, boron-centred prisms are joined together so that the metal atoms beyond the rectangular faces are replaced by boron atoms in adjoining prisms, although the metal lattices are all still quasi-hexagonal. The boron atoms can thus associate in pairs (M_3B_2: Fig. 1b), chains (M_4B_3, MB: Fig. 1c), branched chains ($M_{11}B_8$, only representative known, $Ru_{11}B_8$: Fig. 1d), cross-linked double chains (M_3B_4: Fig. 1e), and finally form a complete hexagonal network (MB_2: Fig. 1f).

It was originally suggested[2] that the cross-linking boron–boron bonds in M_3B_4 were shorter than normal (about 1·5 Å, compared with 1·75—1·85 Å along the chains), although it was noted that an arrangement with all boron–boron distances equal (1·72 Å) was also possible. A re-examination of Cr_3B_4 has shown that, in this case at least, these distances are the same within experimental error (observed distances 1·69 and 1·77 Å;

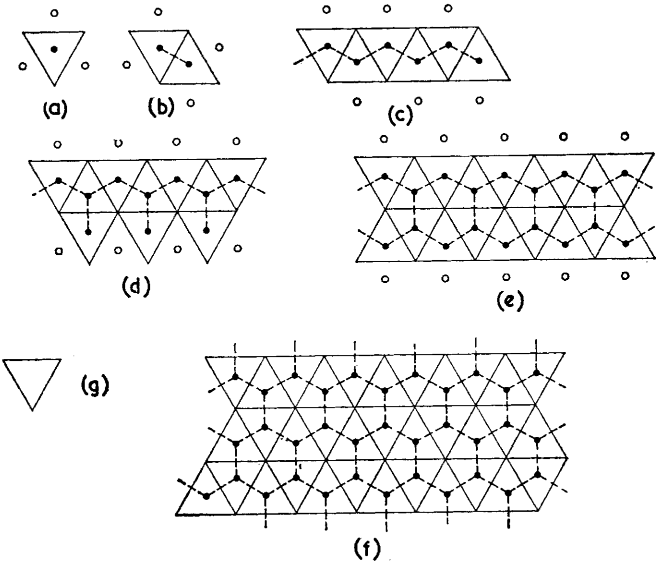

FIG. 1. *Arrangement of trigonal prisms in metal-rich borides.* (a) M$_3$B, (b) M$_8$B$_2$, (c) MB, (d) M$_{11}$B$_8$, (e) M$_3$B$_4$, (f) MB$_2$, (g) *trigonal prism of metal atoms.*
● *Boron atoms* ○ *extra prismatic metal atoms.*

$\sigma = 0{\cdot}02$ Å).[14] It seems likely that the boron–boron distances will be equal in all borides of this type. The double chains thus appear as fragments of the diboride hexagonal nets.

The diborides are strictly hexagonal and form the link between the two structural classes of boride. They have the ultimate structure obtainable by the condensation of trigonal prisms and are also the first type in which a discernible extended boron lattice occurs. The phases M$_2$B$_5$ have structures similar to that of the diborides except that alternate boron layers are puckered, rather than planar. A similar puckering occurs in ReB$_2$.

(b) Boron Lattices (MB$_2$ to MB$_{12}$).—In the higher borides the structure is dominated by the rigid boron framework. Again, simple units can be seen and the structures are mostly formed from cubic arrays of these units with the metal atoms forming a second, interpenetrating cubic lattice. Thus in MB$_6$ the boron atoms form octahedral clusters which are linked together in three dimensions to give a cubic lattice; the metal atoms are accommodated in the holes between eight octahedra (Fig. 2a) and are thus surrounded by twenty-four boron atoms in a cubo-octahedron (Fig. 2b). Fourier analysis for ThB$_6$ is compatible with co-ordinates ± (0·293, 0, 0), etc., for the boron atoms, implying that the inter- and intra-octahedral boron–boron distances are the same.[15] This result is unaffected by sub-

[14] M. Elfstroem, *Acta. Chem. Scand.*, 1961, **15**, 1178.
[15] P. Blum and F. Bertaut, *Acta Cryst.*, 1954, 7, 81.

stitution of sodium up to the limiting concentration of $Th_{0.23}Na_{0.77}B_6$. The actual value of the boron–boron distance (a/2·414) varies with the metal, although the range of a values is considerably less than the range of metallic radii, which implies a considerable rigidity of the boron lattice.[15]

The tetraborides, MB_4, have a structure intermediate between those of the di- and hexa-borides. Boron atoms are arranged in planar layers in which boron octahedra are inserted. The layers are made up of heptagons joined together and connected by octahedra, with metal atoms at the centres of the heptagons (Fig. 2c). The over-all arrangement is tetragonal.

A more complex, although cubic, lattice is found for the dodecaborides, MB_{12}. The boron atoms form a network which can be regarded as a cubic array of cubo-octahedra, each of which contains twelve boron atoms (Fig. 2d). The metal atoms are located in the large holes between eight of these groups, having as their immediate environment twenty-four boron atoms in the form of the third possible type of cubo-octahedron (Fig. 2e).

It appears that BeB_{12}[16] and AlB_{12}[17] (and perhaps BeB_6[18]) may have a related (rhombohedral) structure formed from icosahedral B_{12} units like those found in elemental boron. Another phase, AlB_{10}, which appears

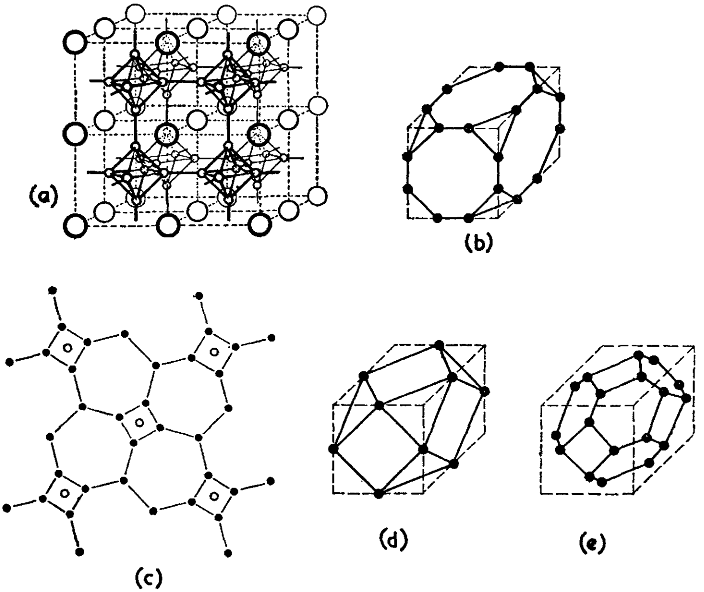

FIG. 2. (a) MB_6 *arrangement,* (b) *metal environment in* MB_6, (c) MB_4 *arrangement,* (d) B_{12} *unit in* MB_{12}, (e) *metal environment in* MB_{12}.

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[16] H. J. Becher, *Z. anorg. Chem.*, 1960, **306**, 266.

[17] J. A. Kohn and D. W. Eckhart, *Z. Krist.*, 1961, **116**, 134.

[18] D. Sands, C. F. Kline, A. Zalkin, and C. L. Hoenig, *Acta Cryst.*, 1961, **14**, 309.

to contain boron icosahedra,[19] probably also contains carbon and the formula AlC_4B_{24} has been suggested.[20]

(c) **Other Structures.**—The only important group of borides which does not fit into the preceding classification is the M_2B type with the $CuAl_2$ structure. The metal atoms are arranged in layers of fused tetrahedra, leaving square antiprismatic holes between the layers in which the boron atoms are accommodated. Borides of the type M_4B have a closely related structure in which half the boron atoms are omitted randomly.

Borides with a very low metal content, corresponding roughly to MB_{70}, have been reported for M = Y, Tb, Ho, and Yb.[21,22] These are probably all cubic but have large unit cells and complicated structures which have not been solved.

The few exceptions to the above generalisations can be listed briefly as follows: (i) Be_2B has the cubic, fluorite structure;[18,23] (ii) PtB and $RhB_{1.1}$ have the anti-NiAs structure, in which the boron atoms form a close-packed hexagonal lattice, each boron atom being at the centre of an octahedron of metal atoms;[24] (iii) RuB and OsB have compositions of $RuB_{\sim 1.1}$ and $OsB_{\sim 1.2}$; both have the AlB_2 structure;[24] (iv) Ru_2B_5 and Os_2B_5 have the W_2B_5 structure, but the compositions are actually $RuB_{\sim 1.5}$ and $OsB_{\sim 1.6}$;[24] (v) RuB_2, OsB_2, $IrB_{1.1}$ adopt the $ThSi_2$ structure with puckered hexagonal boron nets similar to those in other diborides, but in which the metal atoms form an open, three-dimensional lattice so that each boron atom is at the centre of a tetrahedron of metal atoms;[24,25] (vi) CrB_6 is not cubic, but tetragonal;[26] (v) NaB_6 is not isotypic with the other hexaborides; the powder pattern has been reported but not indexed.[27]

It is noteworthy that many of the arrangements of boron atoms in metal borides occur also in discrete molecules or ions, as in the boron hydrides and related systems. For instance, Nöth and Hermannsdörfer have been able to stabilise boron chains by attaching R_2N side groups. So far, compounds in the series $R_n(R_2N)_{n+2}$ with n up to 8 have been isolated.[28] Clusters of boron atoms occur in $B_6H_6^{2-}$ (octahedra)[29] and $B_{12}H_{12}^{2-}$ (icosahedra),[30] and their derivatives. The cubo-octahedral

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[19] G. Will, *J. Amer. Chem. Soc.*, 1963, **85**, 2335.

[20] V. I. Matkovich, J. Economy, and R. F. Geise, *J. Amer. Chem. Soc.*, 1964, **86**, 2337.

[21] A. U. Seybolt, *Trans. Amer. Soc. Metals*, 1960, **52**, 971.

[22] S. La Placa, personal communication to B. Post.[3]

[23] L. Ya. Markovskii, Yu. D. Kondrashev, and G. V. Kaputovskaya, *Zhur. obshchei Khim.*, 1955, **25**, 1045.

[24] B. Aronsson, E. Stenberg, and J. Aselius, *Acta Chem. Scand.*, 1960, **14**, 733; *Nature*, 1962, **195**, 377.

[25] B. Aronsson, *Acta Chem. Scand.*, 1963, **17**, 2036.

[26] V. A. Epel'baum, N. G. Sevast'yanov, M. A. Gurevich, and G. S. Zhdanov, *Zhur. strukt. Khim.*, 1960, **1**, 64.

[27] P. Hagenmuller and R. Naslain, *Compt. rend.*, 1963, **257**, 1294.

[28] H. Nöth and K. H. Hermannsdörfer, personal communication.

[29] R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, 1965, **4**, 917.

[30] J. Wunderlich and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1960, **82**, 4427.

grouping has been postulated as an intermediate in the rearrangement reaction of carborane to neo-carborane.[31] One might also speculate whether ternary metal–boron–carbon systems contain hetero-clusters analogous to the carboranes ($B_4C_2H_6$,[32] $B_{10}C_2H_{12}$[31]) or whether other boron atom arrangements are possible, such as the tetrahedron or square antiprism found in the lower halides.

It can be seen from the structures reviewed in this Section that there are extensive similarities in the metal-rich systems to the structures of metal-rich carbides, silicides, nitrides, and phosphides in which the non-metal is also surrounded by a trigonal prism of metal atoms.[1,1a] However, with the possible exception of Be_2B, there is no boride structure corresponding to those of the ionic carbides and nitrides. This is presumably because the greater electropositivity of boron inhibits anion formation. The system in which boron has the most negative charge [see Section 5(c)] is probably MB_2, which approaches $M^{2+}(B^-)_2$. In this system there is scope for considerable stabilisation by electron delocalisation. Equally, there is no carbide or nitride structure analogous to those of the boron-rich borides, in which the electron-deficient nature of boron allows the formation of clusters of atoms which cannot occur for carbon or nitrogen.

4. Non-stoicheiometry

Clearly, there is considerable scope for non-stoicheiometry in metal borides. The boron content of the metal-rich borides can be varied simply by adding or omitting boron atoms. In the monoborides, for example, molybdenum and tungsten show variable boron content in the ranges $MoB_{0.95-1.06}$ and $WB_{0.92-1.02}$ respectively.[33] Kiessling has suggested that boron atoms may either be removed from the chains, leaving gaps, or added to them, giving a compressed chain.[2] Similarly Mn_4B has a variable composition which could, in principle, extend up to Mn_2B, if boron atoms were placed on all the available sites. Actually, Mn_2B itself adopts the $CuAl_2$-type lattice and appears to be stoicheiometric.[34]

In the diborides, vacancies can presumably appear in either lattice, although Kiessling again favours a complete metal lattice with boron atoms either missing or being inserted at the centre of the hexagons. For example, the composition of the phase "TaB_2" varies from $TaB_{1.78}$ to $TaB_{2.57}$.[35]

The higher borides, with their rigid boron frameworks are more likely to show variation in composition by metal vacancies. For instance, LaB_6 can tolerate metal deficiency until the composition $La_{0.82}B_6$ is

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[31] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, 1964, **3**, 1673; D. Voet and W. N. Lipscomb, *ibid.*, p. 1679.

[32] I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *J. Amer. Chem. Soc.*, 1963, **85**, 3167.

[33] R. Kiessling, *Acta Chem. Scand.*, 1947, **1**, 893.

[34] R. Kiessling, *Acta Chem. Scand.*, 1950, **4**, 146.

[35] R. Kiessling, *Acta Chem. Scand.*, 1949, 3, 603.

reached.[36] It is presumably this ability, coupled with the high mobility of the metal atoms, which makes LaB_6 such a good thermionic emitter.

It has been suggested[18] that there may be a continuous range of homogeneity from BeB_6 through BeB_{12} to rhombohedral boron, as these phases have almost identical *X*-ray diffraction patterns.

Many borides do not exhibit such variation in composition but nevertheless have compositions which deviate markedly from the ideal stoicheiometry suggested by their crystallography. Several striking examples have been mentioned at the end of the previous section; *e.g.*, $RuB_{1.1}$, $OsB_{1.2}$, and $IrB_{1.1}$ all have an ideal composition of MB_2.[24] Less extreme examples are Ta_2B and Ta_3B_2 which actually have compositions corresponding to $Ta_{2.4}B$ and $Ta_{3.2}B_2$.[37]

5. Bonding

The nature of the bonding in metal borides has been discussed by many authors, particularly from the point of view of gain or loss of electrons by the boron atoms relative to the metal atoms. It has frequently been suggested that such electron transfer must be in the same direction for all types of boride; for instance, the relative electronegativities of boron and transition metals might be taken to imply that transfer should always occur from metal to boron. Clearly, however, there will be as many types of electron distribution as there are types of boride and the actual electronic structure will depend on the detailed requirements of the particular boron and metal lattices involved. Each type of boride must be treated individually but the following generalisation can be made: in metal-rich borides such as M_2B electron transfer is to the metal, whereas for the boron-rich borides such as MB_6 it is to the boron lattice.

(a) Metal-rich Borides.—For the metal-rich borides arguments of varying congency and validity have been used to infer the direction of electron transfer. The suggestion that electron transfer is from metal to boron is due to Pauling.[38,39] Using his relation between bond length and bond order and taking into account the relative electronegativities, Pauling concluded that, in borides of the type MB, one-third to one quarter of an electron would be transferred to the boron. For borides of the type M_2B, this argument suggests that either the order of the metal–boron bond rises[2,40] or that the percentage *d*-character in this bond increases as M varies through the series Mn, Fe, Co, Ni. In either case the metal–boron bond is expected to become stronger as the atomic number of the metal rises.[39] It has been stated that such a trend in bond strengths is incom-

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[36] R. W. Johnson and A. H. Daane, *J. Phys. Chem.*, 1961, **65**, 909.

[37] J. M. Leitnaker, M. G. Bouman, and P. W. Gillies, *J. Electrochem. Soc.*, 1961 **108**, 508.

[38] L. Pauling, *Proc. Roy. Soc.*, 1949, *A*, **196**, 343.

[39] L. Pauling and R. Kiessling, *J. Electrochem. Soc.*, 1951, **98**, 518.

[40] R. Kiessling, *J. Electrochem. Soc.*, 1951, **98**, 166.

patible with the observed partitioning of pairs of metals between the phases MB and M_2B at equilibrium.[41] In all cases studied the metal of lower atomic number concentrated in the phase which was richer in boron (MB); this was interpreted as implying a greater strength for the metal–boron bond for the lighter metal. However, such a partition ratio is determined by the balancing of metal–boron (as well as boron–boron and metal–metal) bond strengths for the two phases. Thus, the observed ratio might result from a higher bond strength (not necessarily to boron) for the lighter metal in the phase MB or for the heavier metal in the phase M_2B.

As evidence of electron transfer in the opposite sense (from boron to metal), Kiessling[40] noted that the maximum boron content in transition-metal borides decreases as the atomic number of the metal increases (*i.e.*, as the number of vacancies in the *d*-band decreases) and that it has not been possible to prepare a boride of copper. However, Table 1 shows the dangers of arguments based on the "non-existence" of compounds. All the transition metals except palladium are known to form monoborides and the majority form diborides. Silver and gold (if not copper) have subsequently been found to give diborides.[42] It is doubtful whether useful comparison of electronic structures for borides with different crystal structures can be made in this way; as will be shown, the diborides are probably to be formulated as $M^{2\delta+}(B^{\delta-})_2$. It might possibly have been better to argue that the apparent non-occurrence of lower borides outside the transition elements (apart from beryllium) could be taken as supporting electron transfer to the metal. It is probably also relevant that the transition elements are just those metals which have the highest heats of atomisation and therefore, presumably, the greatest tendency to preserve a metal lattice.

More direct evidence concerning the direction of electron transfer comes from magnetic measurements which have been made for CrB, MnB, CoB, NiB,[43,44] Fe_2B,[45] and Co_2B[46] and which can be interpreted as follows. For the monoborides it was assumed[44] that interaction between the orbitals of the metal atoms would give two energy bands: (*a*) a dense, fairly narrow 3*d* band, in which the electrons are virtually localised on the metal atoms, and (*b*) a broad, shallow 4*s* band, the conduction band. Bonding between the boron atoms (which form zig-zag chains through the metal lattice) must be by 2*s*2*p* bonds which will give another band. The distribution of electrons between these bands will depend on the energies of the bands relative to each other and to the Fermi level. The variation of Bohr magneton number for the ferromagnetic monoborides is linear with the total

[41] G. Hägg and R. Kiessling, *J. Inst. Metals*, 1952-3, **81**, 57.

[42] W. Obrowski, *Naturwiss.*, 1961, **48** 428.

[43] N. Lundquist and H. P. Myers, *Arkiv Fysik*, 1961, **20**, 463.

[44] N. Lundquist, H. P. Myers, and R. Westin, *Phil. Mag.*, 1962, **7**, 1187.

[45] P. Weiss and R. Forrer, *Ann. Physique*, 1929, [10] **12**, 279.

[46] R. Fruchart, *Compt. rend.*, 1963, **256**, 3304.

electron content, suggesting that one spin sub-band is full. The Bohr magneton number may then be interpreted as the number of vacancies in the other sub-band. The number of 3*d* electrons per metal atom is thus estimated to be 8·1 (MnB), 8·9 (FeB), 9·7 (CoB), and 10·0 (NiB). Similar considerations give the figures 8·2 (Fe_2B) and 9·2 (Co_2B). In every case except for Ni, where the two numbers are equal, the number of 3*d* electrons is greater than the total number of valence electrons for the free atoms, even when the conduction electrons are not considered. The metal electrons have therefore gained electrons at the expense of the boron atoms. Lundquist *et al.* suggested[44] that the 2*sp* band lay close to the Fermi level and, in order to explain the conductivity in MnB, this band must be cut by the Fermi level in this compound (Fig. 3).

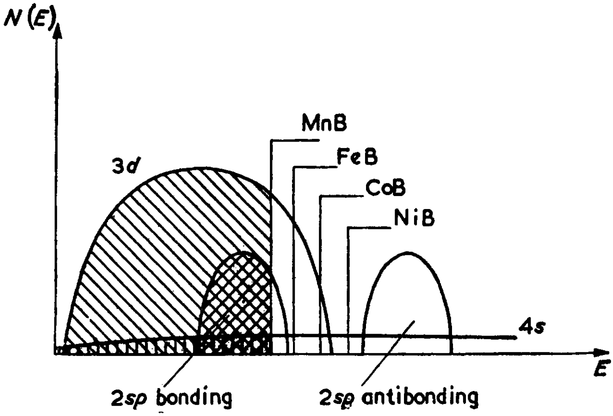

FIG. 3. *A postulated schematic energy band arrangement for the monoborides of* Mn, Fe, Co, *and* Ni. *The vertical lines mark the suggested Fermi levels for the different substances.*

For the two iron borides Mössbauer measurements have given values for the isomer shift and hyperfine magnetic field which are entirely consistent with this interpretation.[47] The hyperfine field decreases from iron metal to Fe_2B to FeB. While it is possible that some of this decrease and of the decrease in Bohr magneton number arises from weakened exchange interactions resulting from distortion or expansion of the metal lattice, it seems most likely that some transfer of electrons from boron to metal has occurred. There is thus a distinction between the boron chains in monoborides and those in $B_n(R_2N)_{n+2}$, in which it is thought that π-electron donation from nitrogen to boron stabilises the chains.[28]

Nothing is known about the electronic structures of the other metal-rich borides. However, Mössbauer measurements have been made on the Fe–Si and Fe–Al systems, both of which are crystallographically similar

[47] J. D. Cooper, T. C. Gibb, N. N. Greenwood, and R. V. Parish, *Trans. Faraday Soc.*, 1964, **60**, 2097.

to the M–B systems, and in both cases the results have been interpreted in terms of electron transfer from the non-metal to the iron atoms.[48,49]

(b) Boron-rich Borides.—The bonding in metal hexaborides has been treated qualitatively by Lipscomb[50] and quantitatively by Longuet-Higgins and Roberts,[51] Yamakazi,[52] and Flodmark.[53] The treatment described here is that due to Longuet-Higgins and Roberts. Molecular orbitals were calculated for an isolated B_6 octahedron using the $2s$ and $2p$ boron orbitals, and the usual approximation that resonance integrals are proportional to overlap integrals. It was found that the orbitals fell into two groups: (*a*) those which had large amplitudes external to the octahedron and which were approximately non-bonding (six orbitals), and (*b*) those which were internal to the octahedron and which were either bonding (seven orbitals) or antibonding (eleven orbitals). The situation is represented diagrammatically in Fig. 4. Bonds between neighbouring octahedra (see Fig. 2a) are then formed by overlap of the outward-pointing orbitals with similar orbitals on adjacent octahedra. If these are considered to be conventional two-electron σ-bonds, this will require six electrons per B_6-unit. The remaining seven bonding orbitals require fourteen electrons to give a "closed shell' configuration. To achieve this, two electrons must be provided by the metal atoms, giving a configuration $M^{2+}(B_6)^{2-}$.

This picture was refined by considering the interactions occurring when the octahedra are brought into the cubic array found in the crystal. With the simplification of considering only the strongest interactions, a set of energy bands was obtained which showed considerable overlapping (Fig. 5). Again, twenty electrons per unit cell are required to fill the bonding levels completely. Comparison of the average energy of the inter-octahedral bonding orbitals with that of intra-octahedral levels showed that the two types of bond would have approximately the same strength. The energy gap between the highest filled level and the lowest unfilled level was estimated[51,52] to be fairly large, 1·0—1·5 ev. Hexaborides of bivalent metals, *e.g.*, CaB_6, would then be expected to be insulators, whereas in fact CaB_6, SrB_6, and BaB_6 are found to be semiconductors with energy gaps of 0·1—0·4 ev.[54] Flodmark's calculation included the boron $3s$, $3p$, and $3d$ orbitals and predicted a much smaller energy gap.[53]

The magnetic properties[55] of the lanthanide hexaborides suggest that the metal atoms are tervalent and conductivity data[56] show that most of

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[48] M. B. Stearns, *Phys. Rev.*, 1963, **129**, 1136.

[49] M. B. Stearns, *J. Appl. Phys.*, 1964, **35**, 1095.

[50] W. H. Eberhart, B. Crawford, and W. N. Lipscomb, *J. Chem. Phys.*, 1954, **22**, 989.

[51] H. C. Longuet-Higgins and M. deV. Roberts, *Proc. Roy. Soc.*, 1955, *A*, **224**, 336.

[52] M. Yamakazi, *J. Phys. Soc. Japan*, 1957, **12**, 1.

[53] S. Flodmark, *Arkiv Fysik*, 1960, **18**, 49; 1959, **14**, 513.

[54] R. W. Johnson and A. H. Daane, *J. Chem. Phys.*, 1963, **38**, 425.

[55] R. Benoit, *J. Chim. phys.*, 1955, **52**, 119.

[56] Y. B. Paderno and G. V. Samsonov, *Doklady Akad. Nauk S.S.S.R.*, 1960, **137**, 646.

these compounds have one conduction electron per metal atom, implying that the other two electrons have been transferred to the boron lattice. The exceptions to this pattern are EuB_6 and YbB_6 which have almost zero conduction electrons per metal atom; these are the two borides whose cell constants are larger than those for the remainder of the lanthanide hexaborides. Similar behaviour with the pure metals was interpreted as a drop in the effective valency of the metal from three to two which, for the hexaborides, is consistent with the conductivity measurements. (The other exception, SmB_6, shows anomalies in both its electrical and magnetic properties.[4])

Neshpor and Samsonov have suggested that complete transfer of two electrons to the boron lattice may not be necessary.[57] It is possible to

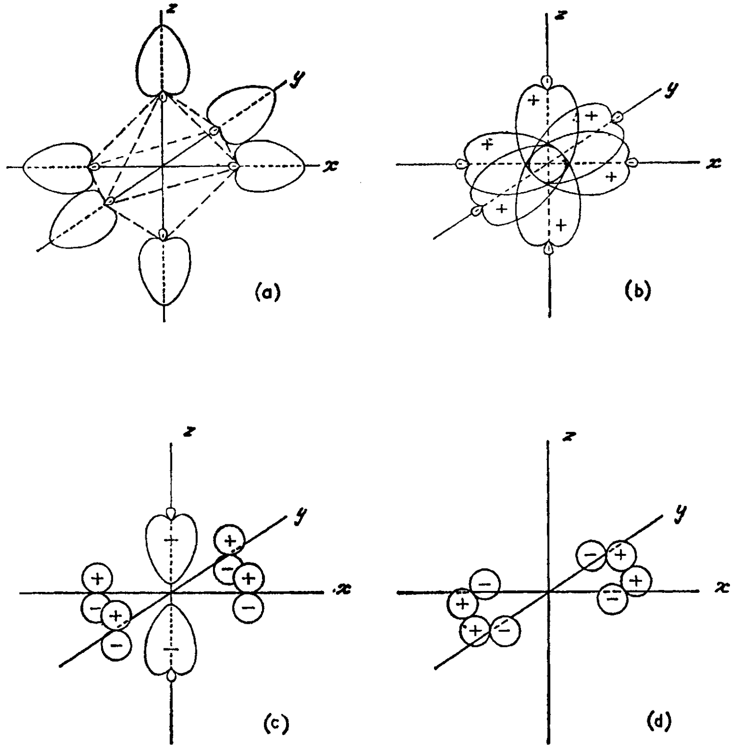

FIG. 4. *Symmetry of orbitals on the B_6 octahedron.*

(a) Six outward-pointing (*sp*) orbitals used for σ-bonding to adjacent octahedra.
(b) Six inward-pointing (*sp*) orbitals used to form the a_{1g} framework bonding molecular orbital.
(c) Components for one of the t_{1u} framework bonding molecular orbitals—the other two molecular orbitals are in the *yz* and *zx* planes.
(d) Components for one of the t_{2g} framework bonding molecular orbitals—the other two molecular orbitals are in the *yz* and *zx* planes.

[57] V. S. Neshpor and G. V. Samsonov, *Russ. J. Inorg. Chem.*, 1959, 4, 893.

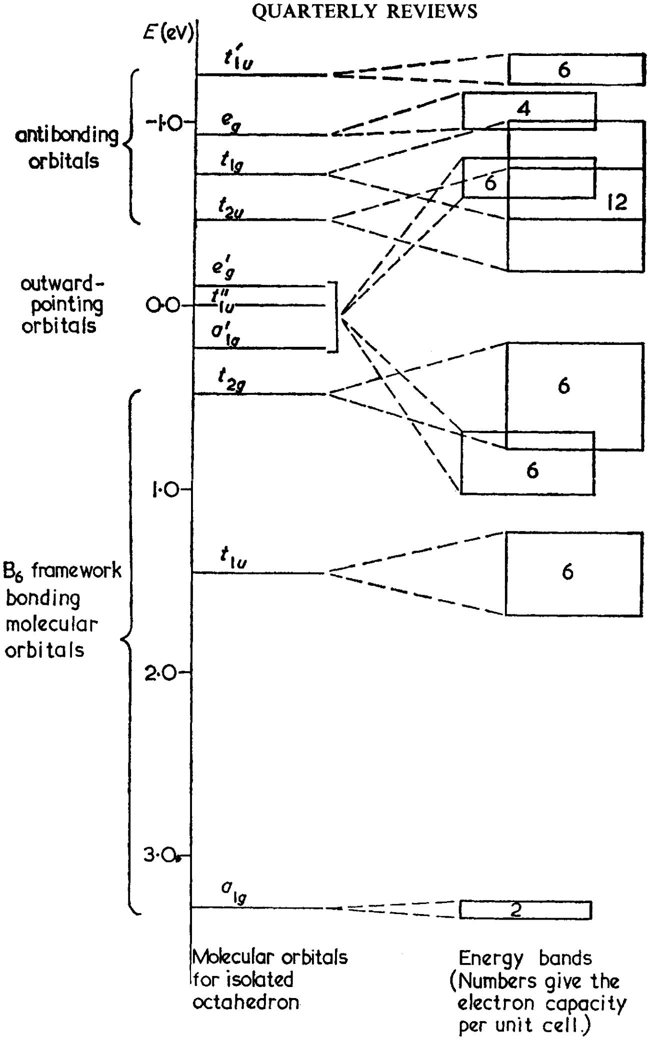

FIG. 5. *Molecular orbitals and energy bands for MB_6.*

substitute sodium for the other metals in CaB_6 and ThB_6 up to limiting concentrations of $Ca_{0.57}Na_{0.43}B_6$ and $Th_{0.23}Na_{0.77}B_6$.[15] The assumption that the metals are fully ionised gives 1·57 and 1·69 electrons, respectively, for transfer to the boron. It is not clear whether the substitution limit is determined by electronic or structural factors. Neshpor and Samsonov have also pointed out[57] that cubic hexaborides are apparently formed only by metals with first ionisation potentials less than about 6·7 ev and second ionisation potentials less than about 12 ev, which neatly excludes the transition metals (6·5—9 ev and 12–20 ev) and beryllium (9·3 ev and 18·2 ev).

It seems therefore that the electronic structure of the cubic hexaborides must approach $M^{2+}(B_6)^{2-}$.

A qualitative treatment of the bonding in dodecaborides has been given by Lipscomb and Britton.[58] Isolated cubo-octahedra are considered to be joined by localised bonds arising from overlap of outward-pointing molecular orbitals. Of the remaining thirty-six molecular orbitals, thirteen are bonding and three non-bonding. A "closed shell" configuration then requires thirty-eight electrons and an $M^{2+}(B_{12})^{2-}$ arrangement is likely. Insufficient physical data are available to test this hypothesis.

(c) **Diborides.**—It was pointed out on p. 445 that diborides (MB_2) represent the transition between the metal-rich and boron-rich types of boride. It is therefore not surprising that electron transfer in each direction has been suggested for them. Measurements of the Hall coefficient and resistivity have been interpreted on a band model in which the boron electrons have been completely transferred to the metal band system,[59] which would imply that any boron–boron bonding would be very weak. However, Post has pointed out[3] that both thermal expansion and lattice-constant results strongly suggest that the boron lattice has considerable rigidity. This is shown, for instance, in an increased axial ratio, c/a, as the size of the metal atom increases (the "a" axis lies in the plane of the boron lattice). Thus, for MgB_2 and AlB_2 the ratios are 1·14 and 1·08 respectively, while for UB_2 it is 1·27. Similarly the c/a ratio increases with metal content in the TaB_2 phase. At the ideal composition, 66·67 atoms per cent. boron, c/a is 1·06. As the boron content increases vacancies occur in the metal lattice allowing the boron network to contract in the "a" direction and c/a becomes 1·08 at 72 atoms %.[35]

Nuclear magnetic resonance suggests that the boron lattice does not contain only σ bonds. Both the ^{11}B coupling constants and the Knight shifts are consistent with π-bonding in the boron layer, which could be achieved by transfer of electrons from the metal to the boron.[60] Complete transfer of one electron per boron atom would give a formulation $M^{2+}(B^-)_2$ in which the boron layers would be isoelectronic with graphite as suggested by Muetterties[61] and by Lipscomb and Britton.[46] The conductivity of YB_2 is consistent with the presence of one free electron per metal atom,[54] in agreement with this model, but conductivities of borides comprising more critical cases, such as BeB_2 and MgB_2, have not been measured.

It is interesting that Neshpor and Samsonov's ionisation-potential criterion[57] does not hold for diborides; these are formed by metals of all types. This could imply that complete transfer of two electrons is not necessary, and this is also suggested by the occurrence of AgB_2 and AuB_2.[42] Alternatively, the charge on the metal could be reduced by back-donation from boron to metal.[61] Finally, it should be noted that the metal lattice in

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[58] W. N. Lipscomb and S. Britton, *J. Chem. Phys.*, 1960, **33**, 275.

[59] H. J. Juretschke and R. Steinitz, *J. Phys. Chem. Solids.*, 1958, **4**, 118.

[60] A. H. Silver and T. Kushida, *J. Chem. Phys.*, 1963, **38**, 865; A. H. Silver and P. Bray, *ibid.*, 1960, **32**, 288.

[61] E. L. Muetterties, *Z. Naturforsch.*, 1957, **12b**, 411.

diborides is hexagonal close-packed, allowing considerable metal–metal bonding, which might stabilise transition-metal diborides. Which, if any, of these factors influence the formation of any particular diboride is not known but it nevertheless seems very probable that some metal-to-boron electron transfer occurs in the diborides.

In summary it is concluded that there is transfer of electrons from metal to boron in diborides and higher (boron-rich) borides, and transfer of electrons from boron to metal in monoborides and metal-rich borides.

6. Chemical Properties

Comparatively little is known of the chemical properties of metal borides; results are scanty and unsystematic. It is therefore more convenient to discuss reactions under the various reagents rather than according to the different boride types. Much of the older work involved impure materials and a large proportion of later investigations has been concerned with the production of boron hydrides by acid hydrolysis. Often the products of reaction are not mentioned and there are conflicting reports of the reactivity of many borides. For example, both TiB_2 and ZrB_2 have been reported both to react[62] and not to react[63] with dilute hydrochloric and sulphuric acids. Reactivity will depend strongly on the purity and state of subdivision of the sample. Borides are characterised by a general inertness, particularly to non-oxidising reagents. In oxidising conditions inertness increases with increasing boron content.

(a) Aqueous Acids.—Of all the reactions, hydrolysis by aqueous acid has been most studied, particularly since Stock's classic preparation and identification of the boron hydrides.[64] Solubilities of borides in aqueous acids are indicated in Table 3. For hydrochloric and sulphuric acids two rough generalisations can be made: (i) for main-group borides resistance to attack increases as the boron content of the boride increases; (ii) for transition-metal borides resistance to attack increases with increasing atomic number in any group or period.

Boron hydrides are obtained in small quantities (about 1 %) from the hydrolysis of most metal-rich borides[23,62,65–72] but the best yield (12·4 %

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[62] L. Ya. Markovskii and G. V. Kaputovskaya, *Zhur. priklad. Khim.*, 1960, **33**, 569.

[63] N. N. Greenwood, R. V. Parish, and P. Thornton, *J. Chem. Soc.*, 1965, 545.

[64] A. Stock, "Hydrides of Boron and Silicon", Cornell Univ. Press, Ithaca, 1933.

[65] G. S. Markevich, Y. D. Kondrashev, and L. Ya. Markovskii, *Russ. J. Inorg. Chem.*, 1960, **5**, 865.

[66] V. I. Mikheeva and V. Yu. Markina, *Zhur. neorg. Khim.*, 1956, **1**, 619.

[67] A. Chrétien and P. Duhart, *Compt. rend.*, 1962, **254**, 1439; *Ann. Chim. (France)*, 1962, **7**, 339.

[68] L. Ya. Markovskii and E. Bezruk, *Zhur. priklad. Khim.*, 1962, **35**, 491.

[69] L. Ya. Markovskii, Yu. D. Kondrashev, and I. A. Goryacheva, *Doklady Akad. Nauk S.S.S.R.*, 1955, **102**, 97.

[70] L. Ya. Markovskii, G. V. Kaputovskaya, and Yu. D. Kondrashev, *Russ. J. Inorg. Chem.*, 1959, **4**, 771.

[71] L. Ya. Markovskii, Yu. D. Kondrashev, and G. V. Kaputovskaya, *Doklady. Akad. Nauk S.S.S.R.*, 1955, **100**, 1095.

[72] E. Wedekind, *Z. Elektrochem.*, 1905, **11**, 850.

total boron hydrides) is obtained by reaction with 8N-phosphoric acid of MgB_2 containing an excess of magnesium (Stock's "Mg_3B_2").[66,73] The principal hydride product is always B_4H_{10} and the other products are hydrogen, boric acid, and the metal in a normal oxidation state. Occasionally up to 25% of the boron in solution after hydrolysis is strongly reducing. Thus MgB_2 and AlB_2 with hydrochloric acid yield a solution in which each reducing boron atom will undergo a two-electron oxidation; it was suggested[67,74] that the reducing species was $BH(OH)_3^-$. Hydrolysis (when it occurs) of TiB_2, ZrB_2, and CrB_2 always yields less hydrogen than would be expected if all the boron were oxidised to boric acid.[62,63,68] The hydrogen deficiency is consistent with the formation of boron(II), as "BO" or $(HO)_2B{\cdot}B(OH)_2$. Similar behaviour is found in the hydrolysis of Be_5B.[65] With VB_2 hydrolysis with hydrochloric acid yields VO^{2+} but no boron in solution. The boron presumably remains as the element. Only two moles of hydrogen are evolved per mole of boride, consistent with the oxidation $VB_2 \rightarrow V^{IV} + 2B^0$.[63] Hexaborides are inert to hydrolysis.

Hot concentrated sulphuric acid attacks all borides with evolution of sulphur dioxide.[5,63,75–81] Similarly, all borides are attacked by nitric acid (see Table 3 for references). The only reported exceptions are Pt_2B_3, NbB_2, TaB_2, and all the borides of chromium, although the last will dissolve on boiling (cf. chromium metal, which is passivated by nitric acid).

Hydrofluoric acid is without effect on most higher borides but attacks the lower borides.

TABLE 3. *Reactivities of metal borides with aqueous acids and alkali*

Acid	Soluble	Insoluble	Refs.
		NaB_6	27
HCl	Be_5B, Be_2B	BeB_2, BeB_6	5*, 23, 65*, 69
	MgB_2, MgB_4	MgB_6, MgB_{12}	66*, 67*, 70, 71
	AlB_2	AlB_{12}	67*, 82
		$M^{II}{\cdot}B_6$	63, 75, 83
		LnB_6	76, 77, 84
	ThB_4	ThB_6	85
	UB_4	UB_{12}	86
	TiB_2	TiB_2	62*, 63, 87

[73] P. L. Timms and C. S. G. Phillips, *Inorg. Chem.*, 1964, **3**, 297.
[74] V. I. Mikheeva and V. U. Surs, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 1133.
[75] J. L. Andrieux, 14ème Congr. Chim. indust., Paris, Oct., 1934.
[76] J. L. Andrieux, *Compt. rend.*, 1928, **186**, 1736.
[77] J. L. Andrieux, *Ann. Chim. (France)*, 1929, **12**, 423.
[78] A. B. du Jassoneix, *Compt. rend.*, 1904, **139**, 1209.
[79] H. Moissan, *Compt. rend.*, 1895, **120**, 173.
[80] H. Moissan, *Compt. rend.*, 1896, **122**, 424.
[81] H. Moissan, *Bull. Soc. chim. France*, 1897, **17**, 1019.
[82] W. Hampe, *Annalen*, 1876, **183**, 75.
[83] N. V. Vekshina and L. Ya. Markovskii, *Zhur. priklad. Khim.*, 1961, **34**, 2171.
[84] N. N. Tvorogov, *Russ. J. Inorg. Chem.*, 1959, **4**, 890.
[85] A. B. du Jassoneix, *Compt. rend.*, 1905, **141**, 191.
[86] J. L. Andrieux and P. Blum, *Compt. rend.*, 1949, **229**, 210.
[87] K. D. Modylevskaya and G. V. Samsonov, *Ukrain. khim. Zhur.*, 1959, **25**, 58.

TABLE 3.—*continued*

Acid	Soluble	Insoluble	Refs.
	ZrB_2	ZrB_2	62*, 63, 87
	VB_2	VB	5, 63*, 87
		NbB_2	5, 63, 87, 88
		TaB_2	5, 87, 88
	Cr_4B, Cr_2B, Cr_5B_3, Cr_3B_2, CrB, Cr_3B_4, CrB_2		62*, 63*, 87, 89, 90
	MoB Mo_3B_4, Mo_2B_5	Mo_2B	5, 63*, 87, 91
		W_2B, WB, W_2B_5	5, 87, 92
	MnB, MnB_2		68*, 72, 78, 93
	Fe_2B, FeB		68*, 79, 94
		CoB	80
		NiB	63, 80, 95
		Pt_2B_3	96
H_2SO_4		NaB_6	27
	Be_2B	BeB_2, BeB_6	5, 23, 69
	MgB_2	MgB_6, MgB_{12}	66, 67, 70, 71, 83
		AlB_{12}	82
		$M^{II}B_6$	63, 75, 81, 83
		LnB_6	76, 77, 84
	ThB_4	ThB_6	85
	UB_4	UB_{12}	86
	TiB_2	TiB_2	5, 63, 87
	ZrB_2	ZrB_2	62, 63, 87
	VB_2	VB	5, 63, 87
		NbB_2	5, 87, 88
		TaB_2	87, 88
	Cr_4B, Cr_2B, Cr_5B_3, Cr_3B_2, CrB, CrB_4, CrB_2		62, 63*, 89*, 90, 97*
	Mo_2B, MoB_2	MoB, Mo_2B_5	5, 63*, 87
		W_2B_5	87
	MnB, MnB_2		78, 93
	Fe_2B	FeB	79, 94
		CoB	80
		NiB	63, 80, 95
		Pt_2B_3	96

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[88] J. L. Andrieux, *Compt. rend.*, 1929, **189**, 1279.

[89] J. L. Andrieux and S. Marion, *Compt. rend.*, 1953, **236**, 805.

[90] A. B. du Jassoneix, *Compt. rend.*, 1906, **143**, 1149.

[91] S. A. Tucker and H. R. Moody, *J. Chem. Soc.*, 1902, **81**, 14.

[92] J. Helgorsky, *Ann. Chim. (France)*, 1961, **6**, 87.

[93] L. Troost and P. Hautefeuille, *Ann. Chim. (France)*, 1875, **9**, 65.

[94] A. B. du Jassoneix, *Compt. rend.*, 1907, **145**, 121.

[95] N. I. Blok, M. N. Kozlova, N. F. Lashko, and K. Ya. Shpunt, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 811.

[96] F. Wohler, H. St. C. Deville, *Compt. rend.*, 1856, **43**, 1088; C. A. Martius, *Annalen*, 1859, **109**, 79.

[97] A. B. du Jassoneix, *Compt. rend.*, 1907, **145**, 240.

TABLE 3.—*continued*

Acid	Soluble	Insoluble	Refs.
HNO_3	Be_2B, BeB_2, BeB_4, BeB_6		5, 69
	MgB_2		5
	AlB_{12}		82
	$M^{II}B_6$		63*, 75, 83, 97
	LnB_6		76, 77, 84
	ThB_4, ThB_6		85
	TiB_2		5, 63*, 87
	ZrB_2		63*, 87
	VB, VB_2		63*, 87
		NbB_2	5, 87, 88
		TaB_2	5, 87, 88
		Cr_4B, Cr_2B, Cr_5B_3, Cr_3B_2, CrB, Cr_3B_4, CrB_2	63, 89, 90, 97
	Mo_2B, MoB, Mo_3B_4, MoB_2, Mo_2B_5		63*, 87, 91
	WB, W_2B_5		63, 87, 91
	MnB, MnB_2		78, 93
	Fe_2B, FeB		79, 94
	CoB		80
	Ni_2B, NiB		63, 80, 95, 97
		Pt_2B_3	96
HF		LnB_6	76, 77
		ThB_6	85
	UB_4	UB_{12}	86
		TiB_2	5
	VB	VB_2	5
	Cr_3B_2, CrB		81*, 89, 91
	FeB		79
Alkali		$M^{II}B_6$	83
		LnB_6	76, 77
		ThB_6	85
	TiB_2	TiB_2	63, 87
	ZrB_2		87
	VB, VB_2		87
	NbB_2		87
	TaB_2		87
	MnB_2		87
		CrB_2	63, 87
		NiB	63
		Pt_2B_3	96

All borides dissolve in oxidising acid mixtures, *e.g.*, aqua regia, HNO_3–H_2SO_4, HNO_3–H_2O_2, etc.[62,72,73]

(b) Aqueous Alkalis.—Most borides are resistant to aqueous alkalis but a few react slowly: MnB_2,[93] VB,[5] TiB_2, ZrB_2, VB_2, NbB_2, Mo_2B_5,[87] (another report gives TiB_2 as insoluble[63]). MnB and MnB_2 are said to react also with aqueous ammonia and even with water.[72,78,93]

(c) **Anhydrous Acids.**—A pyridine solution of hydrogen chloride reacts at 200° with CrB_2 to give py_3CrCl_3 and with NiB to give a mixture of py_4NiCl_2 and $(pyH)_2NiCl_4$.[63] NiB reacts with molten anilinium chloride to give the polymeric $(PhNH_2)_2NiCl_2$.[63]

Anhydrous acetic and benzoic acids react with VB_2 to give hydrogen and $(V(O_2CR)_3)_2$. Both complexes appear to be typical dimeric carboxylates in which the two metal atoms are united by four bridging carboxylate groups.[98]

Chlorosulphonic acid reacts completely at 140° with the diborides of V, Nb, and Cr and CaB_6 to give sulphur dioxide and hydrogen chloride. Sulphuryl chloride (VB_2, NbB_2, CaB_6) and chlorine (VB_2, NbB_2) are formed and the metals are converted into VCl_4, $Cr_2(SO_4)_3$, Nb_2O_5, and $CaSO_4$. In all cases except that of CrB_2, the excess of acid was completely decomposed although it is quite stable in the absence of borides.[63]

(d) **Hydrogen Halides.**—In only a few cases has reaction with gaseous hydrogen halides been investigated. CaB_6, TiB, and MoB react with hydrogen fluoride at 225°;[99] MnB is also attacked.[78] CaB_6, SrB_6, BaB_6,[81] ThB_6,[85] MnB_2,[93] MnB,[72,78] and CrB[100] react with hydrogen chloride at red heat (*ca.* 500°) and ThB_4 rather below this temperature.[85] The products are described only for the last three borides:

$ThB_4 \rightarrow H_2 + BCl_3$; $CrB \rightarrow H_2 + CrCl_2$; $MnB \rightarrow H_2 + BCl_3 + MnCl_2$.
FeB does not react with hydrogen iodide at 1100°.[79]

(e) **Halogens.**—Fluorine reacts vigorously with borides of all types, frequently with incandescence. The other halogens are less reactive, usually requiring strong heating. The products of reaction are described only for the reaction of MnB and CrB with chlorine, when $MnCl_2$ and $CoCl_2$ are formed,[72,78,100] and for the fluorination of HfB_2, which gives HfF_4.[101] The systems investigated are shown in Table 4.

TABLE 4. *Reaction of metal borides with halogens*

Boride	CaB_6	BaB_6	LnB_6	HfB_2	ThB_4	ThB_6	CrB	Cr_2B_3	MnB	FeB	CoB	NiB
F_2	+	+	+	+	+	+	+	+	+			
Cl_2	+	+	+		+	+	+	+	+	+	+	+
Br_2	+	+	+					+	+		+	+
I_2									×	×	+	
Ref.	75, 81	81	81	101	85	85	100	90	72, 78	79	80	80

+ Reaction occurs
× No reaction

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(f) Oxygen and Sulphur.—Borides, like the parent elements, are resistant to atmospheric oxidation at room temperature. At elevated temperatures all borides are oxidised although the rates of attack vary widely. Some borides (those of Be,[102] Cr,[90,100] TiB_2[103,104]) form a protective film of oxide or borate and the rate of oxidation is controlled by diffusion of oxygen through this film. The temperatures at which extensive oxidation occurs vary widely from one report to the next, owing to differences in purity and degree of subdivision of the borides, but a rough order of reactivity may be given.[5,79,80,83,88,93,105] The reaction temperatures lie in the range 400—1700°: (CoB, NiB) $>$ (FeB, Fe_2B, WB) $>$ (MoB) $>$ (W_2B, VB_2) $>$ ($M^{II}B_6$, NbB_2, TaB_2, MoB_2) $>$ (TiB_2, ZrB_2, HfB_2) $>$ (CrB, CrB_2).

Oxidation by elemental sulphur does not lead to the production of protective films and reaction proceeds readily at 400–700° giving B_2S_3 and the metal sulphide.[79,80,85,90,100]

(g) Nitrogen and Ammonia.—Borides of all types appear to be as resistant to nitriding as they do to oxidation. The alkaline-earth hexaborides are unaffected by nitrogen or ammonia at high temperatures[81,83] and CaB_6 is stable up to at least 2000°.[99] In one case at least, lack of reaction is attributable to the formation of a protective film; the borides of beryllium become coated with Be_3N_2 but no boron nitride was detected.[102] In a careful study[106] of the nitriding (in ammonia vapour) of borides of Cr, Fe, and W the products were mixtures of boron nitride and nitrides of the metal. The particular nitrides formed depended, as might be expected, on the temperature and not on the starting material. With the chromium and iron borides, initiation of reaction required higher temperatures the higher the boron content of the boride, but this trend was not noticeable with tungsten. No evidence was found for any ternary phases.

(h) Carbon.—A few borides have been reported to form the corresponding carbide when heated with elemental carbon. For instance, beryllium borides are converted into Be_2C, the reaction again requiring progressively higher temperatures as the boron content rises.[102] Tungsten borides are apparently all converted into tungsten monoboride by heating with carbon.[92] The alkaline earth hexaborides are stable up to at least 2000°[83] and ZrB_2 up to 1600°.[92]

(i) Molten Salts.—All types of boride react with oxidising molten salts (hydroxides, nitrates, etc.) and this is a common method of decomposing them for analysis. The reported reactivities are summarised in Table 5. Several borides are reported not to be affected by non-oxidising salts (halides and cyanides).[63]

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[106] R. Kiessling and Y. H. Liu, *J. Metals*, 1951, 639.

TABLE 5. *Reaction of metal borides with fused salts*

Boride	M_2CO_3	MOH	$MHSO_4$	MNO_3	$MClO_3$	MO_2	PbO_2	Refs.
BeB_2, BeB_6	+							5, 69
CaB_6	+	+	+	+		+	+	75, 81
LnB_6	+	+	+	+		+	+	76, 77
ThB_4		+						85
UB_4, UB_{12}						+	+	86
TiB_2	+	+	+			+	+	5
VB_2	+	+	+			+	+	5
NbB_2	+	+						5, 88
TaB_2		+						5, 88
Cr_3B_2	+	+		+				90
CrB		+	+		+	+		100
Mo_2B		+						5
MnB	+							72,78
FeB	+	+		+	+			79
CoB	+	+		+	+			80
Pt_2B_3	+	+		×	+			96

+ Reaction occurs
× No reaction

To summarise: metal borides are chemically inert except under oxidising conditions. Reaction always occurs with complete disruption of the boride lattice and it has never been possible to isolate polyboron fragments from the boron lattice. The only apparent exceptions to this are in the formation of boron hydrides and diboronic acid in hydrolysis reactions with aqueous acids. These products are presumably formed from polymerisation and hydrolysis of nascent BH_3.

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