

On the bindings in  $AB_M$  phases

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(Received: March 1988)

**Abstract**

A decisive stability argument for borides is afforded by the influence of the spatial correlation of the electrons on the bonding. The analysis of the relations between electron numbers and stability suggests that more electrons take part in the bonding than merely the electrons outside the peripheral closed shell. Furthermore, it may be assumed that electrons belonging to different bands may accommodate to one and the same correlation lattice (collective binding). These assumptions and the earlier rules of the plural correlations model allow to assign to most borides simple bonding types (bindings) which express intrastuctural and quasihomologic numero-metrical relations providing useful interpretations of the stability. These relations are empirical rules being valid in the field of numerical data of crystal structures and conveying intermediary results of the systematic crystal chemistry.

**Introduction**

The crystal data of  $AB_M$  phases (borides) have been reviewed by 54Kie, 63Now, 64Ada, 64Sch, 65Aro, 67Gol, 67Hoa, 69Tho, 71Eck, 72Now, 72Pea, 73Gre, 75Wel, 76Spe, 77Lun, 77Now, 77Spe, 85Vit, 86Mas. With respect to these reviews, in the present study the references to structural communications are replaced by Structure Reports references for the sake of brevity. These reviews also permit the restriction of lattice-constant data to two decimals of an Å.

The assignment of bonding types (bindings) to the phases is not yet in an advanced state. It is well known that boron very rarely forms an anion, so that Lewis' rule of octet completion applies only where B is a cation. In the remaining borides various special rules

have been reported, for instance the formation of characteristic simple partial structures of B (54Kie), or the rule that the  $\text{CaB}_6$  type occurs for  $\text{A}^{1...3}$  but not for  $\text{A}^{4...10}$ . Such special rules may be formulated as relations between the structure of a phase and its electron numbers. They have not yet been appreciated much because the two-electron bond concept of molecular chemistry as applied in crystal chemistry tends to obscure the energetical cause of the rules, namely the lattice like property of the electron spatial correlations (64,83, 86Sch). Furthermore, this bond concept hampers the recognition that electrons below the valence bands have some influence on the bonding. These views have been applied in recent discussions of bindings in  $\text{AB}_M$  phases (79,82Sch). However, continued binding analyses uncovered additional valence rules suggesting various changes of binding proposals. For example one of these rules proposes that the correlation  $b$  of the valence electrons, and the correlation  $c$  of the peripheral core electrons may obey the same correlation lattice  $g=b \sim c$  (collective correlation). This phenomenon simplifies the binding analysis and the reading of binding formulae. If  $d$  electrons take part in  $b$  it may be written  $b' = b \sim c$ , and if  $d$  or  $f$  electrons take part in  $c$  it may be written  $c' = c \sim f$ . Therefore  $g$  may also be equal to  $b' \sim c'$ . The collective correlations do not necessarily cause a highly uniform electron density as may be inferred from the example 83Sch Fig.1.

In the following the present state of the interpretation of borides is described. However, there is no doubt that additional valence rules will be found later on and make necessary a further revision of the binding proposals. In the subsequent text the brackets behind the crystal cell  $a$  contain the numbers of electrons per  $a$  for the various bands; the earlier added " $N="$  is omitted for brevity. Behind the prototype of a phase name, a previous quasihomologic isotype may be added to refer to additional structural remarks. For further abbreviations and formal conventions see 86,87,88Sch. Since the search for a binding interpretation is a search for hypotheses explaining observations, each proposal must be considered as a possibility. However, in order to simplify the presentation it is frequently described here as a fact. While a binding proposal for a crystal with a small cell is frequently quite plausible, a proposal for a crystal with a large cell is necessarily less certain. The assignment of bindings to the borides is now examined.

### Analysis

It may be appropriate to consider briefly the structures of B before inquiring for bindings of borides. The B structures should be seen in conjunction with the structures of Be and C.

Be.r(Mg,H2,SR1.40,23.46), the room temperature phase of Be, may have the binding (see 82Sch1)  $a[4+4+8]=H2.29;3.58\text{\AA}=b_{\text{CH}}(1;3.8/3)=c_{\text{UH}}(2;3.8/2)$ , where  $a$  is the cell matrix of Be.r,  $[4+4+8]$  contains the numbers of electrons per  $a$  in the valence band  $b$  and in the core electron band  $c$  and also their sum. H... $\text{\AA}$  is the abbreviated notation (86Sch) of the numerical value of  $a$ ,  $b_{\text{CH}}$  is the cell of the  $b$  correlation, being cubic primitive (C), in hexagonal aspect (H),  $c_{\text{UH}}$  is the tetragonal bodycentered isometric correlation (U) in H-aspect and somewhat contracted along the quasihexagonal axis (-),  $(1;3.8/3)$  and  $(2;3.8/2)$  are commensurability matrices in abbreviated notation; the multiplication crosses  $\times$  will be omitted below, and  $[\ ]$  will be replaced by  $(\ )$ . The observation that the number of  $b$  sites per  $a$  is 3.8, instead of 4, indicates that the  $b$  and  $c$  correlations form a collective correlation,  $b\cdot c=g$ , obeying  $a=g_{\text{UH}}(2;3.8/2)$  and thus yielding the number of  $g$  sites per atom  $N_{\text{S}(g)}^{\text{At}}=7.6$ . The  $\text{UH}$  type is no longer isometric like  $\text{UH}$ , but provides an improved spin compensation. However, another interpretation is  $a=g_{\text{H}}(\sqrt{3};3)$  yielding  $N_{\text{S}(g)}^{\text{At}}=4.5$ . With respect to the spins,  $g_{\text{H}}$  must be twinned in  $a$ .

Be.h(W,SR23.45) yields  $a(4,4)=2.55\text{\AA}=b_{\text{F}}(1)=c_{\text{C}}(2)$  or  $a=g_{\text{B}}(2)$  with  $N_{\text{S}(g)}^{\text{At}}=8$ , being greater than 7.6 of r, conforming to the rule of site numbers (86Sch). It might be suspected that a correlation  $a=g_{\text{B}}(2)$  would cause a uniform electron density. That this is not the case may be seen, as noted above, from Fig.1 in 83Sch or Fig.1 in 86Sch. An alternative proposal is  $a=g_{\text{F}}(\sqrt{2};1.4)$  with  $N_{\text{S}(g)}^{\text{At}}=5.5$ .

C.r(H4,SR1.28,drw64Sch.180) is composed of close packed  $a$  layers in which every third atom is missing.  $a(16,8)=H2.46;6.71\text{\AA}=b_{\text{FH}}(\sqrt{3};6/3)=c_{\text{CH}}(\sqrt{3}.12/3)$  (82Sch1) or  $a=g_{\text{CH}}(\sqrt{3};12/3)$  with  $N_{\text{S}(g)}^{\text{At}}=9$ . The contraction of  $b$  and  $c$  to  $g_{\text{CH}}$  instead of to  $g_{\text{BH}}$  as in Be.h becomes possible by the loose packing. The high  $b$  electron number causes the lacunae in the  $a$  layers and the support number 1 of the  $a$  layer stacking. Because of the low occupation of  $g$  its cell is compressed, while  $a$  is strained in  $a_3$  direction. For C.hp<sub>2</sub>(F2,SR1.46) comes  $a(32,16)=3.57\text{\AA}=b_{\text{F}}(2)=c(4)$  (82Sch1), or  $a=g_{\text{C}}(4)$  with  $N_{\text{S}(g)}^{\text{At}}=8$

being smaller than 9 of  $r$  because of the high pressure. The reason why also here  $g_C$  occurs instead of  $g_B$  in Be lies in the higher  $b$  concentration.

B.h<sub>1</sub>(R12,SR23.270,drw 64Sch.178) is formed at 800...1200°C and is composed of close packed layers parallel to  $a_1, a_2$  in which every forth atom is missing. While in C.r there are layers parallel to  $a_1, a_2$  with weakly occupied  $g$  sites, in this structure there are strings parallel to  $a_3$  with weakly occupied  $g$  sites. Just as in C.r foreign atoms may enter the empty layers, here the empty strings may be filled by foreign atoms (B<sub>4</sub>C). Just as in C.r the atom layers keep distant from the empty layers, here the atoms recede from the empty strings to form B<sub>12</sub> icosehedra. This must be understood as a first step towards molecule formation as in N<sub>2</sub>O<sub>2</sub> etc. In the weakly occupied regions no  $c$  electrons may be found, only  $b$  electrons. In the strongly occupied regions the  $c$  electrons are an essential stabilizing factor. To be sure the empty strings are not infinitely extended but the B<sub>12</sub> are in a F<sub>H</sub> packing,  $a(108,72)=H4.91;12.57\text{\AA}=b_H(\sqrt{12};9)=c_{CH}(\sqrt{12};24/3)$  or  $a=g_{CH}(\sqrt{12};24/3)$  with  $N_{S(g)}^{At}=8$ . Another probable binding is  $a=g_{CH}(3;21/3)$ ,  $N_{S(g)}^{At}=5.2$ .

B.r(R105,SR35.127,38.37,43.34,drw67Hoa,73Gre.677) is said to be stable at room temperature (73Gre).  $a(945,630)=H10.94;23.81\text{\AA}=g_{CH}(\sqrt{49};37/3)$ ,  $N_{S(g)}^{At}=5.7$ . Because of the high number of atoms per cell the binding must remain tentative.

B.h<sub>2</sub>(T190,SR44.34,45.41,drwSR43.6) was obtained by decomposition of purified BBr<sub>3</sub>+H<sub>2</sub> on Ta filament at 1200°C (79Vla). It is closely htpc to AlB<sub>12</sub>.r.  $a(570,380)=10.14,14.17\text{\AA}=g_C(9;13)$ ,  $N_{S(g)}^{At}=5.5$ .

"B(T50,SR15.137,22.211,drwSR22.212)" is in reality B<sub>50</sub>C<sub>2</sub> or B<sub>50</sub>N<sub>2</sub> (SR38.39,40.38,42.52).

It is well known that the B phases belong to the most complicated structures of the chemical elements. The bindings proposed can therefore only be a first attempt to find the energetical reason for their structure. We now consider the borides.

In A<sup>1</sup>B<sub>M</sub> mixtures Lewis-phases are not expected since the compositions A<sub>5</sub><sup>1</sup>B or A<sub>3</sub><sup>1</sup>B do not provide a good Coulomb interaction. Therefore all stable phases are superborides. Furthermore, the low  $b$  electron contribution of A<sup>1</sup> causes that the A<sup>1</sup> cores are close together and do not give much room for B atoms. Only when the mole fraction of B is  $N_B^>0.75$  compounds are formed.

Li(W,SR1.32),  $a(2,4)=3.51\text{\AA}=b_{\text{B}}(1)=g_{\text{C}}(2)$ .

Li<sub>3</sub>B<sub>3</sub>(T4.12,84Mai) is a read semiconductor, filling-homeotypic to CaB<sub>6</sub> since the atomic volume fulfills  $V_{\text{Ca}}=21V_{\text{Li}}$ . It is isodesmic to CaB<sub>6</sub>,  $a(4+36,32)=5.98;4.19\text{\AA}=g_{\text{B}}(\sqrt{18};3)$ . The number of  $g$  sites per atom is  $N_{\text{S}(g)}^{\text{At}}=6.75$ .

Li<sub>6</sub>B<sub>19</sub>(I16.19,84Mai) contains B<sub>6</sub> octahedra bonded through corners,  $a(6+57,50)=118.23;4.16\text{\AA}=g_{\text{B}}(6;10;3)$ ,  $N_{\text{S}(g)}^{\text{At}}=7.2$ .

Li<sub>3</sub>B<sub>14</sub>(U12.56,84Mai) contains B<sub>8</sub> and B<sub>10</sub> polyhedra,  $a(24+336,272)=10.77;8.95\text{\AA}=g_{\text{B}}(\sqrt{61};6.5)$ ,  $N_{\text{S}(g)}^{\text{At}}=5.8$ . The binding is tentative.

NaB<sub>6</sub>(73Gre,77Mat).

NaB<sub>15</sub>(P2.30,SR35.39) is homeotypic to MgB<sub>7</sub> and contains B<sub>12</sub> icosahedra in H1 packing. Because of  $V_{\text{Na}}=V_{\text{Mg}}+V_{\text{Al}}$  the phase is homeotypic to MgAlB<sub>14</sub> (P2.2.28, SR35.4,drw ibid.),  $a(4,212,128)=5.85;8.42;10.30\text{\AA}=g_{\text{B}}(4;6;7)$ .

KB<sub>6</sub>(CaB<sub>6</sub>,71Eck) is a CsCl structure of K and B<sub>6</sub>,  $a(1,26,20)=4.23\text{\AA}=g_{\text{B}}(3)$  where  $g=b-c-f$ . The assumption that there is not only a binding  $a=(b-c)_{\text{C}}(3)$  (82Sch2) is supported by the stability of the isotypes CaB<sub>6</sub> and YB<sub>6</sub> having more electrons.

The bindings of Be.r and Be.h have been considered above. The phase "Be<sub>5</sub>B"(SR 24.58) is in fact Be<sub>4</sub>B(SR27.65).

Be<sub>4</sub>B(T8.2,SR27.65,drw ibid.) is htpe to Be.h(W) with  $a=a\text{Be.h}(\sqrt{2};3)$ . The lacunae caused by the higher electron contribution of B are neighbouring the B atoms. Since every B causes one lacuna the electron content as compared to Be is decreased,  $a(22,20)=3.37;7.05\text{\AA}=b_{\text{FU}}(2;5.5/2)=c_{\text{C}}(\sqrt{8};5.5)$  or  $a=g_{\text{C}}(\sqrt{8};5.5)$ . The little strain of the binding causes full occupancy of  $b$  and a small contraction of  $a$  in  $a_3$  direction.

Be<sub>2</sub>B.h(CaF<sub>2</sub>,SR26.57),  $a(28,24)=4.66\text{\AA}=g_{\text{C}}(4)$ . The high  $g$  site number 5.4 seems to be the reason for instability at room temperature.

Be<sub>2</sub>B<sub>3</sub>(T24.36;73Ste),  $a(156,120)=7.25;8.46\text{\AA}=b_{\text{FU}}(\sqrt{20};7.5/2)=g_{\text{C}}(\sqrt{40};7.5)$ . The binding is tentative since the cell content is not yet certain;  $N_{\text{S}(g)}^{\text{At}}=5$ .

BeB<sub>3</sub>(H27.82,SR39.27) contains icosahedra and other polyhedra,  $a(300,218)=\text{H9.80};9.53\text{\AA}=b_{\text{FH}}(6;7/3)=c_{\text{CH}}(6;14/3)$  or  $=g_{\text{CH}}(\sqrt{39};15/3)$  with  $N_{\text{S}(g)}^{\text{At}}=5.4$ .

BeB<sub>6</sub>(T28.168,SR26.57) is htpe to AlB<sub>12</sub>,  $a(560,392)=10.16;14.28\text{\AA}=b_{\text{FU}}(\sqrt{40};12)=g_{\text{C}}(9;12)$ .

$\text{BeB}_{12}$ (T4.48,SR24.59),  $a(152;104)=8.80;5.08\text{\AA}=g_{\text{C}}(8;4.5)$ . This phase is htpc to  $\text{B}_{50}\text{C}_2$  and  $\text{B}_{50}\text{N}_2$  (drwSR22.212) and displays a  $\text{B}_{12}$  packing of the U type.

$\text{Mg}(\text{H}_2,\text{SR}1.40)$ ,  $a(4,16)=\text{H}3.21;5.21\text{\AA}=g_{\text{H}}(3;5)$ . The high site number comes from the neighbourhood to Na.

$\text{MgB}_2$ (AIB<sub>2</sub>,SR17.71,drw64Sch.270) decomposes at 1600°C (77Spe). It contains B-layers parallel to  $a_1, a_2$  of the graphite type, and displays an unusual axial ratio.  $a(2,14,6)=\text{H}3.08;3.52\text{\AA}=b_{\text{CH}}(1;2.75/3)=c_{\text{CH}}(2;5.5/3)$  or simplified  $a=g_{\text{CH}}(2;5.5/3)$ . The  $g$  correlation is highly occupied and causes therefore the unusual axial ratio of  $a$ . Surprisingly AIB<sub>2</sub>(H1.2,SR20.5) has a lower axial ratio,  $a(3,14,6)=\text{H}3.01;3.26\text{\AA}=g_{\text{CH}}(\sqrt{(13/3)};5.5/3)$  might be an interpretation for it. The commensurability in the basal plane has been changed from  $2=\sqrt{(12/3)}$  to  $2.08=\sqrt{(13/3)}$ , see 86Sch.

$\text{MgB}_4$ (O4.16,SR38.50,drw ibid.) decomposes at 1800°C (77Spe), it contains  $\text{B}_{2+4/2}$  pyramids forming chains in  $a_2$  direction.  $a(8,80,40)=5.46;4.43;7.47\text{\AA}=b_{\text{F}}(1.25;1;1.75)=g_{\text{C}}(5;4;7)$ . The number of  $g$  sites per atom is 7 while it was 7.3 in  $\text{MgB}_2$ .

$\text{MgB}_7$ (P4.28,SR48.34,drw ibid.) contains  $\text{B}_{12}$  icosahedra in H1 packing and six  $\text{B}_{12}$  surrounding one Mg.  $a(16,232,128)=5.97;8.13;10.48\text{\AA}=g_{\text{C}}(5.5;7.5;9.5)$ .

$\text{MgB}_{12}$ (65Ell, but see 69Shu). The explanation of the constitution needs further work.

$\text{CaB}_4$ (ThB<sub>4</sub>,T4.16,SR26.74,drw64Sch.273) is htpc to  $\text{CaB}_6$  with  $a=a_{\text{CaB}_6}(2;1)$ , every second Ca cube is filled by a  $\text{B}_2$  dumbbell.  $a(8,80,64)=7.11;4.11\text{\AA}=g_{\text{B}}(\sqrt{26};3)$ . The  $g_{\text{C}}$  of  $\text{MgB}_{12}$  becomes  $g_{\text{B}}$  because of higher number of  $f$  electrons involved.

$\text{CaB}_6$ (C1.6,SR2.37,drw64Sch.273) decomposes near to 2500°C (77Spe).  $a(2,26,20)=4.15\text{\AA}=b_{\text{B}}(1)=g_{\text{B}}(3)$ . Below, it is found why  $\text{LaB}_6$ (C1.6) is stable but "HfB<sub>6</sub>(C1.6)" not. Comparing the electron distance  $d_g$  with  $d_b(\text{B.h})=1.4\text{\AA}$  reveals that a strong compression of  $d_b(\text{B.h})$  is caused by the core electrons of Ca. Since at lower B content the boron electrons tend to increase their distance, the  $g$  correlation is there not possible and intermediate phases are not longer stable.

$\text{SrB}_6$ (CaB<sub>6</sub>,SR17.63),  $a(2,26,22)=4.20\text{\AA}=g_{\text{B}}(3)$ .

$\text{BaB}_6$ (CaB<sub>6</sub>,SR17.63),  $a(2,26,22)=4.27\text{\AA}=g_{\text{B}}(3)$ .

$\text{ScB}_2$ (AIB<sub>2</sub>,SR22.65,44.108) has a congruent melting point at 2250°C (cmp).  $a(3,14,12)=\text{H}3.15;3.52\text{\AA}=b_{\text{CH}}(1;2.75/3)=g_{\text{BH}}(2;11/3)$ . The phase is isodesmic to  $\text{MgB}_2$  if the

participation of the Sc2s<sub>p</sub> electrons is disregarded. The influence of these *f* electrons can only be weak in the sense of 83SchFig.1. For the  $g_C^1$  part of the binding the site number is  $\sqrt[3]{\frac{At}{S(g)}} = 8$ . The less perfect commensurability element 11/3 has no influence since there is no possibility of stacking homeotypism.

ScB<sub>4</sub>(73Gre).

ScB<sub>6</sub>(CaB<sub>6</sub>,85Vil),  $a = 4.44\text{\AA} = g_B(3)$ .

ScB<sub>12</sub>(U1.12,SR30.116,44,100) is a Sc<sub>F1</sub> structure with B<sub>12</sub> cubooctahedra in octahedral interstices.  $a(6,88,64) = 5.22; 7.35\text{\AA} = g_B(4;5)$ . This binding is not compatible with a cubic UB<sub>12</sub> structure (SR12.34).

YB<sub>2</sub>(AlB<sub>2</sub>,MgB<sub>2</sub>,71Eck),  $a(3,14,10+4) = 113.30; 3.84\text{\AA} = b_C(1;2,75/3) = g_{BH}(2;11/3)$ . The participation of the B1s<sup>2</sup> electrons in *g* becomes possible because of the weaker attraction by the nucleus as compared with C,N,O.

YB<sub>4</sub>(ThB<sub>4</sub>,CaB<sub>4</sub>,SR30.31,46,41,drw64Sch.237) cmp (77Spe),  $a(12,80,40+32) = 7.09; 4.01\text{\AA} = g_B(\sqrt{29};3)$ . The phase is only homeodesmic to CaB<sub>4</sub>(ThB<sub>4</sub>) because of its higher electron contribution.

YB<sub>6</sub>(CaB<sub>6</sub>,SR17.63),  $a(3,26,22) = 4.11\text{\AA} = g_B(3)$ . The stability of the CaB<sub>6</sub> type with A<sup>1</sup>,A<sup>2</sup>,A<sup>3</sup>, confirms the assumption of a collective binding. That the A<sup>2</sup>B<sub>6</sub> phases are semi-conductors while YB<sub>6</sub> is a metallic conductor (67Hoa) comes from the good fit of *b* in CaB<sub>6</sub>.

YB<sub>12</sub>(UB<sub>12</sub>,F1.12,SR30.29,drw64Sch.273),  $a(12,176,136) = 7.50\text{\AA} = g_B(6;9/2)$ . The commensurability to the structure in the basal plane is excellent and spin compensation is possible since  $(g_B)_3 / (g_B)_1 < \sqrt{2}$ .

YB<sub>66</sub>(F6.396,SR34.43;drw ibid.) is an intermediate phase containing many B<sub>12</sub> icosahedra.  $a(72,4944,3408) = 23.44\text{\AA} = g_B(16;17)$ . Because of the high electron number the proposal is tentative.

LaB<sub>2</sub>(73Gre).

LaB<sub>4</sub>(ThB<sub>4</sub>,CaB<sub>4</sub>,SR6.75),  $a(12,80,72) = 7.32; 4.18\text{\AA} = g_B(\sqrt{29};3)$ .

LaB<sub>6</sub>(CaB<sub>6</sub>,SR26.74) cmp (77Spe),  $a(3,26,22) = 4.16\text{\AA} = g_B(3)$ . For "HfB<sub>6</sub>" would come  $a(4,26,26)$ , this phase cannot be stable therefore. A review of LnB<sub>M</sub> phases is found in 76Spe. The crystal chemistry of these phases provides the possibility to analyse the

influence of the filling of the  $4f$  shell. For instance  $\text{HoB}_6(\text{CaB}_6, \text{SR}23.61)$ ,  $a(3,26,22)$  is stable while " $\text{ErB}_6(\text{CaB}_6)$ ",  $a(3,26,23)$  could not be prepared (76Spe). Also " $\text{TbB}_6$ " and " $\text{CpB}_6$ " could not be prepared (76Spe). This shows that the limit of stability lies at  $\sqrt[3]{\frac{a}{b+c+f}}=51$ . Complete filling of the  $g$  sites is not possible, since for optimum position of the  $g$  lattice with respect to  $\text{B}_6$  one  $g$  site coincides with the La nucleus.

In the mixture  $\text{TiB}_3\text{M}$  the intermediate phases are no longer restricted to the mole fractions  $N_{\text{B}} > 0.66$ , as in  $\text{A}^{1\dots3}\text{B}_3\text{M}$ . This must be caused by the  $\text{Ti}3d^4$  electrons which more strongly separate the Ti cores so that B atoms may easier enter the structure. The intermediate phases thus occur in all parts of the mixture and the bindings must be compatible with the bindings assumed for Ti. For  $\text{Ti.h}(\text{W}, \text{SR}4.84, 13.148)$  was proposed (82Sch1)  $a(8, 16)=3.31\text{\AA}=b_{\text{B}}(1)=r_{\text{C}}(2)=r_{\text{F}}(2)$ . Here  $r_{\text{F}}(2)$  appears questionable since it does not provide good spin compensation. A collective binding fitting to this proposal might be  $a=g_{\text{C}}(\sqrt{8}; 2.8)$ . However, this would suffer from slight overoccupation. Therefore it may be assumed  $a=(8, 16, 16)=g_{\text{B}}(\sqrt{8}; 2.8)$  so that  $N_{\text{S}}^{\text{A}1(g)}=22$  being appropriate up to Cr. For  $\text{Ti.r}(\text{Mg}, \text{SR}1.53)$  comes  $a(8, 16, 16)=\text{H}2.95; 4.68\text{\AA}=g_{\text{H}}(3; 5)$ . This binding is nearly fully occupied, and the matrix element 5 favours the Mg type stacking.

$\text{Ti}_2\text{B}(\text{HtpMg}, \text{SR}12.34)$  is htpc and hdmc to Ti.r, see  $\text{Ti}_4\text{N}, \text{Ti}_6\text{O}, \text{Ti}_3\text{O}$ .  $a(24, 57, 54)=\text{H}5.95; 4.79\text{\AA}=g_{\text{H}}(6; 5)$ . This favours the Mg type stacking of Ti layers following rules of 84Sch.

" $\text{Ti}_2\text{B}(\text{T}, \text{SR}18.67)$ " was doubted (65Ell).

$\text{TiB}(\text{FeB}, \text{O}4.4, \text{SR}18.69, \text{drw}64\text{Sch}, 265)$  displays parallel to  $a_1, a_2$  a quadratic Ti-net, like as in  $\text{TiC}(\text{NaCl})$ , but pleated, so that it allows the formation of B-chains. The separate B-B bonding, earlier discussed by 54Kie, may be caused by the fact that the  $\text{B}2\text{sp}$  electrons do not fit as well into the  $\text{Ti}3\text{sp}$  electron correlation as the  $\text{C}2\text{sp}$  electrons. In  $\text{ABe}_3\text{M}$  phases the formation of  $\text{Be}_{13}$  icosahedra may have a similar reason. However, the binding to be proposed now still reveals another cause:  $a(16, 44, 40)=6.12; 3.06; 4.56\text{\AA}=b'_{\text{B}}(2\sqrt{2}; \sqrt{2}; 1.88)=g_{\text{B}}(4\sqrt{2}; 2\sqrt{2}; 3.75)$  with the site number  $N_{\text{S}}^{\text{Ti}(g)}=30$  while in  $\text{TiC}(\text{NaCl})$ ,  $a=4.33\text{\AA}=g_{\text{B}}(4)$ ,  $N_{\text{S}}^{\text{Ti}(g)}=32$ . From this proposal may be seen that a sufficient occupation of  $b'-c'$  is more important than a full occupation of  $b'$ . The participation of  $f$  electrons makes possible the homeodesmism  $g_{\text{B}}-g_{\text{B}}$  as  $g_{\text{C}}-g_{\text{C}}$  is less favourable. The strain  $\text{B}-\text{B}$  disturbs the com-



measurability found in TiC. The generated dipole vectors in  $g_{\text{B}}$  direction at Ti favour the pleating of the quadratic Ti-nets and hence the formation of B-chains.

$\text{Ti}_3\text{B}_4$  (Ta<sub>2</sub>B<sub>4</sub>, P3.4, 71Eck, drw64Sch.263) contains double chains of B or hexagon tapes, the quadratic Ti-nets are not pleated but slightly strained for structural reasons.  $a(24,72,64)=3.26;13.73;3.04\text{\AA}=b_{\text{B}}(\sqrt{2};6)=g_{\text{B}}(\sqrt{8};12)$ . Like as in TiB,  $g_{\text{C}}:g_{\text{B}}$  is fully occupied by *b-c*. Since there are 6 Ti layers parallel to  $a_1, a_3$ , dipole vectors are not formed and pleating is not possible. The strong decrease of  $d_g$  as compared with TiB presumably indicates that *g* has more the property  $g_{\text{C}}$  than the property  $g_{\text{B}}$ .

$\text{TiB}_2$ (AlB<sub>2</sub>, SR13.46) has a congruent melting point at 2790°C (cmp 2790°C),  $a(4,14,12)=\text{H}3.03;3.23\text{\AA}=g_{\text{B}}(\sqrt{8};4.5)$  as written for  $g_{\text{C}}$ . It would be of interest whether at low temperatures a structural transformation occurs. Another probable interpretation is  $a=g_{\text{BH}}(2;9/3)$ . The striking strain of  $\hat{\text{B}}_{\text{H}}$  must be caused by a special spin distribution.

$\text{Ti}_2\text{B}_5$ (W<sub>2</sub>B<sub>5</sub>, H4.10, SR16.33, drw64Sch.270) is a filling htp of AlB<sub>2</sub>.  $a(16,62,52)=\text{H}2.98;13.98\text{\AA}=g_{\text{BH}}(2;45/3)$ . The energetic advantage against  $\text{TiB}_2$  is the integral value  $(g^{-1}a)_{33}=15$  without a strain  $\hat{\text{B}}_{\text{H}}$ .

$\text{Ti}_2\text{B}_{50}$ (T2.50), SR41.40, drw ibid.),  $a(8,166,116)=8.83;5.07\text{\AA}=g_{\text{B}}(\sqrt{45};3.9)$ , see B<sub>50</sub>C<sub>2</sub>.

ZrB<sub>2</sub>.ih(NaCl, SR16.34),  $a(16,44,48)=4.65\text{\AA}=g_{\text{B}}(4)$ . Strikingly, the NaCl type is avoided in borides. If the impurity is N or O then the isodesmism to ZrC is favoured.

ZrB<sub>2</sub>(AlB<sub>2</sub>, SR16.34),  $a(4,14,10+4)=\text{H}3.17;3.53\text{\AA}=g_{\text{BH}}(2;11/3)$ . The low occupancy indicates that the *f* correlation is not very important. If here also  $a=g_{\text{BH}}(2;9/3)$  is assumed then the full occupation of *b-c* is attained.

ZrB<sub>6</sub>(73Gre).

ZrB<sub>12</sub>-h(UB<sub>12</sub>, F1.12, SR16.35, drw64Sch.273),  $a(16,176,136)=7.41\text{\AA}=g_{\text{B}}(6;9.2/2)$ .

HfB<sub>2</sub>.i(NaCl, SR17.70),  $a(16,44,64)=4.62\text{\AA}=g_{\text{B}}(4)$ .

HfB(FeB, 71Eck),  $a(16,44,64)=6.50;3.21;4.83\text{\AA}=b_{\text{B}}(2\sqrt{2};\sqrt{2};1.9)=g_{\text{B}}(4\sqrt{2};2\sqrt{2};3.75)$ . Remarkably the *g* correlation is slightly overoccupied.

HfB<sub>2</sub>(AlB<sub>2</sub>, SR17.69),  $a(4,14,18)=\text{H}3.14;3.47\text{\AA}=g_{\text{BH}}(2;9/3)$ .

HfB<sub>12</sub>(UB<sub>12</sub>, 85Vil),  $a(16,176,152)=7.38\text{\AA}=g_{\text{B}}(6;10/2)$ .

V(W, SR1.56, 26.275),  $a(10,16,16)=3.02\text{\AA}=g_{\text{B}}(\sqrt{8};2.8)$ .

V<sub>2</sub>B(73Gre).

$V_3B_2(U_3Si_2, T6.4, SR23.72, drw64Sch.252)$  contains W and  $AlB_2$  elements, the B combine to pairs displaying thus a specific interaction of the light atoms which appears less developed in  $AC_{11}$  phases.  $a(30,60,56)=5.75;3.03\text{\AA}=g_B(\sqrt{29};2.8)$ , the phase is closely homeodesmic to V. The tetragonal  $V_3B_2$  suggests twinning of  $g_B$  in V.

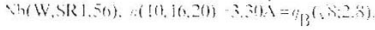
$VB(TII, O2.2, SR23.72, drw64Sch.263)$  is a shear htp of NaCl permitting all B to condense to chains.  $a(20,44,40)=3.06;2.97;8.04\text{\AA}=g_B(\sqrt{8};7.5)$ . Remarkably the  $b'-c$  correlation does not find place in the  $g_C$  part of the  $g_B$  correlation providing only 60 sites. This indicates that  $g_C$  does not accept all  $b'$  electrons and that in slight deviation from Hunds rule only  $V3d^4$  electrons have a +spin while one  $V3d^1$  electron has a -spin. It becomes clear that  $V2sp$  electrons weakly take part in  $g_B$ , because they make it possible that a  $g_C$  correlation of one spin direction is formed. The unoccupied sites of  $g_B$  are remote of the atom cores. In  $a$  there are 4 approximately equidistant V layers parallel to  $a_1, a_2$ , and 15  $g_B$  layers. It may easily be seen that this favours the shear since it causes two neighbouring V layers to have the same momentary electro dipole component in  $a_3$  direction.

$V_5B_6(O5.6, 69Spe, drw ibid.)$  is closely htpc to VB, it contains 10 V-layers and 6 nonequidistant shear planes parallel to the smallest cell-face. Since a shear plane contains B zigzag chains, in the closely neighbouring shear planes a tape along  $a_3$  of B-hexagons sharing edges is formed (see  $Ta_3B_4$  in 64Sch.263).  $a(40+10, 116, 104)=3.06;21.25;2.97\text{\AA}=g_B(\sqrt{8};20)$ . The correlation  $g_C^c g_B$  is nearly filled by  $b^+ - c$  where  $N_{b^+}^c = 40$  and the + sign refers to the spin.

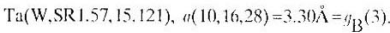
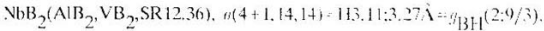
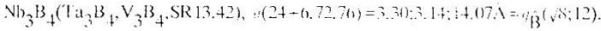
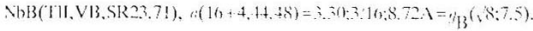
$V_3B_4(Ta_3B_4, P3.4, SR20.56, drw64Sch.263)$  contains 6 V-layers, 4 shear planes, and two B-hexagon tapes.  $a(24+6, 72, 64)=3.03;2.99;13.18\text{\AA}=g_B(\sqrt{8};12)$ . The  $g_B$  correlation is strained to reach the good commensurability as in  $Ti_3B_4$ . The  $V_3B_4$  phase is homeodesmic and heterotypic to  $TiC$ .

$V_2B_3(Q4.6, 69Spe, drw ibid.)$  contains 8 V-layers and 2 double tapes of B-hexagons.  $a(32+8, 100, 88)=3.06;2.98;18.40\text{\AA}=g_B(\sqrt{8};16)$ . The B type is more strained to conserve the good commensurability.

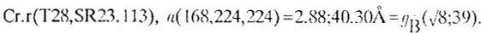
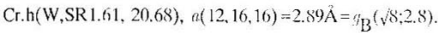
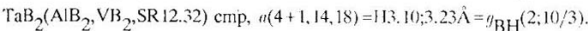
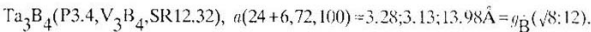
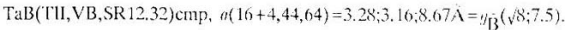
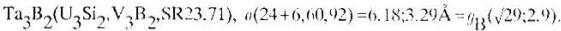
$VB_2(AlB_2, SR12.36)$  has a congruent melting point (cmp),  $a(5, 14, 12)=H3.00;3.06\text{\AA}=g_{B11}(2;10/3)$  or  $a_C(10, 28, 24)=3.00;3.06;5.20\text{\AA}=g_B(\sqrt{8};5)$ . The commensurability per V layer has jumped from 2 in  $V_2B_3$  to 2.5 in  $VB_2$ .



$\text{Nb}_3\text{B}_2(\text{U}_3\text{Si}_2, \text{V}_3\text{B}_2, \text{SR}23.71)$ ,  $a(24+6,60,68)=6.19;3.29\text{\AA}=g_{\text{B}}(\sqrt{29};2,9)$ . The  $e_{\text{C}}$  correlation is filled by  $f^{\uparrow}$ .

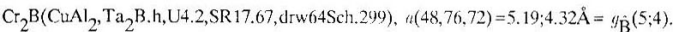


$\text{Ta}_2\text{B.h}(\text{CuAl}_2, \text{U}4.2, \text{SR}26.80, \text{drw}64\text{Sch.}299)$ ,  $a(70,76,120)=5.78;4.86\text{\AA}=g_{\text{B}}(\sqrt{26};4,3)$ .  $g$  is here and in the next three phases somewhat overoccupied, perhaps the  $f$  band donates electrons to a lower band, or a separate  $b$  correlation is formed.

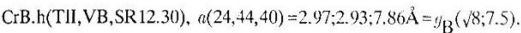


$\text{CrB}_{0.2}(\text{FhtpMg}, \text{SR}21.56)$ ,  $a(12,17.5,16.5)=112.58;4.45\text{\AA}=g_{\text{BH}}(\sqrt{3};15/3)$ . The slight overfilling may be removed by a little change in the mole fraction  $N_{\text{B}}$ .

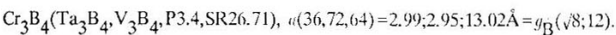
$\text{Cr}_4\text{B}(\text{Mn}_4\text{B}, \text{S}8.2, \text{SR}17.67, \text{drw}64\text{Sch.}254)$  contains parallel to the smallest cell face quasihexagonal layers as in  $\text{CuAl}_2(110)$ . These layers are sheared against one another.  $a(192,280,272)=4.26;7.38;14.71\text{\AA}$ . For the isotypic  $\text{Mn}_2\text{B}_{0.98}$  a tentative proposal is noted.



$\text{Cr}_5\text{B}_3(\text{U}10.6, \text{SR}17.67, \text{drw}64\text{Sch.}254)$  appears intermediary between  $\text{Cr}_2\text{B}(\text{CuAl}_2)$  and  $\text{V}_3\text{B}_2(\text{U}_3\text{Si}_2)$  and contains 4 filled Cr layers,  $a(120,196,184)=5.46;10.64\text{\AA}=g_{\text{B}}(\sqrt{26};10)$ .



CrB.r(MoB,U4.4,SR39.107,drw64Sch.263),  $a(48,88,80)=2.94;15.72\text{\AA}=g_{\text{B}}(\sqrt{8};14)$ . The structure has 8 Cr layers parallel to  $a_1, a_2$  and 4 shear planes as compared to the NaCl type. The proposal is not certain because of MoB.r and WB.r. Perhaps a separate  $b$  is precipitated.



$\text{CrB}_2(\text{AlB}_2, \text{SR}12.36)$ ,  $a = \text{H}2.97:3.07\text{\AA}$ . With respect to the homeotypism of  $\text{CrB}_2$  with the earlier phases ( $\text{Cr}_3\text{B}_4$  etc.) it is of interest to consider the pseudotetragonal cell:  $a_1$  (12.28,24) = 2.97:3.07:5.14 $\text{\AA} = g_{\text{B}}(\sqrt{8};5)$ . Alternatively  $a = g_{\text{BH}}(2;9/3)$ .

$\text{CrB}_4(\text{P}1.4, \text{SR}33.46, \text{drw ibid.})$  contains  $\text{B}_4$  squares parallel to  $a_1, a_2$ , surrounded by six Cr.  $a(12,40,32) = 4.74:5.48:2.87\text{\AA} = g_{\text{B}}(4;5;2.5)$  is a tentative proposal.

$\text{CrB}_4(\text{R}8.328, \text{SR}35.34)$  is htpc to B.h(R12).  $a(48,1048,720) = \text{H}10.96:23.85\text{\AA}$ .

$\text{Mo(W, SR}1.61, 24.88)$ ,  $a(12,16,20) = 3.15\text{\AA} = g_{\text{B}}(\sqrt{(34/4)};2.9)$ .

$\text{Mo}_2\text{B}(\text{CuAl}_2, \text{Ta}_2\text{B.h, SR}11.52)$ ,  $a(48,76,88) = 5.54:4.74\text{\AA} = g_{\text{B}}(\sqrt{26};4.3)$ . The axial ratio  $|a_3|/|a_1|(\text{Mo}_2\text{B}) = 0.86 > |a_3|/|a_1|(\text{Cr}_2\text{B}) = 0.83$  is an indication for the influence of the Mo3d electrons on the stability.

$\text{Mo}_3\text{B}_2(\text{U}_3\text{Si}_2, \text{V}_3\text{B}_2, 71\text{Eck})$ ,  $a(36,60,68) = 6.00:3.15\text{\AA} = g_{\text{B}}(\sqrt{29};2.85)$ . The non-integral commensurability element 2.85 might cause very distant shears with plane  $a_1, a_2$ .

$\text{MoB.h(TII, VB, SR}11.51)$ ,  $a(24,44,48) = 3.16:3.08;8.61 = g_{\text{B}}(\sqrt{8};7.5)$ .

$\text{MoB.r(U}4.4, \text{CrB.r, SR}16.31)$ ,  $a(48,88,96) = 3.10;16.95\text{\AA} = g_{\text{B}}(\sqrt{8};14.5)$ .

$\text{MoB}_2(\text{AlB}_2, \text{SR}16.32)$ ,  $a(4+2,14,14) = \text{H}3.04;3.06\text{\AA} = g_{\text{BH}}(2;9/3)$ . The low occupation is only in the partial correlation occupied by the *f* electrons.

$\text{Mo}_2\text{B}_5(\text{R}2.5, \text{SR}11.49, \text{drw}64\text{Sch.}270)$  is closely htpc to  $\text{W}_2\text{B}_5$  and  $\text{Ti}_2\text{B}_5(\text{W}_2\text{B}_5)$ ,  $a(36,93,90) = \text{H}3.01;20.93\text{\AA} = g_{\text{BH}}(2;60/3)$ .

$\text{Mo}_{0.8}\text{B}_3(\text{H}(3.2).12, \text{SR}39.39)$ , has a filled B site set as in  $\text{MoB}_2$  while the corresponding Mo site set is only partially occupied.  $a(19,62,56) = \text{H}5.20;6.35\text{\AA} = g_{\text{CH}}(\sqrt{12};12/3)$ . The similarity of *a* to  $a(\text{WB}_4)$  suggests that both structures need confirmation.

$\text{MoB}_{12}(73\text{Gre})$ .

$\text{W(B1, SR}1.61, 24.88)$ ,  $a(12,16,28) = 3.17\text{\AA} = b_{\text{B}}(1) = (c \cdot c')_{\text{B}}(3)$ . The slight overfilling of  $a = g_{\text{B}}(3)$  suggests a separate *b* correlation.

$\text{W}_2\text{B}(\text{CuAl}_2, \text{Ta}_2\text{B.h, SR}11.52)$ ,  $a(48,76,120) = 5.56;4.74\text{\AA} = g_{\text{B}}(\sqrt{29};4.5)$ . Just as in  $\text{TaB}_M$  the correlation appears overoccupied.

$\text{WB.h(TII, VB, SR}11.51)$ ,  $a(24,44,64) = 3.19;8.40;3.07\text{\AA} = b_{\text{B}}(\sqrt{2};3.75) = g_{\text{B}}(\sqrt{8};7.5)$ . It is remarkable that the structure contains a separate *b* correlation signaling that the type will become unstable in  $\text{A}^7\text{B}$  phases.

$\text{W.r(MoB.r, CrB.r, SR}16.31)$ ,  $a(48,88,128) = 3.12;16.93\text{\AA} = b_{\text{B}}(\sqrt{2};7.25) = g_{\text{B}}(\sqrt{8};14.5)$ . A

phase 'WB<sub>3</sub>(AlB<sub>2</sub>)' is no longer stable because  $a(6,14,18)$  would not tolerate the commensurability element  $9/3$  since more free sites are required.

WB<sub>2</sub>(H4.8,SR34.41) is a stacking htp of AlB<sub>2</sub> with 4 W layers.  $a(24,56,72)=112.98; 13.88\text{\AA}=g_{\text{BH}}(2;45/3)$ . The cell is the same as that of W<sub>2</sub>B<sub>5</sub>h so that both phases might be identical.

W<sub>2</sub>B<sub>5</sub>h(H4.10,SR11.49,drw64Sch.270),  $a(24,62,76)=112.98; 13.87\text{\AA}=g_{\text{BH}}(2;45/3)$ .

W<sub>2</sub>B<sub>5</sub>r(Mo<sub>2</sub>B<sub>5</sub>,SR32.139),  $a(36,93,114)=3.01; 20.93\text{\AA}=g_{\text{BH}}(2;69/3)$ .

WB<sub>4</sub>(H4.16,SR31.29) is htpc to Mo<sub>0.8</sub>B<sub>3</sub>.  $a(24,80,88)=5.20; 6.34\text{\AA}=g_{\text{BH}}(\sqrt{12};21/3)$ .

The very low occupancy suggests that a  $g_{\text{CH}}$  correlation is locally filled to  $g_{\text{BH}}$ .

WB<sub>12</sub>(H,71Eck).

Mn.h<sub>3</sub>(W,SR18.210),  $a(14,16,16)=3.08\text{\AA}=g_{\text{B}}(\sqrt{8};2.8)$ .

Mn.h<sub>2</sub>(Cu,SR18.210),  $a(28,32,(32))=3.86\text{\AA}=g_{\text{C}}(4)$ .

Mn.h<sub>1</sub>(C20,SR1.757,2.3,20,149),  $a(140,160,160)=6.31\text{\AA}=b_{\text{B}}(3)=(r-c-f)_{\text{B}}(6)$ .

Mn.r(B29,SR2.2),  $a(406,464,464)=8.91\text{\AA}$ .

Mn<sub>4</sub>B(S8.2,SR13.38,drw64Sch.254) is L-htpc to Mn<sub>2</sub>B<sub>0.98</sub>.

Mn<sub>2</sub>B<sub>0.98</sub>(S8.4,SR48.35) is a shear htp of CuAl<sub>2</sub>.  $a(224,304,288)=14.54; 7.29; 4.21\text{\AA}=g_{\text{B}}(11\sqrt{2};5\sqrt{2};4)$ . The commensurability element 11 appears to introduce the shear following the mechanism described for Cu<sub>3</sub>Au in 64Sch.

Mn<sub>2</sub>B(CuAl<sub>2</sub>,Ta<sub>2</sub>B.h,SR13.40),  $a(32+24,76,72)=5.15; 4.21\text{\AA}=g_{\text{B}}(\sqrt{26};4)$ . The binding provides 104 sites for +spin so that Mn contributes only 4 +spins in slight contradiction to Hunds rule.

MnB(FeB,O4.4,SR4.101,drw64Sch.265) is htpc to CrB.h(TII), the B chains being in different manner distributed.  $a(16+12,44,40)=5.56; 2.98; 4.15\text{\AA}=g_{\text{B}}(3.75\sqrt{2};2\sqrt{2};4)$ . In the electron contribution there are 62 +spins while the CrB.h type provides only 60 +spin sites. The type is found also in FeB and CoB but not in NiB.

Mn<sub>3</sub>B<sub>4</sub>(Ta<sub>3</sub>B<sub>4</sub>,P3.4,SR13.40),  $a(42,72,64)=3.03; 12.86; 2.96\text{\AA}=g_{\text{B}}(\sqrt{8};12)$ .

MnB<sub>2</sub>(AlB<sub>2</sub>,SR24.79),  $a(7,14,12)=H3.01; 3.04\text{\AA}=g_{\text{BH}}(2;9/3)$ .

MnB<sub>4</sub>(Ni.4,SR35.38) is deformation htpc to CrB<sub>4</sub>. Analysis must be postponed.

Tc(Mg,SR11.183,26.254),  $a(14,16,20)=112.74; 4.40\text{\AA}=g_{\text{BH}}(2;15/3)$ . The commensurability element  $15/3=5$  favours the Mg type (84Sch).

$\text{Te}_3\text{B}(\text{Re}_3\text{B}, \text{Q6.2}, \text{SR29.104}, \text{drw65Aro.55})$  is like to  $\text{CrB}$ , so that the B are in trigonal prismatic  $\text{Te}_6$  coordination. However, the prisms do not share quadratic faces but trigonal faces.  $a(84, 108, 128) = 2.89; 9.16; 7.25\text{\AA} = g_{\text{B}}(2\sqrt{2}; 9; 5\sqrt{2})$ . The commensurability elements 9 and  $5\sqrt{2}$  cause shears that forbid common tetragonal faces of  $\text{Te}_6$  prisms and generate a 9-coordination of Te around B.

$\text{Te}_7\text{B}_3(\text{Th}_7\text{Fe}_3, \text{H14.6}, \text{SR29.104}, \text{drw64Sch.266}, \text{SR23.58})$  is a more symmetrical homeo-type of  $\text{Cr}_7\text{C}_3$ . On a column of  $\text{Te}_6$ -octahedra sharing faces, trigonal prisms centred by B are erected.  $a(98, 130, 152) = \text{H}7.42, 4.78, = g_{\text{BH}}(\sqrt{27}; 16/3)$ .

$\text{TeB}, \text{Te}_3\text{B}_4(73\text{Gre})$ .

$\text{TeB}_2(\text{ReB}_2, \text{H2.4}, \text{SR29.104})$ ,  $a(14, 28, 28) = \text{H}2.89; 7.45\text{\AA} = g_{\text{B11}}(2; 24/3)$ . In  $\text{ReB}_2$  are on the B rich side 6B in the cell. Therefore  $(b-c)_{\text{C11}}$  is nearly fully occupied. For a  $\text{AlB}_2$  type too many electrons are in the cell.

$\text{Re}(\text{Mg}, \text{SR2.193}, 26, 240)$ ,  $a(14, 16, 28) = \text{H}2.76; 4.46\text{\AA} = g_{\text{B11}}(2; 15/3)$ .

$\text{Re}_3\text{B}(\text{Q6.2}, \text{Te}_3\text{B}, \text{SR24.73})$ ,  $a(84, 108, 176) = 2.89; 9.31; 7.26\text{\AA} = g_{\text{B}}(2\sqrt{2}; 9; 5\sqrt{2})$ . Somehow the binding tolerates a little overoccupation as in  $\text{TaB}_{11}$  and  $\text{WB}_{11}$ .

$\text{Re}_7\text{B}_3(\text{Th}_7\text{Fe}_3, \text{Te}_7\text{B}_3, \text{SR24.71})$ ,  $a(98, 130, 208) = \text{H}7.50; 4.77\text{\AA} = g_{\text{B11}}(\sqrt{27}; 16/3)$ .

$\text{ReB}(72\text{Now})$ .

$\text{ReB}_2(\text{H2.4}, \text{SR24.71}, \text{drw64Sch.270})$  is homogeneous up to  $\text{ReB}_3(77\text{Mof})$ .  $a(14, 34, 40) = \text{H}2.90; 7.48\text{\AA} = g_{\text{B11}}(2; 24/3)$ . The underoccupation comes from the  $f$  part ( $\text{Re}4f^{14}$ ) of the correlation.

$\text{Re}_2\text{B}_5\text{-h}(\text{W}_2\text{B}_5, \text{H4.10}, 71\text{Eck})$ ,  $a(28, 62, 76) = \text{H}2.97; 13.80\text{\AA} = g_{\text{BH}}(2; 45/3)$ .

$\text{Fe.h}_3(\text{W}, \text{SR19.198})$ ,  $a(16, 16, 16) = 2.93\text{\AA} = g_{\text{B}}(\sqrt{8}; 2.8)$ , presumably  $\text{h}_3$  contains lacunae.

$\text{Fe.h}_2(\text{Cu}, \text{SR19.198})$ ,  $a(32, 32, (32)) = 3.65\text{\AA} = (b-c)_{\text{C}}(4)$ . It appears that the  $\text{Fe}2\text{sp}$  electrons fall out of the  $g$  correlation, and there is not much spin correlation so that  $b$  and  $c$  may be considered as having the F type. When the spin correlation sets in, a transition  $\text{F}-\tilde{\text{B}}$  must occur first in  $c$ . Because of a possible twinning of the binding the  $a$  correlation transforms from  $\text{F1}(\gamma\text{-Fe})$  immediately to  $\text{B1}(\beta\text{-Fe})$ :

$\text{Fe.h}_1(\text{W}, \text{SR19.198})$ ,  $a(16, 16) = 2.90\text{\AA} = b_{\tilde{\text{B}}}(\sqrt{5}; 1.92) = c_{\tilde{\text{B}}}(\sqrt{5}; 1.92)$  (87Sch). Below  $770^\circ\text{C}$  the  $b$  correlation precipitates from  $b'$ , leaving  $c$ .

$\text{Fe.r}(\text{W}, \text{SR19.198})$ ,  $a(16, 16) = 2.87\text{\AA} = b_{\tilde{\text{C}}}(\sqrt{1.25}; 0.96) = c_{\tilde{\text{B}}}(\sqrt{5}; 1.92) = c_{\tilde{\text{B}}}(\sqrt{5}; 1.92)$ . The

magnetic data show that the binding in pure Fe is no longer collective (87Sch). However, the phenomenon of isotypism of  $\text{FeB}_{1/2}$  phases with  $\text{MnB}_{1/2}$  phases suggests to seek for intermediate phases a collective binding.

$$\text{Fe}_{23}\text{B}_6, \text{m}(\text{Cr}_{23}\text{C}_6, \text{F23.6, SR44.107}), a(736, 808) = 10.67\text{\AA} = b_{\text{C}}(4, 5) = (c \sim c')_{\text{B}}(9).$$

$\text{Fe}_3\text{B.h}_2(\text{U12.4, Fe}_3\text{P.78Wal, 87Kne})$ , is closely homeotypic to  $\text{h}_1$  (SR27.99),  $a = 8.63; 4.29\text{\AA}$ .

$\text{Fe}_3\text{B.h}_1(\text{T24.8, Fe}_3\text{B}_{0.6}\text{P}_{0.4}, \text{SR44.107, 87Kne})$ ,  $a(192, 216, 208) = 8.75; 4.36\text{\AA} = b_{\text{C}}(\sqrt{18}; 2) = g_{\text{B}}(\sqrt{72}; 4)$ . The strain of  $g_{\text{B}}$  may indicate the existence of a separate  $b$  correlation (87Sch).

$$\text{Fe}_2\text{B}(\text{CuAl}_2, \text{Ta}_2\text{B.h, SR2.286}), a(64, 76, 72) = 5.11; 4.25\text{\AA} = b_{\text{C}}(2.5; 2) = (c \sim c')_{\text{B}}(5; 4).$$

$\text{FeB}(\text{O4.4, MnB, SR2.241})$ ,  $a(32, 44, 46) = 5.51; 2.95; 4.06\text{\AA} = g_{\text{B}}(3.75\sqrt{2}; 2\sqrt{2}; 4)$ . The Fe partial structure in  $\text{Fe}_2\text{B}$  is approximately of the C1 type. It might therefore be surprising that with a higher B content the Fe partial structure is closer packed in FeB. However, the commensurability of  $g_{\text{B}}$  to the quasiquadratic Fe meshes is different.

$$\text{FeB}_2, \text{m}(\text{AlB}_2, 85\text{Vil, 77Mof}).$$

$$\text{FeB}_{4/9}(\text{R2.98, SR42.57}), a = 10.96; 23.87\text{\AA}.$$

$\text{Ru}(\text{Mg, SR1.69, 24.222})$ ,  $a(16, 16, 20) = \text{H2.71}; 4.28\text{\AA} = g_{\text{BH}}(2; 15/3)$ . The commensurability element  $15/3 = 5$  is favourable for the Mg type stacking. The binding of Ru is closer packed than that of Fe. This may be caused by the influence of the Ru3d electrons which is stronger than the influence of the Fe2sp electrons.

$$\text{Ru}_7\text{B}_3(\text{Th}_7\text{Fe}_3, \text{Tc}_7\text{B}_3, \text{SR23.57}), a(112, 130, 152) = \text{H7.47}; 4.71\text{\AA} = g_{\text{BH}}(\sqrt{27}; 15/3).$$

$\text{Ru}_{11}\text{B}_8(\text{U22.16, SR24.73, drw72Pea.527})$  is homeotypic to  $\text{Ni}_4\text{B}_3$ , all B have a trigonal prismatic  $\text{Ru}_6$  surrounding.  $a(176, 224, 252) = 11.61; 11.34; 2.84\text{\AA} = g_{\text{B}}(10.5; 8\sqrt{2}; 2\sqrt{2})$ .

$\text{RuB}_{1.1}(\text{WC, SR27.93})$ ,  $a(8, 12, 12) = \text{H2.85}; 2.85\text{\AA} = g_{\text{BH}}(2; 9/3)$ . The WC type replaces the  $\text{AlB}_2$  type found still in  $\text{MnB}_2$ . The +spin offer is too high for a TII type.

$\text{Ru}_2\text{B}_3(\text{W}_2\text{B}_5, \text{H4.10, SR34.41})$ ,  $a(32, 50, 52) = \text{H2.89}; 12.81\text{\AA} = g_{\text{BH}}(2; 39/3)$ . The reason for the B defect becomes clear when it is assumed that B contributes only +spins. In this case the +spin offer in a " $\text{Ru}_2\text{B}_5$ " phase would be  $20 + 16 + 30 + 20 + 10 = 96$ .

$\text{RuB}_2, \text{I}(\text{O2.4, SR27.94})$  is an inhomogeneous deformation of  $\text{AlB}_2$  with pleated Ru layers.  $a(16, 28, 28) = 4.65; 2.84; 4.05\text{\AA} = g_{\text{B}}(3\sqrt{2}; 2\sqrt{2}; 4)$ . An  $\text{AlB}_2$  type would be impossible since the +spin offer would be 22 while  $\text{AlB}_2$  admits only 18 +spin sites.

O<sub>2</sub>(Mg,SR1.70,5.35),  $a(16,16,28)=12.74;4.32\text{\AA}=g_{\text{BH}}(2;15/3)$

O<sub>2</sub>B<sub>1,2</sub>(WC,SR27.43),  $a(8,12,14)=12.88;2.87\text{\AA}=g_{\text{BH}}(2;9/3)$ .

O<sub>2</sub>B<sub>1,6</sub>(W<sub>2</sub>B<sub>3</sub>,SR27.93),  $a(32,50,68)=12.91;12.91\text{\AA}=g_{\text{BH}}(2;42/3)$ .

O<sub>2</sub>B<sub>2,2</sub>(RuB<sub>2</sub>,SR27.94),  $a(16,31,38)=4.68;2.87;4.10\text{\AA}=g_{\text{B}}(3\sqrt{2};2\sqrt{2};4)$ .

"O<sub>2</sub>B<sub>5</sub>" (SR26.76) is not confirmed, SR27.93.

Co.h(Cu,SR18.118),  $a(36,32,32)=3.54\text{\AA}=b_{\text{C}}(\sqrt{2};1.25)=r_{\text{B}}(\sqrt{8};2.5)=r_{\text{B}}(\sqrt{8};2.5)$ .

Co.r(Mg,SR22.101),  $a(18,16,16)=12.51;4.07\text{\AA}=b_{\text{H}}(1;1.66)=r_{\text{UH}}(2;5/2)$ .

Co<sub>3</sub>B(Fe<sub>3</sub>C.m,O12.4,SR22.58,drw64Sch.253),  $a(108,108,104)=4.41;5.22;6.63\text{\AA}=g_{\text{B}}(4.5;5.5;7)$ . The distance  $d_g$  does not fit very well to the distance of Co<sub>2</sub>B.

Co<sub>2</sub>B(CuAl<sub>2</sub>,Ta<sub>2</sub>B.h,SR3.619),  $a(72,76,72)=5.02;4.22\text{\AA}=b_{\text{B}}(2.5;2)=g_{\text{B}}(5;4)$ .

CoB(FeB,MnB,SR3.619),  $a(36,44,40)=5.25;3.04;3.96\text{\AA}=g_{\text{B}}(5;3;4)$ . The phase is somewhat heterodesmic to FeB and  $a(\text{CoB})$  is quite different from  $a(\text{FeB})$ .

Rh(Cu,SR1.69,24.223),  $a(36,32,40)=3.80\text{\AA}=g_{\text{B}}(4)$ .

Rh<sub>7</sub>B<sub>3</sub>(Th<sub>7</sub>Fe<sub>3</sub>,Tc<sub>7</sub>B<sub>3</sub>,SR23.57),  $a(126,130,152)=12.47;4.78\text{\AA}=g_{\text{BH}}(\sqrt{27};16/3)$ .

Rh<sub>5</sub>B<sub>4</sub>(H10.8,SR48.37). The Rh form a close packing with stacking  $-+-+++\overset{\curvearrowright}{+}$  and the B are in Rh<sub>6</sub> coordination.  $a(90,104,116)=12.31;20.39\text{\AA}=g_{\text{UH}}(\sqrt{12};28/2)$ . For a simple close packing a stacking would be  $+--+--+--+$ . However, the interference of the B atoms causes a stacking sequence which disregards the equal sign clustering prohibition (84Sch).

RhB<sub>1,1</sub>(NiAs,SR27.71) has Rh in  $+-$  type packing while B form straight strings.  $a(18,22,24)=12.31;4.22\text{\AA}=g_{\text{UH}}(\sqrt{12};6/2)$ . The commensurability element  $6/2=3$  favours the  $+-$  stacking.

Ir(Cu,SR1.70,3.182),  $a(36,32,56)=3.84\text{\AA}=g_{\text{B}}(4)$ .

IrB<sub>0,9</sub>.h(WC,SR37.40),  $a(9,11,16)=12.82;2.82\text{\AA}=g_{\text{BH}}(2;9/3)$ .

IrB<sub>0,9</sub>.r(Q4.4,SR37.40),  $a(72,88,128)=2.71;7.58;7.31\text{\AA}=g_{\text{B}}(2\sqrt{2};8;5\sqrt{2})$ .

IrB<sub>1,1</sub>(ThSi<sub>2</sub>,U2.4;SR24.71,drw64Sch.313) is htp to TII.  $a(36,56,72)=2.81;10.26\text{\AA}=g_{\text{B}}(\sqrt{8};10.3)$ .

Ir<sub>4</sub>B<sub>5,4</sub>(N4.5,SR39.38) is quasiorthogonal.

Ni(Cu,SR1.68,13.88),  $a(40,32,32)=3.52\text{\AA}=b_{\text{C}}(\sqrt{2};1.25)=r_{\text{B}}(\sqrt{8};2.5)=r_{\text{B}}(\sqrt{8};2.5)$ .

Ni<sub>3</sub>B(Fe<sub>3</sub>C.m,Co<sub>3</sub>B,SR32.32),  $a(120,108,104)=4.39;5.21;6.62\text{\AA}=g_{\text{B}}(4.5;5.5;7)$ .



- $\text{Ni}_2\text{B}(\text{CuAl}_2, \text{Ta}_2\text{B}, \text{h}, \text{SR}23.64)$ ,  $a(80, 76, 72) = 4.99; 4.25 \text{ \AA} = g_{\text{B}}(\sqrt{2}; 4, 4)$ .
- $\text{Ni}_4\text{B}_2\text{O}(\text{O}16.12, \text{SR}32.32, \text{drw}64\text{Sch}.265)$  is htpc to FeB, but besides B chains there occur isolated B atoms,  $a(160, 164, 152) = 11.95; 2.98; 6.57 \text{ \AA} = g_{\text{B}}(12; 3; 6, 7)$ .
- $\text{Ni}_4\text{B}_3(\text{N}8.6, \text{SR}32.33)$ ,  $a = \text{M}103.3^{\circ} 6.43; 4.88; 7.82 \text{ \AA}$ .
- $\text{NiB}(\text{TII}, \text{VB}, \text{SR}16.32)$ ,  $a(40, 44, 40) = 2.93; 7.39; 2.96 \text{ \AA} = g_{\text{B}}(3; 7.5)$ .
- $\text{NiB}_2(73\text{Gre})$ .
- $\text{NiB}_{12}(\text{F}1.12, 71\text{Eck})$ ,  $a(40, 176, 128) = 7.53 \text{ \AA} = g_{\text{C}}(7)$ . Apparently the dilution of Ni makes possible a strong increase of  $d_g$ .
- $\text{Pd}(\text{Cu}, \text{SR}1.70)$ ,  $a(40, 32, 40) = 3.89 \text{ \AA} = g_{\text{B}}(4)$ . Therefore Ni and Pd are hdmc isotypes.
- $\text{Pd}_{16}\text{B}_3(\text{F}8.(1.5), 82\text{Alq})$  is a superstructure of Pd (Cu type) with inserted B atoms.  $a(320, 274, 332) = 8.01 \text{ \AA} = g_{\text{B}}(8; 8; 7.5)$ . The doubled lattice constant permits a more economical commensurability.
- $\text{Pd}_3\text{B}(\text{Fe}_3\text{C}, \text{m}, \text{Co}_3\text{B}, \text{SR}26.77)$ ,  $a(120, 108, 128) = 4.85; 5.46; 7.57 \text{ \AA} = b_{\text{B}}(2.3; 2.5; 3.5) = g_{\text{B}}(4.5; 5; 7)$ .
- $\text{Pd}_5\text{B}_2(\text{Mn}_5\text{C}_2, \text{N}10.4, \text{SR}26.76)$ .
- $\text{Pd}_2\text{B}(\text{CaCl}_2, \text{SR}46.40, \text{drw}64\text{Sch}.257)$ ,  $a(40, 38, 44) = 4.69; 5.13; 3.11 \text{ \AA} = g_{\text{B}}(4.5; 5; 3)$ . For the  $\text{CuAl}_2$  type the electron numbers would have been (80, 76, 88) i.e. too large.
- $\text{Pt}(\text{Cu}, \text{SR}1.71; 11.174)$ ,  $a(40, 32, 56) = 3.92 \text{ \AA} = g_{\text{B}}(4)$ .
- $\text{Pt}_4\text{B}(\text{C}24.6, 79\text{Has})$ ,  $a(240, 210, 348) = 7.57 \text{ \AA} = g_{\text{B}}(7.5)$ , tentative.
- $\text{Pt}_3\text{B}(\text{T}2.(0.7), \text{SR}30.116)$ ,  $a = 2.63; 3.83 \text{ \AA}$ .
- $\text{Pt}_2\text{B}(\text{H}4.2, 79\text{Has})$ ,  $a(40, 38, 60) = \text{H}2.79; 10.49 \text{ \AA} = g_{\text{BH}}(2; 36/3)$ .
- $\text{Pt}_2\text{B}_{1,3}(\text{anti NiAs}, \text{RhB}_{1,1}, 85\text{Vil})$ ,  $a(20, 20, 31) = 3.37; 5.82; 4.05 \text{ \AA} = g_{\text{UH}}(\sqrt{12}; 6/2)$ . The deformation of  $g$  might be caused by the participation of electrons below  $f$  in the binding. Also the orthorhombic deformation of  $a$  may depend on it.
- $\text{CuB}_{23}(\text{B}, \text{h}, \text{R}108, \text{SR}40.41, 42.55)$ , no intermediate phase (nip) (77Mof).
- " $\text{AgB}_2$ " (SR26.73) not confirmed, Hildebrands rule (50Hil) for miscibility gap is obeyed. (65Wal), nip(77Mof).
- " $\text{AuB}_2$ " (SR26.73) not confirmed (65Wal), nip(77Mof).
- $\text{ZnB}_{25}(64\text{Pic})$ .
- $\text{CdB}_M$  nip(77Mof),  $\text{HgB}_M$  nip(77Mof).

$\text{AlB}_2$ (H12, MgB<sub>2</sub>, SR20.5),  $a(3,17,6) = \text{H}3.01; 3.26\text{\AA} = g_{\text{CH}}(2;6/3)$ , see MgB<sub>2</sub>.

$\text{AlB}_{10}$ (O5.52, SR32.3) is mainly composed of B<sub>12</sub> icosahedra. The phase probably contains C (SR32.4).

$\text{AlB}_{12}$ -h(O348.29, SR26.5),  $a = 16.56; 17.35; 10.16\text{\AA}$ .

$\text{AlB}_{12}$ -r(T13.176, SR43.6, drw ibid.),  $a(39,632,378) = 10.16; 14.28\text{\AA} = g_{\text{B}}(\sqrt{52};10)$ .

$\text{GaB}_{12}$ (T10.120, SR26.72), doubtful.

$\text{InB}_{12}$ nip(77Mof),  $\text{TlB}_{12}$ nip(77Mof).

$\text{B}_{12}\text{BC}_2$ (R13.2, SR42.52, drw64Sch.179) was earlier named B<sub>4</sub>C. It is composed of B<sub>12</sub> icosahedra and CBC strings.  $a(141,90) = \text{H}5.63; 12.14\text{\AA} = g_{\text{CH}}(4;21/3)$ . The commensurability explains why  $a_1$  is very different from  $a_1(\text{B}, h_1)$ .

$\text{B}_8\text{C}$ (O348.48, 85Vil).

$\text{B}_{50}\text{C}_2$ (T50.2, SR42.52, drwSR22.212),  $a(158,104) = 8.75; 5.09\text{\AA} = g_{\text{B}}(\sqrt{413};75)$ , see

$\text{B}_{50}\text{N}_2$ .

$\text{B}_4\text{Si}(\text{B}_4\text{C}, \text{R}12.3, \text{SR}24.255)$ ,  $a(36,180,90) = \text{H}6.35; 12.69\text{\AA} = g_{\text{B}11}(\sqrt{10.5};30/3)$ , tentative.

$\text{B}_6\text{Si}_i(\text{CaB}_6, \text{SR}20.209)$ ,  $a(4,26,14) = 4.13\text{\AA} = g_{\text{B}}(3)$ . SiC and SiO<sub>2</sub> were in the samples.

$\text{B}_6\text{Si}(\text{O}240.40, \text{SR}22.65, 23.278)$ ,  $a(160,1040,560) = 14.39; 18.27; 9.89\text{\AA}$ .

$\text{B}_{14}\text{Si}(\text{B}, \text{r}, \text{R}108, \text{SR}30.116)$  probably marginal.

$\text{B}_{36}\text{Si}(\text{R}102.3, \text{SR}48.37)$  is htpe to B.r(R105).  $a = \text{H}11.01; 23.90\text{\AA}$ .

$\text{BGe}_M$ nip(77Mof),  $\text{BSn}_M$ nip(77Mof),  $\text{BPb}_M$ nip(77Mof).

$\text{BN}(\text{H}2.2, \text{SR}13.44, \text{drw ibid.})$  is homeotypic to C.r(drw64Sch.180), its structure provides a better Coulomb interaction. However, it is isodesmic to C.r:  $a(16,8) = \text{H}2.52; 6.69\text{\AA} = g_{\text{CH}}(\sqrt{3};12/3)$  displaying  $N_{\text{S}}^{\text{At}}(g) = 9$ .

$\text{BN.hp}(\text{ZnS}, \text{F}1.1, \text{SR}21.194)$ ,  $a(32,16) = 3.62\text{\AA} = b_{\text{F}}(2) = c_{\text{C}}(4)$  or  $a = g_{\text{C}}(4)$ . While BN has a site number  $N_{\text{S}}^{\text{At}}(g) = 9$ , the phase BN.hp has  $N_{\text{S}}^{\text{At}}(g) = 8$  conforming to the site number rule.

$\text{BN.rp}(\text{ZnO}, \text{H}2.2, 67\text{Hoa}.147)$ ,  $a(16,8) = \text{H}2.55; 4.20\text{\AA} = b_{\text{B}11}^{\text{B}}(1;7/3) = g_{\text{CH}}(2;7/3)$ . The reason for the stability is presumably the decreased site number 7. The axial ratio of  $a$  needs not to express the strain of  $g$  because of an independent part of  $g$ .

$\text{B}_{50}\text{N}_2$ (T50.2, SR42.52, drwSR22.212),  $a(160,104) = 8.63; 5.13\text{\AA} = g_{\text{CH}}(15/3; \sqrt{13})$ .  $\text{B}_{50}\text{N}_2$  is assumed to be homeodesmic to B.h<sub>1</sub>(R12).  $N_{\text{S}}^{\text{At}}(g) = 7.5$ . However, see  $\text{B}_{50}\text{C}_2$ .

$B_{12}B_{0,6}P_{1,4}$ (R12.2,SR40.43) is htpe to  $B_{13}C_2$  ( $a(20,124,84)=H5.98;11.85\text{\AA}=g_{CH}(4;20/3)$ ). In  $g_{CH}$  is contained  $a=g_{FH}(2;5/3)$  determining the P content.

BP.r(ZnO,SR28.43,296) obeys Lewis' rule.  $a(10,22,8)=H3.56;5.90\text{\AA}=g_{BH}(2;15/3)$ . The  $a$  cell needs confirmation. The strain of  $g_{BH}$  has the same reason as the strain in SiC.

BP.r(ZnS,SR28.43,296) is htpe to SiC.r.  $a(20,44,16)=4.53\text{\AA}=g_B(4)$ . According to Lewis' rule there are  $16+16+8=40$  +spins and  $4+16+12+8=40$  -spins.

$B_6P$ (R12.2,SR40.43),  $a(138,120)=H5.96;11.81\text{\AA}=g_{CH}(4;20/3)$ .

$B_{12}B_{0,6}As_{1,4}$ ( $B_{12}B_{0,6}P_{1,4}$ ;SR26.79 changed according to SR40.43),  $a(20,185,108)=H6.14;11.89\text{\AA}=g_{CH}(4;20/3)$ . The low As content enhances the expansion of As so that a  $g_{CH}$  correlation becomes possible.

BAs(ZnS,SR22.39),  $a(20,40,44,(40))=4.78\text{\AA}=g_B(4)$ . Perhaps the As2sp electrons do not participate in the correlation.

BSb<sub>M</sub>nip(77Mof), BBi<sub>M</sub>nip(77Mof). The formation of the Lewis phases of these mixtures is impossible because of the  $f$  electrons.

$B_6O$ (H24.4,75Pie),  $a(96,56)=H5.40;12.34\text{\AA}=g_{UH}(\sqrt{13};12/3)$ .

$B_2O$ .hp(H36.18,75Pie),  $a(216,108)=H7.98;9.09\text{\AA}=g_{CH}(\sqrt{31};15/3)$ .

$B_2O_3$ (H6.9,SR33.258,drwSR33.259),  $a(72,30)=4.34;8.34\text{\AA}=g_{CH}(3;14/3)$ . Since the  $g$  correlation contains numerous lacunae a p-phase becomes stable.

$B_2O_3$ .p(Q4.6,SR33.259,drwSR33.261),  $a(96,40)=4.61;7.80;4.13\text{\AA}=g_B(3.5;6;3.3)$ .

$B_{12}S$ (htp $B_4C$ , $B_{13}P$ ,SR26.79).

$BS_2$ (M16.32,SR46.408).

$B_2Se_3$ (M16.24,SR43.37).

$B_2F_4$ .l(M4.8,SR22.230).

$BCl_2$ (O8.16,SR19.314),  $BCl_3$ .l(H2.6,SR19.317),  $a=H6.08;6.55\text{\AA}$ .

$BI_3$ (H2.6,SR27.438),  $a=H7.00;7.46\text{\AA}$ .

## Discussion

Numerous metrical data on solid phases are excellently accumulated; sometimes they have been applied to derive atomic radius ratio criteria for stability. However, the relation of electron numbers with metrical data has remained unexploited. Some authors believe

that only extended computations can reveal these relations. The present study attempted to show that the inductive chemical systematics can provide rules for these relations which are quite easily accessible. These rules are useful because of their influence on the systematics of chemical and physical properties as for instance the energy of formation. A systematics of these energies is a condition for the calculation of phase diagrams strongly condensing the knowledge on constitution. The inductive chemistry makes use of general theoretical concepts, but conversely the deductive chemistry will utilize results of inductive research. To be sure, the experimental chemist sometimes prefers to use inductive rules to find a promising direction for his work since they are easier accessible than the extended computations. Some examples of questions of the experimental chemists are the following:

Why is  $\text{LiB}_3$  homeotypic to  $\text{CaB}_6$ ? The volume of  $\text{Li}_2$  approximately equals the volume of Ca so that a homeotypic binding may develop.

Why is  $\text{SrB}_6$  a semiconductor and  $\text{YB}_6$  a metallic conductor? The  $b_B$  correlation is favourable in  $\text{SrB}_6$  but unfavourable in  $\text{YB}_6$ .

Why is  $\text{LaB}_6$  stable but "HfB<sub>6</sub>" not? In "HfB<sub>6</sub>" the binding of  $\text{LaB}_6$  type would be overoccupied.

Why is TiB of the FeB type while TiC is of NaCl type? The  $g$  correlation tends to high occupancy so that in TiB the correlation is deformed and with it the structure, while in TiC it is not deformed.

Why are the closely neighbouring phases  $\text{V}_5\text{B}_6$ ,  $\text{V}_3\text{B}_4$ ,  $\text{V}_2\text{B}_3$  stable? There is the  $g$  correlation in such a harmony that on each V layer parallel to the smallest cell face there come 4  $g$  layers.

Why is a phase " $\text{WB}_2(\text{AlB}_2)$ " not stable? The electron offer exceeds the electron site number of the  $\text{AlB}_2$  type.

Why is  $\text{MnB}_2$  of the  $\text{AlB}_2$  type although " $\text{WB}_2(\text{AlB}_2)$ " was not stable? There are less  $f$  electrons contributed by Mn.

Why is RuB of the WC type and not of the TII type like MoB,h? The +spin offer is too high.

Why is  $\text{IrB}_{0.9}$  not of the WC type? The Q4.4 structure has a better commensurability.

Why is NiB(TII) not of the FeB type like CoB? The  $q$  correlation has acquired a new favourable commensurability.

Why does CuB<sub>M</sub> and ZnB<sub>M</sub> not form intermediate phases? The  $b$  electrons press the metal atoms together and prevent insertion of B.

Why is BN.hp(ZnS,F1.1) and BN,rp(ZnO,H2.2) stable? At the lower temperature the site number is reduced and this is possible only in the hexagonal structure.

It is clear that a first attempt of binding analysis cannot answer all questions. The considerable frequency of deformed correlations suggests that details of spin correlations are still to be investigated. Also, the somewhat uneven fit of the bindings of Fe to those of Fe<sub>2</sub>B, or the compatibility in CoB<sub>M</sub> needs further attention.

Some of the arguments used above belong to a Madelung theory of the pair density, as for instance the dependence of the stacking sequence on the binding. Since this theory seems to be not yet worked out, the interpretative possibilities of the plural correlations model are not yet exhausted. The present interpretation provides numerous applications for a future Madelung theory of the pair density. A further missing support is a theory of the influence of electron correlation on conductivity. When such a theory exists, with conductivity measurements the binding can be examined.

#### **Acknowledgement**

The author wishes to thank Prof. H.G. v. Schnering for informations on LiB<sub>M</sub> alloys prior to publication and Drs. E.A.Clark and F. Hehmann for stylistic help.

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