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ON THE BINDING IN TWO-COMPONENT BORIDES

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Summary

Using a somewhat modified electron count for the transition elements, the two-correlations model interpretation of two-component borides is improved. The valence electrons of the boron atoms are in correlation with the peripheral d electrons of the transition elements. Even the peripheral noble gas shells of several transition elements display a correlative interaction with the valence electrons. An intermediary phase becomes stable when a favourable binding is possible. The intermediary phase has an elevated melting temperature when the commensurability between the correlations is especially good, for instance when it is factorial. The rules of the two-correlations model explain not only the stability of phases but also the stability of their structures. The rules are therefore a useful supplement to the rules connected with atomic radii and atomic charges.

Über die Bindungstypen in zweikomponentigen Boriden

Zusammenfassung

Durch Berücksichtigung einer etwas geänderten Elektronenabzählung für Übergangselemente wird die Zweikorrelationenmodell-Deutung zweikomponentiger Boride verbessert. Die Valenzelektronen der Boratome sind in Korrelation mit den peripheren d Elektronen der Obergangselemente. Selbst die peripheren Edelgasschalen von Übergangselementen zeigen eine korrelative Wechselwirkung mit den Valenzelektronen. Eine Zwischenphase wird stabil, wenn ein günstiger Bindungstyp möglich ist. Die Zwischenphase hat eine erhöhte Schmelztemperatur, wenn die Kommensurabilität zwischen den Korrelationen günstig ist, zum Beispiel, wenn sie faktoriell ist. Die Regeln des Zweikorrelationenmodells erklären nicht nur die Stabilität einer Phase, sondern auch die Stabilität ihrer Struktur. Die Regeln sind daher eine nützliche Ergänzung zu den Regeln, die zusammenhängen mit Atomradien und Atomladungen.

Introduction

Various descriptions of the bonding in borides have been given [1a-g] and an attempt to account for the stability of any two component boride by a bonding classification has been made [2] on the basis of the two-correlations model [3]. This model analyses the spatial correlation of the loosest bound electrons (b correlation) and of the peripheral core electrons (c correlation) and both correlations are assumed as lattice like [3]. A bonding type (named binding) is given by the lattice types of the b and c correlations and by their commensurabilities K' and K" to the crystal cell a. The probability of a binding assumption is assessed by a set of rules [3], and if some of the rules are not obeyed the binding analysis may be mislead. In the analysis [2] the proper electron count, i.e. the distribution of the electrons on b and c correlation, was not found in all cases, this proper electron count emerged only in later investigations [4], therefore a new review of the two-component borides was desirable. Also in [2], the old Strukturbericht designation for correlation types was used which was changed in [3c] and applied in [4], so that it appeared desirable to describe the bonding-types of the borides too by the new symbols.

The main questions to be answered for two-component borides are in the present state:

(1) Is the electron count which was successfull for carbides, nitrides, oxides, fluorides [4] able to lead to an acceptable interpretation also for borides?
(2) Is the strong ionization assumed in [2] for boron in its compounds with transition elements realistic, or may it be replaced by other assumptions which give a more probable overall interpretation?
(3) Can several simple phases which did not yield a reasonable bonding type in [2] be interpreted on the basis of the modified assumptions?
(4) Are several binding proposals of [2] which appeared rather artificial, like the bonding type of CoB, now replaced by more plausible bindings?
(5) Can the conspicious phenomenon of high melting temperatures be brought in relation to the binding?

At this point it is appropriate to avoid a common misunderstanding: The electrons do not form a fine lattice in the electron density. In most cases the electron density does not disclose the electron spatial correlation. The probability density which uncovers the spatial correlation is the D_x^{av} function, the averaged spatial correlation [3c-f], which is quite independent of the electron den-

sity. Therefore it is necessary to inquire which type of D_x^{av} might exist in a given crystal, and this kind of analysis is the binding analysis.

The aim of the present paper is to give an improved version of the binding analysis of two component borides. The main content of the analysis is Table 1, the text should be considered as a commentary to Tab.1. The format of Tab.1 has been described in [3,4], it is self-explanatory when the structure description [1c] and the abbreviated matrix symbolism [3c-f] is understood.

It was, unfortunately, not possible to mention all the authors who have made so many valuable contributions to our knowledge of two-component borides. However, using the Structure Reports references given in Tab.1 the authors readily may be found.

Analysis

The lithium borides and NaB_6 are not known sufficiently to warrant a binding analysis. In the structure of NaB_{15} two B_{12} icosahedra are close packed in the $(\underline{a}_1,\underline{a}_2)$ plane and from each icosahedron starts a chain of icosahedra in $\underline{a}_3$ direction (see drawing SR35.5). The binding proposal of Tab.1 is merely a trial, as the great cell cannot make a proposal very probable. Contrary to this phase the compound KB_6 has a very small cell, its CaB_6 type of structure may be considered as a CsCl structure of K and B_6, octahedra. The $\underline{c}_C(3)$ correlation of KB_6 has been correctly found in [2] but the electron count should be assumed as $K^{1,0}B_6^{0,3}$ (contrary to [2]), so that $\underline{a}=\underline{b}_C(1)$ follows now which gives a CC3 binding (cf. Tab.1). In YB_6(CaB_6 type) a CC2 binding might exist, i.e. the $\underline{c}$ correlation is conserved and the $\underline{b}$ correlation chooses a new possibility.

The boron poor phases $Be_4^{2,2}B^{3,2}$ and Be_2B.h are vacancy-homeotypic and homeodesmic to Be.h(W,SR23.45)2.55Å$=\underline{b}_F(1)=\underline{c}_C(2)$: the vacancy formation caused by increase of valence electron concentration and unchanged binding may be named a Bradley homeotypism (see [1c] p.131). The cell content of Be_2B_3 noted in Tab.1 is assessed from atomic volume and binding, it needs experimental confirmation. Its BF1 binding (see Tab.1) seems to apply also to BeB_3, therefore one and the same binding may belong to neighboring phases when its commensurability to the crystal is different. The $\underline{d}_C$ value of Be_2B_3, easily calculated from the data of Tab.1, makes a little jump as compared with $\underline{d}_C$ of Be_2B.h, this is compatible with the distance rule [3]. The phases rich in boron are closely homeotypic to phases of boron, even BeB_3 is commensurable to B(R12).

The B_2Al type of MgB_2 occurs with many different T-components so that the

frequently noted influence of the B skeleton becomes apparent. The CF1 binding may be filled in the $\underline{c}_F$ correlation by Hund insertion [3], so that the extended occurrence of the structure type (see Tab.1) becomes comprehensible. The phase MgB_4(O4.16, drawing SR38.51) is homeotypic to MgB_2 and a FF2 binding becomes possible. The binding analysis of MgB_7, which is homeotypic to NaB_{15} may be postponed as the cell is fairly great.

$Ca^{2,8}B_4^{0,3}$ (ThB_4, drawing [1c] p.273) is homeotypic to CaB_6 and B_2Al, it yields a CC2 binding which was partly found earlier [2]. CaB_6 is isodesmic to KB_6.

The earlier assumption [2] of a strong change of the electron distance $\underline{d}$ in the boron atoms upon alloying could not be confirmed by [4] and the above binding proposals, therefore the interpretation of $Sc^{1,10}B_2^{0,3}(B_2Al)$ must be improved to a CF'1 binding as it was found in MgB_2. ScB_{12} (deformation homeotype of UB_{12}, drawing [1c] p.273) might have a FF2 binding.

Most YB_M phases ($\underline{M}$ = undetermined mole number) are isotypic and isodesmic to phases discussed before. The $\underline{c}$ correlation is decisive for the stability, while the $\underline{b}$ correlation is less certain here because of uncertainty in the electron count. Calculating the $\underline{d}_C$ distances shows that the distances of $\underline{c}_C$ in YB_4 and YB_6 are contracted relative to $\underline{d}_C$ of YB_2 and YB_{12} in agreement with the distance rule. The same is valid for LaB_M. The finding of vacancies in $Th_{0.78}B_6(CaB_6)$ must be understood by the overfilling of the binding (Bradley homeotypism).

In the mixture TiB_M many new structure types appear. This is indicative for a new electron count: $Ti^{1,3}B_M^{0,3}$. This count was not yet understood earlier [2] so that several binding proposals became incorrect. Assuming Ti.r(Mg,SR1.53)-H2.95;4.68A=$\underline{b}$FH(1;2/3)=$\underline{c}$H(2;3) leads for Ti_2B (homeotypic to Mg) to a FHH2 binding. This binding would be overfilled in the $\underline{c}$ correlation for TiB (homeotypic to Mg), the phase is therefore of the FeB(O4.4) type where the Fe position is more remote homeotypic to Mg and the $\underline{a}_3$(Mg) axis is strongly strained. It is seen that the FHH2 binding is conserved and takes a different commensurability to $\underline{a}$, yielding more places in the comparable cell. In $Ti_3B_4(Ta_3B_4$, drawing [1c] p.263), an overfilled NaCl homeotype, the zigzag boron chains of TiB grow together to double chains. The binding is of a FUHT2 type supplemented by an $\underline{e}_C$ correlation, which was correctly found in [2] and which accounts for the high melting temperature. Finally in $TiB_2(B_2Al)$ the boron atoms form nets and a very stable FF2C4 binding is attained; following the rule of commensura-

bility TiB_2 has therefore a congruent and high melting point. The phase Ti_2B_5 (W_2B_5, drawing [1c] p.270) is a FS-homeotype of TiB2 (F=filling, S=shear) and it is also homeodesmic to TiB_2. The HFH2 binding contains a strained $\underline{b}$ correlation and a compressed $\underline{c}$ correlation in consequence of the fact that the $\underline{b}$ electron concentration has decreased while the $\underline{c}$ electron concentration has increased. The new electron count of TiB_M therefore not only permits to interpret Ti_2B and TiB not explained earlier [2] but also the congruent and high melting point of TiB_2.

In ZrB_M the congruent melting point of ZrB_2 with FF2 binding is quite conspicious. The phase $ZrB_{12}.h$(UB_{12},Fl.12) becomes now comprehensible: as a high temperature phase it accepts many excited electrons into the $\underline{b}$ correlation, therefore the UU2 binding may be stablilized which is well adapted to the UB_{12} structure.. Satisfactorily $ZrB_{12}.h$ has a congruent melting point. The binding proposal [2] was homeotypical to the present one.

The structure of V_3B_2(U_3Si_2, drawing [1c] p.252) is composed of W and B_2Al cells, a FUHT2 binding is probable as a FF2 binding would give too low an occupation of the $\underline{c}$ correlation. The following NaCl homeotypes, VB up to VB_2, are as Table 1 shows also homeodesmic. The TlI structure of VB is homeotypic to TiC(NaCl) [4c], and the present binding clearly shows why VB is not of the NaCl type: the V atom contributes 4 electrons into the $\underline{c}$ correlation; as it is more polarisable then C in TiC, it allows a higher occupation of the $\underline{c}$ correlation and generates therefore the TlI type. The phases of NbB_M are isotypic and isodesmic to VB_M phases. The phase Ta_2B(Cu_2Al, drawing [1c] p. 299) has many isotypes in the following mixtures. While the TlI type is homeotypic to NaCl, the $CuAl_2$ is homeotypic to CsCl and indicates an influence of the great radius r_{Ta}. The remaining TaB_M phases are isotypic and isodesmic to VB_M phases. Quite remarkable is the curved dependence of $\underline{d}_c$ on the mole fraction $\underline{N}_2'$ as a consequence of the bindings; the increase of B content first increases the $\underline{d}_c$ values under the $\underline{b}$ pressure and the decrease of V content afterwards decreases the values (see [3b]).

In $CrB_{0.2}$(Mg homeotype) the great axial ratio $|\underline{a}_3|/|\underline{a}_1| = 1.73$ is explained by the UHH2 binding, the axial ratio permits a 0.8 occupation of the $\underline{c}$ correlation. The pseudo hexagonal Cr_4B(Mn_4B, drawing [1c] p.254) is homeotypic to $CrB_{0.2}$ and Cr_2B. It might have a HH2 binding. The fact of low $\underline{c}$ correlation occupation permits the stabilisation of the structure also for Mn_4B. The phases Cr_2B($CuAl_2$) and Cr_5B_3(U10.6, drawing [1c] p.254) are homeotypic and

isodesmic. In the NaCl homeotypes CrB(TlI), Cr_3B_4 and CrB_2 there are found indications for Hund insertion at Cr when the number of $\underline{c}$ electrons is compared with the number of $\underline{c}$ places. This phenomenon should cause magnetic superstructures which could give additional insight into the binding. The binding analysis of CrB_{41} may be postponed. Cr_4B, a lacuna homeotype of $CrB_2(B_2Al)$ permits a HFH2 binding.

It is satisfactory that in MoB_M the phase MoB.h(TlI) has the maximum melting temperature, as the axial ratio favours a fully factorial binding. With decreasing temperature probably some Hund insertion develops, therefore the commensurability in the direction of the long axis is changed and in consequence of this the stacking homeotypism occurs. Also $MoB_2(B_2Al)$ displays Hund insertion which decreases the stability and therefore the melting temperature. The FS-homeotypic Mo_2B_5 clearly shows Hund insertion. $Mo_{0.8}B_3$ is a lacunahomeotype of MoB_2; the HH2 binding yields $N_p^{/C}=6$ $\underline{b}$-places so that it becomes probable that $Mo_{0.8}B_3$ is only stable at elevated temperatures were additional electrons are excited into the $\underline{b}$ correlation. Also in MoB_M the curved dependence of $\underline{d}_{\underline{b}}$ and $\underline{d}_{\underline{c}}$ on $\underline{N}'_B$ is found.

The WB_M phases are mostly isotypic and isodesmic to earlier phases. The phase WB_4 does not very well compare with $Mo_{0.8}B_3$, a scrutiny of this point appears desirable.

In Mn_4B(S8.2, drawing [1c] p.254) the $(\underline{a}_2,\underline{a}_3)$ plane displays a quasi hexagonal array of Mg atoms. The $\underline{b}$ correlation is similar to that in Ti.r while the $\underline{c}$ correlation leads to a HH2 binding. The low occupation of the $\underline{c}$ correlation prevents a congruent melting point [5], it is caused by the small $\underline{d}_{\underline{c}}$ of the Mn atoms. Following a very precise structure determination [6] more B atoms then described by the nominal composition are said to be in the cell; this would be compatible with the proposed binding. In $Mn_2B(CuAl_2)$ the HH2 binding is once more stable; it is now better occupied in the $\underline{c}$ correlation and the melting point is now congruent. The come-back of the FeB type in MnB may be caused by a BB2 binding. As a factorial binding it affords a congruent melting point to FeB. The phase Mn_3B_4 probably contains a statistical Hund insertion and therefore has not a congruent melting point. In $MnB_2(B_2Al)$ the $\tilde{U}\tilde{H}UH2$ appears. $\tilde{U}H$ is a hexagonally compressed heterometric UH correlation which has the distance $\underline{d}/\sqrt{2}$ between the close packed planes with internal distance $\underline{d}$, and presupposes spin ordering [3f].

The phase $Tc_3B(Re_3B)$ is homeotypic to $CuAl_2$. It is stabilized by the FF2C4 binding, which has shifted to T-atom rich compositions as the d electron con-

tribution of T has increased: no more as much boron insertion is necessary to favour the FF2 binding than with components contributing less d electrons. It is interesting that the old binding [2] is homeotypic to the present one, this is an example of the self stabilizing properts of the inductive conclusions. The satellite phase Tc_7B_3(Th_7Fe_3, drawing [1c] p.266) is, as to be expected, isodesmic. The electron distances are probably smaller as the structure is more closely packed. TcB_2(ReB_2) is homeotypic to MnB_2(B_2Al) but the $\underline{a}_3$ axis is strongly strained, and the binding is of the HFH2 type. The B_2Al type is not stable as too many d electrons are contributed by the T component.

ReB_M is essentially isodesmic to TcB_M.

Fe_2B($CuAl_2$) has not a congruent melting point while Mn_2B had. In fact the HH2 binding of Mn_2B does no more fit to Fe_2B, a HTFU2 binding must be assumed and this is not factorial and therefore permits only a lower melting temperature. For FeB(O4.4, drawing [1c] p.263) a BB2 binding may be assumed as in MnB(FeB). In Ru_7B_3(Th_7Fe_3) some Hund insertion at Ru must be assumed. $Ru_{11}B_8$ is homeotypic to WC, a FF'2 binding appears possible once more; the strong Hund insertion causes a low symmetric atomic site. $RuB_{2.1}$ is homeotypic to FeB, the binding might be a CFU1 type. The mixture OsB_M is isotypic and isodesmic to RuB_M.

In Co_3B(Fe_3C) a DI-homeotype of Cu_3Au is found (D=homogeneous deformation, I=inhomogeneous deformation), and the instability of the type in "Fe_3B" is an argument for the present electron count. A FF'2 binding is probable. This is homeotypic to the HTFU2 binding of Co_2B($CuAl_2$), and in CoB(FeB) the FF'2 binding seems to return. The FF2 binding of Tc_7B_3 is stabilized here with the same commensurability as a FF'2 binding. The stacking-homeotype Rh_5B_4(H10.8) [7] displays a strong increase in length of the $\underline{a}_1$ axis as compared with $RuB_{1.1}$ (WC), therefore a UHF'H2 binding is assumed with a somewhat rare commensurability. The phase $RhB_{1.1}$(anti NiAs) confirms the great $\underline{a}_1$ axis and permits a HF'H2 binding. In the phases of IrB_M the short $\underline{a}_1$ axis is stable. $IrB_{0.9}$.h(WC) has a FF'2 binding with 1.25 $\underline{b}$ places per cell and shows Hund insertion in the $\underline{c}$ correlation. When in h the full $\underline{b}$ occupation is reached by excitation of electrons into the $\underline{b}$ correlation, than at lower temperature, another structure is to be expected. As $(-\underline{a}_1+\underline{a}_2)_h$ is strained strongly in r, the interpretation of a CFU2 binding appears probable. It should be appreciated that also in r Hund insertion is possible and that Hund insertion brings some asymmetry into the structure so that the structure may become more complicated.

The stability of $Ni_3B(Fe_3C)$ is an indication that the additional d electrons of Ni as compared with Co are of minor influence on the structure because of Hund insertion. As in Ni the electron pairing is essentially completed a FHR2 binding appears possible. It should be admitted that because of increasing difference of the T-atom core and the boron valence shell the uniform $\underline{c}$ correlation is no more a good approximation. Therefore the commensurability elements apparently become non whole numbered. In $Ni_2B(CuAl_2)$ the $\underline{b}$ correlation is isotypic to that in Co_2B while the $\underline{c}$ correlation chooses the B type; at any case this binding is closely homeotypic to that of [2]. It would be of interest to study the mixed crystal $Co_{2-n}Ni_nB$ and see how the different bindings are connected. For the ideal compound "Cu_2B" the difference between the Cu core and the B valence shell becomes so great that the structure is no more stable. The phases $Ni_4B_{2.9}$ (see [8]) and Ni_4B_3 are homeotypic to NiB(TII). Because of the limited approximation of the model only NiB be considered here. At elevated temperatures a $\underline{b}_B$ correlation or even $\underline{b}_U$ correlation may be stable, but at lower temperatures a deformed $\underline{b}_{FU}$ correlation appears probable. The temperature dependent $\underline{b}$ electron contribution of Ni suggests the expectation that at lower temperatures NiB might substitute Cu for Ni.

In $Pd_3B(Fe_3C)$ the latice constants do not fit very well to the proposed binding. This might be the reason for the stability of the Fe_3C-homeotype Pd_5B_2. The phase Pt_3B_2.h (see [5]) has an orthorhombically deformed anti-NiAs structure [9] which is remotely homeotypic to $IrB_{0.9}(WC)$. The corresponding $\underline{c}_{CH}$ correlation of Tab.1 fits very well to the structure and the $\underline{b}_{UH}$ correlation might give a reason for the orthorhombic deformation. Contrary to many other bindings found, the commensurability is UHCH$\sqrt{3}$.

With the B^1 elements (Cu,Ag,Au) and B^2 elements no borides are formed, probably as there is no good correlation possible between the d^{10} shells and the boron valence shell. This is also valid for B^3 elements with the exception of Al. The electron count of B_2Al may be assumed as $B_2^{0,3}Al^{3,8}$ conforming to MgB_M. Surprisingly a $\underline{c}_{F'H}$ correlation is well commensurable to the cell, near Al the $\underline{c}_F$ correlation is filled to a $\underline{c}_C$ correlation. The phases $B_{10}Al$ and $B_{12}Al$.h,r should be postponed.

In B_4C(R12.3, drawing [1c] p.179) the count $B_4^{3,2}C^{4,2}$ is without doubt and a HR1 binding is found, and this is modified in $B_4Si(B_4C)$ to a UHR1 binding. Remarkably in $B_6Si(CaB_6)$ another electron count seems to be stable ($B_6^{0,3}Si^{4,8}$). Perhaps therefore another phase B_6Si is found, the binding analysis of which may be deferred.

The electron count $B^{3},^{2}P^{5},^{8}$ is confirmed by the stability of BP.r(ZnS) which obeys Lewis' rule. $B_{13}P_2$ is isodesmic to B_4Si and $B_{13}As_2(B_{12}C_3)$ is isodesmic too.

The mixture BS_M does not contain a phase obeying Lewis' rule, but a homeotype of B_4C is stable. The boron-chalcides and boron-halides have molecular structures which are generated by Hund insertion at the $B^{6\cdots7}$atoms. Since these bindings are more difficultly to analyse they will be postponed here.

Concluding remarks

The foregoing analysis has answered the questions of the Introduction.

(1) The previous electron count [4] has proved true also for borides.

(2) The strong ionisation of boron [2] is no more necessary.

(3) Several simple phases could now be interpreted, for instance $CrB_{0.2}$.

(4) Several artifical proposals became more plausible, CoB e.g.

(5) The phenomenon of high melting temperatures can now be understood by the interaction of a third correlation and factorial commensurability.

These results suggest some confidence into the improvement of the interpretation of the two component borides. Also with respect to earlier interpretations some better understanding is attained:

Following Kiessling [1] and other authors there exists a tendency of the boron atoms to form covalent bonds with each other of a length 1.6 to 1.9 Å. The ordering of the boron atoms in zigzag chains, double chains, nets and lattices is a well confirmed result of observation, but the statement that the stability of these partial structures is a consequence of bond hyphens between the boron atoms is a matter of interpretation and therefore open to discussion. If the electrons are concentrated near the bond hyphen there is certainly only a poor spatial correlation possible. If however, as electron density knowledge confirms, the valence electrons are fairly uniformly distributed, a lattice like spatial correlation appears possible. The above analysis has shown that the valence electrons of the boron atoms occupy the $\underline{c}$ correlation which is often of the F1 type with an electron distance $\underline{d}_{\underline{c}} = 1.5\pm0.1$ Å (see Tab.1). Assuming that two neighbored B atoms "are in electron triangles" sharing corners, a boron distance of $\underline{d}_{\underline{c}}2/\sqrt{3}=1.73$ Å results, i.e. just the average of the above empirically found bond distance. The array of the boron atoms is therefore not caused by bonds but by a lattice like spatial correlation in which the boron atoms are distributed as to find a low energy. The model of a

bond hyphen describes a spatial correlation of electrons too, but it does not describe appropriately the energetic situation. The old bond hyphen model has contributed to the surprising phenomenon that the important concept of commensurability of correlations has remained hidden so long and that the interaction of valence electrons with the peripheral core electrons escaped the attention so often. Just this analysis shows that even three correlations may be of influence.

It is not quite satisfactory to state that different aggregations of boron atoms cause different phases, the question of structural systematics is why these different phases become stable. The two correlations model answers: When the b electron concentration and the c electron concentration have values which yield an energetic favourable binding. Therefore the two correlations model is in fact a new valence model for borides.

Sometimes [1] the question is raised why in borides with such evidently strong covalent bonding there exists a considerable electro conductivity, also when the transition atoms are isolated in the structure (e.g. ZrB_{12}). The present interpretation simply points to the b correlation which is sometimes not completely occupied because of temperature dependent Hund insertion.

The present analysis is only a first step towards an improved systematics of borides. Many new problems emerge, for instance, why certain geometrically possible bindings do not appear. This leads to a further refinement of the energetical assessment of the bindings. The present analysis tries to find out which binding is present in the allowy phases observed. Later steps of analysis will find out why certain possibilities are not stabilized.

The question could be asked how it is possible that the binding analysis may lead to erroneous results. This possibility occurs just as in crystal structure determination: many phenomena are of influence on the final result and when one phenomenon is wrongly interpreted the whole result may become incorrect. In the course of time the precision of the analysis will be increased and the probability of errors will then decrease. The sharpening of the analysis is attained by finding new rules i.e. new criteria to judge the correctness of an interpretation. In fact the two-correlations model is nothing else than an integrated system of crystal chemical rules, and the concepts like "commensurability" or "Hund insertion" are supported by many observed structures. The rules may only be confirmed by applying them to more and more observations. Since the rules mostly apply to facts for which no other interpretation has been advanced they may only be falsified by finding an inherent

error in the model.

It should be appreciated that, following the inductive logic, the model is not yet falsified when one interpretation is shown to be wrong, only when the majority of interpretations is improbable, something must be wrong with the model. It would be quite unreasonable to pretend that we do not need a valence theory for borides. Since the two correlations model affords such a valence theory, a possible argument against the model would in fact be another model which is so different from the two-correlations model as to be not an improvement of it and which gives an analogous or better phase classification and energetic explanation of borides. As long as such a new model is not yet found the present model should serve as a compass in the field of crystal chemistry. Especially the systematics of three-component borides (see [1f] article by Nowotny and Rogl) might be improved by the consideration of the electron spatial correlations. Since the two component boride bindings are, as shown above, now quite homeotypic to the carbide bindings [4c] and the nitride bindings [4d] the borocarbides and boronitrides should also fit to the above interpretation.

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Table 1: Two-component Borides (excepting lanthanoid and actinoid borides)

LiB2(Shunk)
LiB10
NaB6(,77Ma)
NaB15(P2.30,SR35.39)5.847;8.415;10.298A=bFU(1;1.5;2.5/2)=cFU(4;6;10/2) N=4,212
KB6(CaB6,71Ec)4.232A=idm CaB6 N=1,26
Be4B(T8.2,SR27.65)3.369;7.050A=bF(√2;6/2)=cC(√8;6) N=22,20
Be2B.h(CaF2,SR26.57)4.663A=bF(2)=cC(4) N=28,24
Be2B3(T22.33,Z.Met64.684)7.25;8.46A=bB(4;4.5)=cF(4;4.5) N=143,110
BeB3(H27.82,SR39.27)H9.800;9.532A=bBH(4;19/3)=cFH(8;9.5/3) N=300,218
BeB6(T28.168,SR26.57)10.16;14.28A corresponds to B(T192)
BeB12(T4.48,SR24,59)8.80;5.08A=bHT(6;4/2)=c U(6;4) N=152,104
MgB2(B2Al,SR17.71)H3.083;3.521A=bCH(1;2.8/3)=cF'H(2;2.8/3) N=2,14
MgB4(O4.16,SR38.50)5.464;4.428;7.472A=bFHO(1;1.75;2.5)=cF'HOK'(2) N=8,80
MgB7(P4.28,JLCM82.1981.325)5.970;8.125;10.480A N=16,232
MgB12
CaB4(ThB4,SR26.74)7.11;4.11A=bCK"/2=cC(√26;3) N=8,80
CaB6(C1.6,SR2.37)4.145A=bC(1)=cC(3) N=1,27
SrB6(CaB6,SR17.63)4.198A=idm CaB6
BaB6(CaB6,SR17.63)4.268A= idm CaB6
ScB2(B2Al,SR22.65)H3.146;3.517A=bCH(1;2.7/3)=cF'H(2;2.7/3) N=3,10
ScB12(U1.12,SR30.116)5.22;7.35A=bFUK"/2=cFU(√13;7) N=6,88
YB2(B2Al,71Ec)H3.298;3.843A=b CH(1;2.8/3)=cF H(2;2.8/3)idm MgB2 N=3,10
YB4(ThB4,SR30.31)7.086;4.012A=bCK"/2=cC(√26;3)idm CaB4 N=12,80
YB6(CaB6,SR17.63)4.113A=bB(1)=cC(3)hdm.CaB6 N=2,27
YB12(UB12,SR30.29)=bHT(√4.5;2.5/2)=cU(√18;5.2) N=12,176
YB66(F24.1584,SR34.43)23.44A
LaB4(ThB4.SR6.75)7.324;4.181A=idm CaB4
LaB6(CaB6,SR26.75)4.156A=idm CaB6
TbB4(ThB4,JLCM82.349),TbB4.1(magn.superstr.)
ErB4(ThB4,JLCM82.349)ErB4.1(magn.superstr.)
ThO.78B6(CaB6,SR37.41)4.111A=idm CaB6
Ti2B(~Mg,SR12.34)H5.946;4.789A=bFH(2;2/3)=cH(4;3) N=8,36
TiB(FeB,SR18.69)6.12;3.06;4.56A=bFHO(2.5/3;1;1.75)=cHT(4;2;3.5/2) N=4,24
Ti3B4(Ta3B 4,71Ec)3.259;13.73;3.042A=bFU(1;6/2;1)=cHT(2;10.5/2;2)=eC(√8;12;√8) N=6,42
TiB2(B2Al,SR13.46)H3.028;3.228A=bFH(1;1.3/3)=cFHK'(2)=eCH(2;5.2/3) N=1.9
Ti2B5(W2B5,H4.10,SR16.33)H2.98;13.98A=bH(1;4)=cFH(2;12/3) N=4,42
ZrB.h(NaCl,SR16.34)4.65A probably impurity stabilized
ZrB2(B2Al,SR16.34)H3.170;3.533A=idm TiB2 N=1,9
ZrB12.h(UB12,SR16.35)7.408A=bU(√4.5;2.6)=cU(√18;5.2)
HfB(FeB,SR17.70)6.502;3.212;4.829A=idm TiB
HfB2(B2Al,SR17.69)H3.141;3.470A=idm TiB2
V3B2(U3Si2,SR23.72)5.746;3.032A=bFU(2;1.5/2)=cHT(4;2.5/2)=eC(√32;3) N=6,36
VB(TlI,SR23.72)3.058;2.966;8.043A=bFU(1;4/2)=cFU(2;7/2)=eC(√8;7.5) N=4,28 10.76
V5B6(Q5.6,HighTemp.Scl.1969.86)3.058;21.25;2.974A=bFU(1;10/2)=cFU(2;19/2)=eC(√8;20)N=
V3B4(Ta3B4,SR20.56)3.030;2.986;13.18A=bFU(1;6.5/2)=cFU(2;12.5/2)=eC(√8;12.5)N=6,48
V2B3(Q4.6,HighTemp.Scl.1969.86)3.061;18.40;2.984A=bFU(1;8.6/2)=cFU(2;17/2)=eC(√8;17)
VB2(B2Al,SR12.36)=bFH(1;1.25/3)=cFH(2;2.5/3)=eCH(2;5/3) N=1,10 N=8,68
Nb 3B2(U3Si2,SR23.71)6.192;3.289A=idm V3B2
NbB(TlI,SR23.71)3.295;8.717;3.164A=idm VB
Nb3B4(Ta3B4,SR13.42)3.305;14.07;3.138A=idm V3B4
NbB2(B2Al,SR12.36)H3.11;3.27A=idm VB2
Ta2B(CuAl2,SR26.80)5.778;4.864A=bHT(2;2/2)=cC(4;3.3)=eC(√32;4.7) N=8,44
Ta3B2(U3Si2,SR23.71)6.184;3.287A=idm V3B2
TaB(TlI,SR12.32)3.276;8.669;3.157A=idm VB
Ta3B4(P3.4,SR12.32)3.284;13.98;3.129A=idm V3B4 N=24,94
TaB2(B2Al,SR12.32)H3.097;3.225A=idm VB2 N=1,10
CrB0.2(Mg,SR21.56)H2.576;4.449A=bUH(1;2/3)=cH(2;3.5) N=2,11.2
Cr4B(Mn4B,S8.2,SR17.67)4.262;7.382;14.71A=bH(√3;3;6)=cH(√12;6;12) N=32,184

Cr2B(CuAl2,SR17.67)5.185;4.316A=bHT(2;2/2)=cHT(4;4/2)=eU(4;4) N=8,52
Cr5B3(U10.6,SR17.67)5.46;10.64A=bHT(√4.25;4.7/2)=cHT(√17;9.5)=eU(√17;9.5)N=20,136
CrB.h(TlI,Q2.2,SR12.30)2.969;7.858;2.932A=bFU(1;√4/2)=cFU(2;7.5/2)=eC(√8;7.5)N=4,32
CrB.r(MoB,MhChem104.1973.933)2.94;15.72A
Cr3B4(Ta3B4,SR26.71)2.986;13.020;2.952A=bFU(1;6/2)=cF'U(2;12/2)=eC(√8;12.5)N=6,54
CrB2(B2Al,SR12.36)H.2.969;3.066A=bFH(1;1.25/3)=cF'H(2;2.5/3)=eCH(2;5/3) N=1,11
CrB4(P1.4,SR33.46)4.744;5.477;2.866A=bHO(1;1.9;1)=cFHO(2;4.5/3;2) N=2,34
CrB4I(R8.328,SR35.34)H10.964;23.848A
Mo2B(CuAl2,SR11.52)5.543;4,735A=idm Cr2B N=8,52
Mo3B2(U3Si2,71Ec)6.00;3.15A=bFU(2;1.5/2)=cFU(4;3/2)=eC(√32;3) N=6,42
MoB.h(TlI,SR11.51)3.16;3.08;8.61A=bFU(1;3.9/2)=cFU(2;7.8/2)=eC(√8;7.8) N=4,32
MoB.r(U4.4,SR16.31)3.103;16.95A=bFU(1;7.75/2)=cFU(2;15.5/2)=eC(√8;15.5) N=8,64
MoB2(B2Al,SR16.32)H3.04;3.06A=bFH(1;1.24/3)=cF'H(2;2.5/3)= =eCH(2;5/3)
Mo2B5(R 2.5,SR11.49)H3.011;20.93A=bH(1;7)=cF'H(2;17/3)=eCH(2;34/3)N=6,75 N=1,11
MoO.8B3(H(3.2).12,SR39.39)H5.203;6.349A=bH(√3;2)=cH(√12;4) N=3,52
W2B(CuAl2,SR11.52)5.564;4.740A=idm Cr2B
WB.h(TlI,SR11.51)3.19;8.40;3.07A=idm CrB

WB.r(MoB.r,SR16.31)3.115;16.93A=idm MoB.r
WB2(B2Al,71Ec) not confirmed (77 Mo)
W2B5.h(H4.10,SR11.49)H2.982;13.87A=bH(1;4.5)=cF'H(2;115) N=4,50
W2B5.r(Mo2B5,SR32.139)H3.011;20.93A=idm Mo2B5
WB4(H4.16,SR31.29)H5.200;6.34A=bH(√3;2)=cF'H(√12;5/3) N=4,68
WB12(H ,71Ec)
Mn4B(S8.2,SR13.38)14.53;7.29;4.21A=bH(6;3;√3)=cH(12;6;√12) N=32,216
Mn2B(CuAl2,SR13.40)5.148;4.208A=bHT(2;2/2)=cHT(4;4/2)=eU(4;4) N=8,60
MnB(FeB,SR4.101)5.560;2.977;4.145A=bB(2.6;1;√2)=cBK'(2) N=4,36
Mn3B4(Ta3B4,SR13.40)3.032;12.86;2,960A=bFU(1;6/2)=cF'U(2;12/2)=eC(√8;12) N=6,60
MnB2(B2Al,SR24.79)H3.009;3.038A=bUH(1;1.5/2)=cUH(2;3/2)=eCH(2;5/3) N=1,12
MnB4(N1,4,SR35.38)M90.30 4.63;5.37;2.95A=bHO(1.5;1;1)=cUHO(4.5/2;2;2) N=2,36
Tc3B(Re3B,Q6.2,SR29.104)2.891;9.161;7.246A=bFU(1;4.5/2;2.5)=cFU(2;9/2;5)=eC(2√2;9;5√2)
Tc7B3(Th7Fe3.H14.6,SR29.104)H7.417;4.777A=bFH(√7;2/3)=cFH(√28;4/3)=eCH(√28;8/3)N=14,102
TcB2(ReB2,H2.4,SR29.104)H2.892;7.453A=bH(1;2.5)=cFH(2;6.3/3) N=2,24
Re3B(Q6.2,SR2 4.73)2.890;9.313;7.258A=idm Tc3B
Re7B3(Th7Fe3,H14.6,SR24.71)H7.504;4.772A=idm Tc7B3
ReB2(H2.4,SR24.71)H2.900;7.478A=idm TcB2
Re2B5.h(W2B5,71Ec)H2.97;13.8A=bH(1;4.6)=cUH(2;13/2) N=4,54
Fe3B(71Ec) questionable (77Mo)
Fe2B(CuAl2,SR2.286)5.109;4.249A=bHT(2;2/2)=cFU(4;4.7/2)=cU(4) N=8,68
FeB(O4.4,SR2.241)5.506;2.952;4.061A=bB(2.6;1;√2)=cB(5.2;2;2√2) N=4,40
FeB2(77Mo)
Ru7B3(Th7Fe3;SR23.57)H7.467;4.713A=idm Tc7B3FF'2 N=14,116
Ru11B8(O22.16,SR24.73)11.61;11.34;2.84A=bFU(5.5/2;4;1)=cF'UK'(2) N=22,202
RuB1.1(WC,SR27.93)H2.852;2.855A=bH(1;1)=cFH(2;2.5/3) N=1,10.3
RuB1.5(W2B5,SR34.41)H2.89;12.81A=bH(1;4,5)=cFH(2;11/3) N=4,46
RuB2.1(O2.4,SR27.94)4.645;2.865;4.045A=bC(1.5;1.5;1)=cFU(4.5/2;2;3) N=2,26
OsB1.2(WC,SR27.93)H2876;2.871A=idm RuB1.1
OsB1.6(W2B5,SR27.93)H2.91;12.91A=idm RuB1.5
OsB2.2(RuB2,SR27.94)4.684;2.872;4.096A=idm RuB2.1
Os2B5(W2B5,SR26.76)H2.91;12.91A=idm W2B5
Co3B(Fe3C,O12.4,SR22.58)4.408;5.223;6.629A=bFH(√3;2;3/3)=cF'HK'(2) N=12,108
Co2B(CuAl2,SR3.619)5.016;4.221A=bHT(2;2/2)=cFU(4;4.8/2) N=8,72,88
CoB(FeB,SR3.619)5.254;3.043;3.956A=bFH(2.1/3;1;1.5)=cF'H(4.2/3;2;3) N=4,44
Rh7B3(Th7Fe3,SR23.57)H7.471;4.777A=bFH(√7;2/3)=cF'H(√28;4/3) N=14,130
Rh5B4(H10.8,JLCM82.1981.303)H3.306;20.394A=bUH(√1.33;8/2)=cF'H(√5.3;18/3) N=10,104
RhB1.1(anti NiAs,SR24.71)H3.309;4.224A=bH(√1.33;1.5)=cF'H(√5.3;3.6/3) N=2,22
IrBO.9.h(WC,SR37.39)H2.815;2,823A=bFH(1;1.25/3)=cF'H(2;2.5/3) N=1,11
IrBO.9.r(Q4.4,SR37,40)2.711;7.578;7.314A=bC(1;√8;√8)=cFU(3/2;√32) N=8,88
IrB1.1(ThSi2,U2.4,SR24.71)2,810;10.263A=bHT(1;4/2)=cF'U(2;10/2) N=4,46
IrB1.35(N4.5,SR39.38)M91.120 10.530;2.904;6.101A=bH(4;1;2)=cF'H(8;2;5.2/3) N=8,94
Ni3B(Fe3C,SR32.32)4.389;5.211;6.619A=bFH(√3;2;3/3)=cR(√12;4;9/3) N=12,120

Ni2B(CuAl2,SR23.64)4.989;4.246A=bHT(2;2/2)=cB(4;3.4) N=8,84
Ni4B2.9(O16.12,SR32.32)11.953;2.981;6.569A=bB(4;1;2)=cU(8;2;5.5) N=16,180
Ni4B3(N8.6,SR32.33)M103.3°6.430;4.882;7.818A
NiB(TlI,SR16.32)2.928;7.391;2.964A=bFU(1;4/2;1)=cU(2;6;2) N=4,48
NiBl2(,71Ec)7.526A
Pd16B3(F8.(1.5),ZMetk73.1982.331)8.010A N=32,306
Pd3B(Fe3C,SR26.77)4.852;5.463;7.567A=bFH(√3;2;3.3/3)=cF'HK'(2) N=12,120
Pd2B(CaCl2,JSolStateChem31.1980.361)4.692;5.127;3.110A=bU(1.5;2;1)=cU(3;4;2) N=4,42
Pd5B2(Mn5C2,N10.4,SR26.76)M97.03°12.79;4.96;5.47A N=20,204
Pt4B
Pt2B
Pt3B2.h(Dhtp anti NiAs,Ellner1982)3.371;5.817;4.045A=bÛH(1.1;2;2/2)=cCHO(2;2;6/3)
CuBM(nic,77Mo),CuB23(B.h,R108,SR40.41)is marginal N=4,42
AgBM(nic,77Mo),AgB2 questionable(JLCM9.1965.423)
AuBM(nic,77Mo),AuB2(SR26.73)questionable(ibid.)
ZnBM(nic,77Mo)
CdBM(nic,77Mo)
HgBM(nic,77Mo)
B2Al(H2.1,SR20.5)H3.009;3.262A=bR(1;3/3)=cF'H(2;2.6/3) N=3,14
B10Al(Q52.5,SR32.3)8.881;9.100;5.690A
B12Al.h(O348.29,SR26.5)16.56;17.35;10.16A
B12Al.r(T180.15,SR26.4)10.161;14.283A
BGaM(nic,77Mo),B12Ga(T120.10,SR26.72)doubtful
BInM(nic,77Mo)
BTlM(nic,77Mo)
B4C(R12.3,SR9.154)H5.60;12.12A=bH(4;9)=cR(4;27/3) N=144,90
B4Si(B4C,R12.3,SR24.255)H6.32;12,75A=bUH(4;9/2)=cR(4;18/3) N=144,144
B6Si(CaB6,SR20.209)4.13A=bHT(1.5,1.8/2)=cC(3) N=4,26
B6Si(O240.40,SR22.65,23.278)14.392;18.267;9.885A N=160,1040
B14Si(B.h,R108,SR30.116)probably marginal phase
BGeM(nic,77Mo)
BSnM(nic,77Mo)
BPbM(nic,77Mo)
B13P2(B13C3,SR26.79)H5.984;11.850A=bUH(4;9/2)=cR(4;18/3) N=147,126
BP.h(ZnO,SR28.43,296)H3.562;5.900A cell needs confirmation
Bp.r(ZnS,SR28.43,296)4.534A=bF(2)=cC(4)
B13As2(B12C3,SR26.67)H6.142;11.892A=idm B13P2 N=147,138
BAs(ZnS,SR22.39)4.777A=idm BP
BSbM(nic,77Mo)
BBiM(nic,77Mo)
B6O(H24.4,75PW)H5.395;12.342A
B2O.hp(H36.18,75PW)H7.981;9.091A
B2O3(H6.9,SR33.258)H4.336;8.340A=bBH(2;18/3)=cFH(4;≈9/3) N=72,30
B2O3.p(Q4.6;SR33.259)4.613;7.803;4.129A=bFH(4;6;4)=cCH(4;6;8/3) N=96,40
B12S(R12.1 B4C,SR26.79)H5.80;11.90A=idm B13P2 N=126,96
BS2(,77Mo)
B2Se3(,77Mo)
BTeM
BPoM
B2F4.1(M4.8,SR22.230)
BCl3.1(H2.6,SR19.317)H6.08;6.55A
B2Cl4(O8.16,SR19.317)11.900;6.281;7.690A
BI3(H2.6,SR27.438)H7.00;7.46A