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Boron and Borides

Boron: Elementary Challenge for Experimenters and Theoreticians

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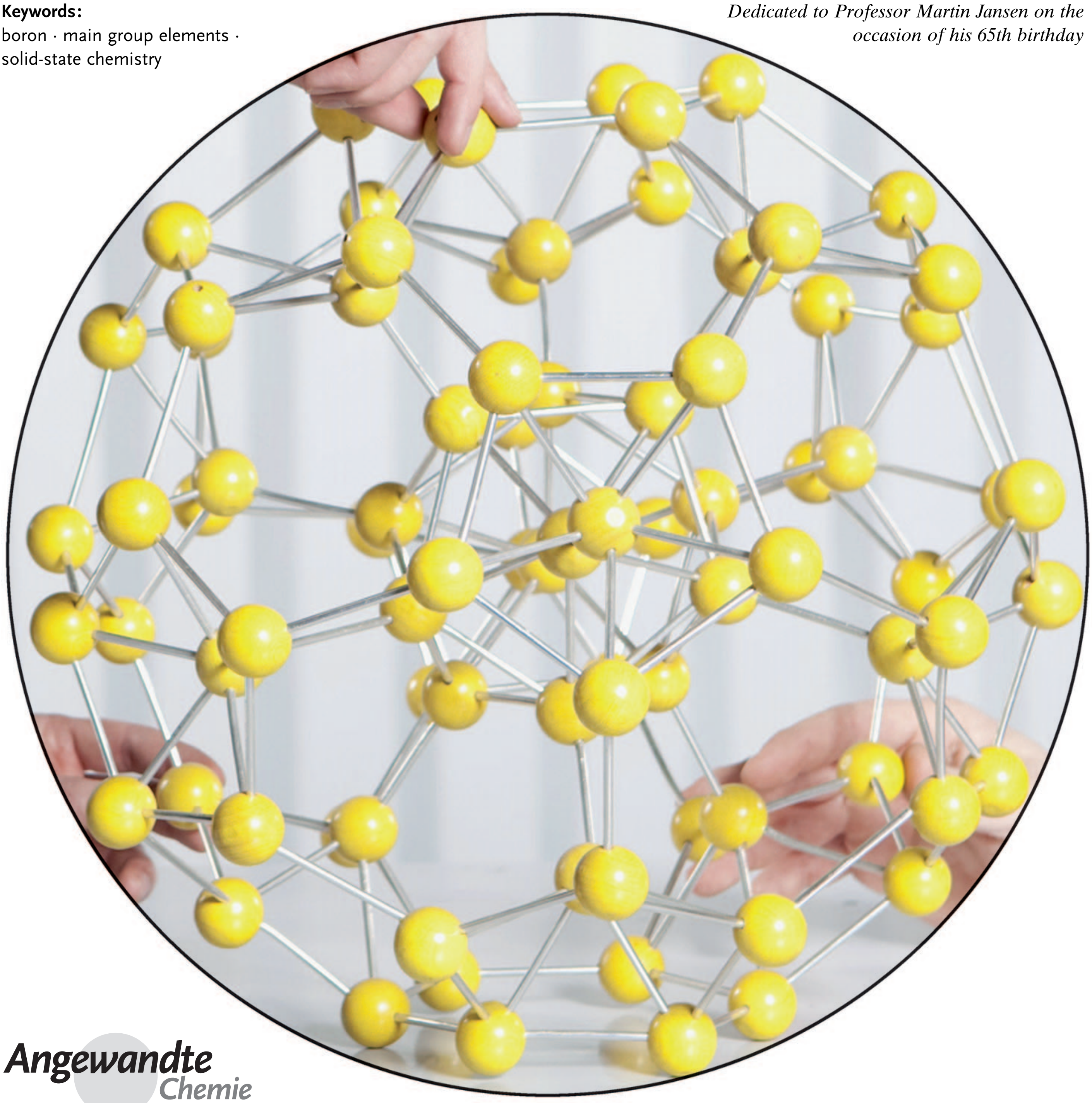
boron · main group elements · solid-state chemistry

Dedicated to Professor Martin Jansen on the occasion of his 65th birthday



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Many of the fundamental questions regarding the solid-state chemistry of boron are still unsolved, more than 200 years after its discovery. Recently, theoretical work on the existence and stability of known and new modifications of the element combined with high-pressure and high-temperature experiments have revealed new aspects. A lot has also happened over the last few years in the field of reactions between boron and main group elements. Binary compounds such as B_6O*,* MgB_2*,* LiB_{1-x}*,* Na_3B_{20}*, and* CaB_6 *have caused much excitement, but the electron-precise, colorless boride carbides* $Li_2B_{12}C_2$*,* $LiB_{13}C_2$*, and* $MgB_{12}C_2$ *as well as the graphite analogue* BeB_2C_2 *also deserve special attention. Physical properties such as hardness, superconductivity, neutron scattering length, and thermoelectricity have also made boron-rich compounds attractive to materials research and for applications. The greatest challenges to boron chemistry, however, are still the synthesis of monophasic products in macroscopic quantities and in the form of single crystals, the unequivocal identification and determination of crystal structures, and a thorough understanding of their electronic situation. Linked polyhedra are the dominating structural elements of the boron-rich compounds of the main group elements. In many cases, their structures can be derived from those that have been assigned to modifications of the element. Again, even these require a critical revision and discussion.*

From the Contents

1. Introduction

The element boron—neighbor of carbon in the periodic system of elements, nonmetallic, hard material—represents structural complexity, electron deficiency, unusual binding situations, and a rich variety of compounds.

Even the question as to the number of existing or hitherto proven elemental modifications cannot be answered. The number of boron modifications that have been the subject of discussion comes to 16,[1,2] even before the recent finding of new high-pressure varieties. There is no doubt about the existence of two crystalline modifications at normal pressure, known as α-rhombohedral boron (α-B, Figure 1) and β-rhombohedral boron (β-B, Figure 2). The latter is believed to be thermodynamically stable at high temperatures, whereas α-B is sometimes called the low-temperature form. A transformation from α-B to β-B, however, has not been proven as yet, while only the different temperatures of synthesis support this categorization (α-B is synthesized at $T < 1300$ K, β-B above about 1400 K).

Tetragonal boron I (t-I) and tetragonal boron II (t-II), two more crystalline elemental modifications to be found in chemistry textbooks (earlier called α-tetragonal and β-tetragonal boron, respectively) have been suggested as being "stabilized by foreign atoms".[3] The question of whether they can be called real allotropes of boron will be discussed in detail later, as well as a new high-pressure modification, γ-B_{28},[4,5] which according to theoretical calculations consists of partially positively charged and partially negatively charged structural units.[4] There are further polymorphs of boron which have been obtained under high pressure, but whose structures have not yet been elucidated. Eremets et al. found a transition to a superconducting phase at pressures above 160 GPa, the critical temperature being between 6 K (175 GPa) and 11.2 K (250 GPa).[6] A structure analogous to α-Ga has been predicted for this phase,[7] and several attempts have been made at an electronic interpretation of the superconductivity (see Ref. [8] for an example).

We also know of (X-ray) amorphous boron, since this is the variety that Henri Moissan obtained in 1892 when he reduced diboron trioxide with magnesium.[9] Moissan's samples were contaminated (but not as badly as those of the discoverers of boron: von Crell, Gay-Lussac and Thenard, and Davy[10–12]), and one of the contaminating substances was magnesium diboride. MgB_2 is thus a well-known binary compound, but it is only since 2001 that we have known it becomes a superconductor at 39 K.[13] It has since become possible to produce it on an industrial scale in the form of

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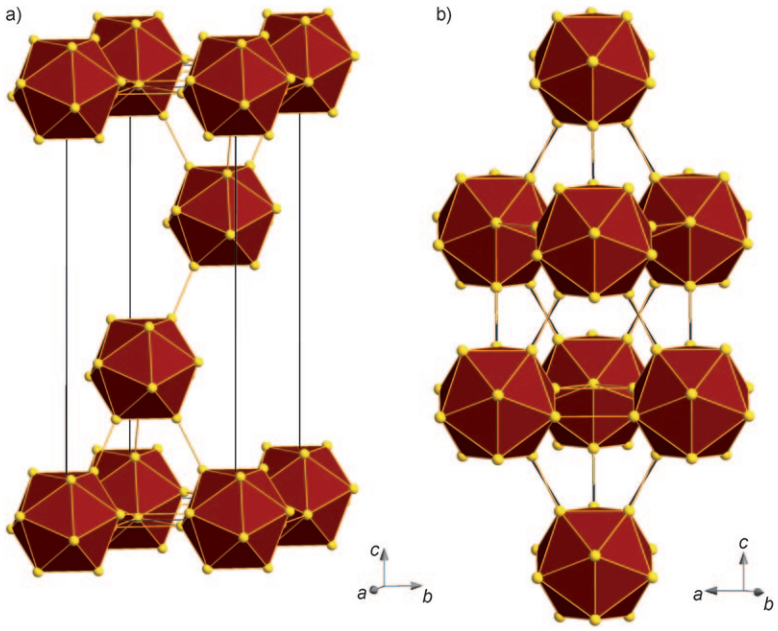


Figure 1. Unit cells of α-B: a) hexagonal setting, b) rhombohedral setting.

wire, and prototypes of magnetic resonance imaging (MRI) magnets and electric current limiters have been tested for application.[14] Pure boron (>99%) was first synthesized by Weintraub in 1909.[15]

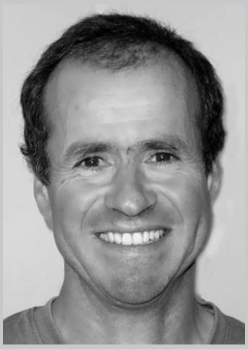
The structures of boron and many boron-rich compounds are characterized by subunits of triangular-defined polyhedra, so-called deltahedra (from the Greek letter Δ), for example, octahedra or icosahedra. In the case of closed polyhedra (Figure 3), one talks of *closo*-clusters, a nomenclature which makes reference to the Wade classification.[16] Wade—and later Mingos,[17] Jemmis,[18,19] and others—derived rules for the existence and structure of certain boron–hydrogen compounds and distinguished between *closo*-hydroborates $B_nH_n^{2-}$ and *nido*-, *arachno*-, *hypho*-, and *conjuncto*-Boranes (for example, B_nH_{n+4}). The variety of these compounds is immense. Boranes (and boron halogenides) are the only group of compounds of boron with main group elements which will not be taken into consideration in this Review, but Wade's concept will be applied to the structural chemistry of boron and boron-rich compounds later and discussed for selected examples.

This Review will discuss binary and selected ternary compounds of boron with main group elements, with the exception of hydrogen and halogens. Table 1 gives an overview of which binary boron compounds can be found in the systems. These are borides of the alkali and alkaline-earth metals, aluminum borides, and compounds of boron and the nonmetals C, Si, Ge, N, P, As, O, S, and Se. Emphasis is put on *boron-rich* compounds of the *main group elements* with extended structures. For well-known compounds, such as B_2O_3 or BN, the reader is referred to the text books,[3,20] and for compounds such as B_8S_{16}, which has been described as an inorganic porphine with a molecular configuration,[21] as well as the selenoborates of the alkali metals, to the work of Krebs and co-workers (review in Ref. [22]), where they are extensively described.

Table 1: Binary compounds of boron with main group elements.

LiB_{1-x}	BeB_3		$B_{13}C_2$	BN	B_2O_3
Li_2B_6	BeB_{15}		$B_{50}C_2$	$B_{13}N_2$	B_6O
Li_3B_{14}				$B_{50}N_2$	
LiB_{10}					
Na_2B_{29}	MgB_2	$Al_{0.9}B_2$	SiB_{36}	BP	B_2S_3
Na_3B_{20}	MgB_7	AlB_{12}	SiB_6	B_6P	B_8S_{16}
	Mg_5B_{44}	AlB_{31}	SiB_3		$B_{12}S$
	MgB_{12}				
	$MgB_{17.9}$				
KB_6	CaB_6		GeB_{90}	BAs	$B_{13}Se$
				B_6As	
	SrB_6				
	BaB_6				

Barbara Ruth Albert is professor at the Technische Universität Darmstadt. She studied chemistry in Bonn and received her PhD in 1995, with Prof. Martin Jansen. This was followed by research at the Materials Research Lab. of the UC at Santa Barbara with Prof. A. K. Cheetham and at the Justus-Liebig-Universität Gießen with Prof. J. Beck, habilitation (Bonn, 2000), and a deputy chair (Giessen), before she accepted an offer of a full professorship for solid-state chemistry and materials science in Hamburg. From there she moved to her current position. Her awards include a grant from the Alexander von Humboldt foundation, a Lise-Meitner grant, the ADUC, and the Bennigsen-Foerder award. She is European editor of Solid State Sciences, member of the board of the GDCh, head of the German solid-state and materials science division, and is currently head of the chemistry department at the TU Darmstadt.



Harald Hillebrecht studied chemistry at the University of Freiburg and recieved his PhD in 1991 with Prof. Thiele. After postdoctoral research at the Max Planck Institute for Solid-State Science in Stuttgart with Prof. H.-G. von Schnering, he returned in 1993 to Freiburg and finished his habilitation (1997). After professorships in Bonn (1997–1999) and Bayreuth (1999–2002) he returned to Freiburg as the chair for solid-state chemistry. His research interests are high-temperature syntheses, reactivity of molten metals, structure–property relationships, hard materials, and intermetallic phases.

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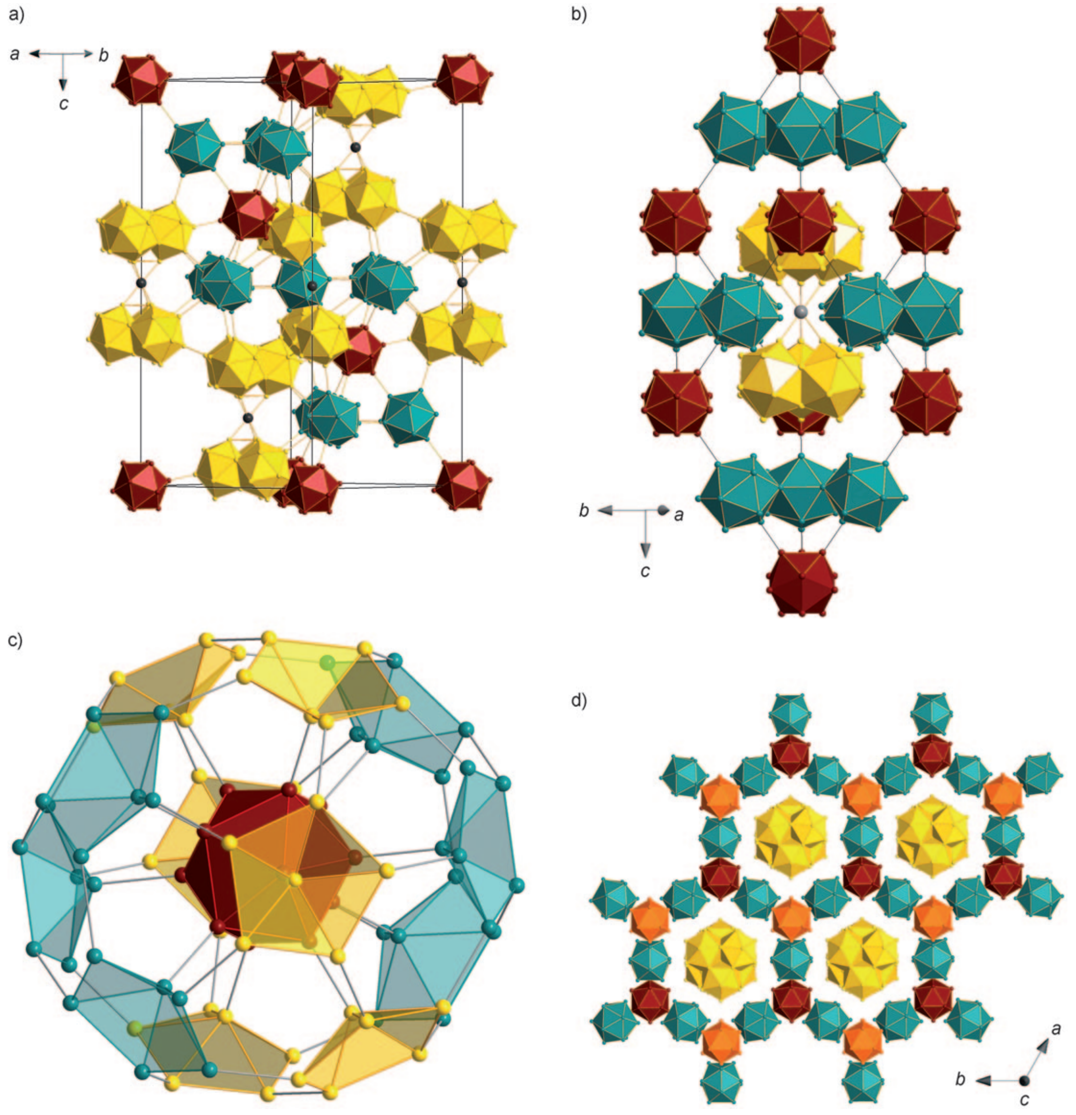

Figure 2. Unit cells of β-B: a) hexagonal setting, b) rhombohedral setting; c) B_{84} unit, d) Kagome net of icosahedra.

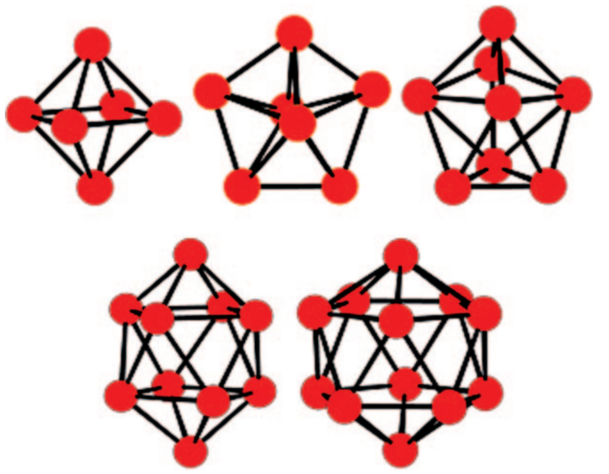

Figure 3. Polyhedra in boron-rich compounds: octahedron, pentagonal bipyramid, trigondodecahedron, double-capped square antiprism, icosahedron.

Many of the boron substructures in boron-rich compounds are derived from elemental modifications, which cause the problems concerning the unambiguous structural characterization indicated above to be mirrored in many facets.

The chemical and physical properties of boron-rich compounds can also be discussed in the context of those of the element, always bearing in mind that the physical properties of boron and its compounds have not in all cases been described beyond doubt. As is well-known, even small amounts of contamination (dopant) can have an influence on the electronic structure of inorganic solids and cause considerable changes in such properties as electrical conductivity and hardness. The preparation and conversion of pure boron usually requires high reaction temperatures, at which the introduction of undesired reaction partners to the base element cannot always be excluded. The postsynthetic purification of boron and the compounds as described here is possible only in exceptional cases. Digestion and analysis of

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boron and its compounds, as well as proving the presence of trace impurities in them, pose particular challenges, which is why in many cases it is unclear what has led to the differences in results and numerical data in the literature. Even modern methods of calculation, which are based on density functional theory, sometimes encounter difficulties when it comes to the description of boron-rich solids with extensive structures, partial occupancies, and large unit cells. Covalent, ionic, and metallic bonding forces exert their influence alongside each other. Diverging data from experiments and theory have led to controversies about basic properties, one case in point being certain borides of apparently simple composition which are variously described as insulators, semiconductors, semimetals, or metals (example: CaB_6 or SrB_6[126]). Theoreticians have developed concepts to try and make boron chemistry more accessible: Longuet–Higgins and de Vries Roberts,[23] Lipscomb (Nobel Prize 1976),[24] and Hoffmann (Nobel Prize 1981)[25,26] are the most eminent among them. It is thanks to them that the bonding situation of molecularly structured boron compounds is understood or can at least be described in most cases. The concept of polycentric bonding has also been proven experimentally in recent experimental determinations of the electron density in *closo*-clusters.[27–29] However, the bridge from molecules to solids—that is, from borane to boron-rich boride—remains one of the great current challenges.[30]

The production of boron and borides in the form of nanomaterials—nanotubes, nanowires, nanoparticular, nanostructured, or in the form of nanolayers—is yet another current challenge. Whereas, for example, nanotubes of carbon are intensively investigated and developed as highly attractive new functional materials, there are comparatively few reliable data regarding nanotubes and wires of pure boron or borides. Bornitride is isoelectronic with carbon, which suggests the possibility of synthesizing it in the form of nanotubes and characterizing it accordingly. Multiwall and pure boron nitride nanotubes were obtained for the first time in 1995 by Chopra et al., who placed BN in an arc between tungsten and copper electrodes.[31] Loiseau et al. later described a synthesis between hafnium diboride electrodes, which resulted in very pure BN nanotubes with just a few walls, and sometimes only a single wall.[32] Following this, seminal contributions were made to their detailed analysis by high-resolution transmission electron microscopy and electron energy loss spectroscopy, including a determination of the optical band gap.[33–36] Boron nitride nanotubes were also deposited as a composite material with carbon,[37] and boron–carbide nanofibers were obtained in an aligned manner by chemical processes from precursor compounds.[38] This chemical process to nanostructured materials, nanoparticles, nanofibers, and nanotubes is very promising; BN (in the form of particles resembling diatoms) and $B_{13}C_2$ were synthesized, for example, from carbaboranes[39] and polyborazylenes.[40]

Nanoparticles of metal borides are less amenable to synthesis than, for example, sulfides, since borides cannot normally be obtained from solution and precipitated at low temperatures (exception in Ref. [41]). We shall discuss selected work which has described nanoboron and nanoborides.[42–44] However, we stress even here that all studies on boron nanomaterials with a t-I structure (α-tetragonal boron, tetragonal boron I) can be shown to relate to boron carbide phases rather than pure boron (for example, Ref. [42]). The same probably goes for the spectacular B/SiO_x, described in 2008 as a nanocomposite reinforced by a nanocollar, with an electrical conductivity which is said to be a thousand times higher than that of bulk boron.[45] However, it seems that nanotubes of 40 nm thickness were obtained by laser ablation that were shown to be free of foreign elements by electron energy loss spectroscopy (EELS) and to consist of t-I boron by electron microscopy.[46]

Boron is used in igniters of airbags, but also in semiconductors and electronic components. Boron fibers serve to reinforce synthetic materials and light metals (in airplane construction and the aerospace industry generally). Its high neutron capture cross-section means that ^{10}B boron also serves to line walls of nuclear reactors; it is also attractive to medicine (boron neutron capture therapy) for the same reason (for example, in Refs. [47,48]). Composite materials of aluminum and boron carbide have been investigated as high-value construction materials.[49] Metal borides—although mostly those of the transition metals and not those of the main group elements—are used to harden tools and mechanical parts exposed to high strain (turbine and rotor blades, sports equipment). Their mechanical and chemical resistance and high electrical conductivity make them a useful electrode material. Ferroboron, an alloy of iron and boron, hardens steel. Lanthanum hexaboride is a thermo-ionic emitter with a very low work function that can be used as an electrode in transmission electron microscopes and especially for electron beam lithography. Metal hexaboride nanowires (for example, La) have recently been proposed for so-called high-performance electronic applications.[50] The well-known CaB_6 was published as a "new and semiconducting material for spin electronics".[51] Boron carbide is a very hard and, at the same time, lightweight material for applications in personal security (bullet-proof vests).[52,53] Its excellent abrasive properties even at high temperatures have resulted in it being used, similarly to aluminum boride, as a grinding material and for sandblasting nozzles.[54–56] Boron hydrogen compounds first came to public attention as rocket fuels, and very recently, as hydrogen-storage materials (for example, $LiBH_4$, $NaBH_4$, NH_3BH_3) for fuel cells.[57–60] Studies on the incorporation of hydrogen into BN nanotubes[61] and on increasing hydrogen absorption through the addition of noble elements, such as Pt nanoparticles, to "$LiB_{0.33}N_{0.67}H_{2.67}$"[62] should be mentioned specifically. The Millenium Cell Corporation is testing a system which uses $NaBH_4$ for hydrogen storage.[63] The attractive properties of the superconductor MgB_2, used for wires in tomographs, have already been mentioned. Last, but not least, it should be mentioned that boron-rich borides could play an important role as thermoelectric materials of resource-sensitive energy conversion, especially in high-temperature applications.[64,65] Elemental boron in its β-rhombohedral form is a p-type semiconductor and can be made into an n-type semiconductor by doping with metals such as iron. If it were possible to enhance their electrical conductivity without a significant increase in thermal conductivity, such systems would become promising for the

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development of thermoelectric devices. Hexagonal boron nitride on the other hand is a soft, electrically nonconducting material of high chemical resistance, and a very good heat conductor, which is used above all as a material for crucibles. Finally, cubic boron nitride is second in hardness only to diamond; it is used for specialized applications because of its excellent oxidation stability.

On a large scale, boron (in all its forms) is nowadays synthesized by reducing boron trichloride with hydrogen, thermal decomposition of diborane, and—most commonly—by reducing boron oxide with magnesium; the annual world production is about 100 tonnes (Germany: Fa. H. C. Starck, ca. 30 tonnes).

2. The Element Boron: Four, Five, or Six Known Modifications?

2.1. Amorphous and α-Rhombohedral Boron (α-B)

2.1.1. Synthesis and Properties

Amorphous, brown, or black boron was obtained as early as 1808 from boron oxide B_2O_3 or boric acid $B(OH)_3$ and potassium, or by electrolysis.[11,12] It was later synthesized, as described in the introduction, from B_2O_3 and magnesium. α-B can be obtained by crystallizing amorphous boron in a platinum melt.[66] Another way of synthesizing α-B is by pyrolytic decomposition of boron trihalogenides on (tantalum) surfaces.[67,68] The reduction of boron trihalogenides with hydrogen at $T > 1200$ K on W or Ta wires or surfaces produces pure samples of crystalline boron.[3] It should, however, be pointed out that so far only three laboratories have been able to obtain single crystals of α-B, and the last time was in 1967.[69]

α-B is red or maroon in color and non- or semiconducting at room temperature. Van Setten et al.[70] calculated an indirect band gap of 1.54 eV and a direct band gap of 1.94 eV; dipole-permitted transitions start at 2.59 eV. A direct optical band gap of about 2 eV and 2.4 eV was determined experimentally by optical absorption[71,72] and EELS,[73] respectively.

α-B is considered to be harder than β-B,[74] the Debye temperature θ_D is 1430 K, and the bulk modulus of 208 GPa (calculated)[70] and 213–224 GPa (experimental)[75] is thus greater than that of β-B. α-B has a density of 2.46 $g\,cm^{-3}$. Numerical data for the physical properties of elemental boron modifications—as far as are known—can be found in Ref. [76].

2.1.2. Structures

The structure of amorphous boron is not known. The EEL spectrum of amorphous boron[73] is similar to that of β-B, which might be taken to suggest that its structure is more similar to that of β-B than to that of α-B. However, since no theory-supported fine-structure analysis was performed, no further conclusions can be drawn from these EELS experiments. Theoretical calculations by Kobayashi et al. show that a possible structure of amorphous boron can be simulated using icosahedral structural units.[77]

The name of α-rhombohedral boron already indicates in which crystal system this modification crystallizes: space group $R\bar{3}m$ (no. 166). The centers of gravity of the B_{12} icosahedra are located on the corners of a primitive rhombohedral unit cell ($a = 505.7$ pm, $\alpha = 58.06°$[78]; Figure 1 shows the unit cell in a hexagonal (a) and rhombohedral (b) setting). In the rhombohedral setting the unit cell contains 12 boron atoms, which is why this modification is sometimes referred to as α-B_{12}. The boron atoms are situated on two sixfold sites which are crystallographically independent of each other. The distances between the boron atoms, which vary between 170 pm and 179 pm, will be further discussed in Section 2.1.3, since they can be attributed to different types of bonds.

The icosahedral arrangement in α-B can be compared to the image of a cubic close packing of spheres with the layer sequence ABC. Each icosahedron is then surrounded by 12 more icosahedra. The rhombohedral angle, which is 60° in a cubic system, is reduced. B–B bonds between icosahedra require rhombohedral angles of about 63° if the fivefold rotation symmetry of the icosahedra is to be retained. The actual rhombohedral angle of 58° is smaller, which can be explained by the influence of the three-center bonds between the icosahedra. The packing density was given as 41 %[70] (based on a boron atom radius of 89 pm). In Refs. [3,20], 37 % was found, while Oganov et al. calculated 34 %.[4]

2.1.3. Bonding Situation

According to Wade, a *closo*-cluster with n vertices needs $2n+2$ electrons to stabilize the polycentric bonding system. An icosahedron consisting of 12 boron atoms has 36 valence electrons, 26 of which may be used for intra-icosahedral bonds (polycentric bonding system of the icosahedron) and 10 for inter-icosahedral bonds. Based merely on calculations, one might imagine that in an icosahedral arrangement, with the cubic close packed motive, each icosahedron forms six two-electron–two-center (2e2c) bonds with the icosahedra of neighboring layers, which requires $6 \times 2/2 = 6$ electrons, as well as six closed 2e3c bonds (two electrons, three centers) with the neighboring icosahedra in its own layer. The B–B distance in the latter is 203 pm. These multicenter bonds require $6 \times 2/3 = 4$ electrons, so that within this image the electrons are balanced for α-B according to Wade ($36 = 26 + 6 + 4$). The 2e2c bonds should be shorter than polycentric bonds. Indeed, one can identify B–B bond lengths of 171 pm in α-B for inter-octahedral contacts; the B–B distances within the icosahedra are 173 pm, 178 pm, and 179 pm.

In 2001 Will and Kiefer published the electron deformation density of α-B, based on a "high order–low order" and multipole refinement ($a = 491.79$ pm, $c = 1258.05$ pm).[69] Analysis of the dynamic deformation density maps confirms the picture of the different intra- and inter-icosahedral bonding types in α-B. The crystal data as well as the experimental data used in this study originated from Horn and Morosin et al.[79,80] The lattice parameters and atomic positions agree excellently with the theoretically calculated values of van Setten et al.[70] In a modern analysis of the

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bonding situation, Hosoi et al. recently managed to investigate crystalline powder of α-B, boron carbide, and boron phosphide by means of a combination of Rietveld refinement of synchrotron data and the maximum entropy method (MEM).[81] The results show a bent inter-icosahedral 2e2c bond, and confirm the proposal made by Fujimori et al. on the basis of electron density analyses.[82] This observation led the authors to discuss the very interesting question: Are inter-polyhedral bonds in boron and boron-rich compounds stronger than intra-polyhedral bonds, as suggested by the bond lengths? This view is generally accepted, and it is for this reason that boron-rich substances have been called "anti-molecular" or "inverse molecules", for example by Emin.[83] Is there a correlation between bond length and bond strength? Experimentally derived and calculated force constants partially contradict each other.[84–87] In both publications quoted above, the authors conclude that multicenter bonds between icosahedra, which make α-B an electron-precise compound, require a reduction of the rhombohedral angle to 58°, thus forcing the system to bend its 2e2c bonds between the icosahedra, thereby resulting in shorter distances than required on the basis of the bond strengths. Analysis of the electron densities led the authors to expect the intra- and inter-icosahedral bonds to have similar strength. This is an interesting hypothesis; however, further experiments are required since in both cases the electron density measurements were made on crystalline powders and not single crystals, and in at least one case the analysis was performed at room temperature. It has been shown that the use of low-temperature data and single crystals is highly advantageous for multipole refinements and the determination of deformation densities, at least for molecular compounds.[88] The influence of the temperature in the range of 550 to 100 K is smaller, however, for boron-rich and hard borides with three-dimensional frameworks.[89]

2.2. β-Rhombohedral Boron (β-B)

2.2.1. Synthesis and Properties

β-B can be obtained from a boron melt,[90] and it can be purified by zone-melting.[91] Whether α-B can be transformed to β-B directly, as described in Ref. [67] and theoretically predicted in Ref. [74], has not been established. Results from in situ heating experiments within an electron microscope (diffraction)[92] were interpreted in different ways since they indicate several metastable intermediate phases.[74,93]

β-B is a semiconductor with an experimentally determined band gap of 1.6 eV,[94] is harder than corundum, and has a grayish black color; the melting point is stated to be between 2450 and 2723 K. Its slightly lower density than α-B (2.33 $\mathrm{g\,cm^{-3}}$), lower bulk modulus (185–210 GPa), and lower Debye temperature (1200–1300 K) has resulted in it being described as "softer" ("diluted"[74]).

2.2.2. Crystal Structure

The crystal structure of β-B (Figure 2a shows the unit cell in a hexagonal arrangement) was first described in a cursory manner by Kolakowski in 1962,[95] and then later, contemporaneously, by Geist et al. and Hoard et al.[96,97] Similar to α-B, it crystallizes in space group $R\bar{3}m$ (no. 166), but the rhombohedral unit cell (Figure 2b, $a = 1013.9$ pm, $\alpha = 65.2°$[96]) is considerably larger than that of α-B. At first, 105 boron atoms were described in 15[96] or 16[97] crystallographically independent positions, with a partially occupied boron atom position in Ref. [97], while in Ref. [96] it was fully occupied, and the additional 16th site was also partially occupied. Callmer refined the structure of β-B with 314.7 atoms per (hexagonal) unit cell, also using 16 boron atom positions, 2 of which were partially occupied.[98] Eleven years later, Slack et al. showed that there are four additional interstitial positions with partial occupations.[99] They described the structure in the hexagonal arrangement with 319–321 atoms in the unit cell. The occupation factors varied from sample to sample.

If the unit cell is drawn in a rhombehedral arrangement (Figure 2b), there will be icosahedra at the corners and in the middle of the edges, that is, there is a total of four icosahedra in the unit cell, which is equivalent to 48 atoms. There are two B_{28} units on the body diagonal, each consisting of three condensed icosahedra and linked via an insulated B atom in the center of the (rhombohedral) unit cell. Visualizing the structure with the help of Samson polyhedra, as explained below, the rhombohedral unit cell has B_{84} units at its corners and B_{10}-B-B_{10} chains on the body diagonal, which makes it vaguely similar to the structure of $B_{13}C_2$ (see Section 4.2), which contains icosahedra at the corners and C-B-C chains on the body diagonal. The single boron atom in the center of the unit cell is coordinated trigonal-antiprismatically (distorted octahedron) by six boron atoms of the $B_{28}(B_{10})$ units (B–B distances ca. 174.5 pm). This results in $4 \times 12 + 2 \times 28 + 1 = 105$ boron atoms per unit cell. In addition, there are positions which are only partially occupied. It should be mentioned that a 2/3 occupancy of one of the boron atom positions, as described by Hoard et al. and Callmer et al., results in a distorted tetrahedral instead of the trigonal-antiprismatic coordination of the single isolated boron atom and the B_{28} unit becomes a B_{27} unit, as described in Section 4.3 for certain metal borides.

The B_{84} units are also called "super-icosahedra", and according to Matkovich[100] the 12 boron atoms of a central icosahedron are linked to 12 half-icosahedra in such a way ($B_{12}(B_6)_{12}$) that an outer, truncated icosahedron is formed (as known from fullerene C_{60}). The packing of these "super-icosahedra" in β-B follows the motif of the cubic close packing of spheres. The B_{10} units are located in the trigonal-antiprismatic gaps of such an arrangement. In addition, there are other, partially occupied interstitial boron atom positions. Such a B_{84} unit is therefore really a well-defined, three-shell "sub-nanoparticle" (with a diameter of ca. 0.8 nm): on the inside a B_{12} icosahedron of typical dimensions, followed by a B_{12} icosahedron with a diameter larger than usual, which is again surrounded by a B_{60} sheath (see frontispiece). The B_{10} units consist of three condensed half-icosahedra (if the missing halves were added, the B_{28} unit described above would result; these latter halves are here counted as part of the B_{84} units). Such structural motifs of β-B are also found for intermetallic Zintl phases, for example in $K_{49}Tl_{108}$.[101,102]

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A third description of the β-B structure uses the image of Kagomé nets (6.3.6.3 nets) of icosahedra (Figure 2d) which have an ABC stacking perpendicular to the *c* axis.[103] In addition, B_{28} units made up of three condensed icosahedra are situated in the gaps of the Kagomé nets, which are formed by a triangle and a hexagon. Two B_{28} (or better B_{27}) units are linked by one B atom. In addition to that, there are further icosahedra between every two triangles of the Kagomé net.

2.2.3. *Stability*

Experimental investigations show that β-B is the modification of boron which is thermodynamically stable at high temperatures.[2] α-B can only be synthesized at comparatively low temperatures.[66] At temperatures above 1500 K, α-B is reported to transform into β-B; as discussed in Section 2.2.1, this is not necessarily a direct transformation, but might occur via metastable intermediate phases.

Van Setten et al. reported in a recent paper[70] that even the ground states of α-B and β-B have not yet been described with any degree of certainty, and the determination of the relative stability of α-B and β-B has been attempted for the past 30 years. Theoretical work undertaken by Jemmis et al. in 2005, however, suggested that α-B is more stable than β-B, which has 105 atoms in the rhombohedral unit cell.[104] β-B with 105 atoms per unit cell is expected to be a metallic conductor, which is in contradiction to experimental observations. However, as explained above, β-B not only has 105 atoms but additional electron density on positions that were partially occupied by boron atoms. Jemmis et al. showed that β-B with its experimentally derived 106.66 boron atoms per rhombohedral unit cell should be an electron-precise substance; this finding is in accordance with the experimental results of Werheit,[94] who suggested that intrinsic structural defects lead to a 0.19 eV split-valence band. The valence band can contain up to 320 electrons. If there were 105 atoms in the unit cell, only 315 electrons would be present. The additional interstitial positions, repeatedly found in experimental investigations, are thus necessary to stabilize the modification through five additional electrons. According to recent theoretical calculations by Masago et al., α-B is the stable form at low temperatures (0 K), which should transform to β-B at 970 K.[74] On the other hand, van Setten et al. have recently calculated a lower ground-state energy for a slightly distorted variant of β-B.[70] They used a first-principles method (density functional theory with generalized gradient approximation) to compare several β-B variants with interstitial atoms and partially occupied sites. The property values they calculated, such as electronic band gap (1.4 eV with a hole trap of 0.35 eV above the valence band), bulk modulus, and lattice vibrations, agreed well with the experimental data. These investigations lead to the conclusion that it is essential to include the zero-point energies in the calculation of the stability of boron modifications, and that only if zero-point energies are taken into account will it be possible to prove that β-B (in a slightly distorted, triclinic form stabilized by partially occupied sites and defects, and with 106 boron atoms per unit cell) should be more stable than α-B by 3 eV. Without these zero-point energies and the partial occupancy, α-B appears as the more stable modification by 1 eV.

Quite recently, another DFT-based calculation was published that predicts a "broken symmetry" structure for the ground state of β-B, with a stable arrangement of fully occupied and fully unoccupied sites in the triclinic space group *P*1.[105] In another new theoretical study on the stability of β-B, Ogitsu et al. confirm the stabilizing effect of a "macroscopic" amount of intrinsic defects and the presence of additional electronic states within the band gap, similar to a self-doping semiconductor.[106] As in earlier studies, these defects continue to be discussed as partially occupied sites. The element boron is called a "frustrated element", a system similar to ice or spin-ice compounds, which contain macroscopic residual entropy. The general underoccupancy of the B13 position, which leads to a B_{27} instead of a B_{28} unit, as described above, was confirmed.

2.3. *Tetragonal Boron I and II (t-I, t-II)*

2.3.1. *Synthesis and Controversy as to Their Existence*

The synthesis and structure of tetragonal boron I (t-I, also referred to as α-tetragonal boron) were described in 1943, 1951, and again in 1958.[107–109] Tetragonal boron I was considered the first known crystal structure of a boron allotrope. Twenty years later, Amberger and Ploog[110] published experimental results that showed that by reducing boron tribromide with hydrogen at 1200–1600 K on a tantalum wire, only α-B and t-II were obtained, never t-I. When the reproducible synthesis of the two binary compounds $B_{48}B_2C_2$ ($=B_{50}C_2$) and $B_{48}B_2N_2$ by pyrolysis of BBr_3/CH_4/H_2 mixtures on tantalum substrates at 1470 K and BBr_3/N_2/H_2 mixtures on BN substrates at 1670 K was proved (which both crystallize with the structure of t-I),[111] suspicion grew that no pure boron modification with this structure exists. Since that time, apart from α- and β-rhombohedral boron, the only modification of boron that is accepted as a crystalline normal-pressure modification of boron is tetragonal boron II (t-II, T-190, T-192, or β-tetragonal boron). Theoretical calculations also show that B_{50} is not stable.[23,112] Black crystals (red in transmission) of t-II were obtained by reduction of BBr_3 with H_2 on tantalum and rhenium wires at 1470–1520 K; they have a density of 2.36 $g\,cm^{-3}$.[1,110] t-II is also said to have been synthesized by sprinkling finely crushed boron into an argon plasma.[113] Since it has not been possible to reproduce the synthesis of t-II in the form of single crystals and hence its structure determination since 1978, slight doubts about the existence of this modification are justified. According to theoretical calculations, there might be a range over which t-II exists: Hayami and Otani recently published DFT studies on t-I[93] and t-II[114] which suggested that t-I and t-II can be more stable than α-B and β-B if the surface energy is taken into account in the calculations. According to this, small particles with 216 to 512 atoms would be expected to preferentially crystallize in the t-II structure.

It is interesting to note that references to t-I have recently started to appear again in the literature: nanocones,[42] nanowires,[43] and nanobelts[44] of boron are said to have

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been synthesized with the structure of t-I, with the nanowires even having unexpected photoemission and electric transport properties. However, suspicion exists that under the synthetic conditions chosen (for example, CVD, ion bombardment), the inclusion of impurity atoms cannot be excluded, so that one would have to speak of $B_{50}N_2$ or $B_{50}C_2$ nanomaterials. The EEL spectrum of a nanowire shown in Ref. [42], which is claimed to consist of tetragonal boron, undoubtedly displays the inclusion of carbon.

2.3.2. Crystal Structures

The structure of t-I (space group $P4_2/nnm$, no. 134) displays an icosahedral framework. According to the original study there are 50 boron atoms in each unit cell which are distributed among four icosahedra and two interstitial positions. The revised structures[111,115,116] show that impurity atoms occupy the two isolated boron atom positions, and the structure was described in several different space groups ($P\bar{4}n2$, $P4/mnm$, $P4_2/mnm$, or $P4nm$). Furthermore, partially occupied boron atom positions were introduced with two boron atoms per unit cell, thus resulting in the formulas $(B_{12})_4B_2C_2 = B_{50}C_2$ or $(B_{12})_4B_2N_2 = B_{50}N_2$. These phases were later given the formulas $B_{48}C_2 = B_{24}C$ and $B_{48}N_2 = B_{24}N$, respectively,[3,20] which is not supported by any convincing experimental evidence. The question of the real composition and structure of the phase earlier named boron modification I can still not be answered.

Tetragonal boron II possibly crystallizes in one of the space groups $P4_1$ or $P4_3$ with four formula units to the cell, but other space groups have also been suggested. The structure was described in 1979 on the basis of single-crystal structure data as consisting of B_{21}, B_{12} (2 ×), and $B_{2.5}$ units (Figure 4) with 190 atoms in the unit cell.[117,118] Three of the 49 sites were partially occupied, thereby resulting in 189.5 atoms per unit cell. The real composition, particularly of the the B_{21} units, is uncertain, since the vibrational parameters given in the original publication differ by about a factor of five, which makes further partial occupancies possible. According to Donohue, there should be 192 atoms in the unit cell,[1] which is why this phase is sometimes called T-192 in the literature. Vlasse et al. called this modification related to α-AlB_{12}, a compound that will be discussed in Section 4.5.

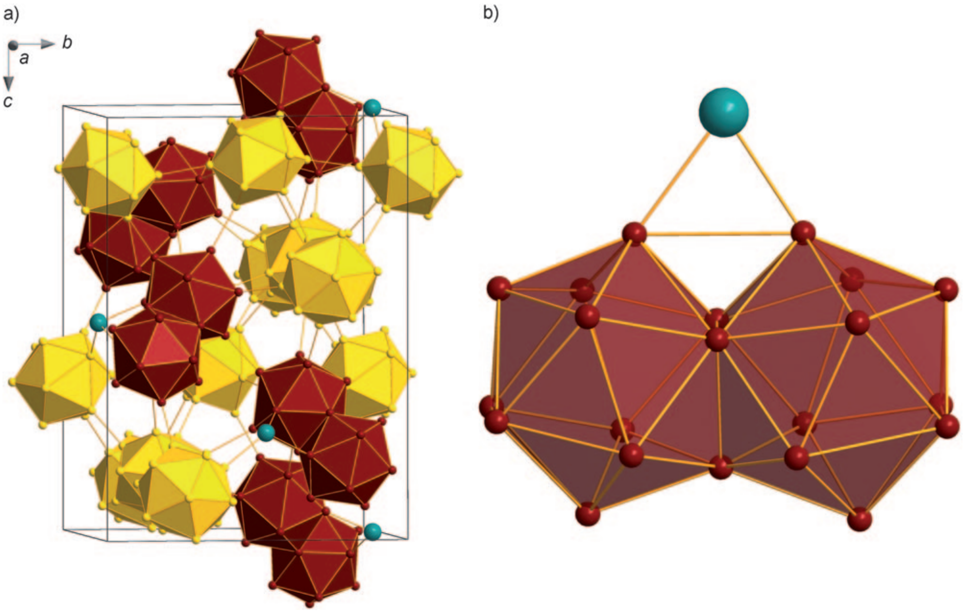

Figure 4. t-II structure type: a) unit cell, b) B_{20} unit.

2.4. Boron under High Pressure: "Ionic" γ-B_{28}

Oganov et al. recently published a structural prediction for a new phase which they obtained from β-B under a pressure of about 20 GPa and 2000 K and were able to characterize by X-ray powder diffractometry and infrared spectroscopy.[4a,b] They called this phase γ-B_{28}. It is possible that this phase was obtained earlier by Wentorf in 1965.[122] It was described independently by Zarechnaya et al.[5a,b] Zarechnaya et al. have since confirmed the crystal structure on the basis of single-crystal data. The band gap of γ-B_{28} is 1.5 eV at normal pressure and changes little up to 200 GPa (1.25 eV). Its crystal structure is similar to that of α-B, with B_2 dumbbells filling gaps each made from six icosahedra. If α-B is viewed as a variant of a cubic close packed arrangement of icosahedra, and the gaps occupied by B_2 dumbbells as octahedron gaps, one can talk of the sodium chloride structural type (Figure 5). The B–B distance within the dumbbell is 173 pm, which is comparable to that in molecular B_2Cl_4. Naming this as a boron boride with $(B_2)^{\delta+}(B_{12})^{\delta-}$ led to its description as "ionic boron".[4a] The calculated positive charge on the B_2 unit varies from +0.2 to +2.2, with the authors favoring values from 0.34 to 0.48 (from Bader theory). The characteristic absorption bands found in the experimental and calculated infrared spectra were taken as proof of charge transfer. Such absorption can be caused by the fact that optical (ε_∞) and static (ε_0) dielectric constants are different in substances with ionic bonds, which leads to a LO-TO splitting (LO-TO = longitudinal and transversal optical phonones). The proportion of ε_0 to ε_∞ is a measure of the ionicity of a compound, and was calculated as 1.16 for γ-B_{28}. For comparison, the authors also calculated values for α-B (1.01) and gallium arsenide, but the value they obtained for GaAs differs by about 5 % from other data.[119] The "ionicity" of the compound is called into doubt in Ref. [5a]; Oganov et al. have now published an addendum in which they describe the bonding situation in γ-B_{28} as being on the whole covalent.[4c]

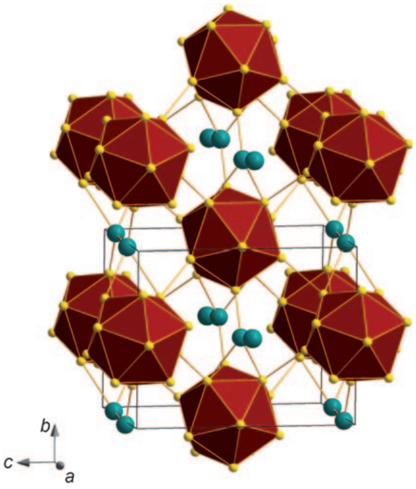

Figure 5. Arrangement of icosahedra and B_2 pairs in γ-B_{28}.

It should be mentioned that the discussion of partially ionic entities in elemental boron is not completely new. Werheit calculated LO-TO splittings, as described above, also for β-B,[120] and Jemmis et al. rationalized the bonding in and stabilization of β-B as early as 2001 by applying their *mno* rule. They reduced the structure to fragments, namely B_{57} clusters with an excess of electrons and B_{12} clusters with an electron deficiency.[121]

Alternatively, the structure of γ-B can be described as a tetragonal body-centered packing of columns. In this case, the icosahedra exhibit short exohedral contacts (165.9 pm), which results in chains parallel to the *a* axis. Each chain is surrounded by four more chains, with the centers of the icosahedra being displaced from each other by half the diameter of an icosahedron, similar to the structure of t-I. This arrangement results in each icosahedron forming eight more exohedral bonds, which are significantly longer (182.6 pm). The boron atom in the B_2 units in the octahedral voids forms bonds with three boron atoms of the icosahedron: a short one (166.8 pm) and two longer ones (192.7 pm) directed towards an icosahedron of a neighboring chain (in the [010] direction). Thus, 16 bonds result for each icosahedron: two plus eight within the packing of columns (chain) and two plus four to the B_2 unit. Such a packing of boron atoms appears to be quite efficient and explains the high density of 2.54 $\mathrm{g\,cm^{-3}}$.

The history of the discovery of this high-pressure modification is symptomatic of the challenges posed by elemental boron to experimenters and theoreticians. Although described as early as in 1965, the powder diagram of γ-B initially proved not to be indexable. Only with modern methods of structure prediction and analysis has it been possible to develop a structural model. Even the most up-to-date theoretical methods result in two quite different interpretations of the bonding situation. One indicates a significant separation of charges between the B_{12} icosahedron and the B_2 dumbbell, while the other emphasizes the covalent character of the arrangement.

3. The Chemistry of Boron-Rich Borides

3.1. Synthesis

Boron-rich borides are obtained by the direct solid-state reaction of the pure elements at high temperatures, or by means of metal-melt conversion.

Since boron only melts at very high temperatures and solid-state reactions, according to Tammann, only reach significant reaction rates at 2/3 to 4/5 of the melting point,[123,124] direct conversion has numerous disadvantages. One problem is posed by the material of the crucible, since many of the substances in use react with the starting materials and lead to undesired by-products or to the incorporation of foreign atoms into the product. Tantalum, for example, which is used in the direct conversion of sodium and boron according to Equation (1)

$$2\,\mathrm{Na} + 29\,\mathrm{B} \rightarrow \mathrm{Na_2B_{29}} \qquad (1)$$

produces undesired tantalum borides at reaction temperatures of around 1250 K. It is for this reason that such crucibles must be converted with excess boron (which is discarded afterwards) in a preliminary step, so as to line the inner surface with an inert, dense layer of tantalum boride. It is also essential that at high temperatures special attention be paid to ensure that the conversion takes place in a controlled atmosphere. Even minimal amounts of oxygen, nitrogen, hydrogen, or carbon from the air will be inserted into boron, which is easily oxidized and can be used as a highly active "getter" substance (similarly to aluminum in sputtering). To avoid this, samples for the conversion of alkali or alkaline-earth metals and boron are prepared in an evacuable, heatable all-glass apparatus under argon which has been passed through phosphorus pentoxide, molecular sieves, blue gel, and titanium sponge ($T = 950$ K). The reactions take place in welded metal tubes and crucibles, the latter are melted into evacuated quartz glass ampoules and heated in conventional tube furnaces or placed in appropriate water-cooled quartz glass reactors for high-frequency heating in induction coils. Prior to reaction, the metals are segregated, distilled, or dissolved in ammonia, and cleaned of any possible impurities in a sintered glass crucible. Impurities in the starting boron material can also be responsible for products not being obtained a in pure phase.

However, perhaps the worst disadvantage of direct conversion into borides is that at the necessarily very high reaction temperatures none of the compounds that disintegrate at those temperatures can be synthesized. On the other hand, the formation of compounds which are stable at high temperatures may be kinetically inhibited because sufficiently high temperatures cannot be reached. Finally, the formation of single crystals is rendered difficult by solid-state reactions.

Of the borides of main group elements, all those that have been synthesized at high temperatures are sensitive to oxygen and water, and unstable in the presence of acids or bases, and thus cannot be further purified after synthesis. Lithium, sodium, and potassium carbaborides, boride carbides, and borides were synthesized in welded, pretreated metal ampoules (tantalum, niobium, molybdenum) which were in turn placed in evacuated quartz ampoules.[125] Such alkali-metal compounds can be cleaned of excess metal by washing in liquid ammonia. If the alkali metal is removed by distillation, a deintercalation or even deterioration of the compound is possible; for example, Na_3B_{20} is transformed into Na_2B_{29}, which has a lower sodium content.[126] It was shown for LiB_{10} that the lithium content and the boron atom arrangement depended on the reaction conditions.[127]

Aluminum, copper, gallium, tin, and also mixtures of these metals (Cu/Mg, Al/Mg, Li/Sn, Li/Ga) have been found to be particularly suitable for the synthesis of borides[129–131] in metal melts (auxiliary metal-bath technique[128]), but metals such as palladium have also occasionally been used.[132] Lower reaction temperatures may be used than in direct conversion, so that another area of the phase diagram becomes accessible. Products are usually more homogeneous since this is a reaction "in solution", or at least a conversion brought about by liquids. It is even possible to recrystallize borides in molten aluminum, a practice which has been used for hexaborides.[133–135] Even though the solubility of boron is very limited in the metals mentioned, the metal can at least serve as a flux or mineralizer.

The disadvantage of conversion in molten metal is that this, too, takes part in the reaction and may be incorporated, so that after reaction it may have to be separated from the product by being dissolved in acids or bases. Despite this, this synthesis route has proved itself: $Li_2B_{12}C_2$, MgB_{12}, $Li_2B_{12}Si_2$, $MgB_{12}Si_2$, and $MgB_{12}C_2$ are some examples of single-phase, highly pure, single-crystal boron compounds which have recently been obtained in this way.[136–140]

There have been occasional reports of the use of chemical transport reactions and chemical vapor deposition (CVD) techniques to synthesize boron and borides.[141] These methods, however, have not so far proved themselves for boron-rich compounds to the extent that it seems necessary to discuss them here in detail. Neither has the reductive conversion of oxides into borides been found to be useful in the quest for a pure-phase product.

3.2. Characterization and Analysis

Since boron-rich borides are practically insoluble, their analysis poses a problem. Preparing samples by means of decomposition can lead to spontaneous combustion, since this is carried out with strongly oxidizing acids; it can also produce volatile boron compounds. Analysis by inductive coupled plasma optical emission spectroscopy (ICP-OES), therefore, requires specialized techniques to ensure a good recovery rate and reproduceable results. The example of the alkaline-earth hexaborides has shown that quite a precise determination of the composition of boron-rich borides is possible.[142] Energy- and wavelength-dispersive X-ray spectroscopy (EDS, WDS) have also been employed[136–140, 143] to quantify the components of borides. Careful handling and preparation of the samples as well as the employment of suitable, well-defined standards are essential. The great hardness of borides means that the preparation of samples with a plane, ground surface is a challenge that must not be underestimated. The standard compounds which are drawn upon for comparison often have to be synthesized by the researchers themselves, since commercial borides seldom have the composition and purity that are required. This holds also for the standards used in X-ray absorption spectroscopy (EXAFS, XANES), which has also been employed to obtain a more detailed characterization of borides. This method is rarely used on main group element compounds of boron (for example, CaB_6[144]), but there have been initial experiments with iron and nickel borides.[145] One of the most valuable methods for characterizing and analyzing substances containing boron is EELS. This method has in the past been used to examine borates and in exceptional cases to analyze elemental boron, boron carbides, and boron oxides.[146, 147] However, more recently the studies of Hofmann et al. have not only shown its great potential for the identification and quality control of boron and borides, but have also allowed structural determination through fine-edge analysis and the theoretical calculation[148, 149] of spectra at the DFT level.[150–152] Figure 6 shows the significant variation of the experimental ELNES (energy loss near edge structure) of B_K ionization edges in highly resolved EEL spectra of boron and borides. Some initial results with CaB_2C_2 and BeB_2C_2 show that the disadvantages of diffractive methods in light-element compounds can be offset by this complementary spectroscopic method.[151, 152] Diffraction methods, especially X-ray structure analysis,

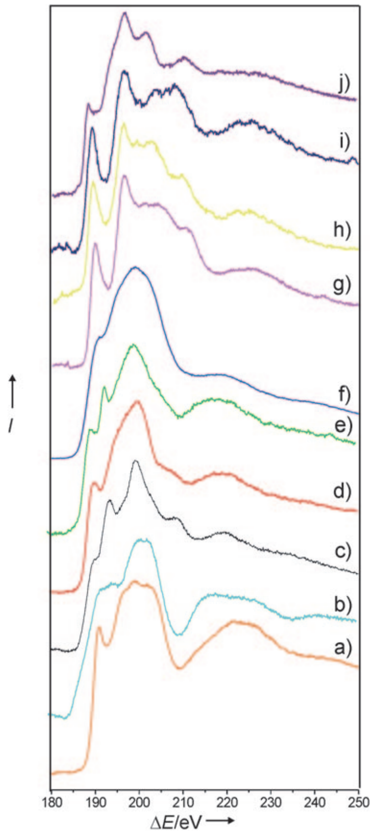

Figure 6. Fine-edge structures in EEL spectra: B_K ionization edge of different borides: a) TaB_2, b) UB_{12}, c) CaB_6, d) KB_5C, e) Na_3B_{20}, f) Na_2B_{29}, g) BeB_2C_2, h) LiBC, i) MgB_2C_2, j) CaB_2C_2.

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have the disadvantage that contaminations and by-products in small amounts cannot be observed, and that, secondly, the electron density of boron atoms—particularly in partially occupied positions or in the presence of heavy elements—is not significant enough to allow a positive localization of the atoms. In addition to that, as has already been mentioned, it is not always possible to grow boride single crystals, so that the limited information that can be derived from a powder diffractogram is the only basis for the determination and refinement of the crystal structure. Whereas powder data may provide a sufficient basis for statements about structure, they usually preclude the refinement of the anisotropic components of the displacement parameters and the occupancy factors of partially occupied sites, so that any results gained this way should not be overinterpreted.

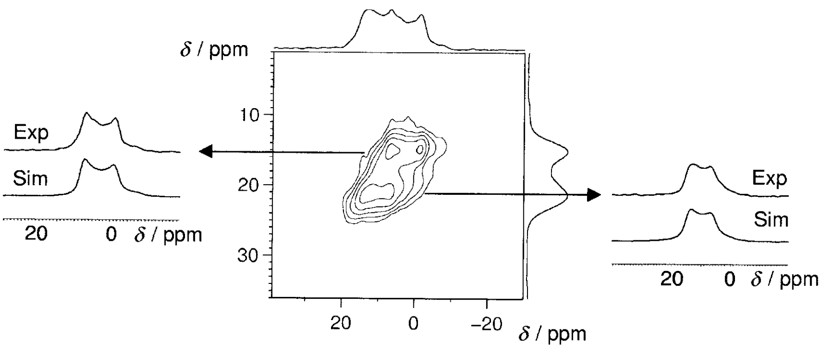

Figure 8. Two-dimensional solid-state NMR spectra of Na_2B_{29} (from Ref. [153]).

Neutron diffraction data are well suited, since the scattering length of boron is greater in neutron radiation than in X-rays. The atoms of ^{11}B, which have a scattering length of 0.60×10^{-12} cm, contribute more to the diffraction image than, for example, sodium (scattering length 0.363×10^{-12} cm). On the other hand, neutron diffraction experiments are rendered difficult by the fact that synthesis has to be carried out with isotopically pure boron, since ^{10}B has a very high absorption coefficient and boron is activated by neutrons. Electron diffraction has also been used to support or refute controversial statements with respect to the symmetry of borides. In some cases this method has supplied very convincing evidence.

The electron microscope can be used with EELS, EDS, and diffraction as described above, but the pictures obtained in the imaging mode of a high-resolution transmission electron microscope are among the most impressive experimental results. When images of structural models can be simulated and a defocus series of pictures taken at different apertures agrees with the images observed (Figure 7), this is a significant indication that a structural model is correct.[153] Errors in the determination of symmetry and composition become immediately evident.

Finally, solid-state NMR spectroscopy has also been employed occasionally to investigate borides. The structural determination of Na_2B_{29} by means of ^{23}Na-triple quantum MAS NMR has shown that the sodium atoms are situated at two crystallographically independent sites (Figure 8), which refutes a structural model published earlier.[153] Boron nuclei can also be studied by NMR spectroscopy; however, the spectra are difficult to interpret because of the broadness of the signals and the complex superimposition of multiple signals in a boron-rich solid. On the other hand, solid-state NMR not only offers special possibilities to understand special features of boron-rich solids, but also to compare the observed spectra (chemical shift, coupling pattern) with the results of calculations. The study of on boron carbide by Vast et al.[154] is a recent example.

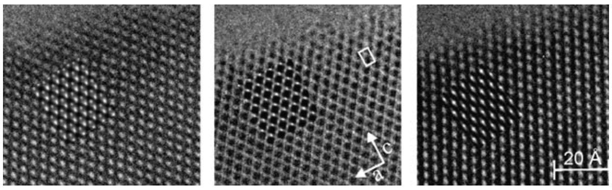

Figure 7. High-resolution TEM images of Na_2B_{29} at different values of defocus ($\varepsilon = -650$, -800, -1020 Å). Projection along [010]; contrast simulations are inserted, the unit cell is indicated with white lines. The crystal thickness along [010] is 6.23 nm.[153]

3.3. Properties and Applications

Boron-rich borides are classical refractory materials: lightweight, very hard, and thermically exceptionally stable.[54–56] Boron-rich compounds are known with various electrically insulating, semiconducting, semimetallic, metallic, and even supraconducting properties—even ionic concuctivity has been observed in borides; examples of all these will be given below. Good electrical conductivity in combination with poor thermal conductivity could produce good thermoelectrical properties in borides with complex covalent boron atom structures, which are believed to be particularly attractive under high temperatures because of the excellent thermal stability of many boron compounds.[155]

The interesting physical properties of boron compounds are melting point, hardness, electrical conductivity, thermal conductivity, and Seebeck coefficients. It should be pointed out, however, that all these values are subject to much variation, depending on their source; this is due to the difficulties associated with the synthesis of boron and borides, and also to the problem of compacting nonmelting powders of very hard particles in such a way that realistic contact and measurement of transport properties becomes possible. Werheit et al. have shown the negative influence of a boron suboxide layer on the thermoelectric properties of boron-rich compounds.[156] Recently, Mori et al. demonstrated the dependence of thermoelectric properties on the porosity of the sintered compact.[157a] Similar observations were made for

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classical thermoelectrics, such as the antimonides of the transition metals.[157b]

The structural complexity of boron-rich borides offers many opportunities to dope or substitute them, thus influencing the electrical properties. Borides of the rare-earth metals have been shown to become either p- or n-type semiconductors (see Ref. [158]).

The large capture cross-section of ^{10}B for thermal neutrons has already been mentioned. In addition to its well-established use as an absorbent of neutrons in reactor technology (^{10}B-enriched concrete), it has been shown that a ^{10}B-enriched boron carbide can be used in neutron detectors.[83] When it decomposes to ^{7}Li and ^{4}He, the material is heated at one side of the detector. The high Seebeck coefficient of boron carbide allows the resulting voltage to be used to detect the signal.

4. Structural Motifs: From Element to Compound

4.1. General Observations

In many cases structures that are observed for boron-rich compounds are well-known from the discussion of the elemental modifications—existing or hypothetical ones.

Metals, but also carbon, silicon, germanium, nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium are incorporated into α-B and β-B. Numerous metal borides are formed that exhibit β-B structures, while transition elements, as well as boron subcarbides, -oxides etc. give α-B structures. Equally well-known are compounds with t-I and t-II structures. We also know many boron-rich compounds without an explicitly crystallographic relationship to elemental boron structures but which still contain very similar structural units (for example, icosahedra). Finally, other linked polyhedra besides icosahedra are found—again well-known, this time from the molecular chemistry of boron (hydrogen and halogen chemistry)—and then there is the disintegration of the three-dimensionality of the boron atom arrangement: strictly speaking, compounds with layers of condensed rings, boron atom chains, and single boron atoms do not belong to the group of boron-rich compounds, but examples will be discussed to round off the picture of the solid-state chemistry of boron compounds with main group elements.

4.2. Boron Compounds Related to the α-B Structure: $B_{13}C_2$, α-SiB_3, $B_{13}N_2$, B_6P, B_6As, B_6O, $B_{12}S$, $B_{13}Se$, Ternary Comounds

At high temperatures, boron reacts with carbon, silicon, nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium to form a boron carbide, silicide, nitride, phosphide, arsenide, oxide, sulfide, and selenide with a structure derived from α-B. An overwiew of the compounds characterized so far is given in Table 2.

These compounds crystallize in the space group $R\bar{3}m$ (no. 166). The B_{12} icosahedra are situated on the corners of a rhombohedron as in α-B (two 18 h sites in hexagonal arrangement), one can speak of the layers ABC being stacked vertically to the spatial diagonal. The non-boron atoms are located on the spatial diagonal of the rhombohedron and link three icosahedra each of one layer (6c site). At the center of the rhombohedral unit cell, that is, between the two non-boron atoms on the spatial diagonal in the pseudooctahedral gap between six icosahedra, there is a 3b site which can be occupied by a further boron atom. The 2e3c bonds in α-B are thus replaced by 2e2c bonds to non-boron atoms, which lead to a significant reduction of the c/a ratio.

Boron carbide is by far the most important and most investigated representative of this structural family. It has been known since 1864, and is synthesized industrially in tonne quantities. The ESK company, for example, uses entire tree-trunks as poking rods (and also as a source of carbon), which are placed in a arc several meters in length, together with large amounts of boron.[176]

It is well known that boron carbides can have various compositions with a carbon content between 10 and 20%. Uncertainties as to the precise determination of the carbon

Table 2: Overview of borides related to α-B.

	a [pm]	*c* [pm]	*c/a*	Structural units	Powder/single crystal	Ref.
α-B	490.75(9)	1255.9(3)	2.559	B_{12}	s.c.	[69,159]
$B_{13}C_2$	561.7(1)	1209.9(4)	2.154	B_{12}, CBC	s.c.	[160]
"B_4C"	560.33(8)	1207.5(2)	2.155	$B_{11}C$, CBC	s.c.	[161]
$B_{10.2}Si_{3.8}$	630.8(1)	1272.9(3)	2.018	$B_{10.2}Si_{1.8}$, Si_2	s.c.	[162]
$B_{12}N_2$	545.7(7)	1224(2)	2.234	B_{12}, N_2	p	[163]
$B_{13}N_2$	544.55(2)	1226.49(9)	2.252	B_{12}, NBN	p	[164]
$B_{12}P_2$	597.71(7)	1185.4(2)	1.983	B_{12}, P_2	s.c.	[165]
$B_{12}P_2$	600.0(4)	1185.7(8)	1.976	B_{12}, P_2	s.c.	[166]
$B_{12}P_{2-x}B_x$	596.78(4)	1180.79(7)	1.981	B_{12}, $P_{1.36}B_{0.64}$	s.c.	[167]
$B_{12}As_{2-x}$	613.88(4)	1197.07(7)	1.950	B_{12}, $As_{1.76}B_{0.24}$, or $As_{1.8}$	s.c.	[168]
$B_{12}As_2$	614.9(2)	1191.4(3)	1.938	B_{12}, As_2	s.c.	[169]
$B_{12}O_{2-x}$	538.24(4)	1232.2(1)	2.289	B_{12},O	p	[170]
$B_{12}O_2$	539.02(1)	1221.25(2)	2.284	B_{12}, O	p	[171]
$B_{12}S$	580	1190	2.05	B_{12}, BS	p	[172]
$B_{12}Se_{2-x}B_x$	590.41(4)	1194.7(1)	2.023	B_{12}, $Se_{2-x}B_x$ ($x=1.06$)	p	[173]
$Al_{2x}B_{13-x}C_2$	565.61(8)	1244.2 (2)	2.200	B_{12}, CBC/2 Al	s.c.	[143,174]
$Li_{0.25}B_{13}C_2$	561.5(2)	1225.6(5)	2.183	B_{12}, CBC, Li	s.c.	[165,175]

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content may be ascribed to their direct synthesis from the elements at high temperatures as well as to the chemical stability of the bonds and the elements involved. Investigations in to the stability range have found a maximum melting point at 2450 °C for a carbon content of about 18.5 %.[177]

At high reaction temperatures and fast cooling rates, an increasing number of defects (vacancies, mixed occupation) and occupation of interstitial sites is to be expected. The synthesis of defined samples is of special importance in the analysis of the physical properties of boron carbides. When examining the distribution of C atoms in powder samples and single crystals thus obtained, partially contradictory results are sometimes encountered, especially when trying to derive structural details from measurements of conductivity or from spectroscopic data.

The basic structural principle of the boron carbide crystal structure was recognized by Matkovich.[172] This ideal description results in a C-B-C chain perpendicular to the direction of the stack of the layers between triangles of icosahedra of neighboring layers.

Similar to α-B, single crystals of boron carbide can be grown in a metal flux. Synthesizing single crystals in copper melts has enabled carbon-rich single crystals to be obtained, which have been assigned the formula "$B_{13}C_2$". These investigations suggest[161] that the icosahedra are connected through ordered C-B-C chains and that icosahedra have a polar position that is occupied with carbon to 1/6. Thus, a composition results that can be described formally as electron-precise ($B_{11}C$)(CBC). Apart from C-B-C chains, C-B-B chains also occur at site disorder. The dominance of $B_{11}C$ icosahedra in carbon-rich phases was confirmed by NMR studies and theoretical calculations.[154]

The existence of the boron-rich phase of composition $B_{13}C_2$ (that is, B_{12}CBC) is well substantiated. Boron-rich single crystals were obtained by pyrolysis of BI_3 and CI_4 at 1000 °C on a tantalum wire. Conventional refinement substantiates the description of B_{12} icosahedra linked via ordered C-B-C units.[160] This was confirmed by Kirfel et al. by multipole refinement based on high-angle data.[178] Multipole refinement also gives indications about the effective charge of atoms: According to this, the boron atoms of the icosahedron are nearly neutral, whereas the boron atom of the C-B-C unit is positively charged (+0.5) and the C atoms have a slightly negative charge (−0.25).

In accordance with the large width of the phase and the relatively slight differences between boron and carbon atoms in the diffraction diagram, the two crystal structures have to be seen as snapshots in an idealized arrangement. It is surely no coincidence that these structural models were generated from data of single crystals which were grown at relatively low temperatures (metal melt and gas-phase generation, respectively). There are considerable uncertainties and contradictions with respect to phases obtained from high-temperature synthesis. Apart from the question as to what extent positions within icosahedra can be occupied by carbon atoms instead of boron atoms, this particularly concerns the constitution of the three-atom units between the icosahedra. The most complete crystal-structure analysis of $B_{13}C_2$ was done by Kwai and Morosin,[179,180] who performed neutron diffraction experiments on samples with different proportions of carbon. They found that crystalline powders obtained at high temperatures have up to 25 % non-occupation of the central B/C position in the center of the chain. Werheit et al. produced infrared and raman-spectroscopic images of the phonone spectra of α-B and compounds derived from it. To this end they studied samples obtained by solid-state reactions at high temperatures. They assert that the ionicity of the bonds is sufficient for absorption in single phonone processes and analyzed the lattice vibrations in detail.[181–184] More importantly, their analysis of the spectra provides quantitative results of the proportions of the various structural units in boron carbide, depending on the composition. A sample of composition $B_{4.3}C$ 100 % $B_{11}C$ versus 0 % B_{12}, for example, 81 % CBC versus 19 % CBB and 0 % B□B, whereas $B_{13}C_2$ contains 58 % $B_{11}C$ versus 42 % B_{12} besides 62 % CBC versus 19 % CBB and 19 % B□B.[185]

The model of charge transport in boron carbide has been the subject of discussion for many years. Emin has formulated the theory that bipolarones, that is, pairs of "singlet holes" resulting from electron deficiency in valence bands, are responsible for the charge transport and account for the observed low spin density (by measuring the magnetic susceptibility or ESR).[83] Werheit rejects this theory on the grounds that it is based on a non-existent, idealized crystal structure without structural defects[185] Instead, he suggests that the experimental observations—for example, the band structure obtained by optical spectroscopy and electric conductivity at high temperatures—could well be explained by the assumption that a high density of structural, intrinsic defects compensates for electron deficiency in the valence band by generating dislocated valency states in the band gap. Hoffmann and co-workers[186] propose a similar interpretation.

There are also indications of ternary compounds of main group elements derived from boron carbide. In 1970, for example, a boron carbide containing aluminum was described[187] in which aluminum atoms replace some of the CBC units. A recent examination of single crystals[143,174] was able to show that the aluminum atoms at the 18h positions only replace boron atoms. The C atoms are slightly displaced in the *z* direction so that the covalent bonding structure is maintained.

The incorporation of lithium in boron carbide has also recently been detected.[165,175] Lithium atoms partially occupied a 6h position above and below the CBC unit in the practically colorless $Li_{0.25}B_{13}C_2$. The lithium incorporation was detected by means of EELS.

Silicium borides are of particular significance because of their interesting material characteristics. They are stable in air above 1270 K, have very low thermal extension, and high chemical stability, for example, to HF/HNO_3. They are binary marginal phases of the important Si/B/C/N and Si/B/N systems, of which numerous amorphous high-performance ceramics have been synthesized (examples in Ref. [206,207]). Silicon atoms can be incorporated into boron atom icosahedra, as has been shown for $SiB_{2.6}$ and SiB_6[208] as well as ternary boron silicides (for example, $YB_{41}Si_{1.2}$[209]). A phase analogous to α-B has been know for over a hundred years in the binary system B/Si,[203] but proposals as to its composition vary considerably ($SiB_{2.5}$ to SiB_4). The extremely high chemical and thermal stability of the silicon borides makes analytical characterization difficult.[204] There has long been no doubt,[205] however, that the structure is based on α-B with a Si_2 group, and that the high silicon content and the relatively large lattice parameters are due to partial incorporation of silicon atoms into the polar position of the icosahedron.

In the case of boron-rich oxide, an arrangement of two O atoms between three icosahedra (the oxygen atoms sit on the spatial diagonal of the rhombohedral unit cell) leads to the composition B_6O ($=B_{12}O_2$). The OO distance was determined as 306–308 pm, and the shortest distance between an oxygen atom and the icosahedra 143 pm. Olofsson and Lundstrom report an underoccupancy of the 6c site, and give an OO distance of 300.4 pm and short OB distances of 147.6 pm.[170] This substance and its structure (determined from powder X-ray diffraction data) have also been known for a long time. Synthesis can be achieved by, for example, the solid-state reaction of boron and B_2O_3, but also with metal oxides such as ZnO. B_6O was reexamined and described in 1998: orange-red, very hard crystals of a very nice icosahedral habit and substantial size (20 μm) were obtained under pressure (1470–2070 K, 2–10 GPa).[188] The microhardness of B_6O was given as 38 GP and the band gap is believed to be 2 eV.[189–191] Electron and X-ray diffraction studies confirmed older investigations, and the scanning electron microscopy images of the crystals show the turned-in corners of an icosahedrally twinned crystal which is said to consist of 20 individual twins. According to EELS examinations, the composition should be described as B_6O_x ($0.86 < x < 0.96$).[163,192] There is special interest in B_6O, since it is the hardest of the boron-rich borides. Its hardness confirms expectations concerning short covalent bonds, which are believed to favor hardness.[193,194]

It should be pointed out that B_6O is probably one of the most frequently overlooked contaminations in boron and borides. The high affinity of boron for oxygen means it is easily formed and, because of its structure, it is often mistaken for elemental boron or a boron-rich compound; since oxygen is difficult to observe or to exclude in analysis, it is often overlooked, and because of its high chemical, mechanical, and thermal resistance, oxygen is—once it is present—hard to get rid of. It has to be assumed that many of the published values meant to quantify the physical properties of known compounds are inaccurate because of the presence of B_6O. The adverse influence of B_6O layers on the thermoelectric properties of boron were discussed earlier on.

One of the studies of B_6O cited earlier also reports the EELS characterization of $B_{13}N_2$.[192] Kurakevych and Solozhenko reject the idea that the phase described in this study is the said subnitride[195] since the ionization edge in the EEL spectrum does indeed look different from that of boron carbide or boron suboxide. The authors have since published a new structural refinement of $B_{13}N_2$.[164,196] They obtained a crystalline powder at high pressure (5 GPa, 2400 K) and determined the structure in the presence of five[195] and three[164] other phases by means of Rietveld refinement. The fitting of a diffractogram that takes into account the reflexes of several different phases—the identity and structure of at least two of which are as yet uncertain—is of course beset with problems. The structure shows N-B-N chains (N in 6c position, B in 3b position, fully occupied) with an N−B distance of 154 pm, which is comparable to distances in cubic BN (156.6 pm as opposed to 144.6 in hexagonal BN). The shortest distance between the nitrogen atoms and the three neighboring icosahedra is 152 pm, which seems reasonable compared with 147.6 pm for O−B in B_6O and 160 pm for C−B in $B_{13}C_2$. The only problem is that the intra-icosahedral distance of 151.4 pm in $B_{13}N_2$ is too short; this suggests that the synthesis of pure phase samples should be targeted to support the result. At this point a possible comparison with nitride borates such as $Ca_3(BN_2)_2$ and $Ca_3(BN_2)N$[197,198] should be noted, but will not be discussed further.

Colorless as well as—more often—bluish black samples are described for $B_{12}P_2$. The crystal structure always shows B_{12} icosahedra and linking P_2 units (Figure 9). Since the P−P distance of about 223 pm corresponds to a single bond, an electronically precise formulation and a large band distance seem likely, so that colorless, transparent crystals would appear plausible. They are formed in the process of treating the elements in nickel melts.[165,199] Characterization gives a fully occupied phosphorus atom position and an optical band gap of 400 nm (3.1 eV) (band-structure calculations: direct semiconductor, $\Delta E = 2.9$ eV).[200]

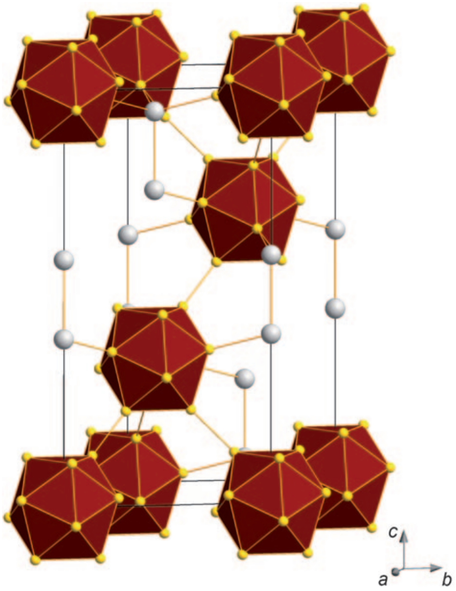

Figure 9. Unit cell of $B_{12}P_2$.

Black samples were obtained in various ways: by thermal decomposition of BBr_3 and PBr_3 in an H_2 atmosphere,[167] by treatment of the elements in an aluminum melt, as a by-product in nickel melts, and in the synthesis of $LiB_{12}PC$.[165]

Colorless and black samples have also been described for $B_{12}As_2$ and $B_{12}As_{2-x}$. No significant differences, apart from the color, were observed for the single crystals obtained from palladium melts.[166,169] The same is reported of a colorless sample obtained by chemical disintegration.[169] Amberger and Rauh, on the other hand, detected an arsenic deficiency of 10% or 88% arsenic content in mixed occupation with boron in their single crystals obtained from H_2 reduction of $AsCl_3$ and BCl_3 in the gaseous phase.

A sulfurous phase is mentioned once in the literature. Matkovich[172] describes the compound as $B_{12}S$ on the basis of the results of the chemical analysis. Powder film methods led to an isotype with $B_{12}P_2$ being concluded. Nothing is said about the nature of the two-atom unit. Lattice constants and the c/a ratio, however, indicate a certain similarity with the analogous Se compound.

There is only one study of a boron-rich boride containing Se in the literature.[173] A sample with 8% Se was obtained by substitution of the elements (ICP-AES) and characterized by X-ray powder investigations. In the subsequent structural determination, Rietveld refinement led to mixed occupancy of the two-atom unit (53(1)% B content). Slightly different positions resulted for B and Se, which is in accordance with expectations.

It has been stated on the basis of theoretical calculations that a hypothetical intercalation compound of α-B and Li (Li_xB_{12} with $1 < x < 3$) should be stable and experimentally accessible, and that such a phase could possibly be superconducting.[210,211] However, experiments have so far not been able to prove the existence of such a phase.[212]

4.3. Boron Compounds with a β-B Structure: $LiB_{\approx 10}$, $MgB_{17.9}$, AlB_{31}, SiB_{36}, GeB_{90}

There are numerous examples of the incorporation of metal atoms in β-B, a process in which the β-B structure is largely preserved. This is caused by the electron deficit in β-B, which has to be compensated for only in partially occupied sites between the linked polyhedra in pure boron by interstitial boron atoms; in boron-rich borides it can be compensated by metal electrons. The metal ions will then be located in the gaps of the icosahedral boron framework. Structures with 15 to 16 boron atom positions have been described. Possible metal atom positions were given as A1, A2, A3, D, E, F1, F2, and G by Anderson and Lundstrom.[213] It has also been reported that the A1 and E positions cannot be occupied at the same time. In most cases, these phases—in as far as they have been discovered and described to date—are transition-metal borides (Cr, Cu, Fe, Mn, Ni, Sc, V, Zn). However, main group elements, too, can react to make boron compounds with β-B structures: such phases have been described for lithium, magnesium, and aluminum. The structural determination of such compounds is often rendered difficult by the fact that no single crystals exist and, secondly, that the allocation of the electron density of a partially occupied site to an individual metal atom can be ambiguous, especially for light metals. For this reason it is not always easy to assign credible sum formulas to these compounds. Furthermore, boron-rich borides have wide phases, because different proportions of metal atoms can be realized. It is possible that interstitial boron atoms in the structure of β-B can be replaced by variable, "tunable" metal partners, as long as the electron deficiency of the framework is balanced. Finally, theoretical calculations of phases with a β-B structure do not always yield as much information as could be desired, since partially occupied sites in large unit cells are difficult to handle.

According to a recent study, boron-rich lithium boride with a β-B structure can be denoted as $LiB_{\approx 10}$ or $Li_{30}B_{309}$.[127] This formula is based on structural examinations performed on highly pure crystal powders and single crystals obtained by metal flux. The same phase was earlier called LiB_{13}.[214] As for magnesium boride with a β-B structure, $MgB_{17.9}$,[217] 15 boron atom positions were found for $LiB_{\approx 10}$; 4 metal atom positions (A1, E, D, F2) were (partially) occupied by lithium atoms. Two boron atom sites are only partially occupied (66% and 90% respectively). The partial occupation of the so-called B11 site is known from several compounds described in the literature. It, therefore, seems confirmed that the B_{28} unit of the elemental structure mentioned in Section 2.2.2 should be denoted as a B_{27} unit. This also means that B1 is subject to a distorted tetrahedral coordination not by six, but only by four atoms in the B11 position.

The same structural motif can be found in $MgB_{17.9}$, and again four interstitial positions are (partially) occupied with magnesium atoms. There are two more recent papers on magnesium borides with a β-B structure: Brutti et al. described the Rietveld refinement of the structure of MgB_{20} based on synchrotron data,[216] while Giunchi et al. also worked on crystalline powders and derived the structure of a compound they termed Mg_2B_{25}.[217] The calculated densities of the three compounds and the volumes of the unit cells are very similar ($MgB_{17.4}$, MgB_{20}, Mg_2B_{25}: 2.45 g cm^{-3} and 2523.48 Å^3, 2.42 g cm^{-3} and 2523.48 Å^3, 2.49 g cm^{-3} and 2554.17 Å^3), which may suggest that all three represent the same compound, with the composition varying slightly depending on the conditions of synthesis. The structure was described with 15 boron atom positions and 4 or 3 magnesium atom positions. Only in the case of $MgB_{17.4}$ were the composition and structure determined on single crystals and confirmed by WDS. From the knowledge currently available it may be assumed that Mg-doped β-B is best described by the sum formula $MgB_{17.4}$. In a recent publication Hyodo et al. reported the incorporation of Mg up to a composition of MgB_{12}.[218] The magnesium was introduced in the gaseous phase at 1073 K, and the characterization was done by Rietveld refinement of powder data.

Higashi et al. described Al-doped β-rhombohedral boron, to which they assigned the formula AlB_{31} as early as 1989.[219] The occupation of the boron atom positions is as in $LiB_{\approx 10}$ and $MgB_{17.9}$, and the aluminum atoms were located in positions A1, B, C, D.

A compound which was described as SiB_{36} with a β-B structure[220] is in need of further investigation since it is unclear as yet to what extent silicon atoms replace boron atoms in the icosahedra. It was also recently shown by EDS[221] that this phase can incorporate a small amount of carbon at an interstitial position, and that this compound would have to be assigned the formula $SiB_{30}C_{0.25}$.

The incorporation of small amounts of germanium has also been documented. Lundstrom und Tergenius describe

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the composition GeB_{90} on the basis of single-crystal investigations.[222] Ge is situated mainly in the A1 position.

4.4. Boron Compounds with a t-I Structure: $B_{50}C_2$, $B_{50}N_2$, $Be_{3.2}B_{48}B_2$, $Mg_2B_{24}C$, $Al_{2.7}B_{48}C_2$

Compounds with a t-I structure should crystallize in a tetragonal crystal system ($P\bar{4}n2$, $P4/mnm$, $P4_2/mnm$, and $P4nm$ have been proposed as possible space groups) and have lattice parameters in the region of 890 pm and 505 pm, or at least display structures which can be derived from this type (see Table 3 for an overview). The tetragonal unit cell consists of four icosahedra, whose centers are situated at the corners and in the central areas of the unit cell (in $P4_2/mnm$ this corresponds to two 8-fold and two 16-fold sites), and two tetrahedrally coordinated, isolated atoms (corresponding to the twofold site for isolated boron atoms), according to a description as $B_{48}X_2$. The discussion of the structures of $B_{50}C_2$ and $B_{50}N_2$ above showed that two additional boron atoms are assumed to be located in the unit cells of these compounds, according to a description as $B_{48}B_2X_2$. A closer look at the geometric disposition in the icosahedral arrangement shows that only two of the four additional atoms are tetrahedrally coordinated by the boron atoms of the icosahedron in a way that corresponds to the length of about 170 pm expected for B−B bonds. The other two positions have distances of about 215 pm, which seems to predispose these sites for metal atoms.

Table 3: Overview of compounds with t-I related structures.

	Space group	*a* [pm], *c* [pm]	Ref.
"t-I boron"	$P4_2/nnm$	875, 506	[108,109]
$B_{25}C$	$P\bar{4}2m$	875.3, 509.3	[110,116]
$B_{25}N$	$P\bar{4}2m$	863.4, 512.8	[110,116]
BeB_{12}	$P4_2/nnm$	885.6, 511.6	[224]
$AlBeB_{24}$	$P4_2/nnm$	882, 508	[225]
$B_{25}AlCu_{0.8}$	$P\bar{4}n2$	900.2, 506.9	[230]
$B_{48}Al_3Si$	"tetragonal"	891, 505	[232]
$B_{48}Al_{2.7}C_2$	orthorhombic distorted (superstructure)		[143]

Up to now, metal borides of the composition MB_{12} and MB_{25} were included with this structural family. When the structure of $BeB_{12} = Be_4B_{48}$ was determined from single crystals obtained from a copper melt[223] it turned out to be $Be_{3.2}B_{48}B_2$, with beryllium atoms in different positions than described earlier. This compound is thought to be identical with a phase that was described as $BeB_9 = Be_{5.3}B_{48}$.[224] In the original study on "BeB_{12}", the synthesis of pure t-I boron was attempted;[223] this is in urgent need of repetition since it would permit very interesting conclusions to be drawn regarding the stability of the controversial boron modification t-I. Beryllium boride was treated with boron trichloride in a closed system, which yielded beryllium chloride and a t-I phase with lattice parameters which were different from those of the starter substance—was this perhaps indeed tetragonal boron?

There is currently some suspicion that compounds of the transition metals, earlier described as MB_{25} (where M = Ti, Ni, Zn, V),[225–229,231,236–239] are really ternary compounds with the formula $MB_{24}C$. One such example is $Mg_2B_{24}C$, which crystallizes with a t-I structure and shows no partially occupied sites (Figure 10).[233] There are indeed some ternary phases which contain carbon and could be discussed as filled variants of t-I. $Al_{2.7}B_{48}C_2$ was obtained as light yellow to maroon single crystals and crystallizes orthorhombically with the icosahedral arrangement described for t-I, but it has additional, partially occupied metal atom positions.[143,234,235] These positions are situated in tetrahedral and octahedral gaps of the icosahedral structure. The aluminum content corresponds to the value needed for an electronically precise compound. This phase was earlier described as β-AlB_{12}.

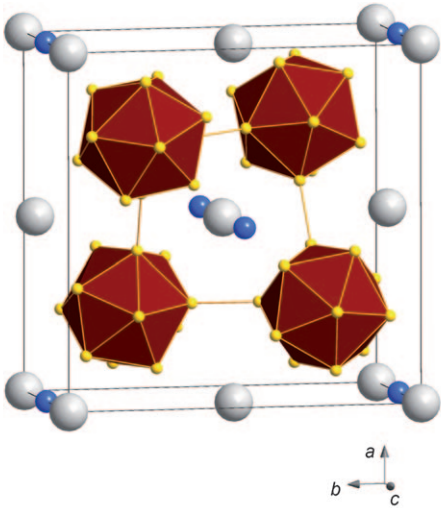

Figure 10. Unit cell of $Mg_2B_{24}C$.

Recent work on the boron subnitride called "$B_{50}N_2$" (space group $P\bar{4}n2$, no. 118, $a = 879.79$ pm, $c = 503.7$ pm) obtained at high pressures[164,195] also introduces a new refinement of a boron-rich boron nitride with a t-I structure. Up to now there has been a lack of precise data on this phase. Theoretical calculations predict that a $B_{50}N_2$ phase in space group $P\bar{4}2m$ is stable to disintegration to BN and α-B.[236] The electrochemical synthesis of nanorods consisting of $B_{50}N_2$ was recently reported.[237]

4.5. Boron Compounds with a t-II Structure: α-AlB_{12}, γ-AlB_{12}, MgB_{12}, Mg_5B_{44}

α-AlB_{12} was first described in 1961, and the structural descriptions by Higashi et al. and Kasper et al.,[238,239] which date from 1977, are still accepted today. Both research groups obtained single crystals from an aluminum melt. The density of these crystals as found experimentally was 2.54 g cm^{-3}[238] and 2.65 g cm^{-3},[239] respectively, which indicates slight deviations in the composition. α-AlB_{12} decomposes to AlB_{31} and aluminum at approximately 2273 K. The compound crystallizes in the space group $P4_12_12$ or $P4_32_12$ (no. 92 or 96, $a =$ 1015.8 pm, $c = 1427.0$ pm[238]). Higashi recently published a reevaluation of α-AlB_{12}.[240] The structure of α-AlB_{12} was originally described as consisting of twinned, incomplete icosahedral B_{19} polyhedra, icosahedra, and isolated atoms. However, the B_{19} polyhedra would be better described as B_{20} units consisting of two condensed icosahedra with a corner missing from each, a common face, and one bridging boron atom. The sum of the occupancies leads to an aluminum content of 13.6 Al atoms per unit cell, which correlates well with the electron demand of 40 calculated according to the *mno* rules.

The compound denoted as γ-AlB_{12} crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$ (no. 16, $a =$ 1657.3 pm, $b = 1751.0$ pm, $c = 1014.4$ pm), and it has so far been impossible to obtain it as a single-phase product.[240] Crystals of γ-AlB_{12} grown together with α-AlB_{12} are transformed into α-AlB_{12} when ground, thus no powder diffractogram of this phase could be obtained. The structure is described with 88 crystallographically independent, fully occupied 4a positions for boron atoms and 11 partially occupied 4a positions for aluminum atoms, which results in the compositions $Al_{6.3}B_{88}$ or $AlB_{\approx 14}$. There are boron atom icosahedra and two different B_{20} units, which are described as double icosahedra with a common face, two missing corners (either both are missing from the same half-icosahedron or one from each half-icosahedron), and an additional boron atom bridge between the icosahedra.

Blue-black crystals of the compound MgB_{12} were recently obtained in a Mg/Cu melt at 1823 K.[136] Even though the dimensions of the unit cell of this compound are nearly identical with those of "γ-AlB_{12}" (MgB_{12}: $a = 1663.2$ pm, $b =$ 1780.3 pm, $c = 1039.6$ pm), it is not isotypic with the aluminum compound described above. MgB_{12} crystallizes in space group *Pnma* (no. 62) with 51 sites occupied by boron atoms (39 eight- and 12 fourfold) and 9 sites partially occupied by magnesium atoms (7 eight- and 2 fourfold). The unit cell is made up of 16 boron atom icosahedra and 8 B_{21} polyhedra; the latter are double icosahedra with a common face and one corner missing and are linked by an additional boron atom, similar to the B_{20} units with two missing corners described above. For more complicated structural units, such as the B_{19}, B_{20}, and B_{21} unit found in the structures of t-I, t-II, as well as (α and γ) AlB_{12} and MgB_{12}, the *mno* rules for condensed, incomplete, or capped or bridged clusters according to Jemmis can be applied.[241] According to this, the number of bonding molecular orbitals in a *closo*-, *nido*-, or *arachno*-cluster is $m+n+o+p-q$ ($m =$ number of condensed polyhedra, $n =$ number of framework atoms, $o =$ number of single molecules bonded to the cluster, $p =$ number of atoms missing from a *closo*-cluster, $q =$ number of atoms capping a B triangle). For the B_{21} unit in MgB_{12}, for example, the number of electron pairs is calculated as $2+21+1+1-0 = 25$; in addition to that, 17 electrons are needed for 2e2c bonds on the outside, which makes a total of 67. The boron atoms can contribute 21 × 3 electrons to the bonding system, and the remaining four electrons must originate from the metal atoms. According to this concept, for a total of 16 icosahedra and 8 B_{21} units in the unit cell, 64 electrons should be transferred by almost 30 magnesium atoms, but this is not possible; however, given the complexity of the structure and the generalizing approximative rule, it seems to be a convincing indication that the concept is sound.

The number of electrons necessary to stabilize the boron polyhedra correlates with the constitution of the polyhedra and the incorporation of metal atoms, which is particularly marked in tetragonal Mg_5B_{44} ($P4_12_12$ or $P4_32_12$, $a = 1035.0$ pm, $c = 1442.5$ pm), which has been observed as a by-product in the synthesis of MgB_7.[242] Mg_5B_{44} has the same framework of boron atom polyhedra as α-AlB_{12} (more correctly $AlB_{13.2}$), that is, B_{12} icosahedra and B_{19+1} units. The requirement of 40 electrons per unit cell is fullfilled by 20 magnesium atoms in 5 partially occupied sites. Compared with MgB_{12} with its modified structure of icosahedra and B_{21} units, the greater electron requirement is demonstrated by the higher magnesium content.

The phases described earlier in the literature as AlB_{10} and β-AlB_{12} do not exist in the form of binary compounds, they are the ternary compounds $B_{51}Al_2C_8$[243] and $Al_{2.7}B_{48}C_2$.

5. No Elemental Structure, but Linked: Polyhedron, Layer, Chain

5.1. Icosahedra: $Li_2B_{12}C_2$, $LiB_{13}C_2$, $Li_2B_{12}Si_2$, $LiB_{12}PC$, $LiAlB_{14}$, Na_2B_{29}, BeB_3, MgB_7, o-$MgB_{12}C_2$, m-$MgB_{12}C_2$, $MgAl_{0.7}B_{14}$, $MgB_{12}Si_2$, SiB_3

The icosahedron is the most common structural unit in the chemistry of boron, and is also found in borides and boride carbides of the main group elements whose crystal structures cannot be directly derived from those of the (postulated) boron allotropes. This is exemplified by BeB_3[244,245] and the new lithium compounds, $Li_2B_{12}C_2$ (1), $LiB_{13}C_2$ (2),[137] $Li_2B_{12}Si_2$ (3),[140] and $LiB_{12}PC$ (4),[246] of which light-green (1), colorless (2, 4), or yellow (3) single crystals have been synthesized from the elements at temperatures of 1570 K and 1770 K in tin melts. The compounds crystallize orthorhombically (space group *Amm*2, no. 38, $a = 470.6$ pm, $b = 901.0$ pm, $c = 565.2$ pm (1); space group *Imma*, no. 74, $a = 566.8$ pm, $b =$ 1082.0 pm, $c = 804.0$ pm (2, 4); space group *Cmce*, no. 64, $a =$ 610.60 pm, $b = 1097.9$ pm, $c = 840.50$ pm (3)). In $Li_2B_{12}C_2$ the arrangement of the boron atom icosahedra follows the motif of a hexagonal primitive arrangement and the sequence of the layers is AAA. Between the layers are lithium atoms and C_2 dumbbells (the C–C distance of 137.4 pm suggests a double bond) and the four boron atoms are linked into a nearly planar rectangle by four icosahedra. $LiB_{13}C_2$ and $LiB_{12}PC$ are variants of the MgB_7 type (see below), with the trigonal prismatic gaps of a slightly different hexagonal primitive arrangement of icosahedra filled by lithium atoms and C-B-C chains, which are similar to those in boron carbide. The C-B-C chains are slightly bent and have a C–B distance of 141.3 pm. Good resolution IR and Raman spectra have been obtained for $Li_2B_{12}C_2$ and $LiB_{13}C_2$. The force constants show the progression which was to be expected on the basis of qualitative considerations ($f_{C=C} > f_{C\text{-}B\text{-}C} > f_{C\text{-}B} > f_{B\text{-}B,exo} > f_{B\text{-}B,endo}$).[247] Orthorhombic *o*-$MgB_{12}C_2$, too, has to be assigned to the MgB_7 family. In this structure C_2 units with a remarkably large CC distance of 173 pm are situated in the trigonal prismatic gaps. According to band-structure calculations the highest electron density is to be found between the C atoms, despite the large distance.[200]

In the silicon compound $Li_2B_{12}Si_2$ there are again boron atom icosahedra, but in this case they are slightly distorted. Layers are formed perpendicular to [010] which can be derived from a hexagonal dense arrangement and have the sequence ABAB. The distorted tetrahedral voids in this packing are occupied by silicon atoms, which link four icosahedra each, and lithium ions. This compound is very hard ($H_V = 20.3$ GPa) and has an optical band gap of 2.27 eV (measured). $MgB_{12}Si_2$ is closely related to this compound; its crystal structure (space group *Pnma*, no. 62) is linked with that of the lithium compound through a group-subgroup relationship.[139] The eightfold site occupied by the lithium atoms is, therefore, divided into two fourfold positions, one of which is occupied by magnesium.

A unique structure type was found for monoclinic *m*-$MgB_{12}C_2$. Here, icosahedra form a cubic close packed arrangement with magnesium atoms in the octahedral voids and carbon atoms in the tetrahedral voids. This compound also exhibits a remarkably high microhardness of $H_V = 30$ Gpa.

SiB_3 was recently obtained from gallium[248] or tin melts[249] and shown to crystallize with similar structural motifs. In this case, zigzag chains are located between the icosahedra formed by Si–Si-linked Si_4 rhomboids. R. Hoffmann et al. investigated such rhomboids with extended Hückel and DFT calculations, and classified them as electron deficient.[250] They described β-SiB_3 as $(B_{12})_4(Si_4)_4$ and assigned formal charges of +2 to the Si_4 units. These "new and nonclassical" Si_4^{2+} units were compared to B_4 rhomboids in Na_3B_{20} (see below).

The icosahedral arrangement in MgB_7 (=Mg_2B_{14}),[253,254] $LiAlB_{14}$,[255] $MgAl_{0.7}B_{14}$,[256] and Na_2B_{29}[153] is similar to that discussed above for $LiB_{13}C_2$. Mg_2B_{14} crystallizes orthorhombically, space group *Imma* (no. 74, $a = 597.0$ pm, $b = 1048.0$ pm, $c = 812.5$ pm). $MgAl_{0.7}B_{14}$ also crystallizes orthorhombically, space group *Imma* (no. 74, $a = 584.8$ pm, $b = 1031.2$ pm, $c = 811.2$ pm). Na_2B_{29} crystallizes in the monoclinic crystal system with an angle close to 90° (space group *I*1*m*1, no. 7, $a = 587.4$ pm, $b = 1040.3$ pm, $c = 835.9$ pm, $\beta = 90.17°$). Its structure is very similar to that of Mg_2B_{14}, but the position occupied by the metal atoms is split into two positions because of symmetry reduction from the orthorhombic to the monoclinic crystal system; these two positions can be clearly distinguished in solid-state NMR spectroscopy. The position of the interstitial boron atom is also split into two positions, one of which is not occupied. The structural model was refined on the basis of powder X-ray diffraction data and confirmed by neutron diffraction and high-resolution transmission electron microscopy. A compound earlier published as NaB_{15} does not exist.

It is remarkable how many compounds can be assigned to the MgB_7 family (Table 4). This indicates that electron-precise structures following the concept of Longuet–Higgins et al. clearly seem to be favored.

Table 4: Overview of borides related to MgB_7.

Compound	Unit	Color	Band gap [eV]		Hardness [GPa]
			observed	calcd	
MgB_7	$B_{12} + B_2$	dark red	1.8[200]	1.9[200]	20[252]
o-$MgB_{12}C_2$	$B_{12} + C_2$	colorless		2.5[200]	25[252]
$LiB_{12}PC$	B_{12} + PC	colorless	3.1[165]		27[252]
$LiB_{13}C_2$	B_{12} + CBC	light green		2.3[200]	
Na_2B_{29}	$B_{12} + B_2 + B$	black			
$ScB_{13}C$[251]	B_{12} + BC	black			
$LiAlB_{14}$	$B_{12} + B_2$	black			
$MgAl_{0.7}B_{14}$	$B_{12} + B_2$	black			

5.2. Other closo-Polyhedra: MgB_9N, MB_6, Li_2B_6, MB_5C, Na_3B_{20}, Li_3B_{14}

Icosahedra may dominate the structural chemistry of boron-rich borides, but there are other polyhedra among the borides of the main group elements: octahedra, the pentagonal bipyramid, the (trigon)dodecahedron, and the double-capped square antiprism, that is, we know of polyhedra with $n = 6$, 7, 8, 10, and 12 among such compounds. In contrast to, for example, ZrB_{12} and UB_{12}, the cuboctahedron has never been observed in boron compounds of main group elements.[257]

Although CaB_6 was first described in 1897,[258] no satisfactory consensus has so far been established with respect to the quantification of the fundamental physical properties of these compounds. Examples include thermal conductivity, electric conductivity, and Seebeck coefficients—all of these properties are described rather differently in the literature. Recently CaB_6 was even shown to take on itinerant ferromagnetic behavior at temperatures above 600 K,[259] which is surprising for a compound without partially occupied d or f orbitals. Solid solutions of the composition $Ca_{1-x}La_xB_6$ had been synthesized and investigated up to $x = 0$. The magnetic behavior of these systems was at first explained by electron correlations, as in the model of a free electron gas with very low density. However, this observation is still subject to debate, including the hypothesis that the sample contains impurities such as FeB and Fe_2B. These compounds have similar Curie temperatures around 600 K.[260,261] Zhitomirsky et al. proposed that the experimental observations agree well with the picture of an exitonic insulator doped with electrons.[262] Other explanations have in the meantime been put forward: Fisk et al., for example, now believe that the ferromagnetism of the compound is caused by a low concentration of intrinsic defects in the calcium or boron structure.[263] They discuss "neutral B_6 vacancies" that are statistically distributed in the structure.

The hexaborides MB_6 (M = Ca, Sr, Ba, rare-earth metals) have a three-dimensional, cubic framework of linked octahedra, space group $Pm\bar{3}m$ (no. 221). The B–B distances between

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the octahedra are shorter than those within the octahedra. There is one metal ion in each of the cuboctahedral gaps between the octahedra. This structural type has been known since 1932;[264] further literature is cited in Ref. [125]. The structure of the metal carbapentaborides MB_5C (M = Na, K), in which one of the six boron atoms is substituted by a carbon atom,[265,266] is derived from this, as is the structure of Li_2B_6, in which two metal ions occupy the cuboctahedral gap.[267] SiB_6 with a CaB_6 structure, which had been postulated in the past, does not exist.

As early as in 1954 Longuet–Higgins and de Vries Roberts compared the *closo*-$B_6H_6^{2-}$ ion with the B_6 octahedron in CaB_6, which formally has a double negative charge.[23] Multipole refinements of the crystal structure based on diffraction data gained from single crystals at low temperature were recently performed for the *closo*-$B_6H_6^{2-}$ ion and the $B_6H_7^-$ ion; the experimental electron density distributions (static deformation density) were also analysed.[27–29] The picture of multicenter bonds as found for *closo*-clusters in textbooks was confirmed without reserve for $B_6H_6^{2-}$ (Figure 11 a). For $B_6H_7^-$, a new type of 2e4c bond was found with ring-critical points in the B_3H rhomboids. It will be interesting to compare these results with experimental determinations of electron density distributions in hexaborides. Relevant experiments have not yet been completed.[268] According to the Wade rule, the polycentric bonding system in the hexaborides would need $2n+2=14$ electrons to be stable. Two electrons are needed for each of the B–B bonds between the octahedra, if they are to be conventional 2e2c bonds (which is suggested by the shorter distance). There are six of these 2e2c bonds per octahedron, to which each B_6 unit should contribute six electrons. This means that within such a boron atom framework, $14+6=20$ electrons are needed per formula unit. However, six boron atoms only have eighteen valence electrons in total. The missing two electrons in this concept are supplied by the metal atom in the sense of the Zintl concept,[269,270] which would have to exist as at least one two-valent or two monovalent cations; this would make the existence of the alkaline earth metal hexaborides and Li_2B_6 plausible. In a carbaboride with the octahedral B_5C unit, the constituting atoms supply 19 valence electrons. According to Wade, these compounds are electronically precise if each metal atom transmits one electron to one octahedron—this would explain the existence of the alkali-metal carbapentaborides.

According to this conceptual model, the compound KB_6 should not occur as a structural type in the hexaborides. This is contradicted by the observations of Etourneau et al., who described the synthesis and structure of potassium hexaboride in 1966 and recently published their reexamination of this system.[271,272] The compound is described as an unusual metal of composition $K_{1-x}B_6$, with a slight deficiency of cations. EPR signals are explained by a localization of electrons in the sense of a bipolaron model. A prerequisite would be the existence of isolated octahedra, which allow a local electron–phonon interaction. The structure was supported by synchrotron data on a crystalline powder.

The existence of NaB_6 was postulated in 1963, but disproved beyond doubt by more recent experiments.[273,274]

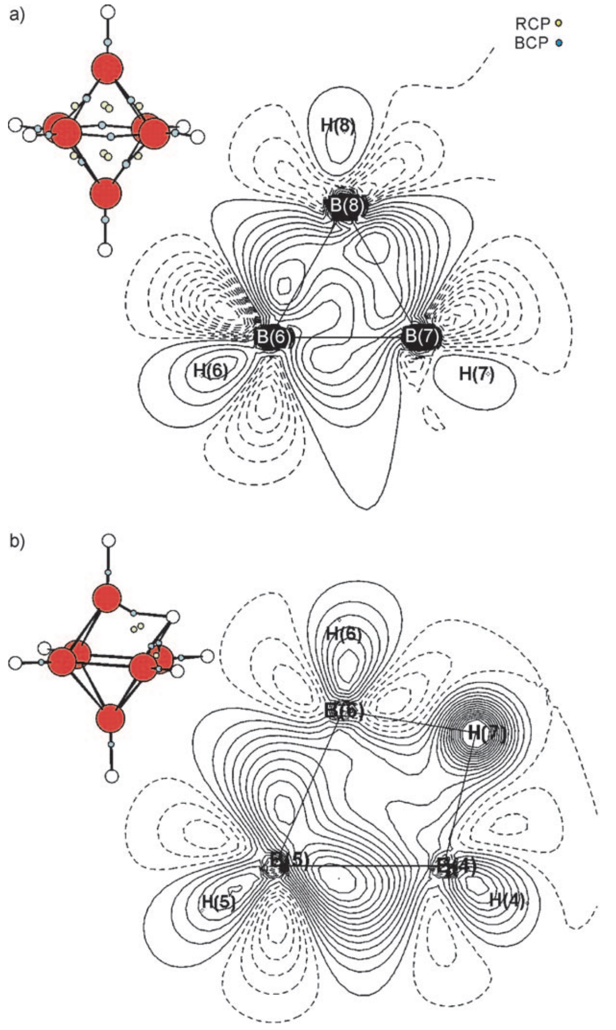

Figure 11. Results of the experimental electron density determination on a) $B_6H_6^{2-}$ and b) $B_6H_7^-$. RCP = ring critical point; BCP = bond critical point.

This compound has been identified as Na_3B_{20}, a sodium boride whose crystal structure displays octahedral and pentagonal-bipyramidal structural units. It was solved and refined by means of powder diffractometry based on X-ray and neutron data, space group *Cmmm* (no. 65, $a=1869.45$ pm, $b=570.09$ pm, $c=415.06$ pm). The unit cell consists of two B_6 octahedra and four B_7 bipyramids, $Na_6(B_7)_3(B_6)_2=2\times Na_3B_{20}$. The octahedra are connected to the other polyhedra through 2e2c bonds, as in the hexaborides. According to Wade, their electron requirement would be 20 electrons per octahedron, 14 per multicenter bond, and 6 for the *exo*-polyhedral bonds. The pentagonal bipyramids, on the other hand, also have a 2e2c bond to the axial positions, but also display unusual B_4 rhomboids in the *a-b* plane, similar to the Si_4 units in β-SiB_3 mentioned above, which link two polyhedra each. This results in one-dimensional infinite, condensed B_7-B_4 chains, to which Balakrishnarajan and Hoffmann, by applying the *mno* rule, assign an electron requirement of 18 pairs of electrons per $(B_7\text{-}B_4)_2$- unit.[250] This discrepancy between the 18 electrons required per bipyramid and the 17.5 available has not yet been explained in the framework of this concept. Even if the rhomboids are described as 2e4c bonds, there would be one electron missing per formula unit. According to Wade, a bipyramid would have to have sixteen electrons for the cluster, four for the four 2e2c bonds with neighboring octahedra, and two for the two 2e4c bonds, which makes 22 electrons altogether, which for two bipyramids and one octahedron would require a grand total of 64 electrons; but Na_3B_{20} only has 63 electrons. The presence of doping substances (C, H) which donate electrons has been excluded by all available means. Balakrishnarajan and R. Hoffmann propose a single errant boron atom capping a triangular plane,[250] which, alas, would be difficult to prove by experiment. Accurate analyses of electron density might be able to clarify the situation, through which it might be possible to quantify the electron requirements of a four-center bond.

Finally, the Li_3B_{14} compound should be discussed. It is the first and so far only example of dodecahedral and double-capped square antiprismatic structural units in a three-dimensional boron atom framework.[275] The positions of the lithium atoms are partially occupied without exception. Measurements on powder samples of the compound, which was obtained in the form of red, transparent crystals and a brown-grayish powder, indicated mixed electronic and ionic conductivity above 600 K. Below this temperature, no observations were possible because of extrinsic conductivity, which were caused by contamination. As for the alkaline earth metal borides described above, a description of the boron atom framework by Wade rules in combination with the Zintl concept is justified, since two electrons can be donated by the metal atoms per *closo*-polyhedron according to $Li^+_6[(B_8)^{2-}(B_{10})^{2-}_2]$.

Assuming complete electron donation from the metal to the nonmetal framework, one would expect nonmetallic or semiconducting behavior of the electronically precise boron-rich borides, with their extensive structures consisting of linked *closo*-polyhedra. Electronic conductivity should only be expected where more electrons are available, for example, for the hexaborides of the rare-earth metals. This is what has been observed beyond doubt for compounds such as LaB_6. However, observations differ as to the electronic situation of CaB_6, SrB_6, and BaB_6. Perkins calculated in 1975 that the metal atoms do not donate 2, but only 0.9 electrons to the octahedron.[276] Measurements on these alkaline earth metal borides have shown insulating, semiconducting, half-metallic, and conducting behavior. Undoubtedly many of these measurements suffer from poor sample quality, since it is extremely time consuming and difficult to synthesize these high-melting borides in a very pure form. It is absolutely essential to check that the very pure boron used as a starting material does not contain carbon, for example, by means of EELS. Recent experimental and theoretical work on SrB_6,[135] LaB_6,[277] and BaB_6[278,279] shows that the hexaborides of the alkaline-earth metals are semiconductors, while those of the rare-earth metals are metals. The size of the band gap, however, depends on the ratio of inter- and intra-octahedral B–B bonds and, therefore, on the position of the boron atoms. It was calculated that the band gap of BaB_6 closes at a positional parameter of $z = 0.205$ (z is the only free positional parameter in the structure), and this is exactly the value found experimentally for the structure.[279] The size of the barium atoms results in this hexaboride exhibiting the longest possible inter-octahedral B–B bonds.

Hexaborides also seem to be attractive as potential thermoelectric materials.[64,65] However, here again, the difficulties in synthesizing the samples and in measuring the Seebeck coefficients lead to nonreproducable and contradictory results. One example is the study of Takeda et al. on CaB_6, SrB_6, and $(Ca,Sr)B_6$, in which the Seebeck coefficient of the calcium compound initially had higher negative values than the strontium compound (Figure 3 in Ref. [280]), but a second publication reported the opposite situation (Figure 3 in Ref. [281]). Very recently, ternary hexaborides in the Ca-Ba-B system have been investigated with respect to this problem.[282,283]

Compounds with a M_6^{2-} octahedron are also known for the higher homologues of boron, indium, and thallium. Corbett and co-workers determined for KTl and Rb_2In_3 octahedral cluster analogues to B_6.[284,285]

In the same way as Na_3B_{20} has both octahedra and pentagonal bipyramids as structural units, the recently described compound MgB_9N has both octahedra and icosahedra, which are three-dimensionally linked into a framework.[286] Black single crystals of the boride were obtained in the reaction of magnesium and boron in and with a BN crucible; high temperatures (1873 K) and an argon pressure up to 100 MPa were applied. The crystal system of MgB_9N is trigonal/rhombohedral (space group $R\bar{3}m$, no. 166, $a = 549.60$ pm, $c = 2008.73$ pm) with 66 atoms in the unit cell, of which 54 boron atoms are distributed between 3 icosahedra (B1, B2) and 3 octahedra (B3). One layer of icosahedra follows the motif of densest spherical packing. Within this layer, nitrogen atoms link three icosahedra each, so that this layer is formally of the composition $(B_{12})N_{6/3} = B_6N$ and resembles the layers in the subcompounds of the α-B type (see Section 2.1.2). In between the icosahedra are octahedra, which are not linked to each other but display inter-polyhedral bonds to icosahedra.

Compounds with icosahedra next to octahedra are well known among the boron-rich borides of rare-earth metals.[287,288] Similar structural motifs have recently been observed for the Zintl compound $Na_{20}Zn_8Sn_{11}$.[289]

An exception is a compound of the approximate composition of SiB_6. It has a complex orthorhombic structure with B_{12} icosahedra and polyhedra formed from 15 atoms, mainly boron atoms, but also with some silicon atoms partially substituting the boron atoms. Further conclusions are not possible before the identity (formula, carbon content) and structure (disorder, partial occupancy) of the compound have been confirmed.[208,290]

5.3. On the Way To Being Dissolved: "MgB_4", $CaB_{4-x}C_x$

BB dumbbells which link polyhedra to make a three-dimensional framework were known before the new boron modification γ-B_{28} discussed in Section 2.4 was discovered.

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These, however, were not “cationic” units of B_2. A charge distribution for metal tetraborides with BB dumbbells appears to suggest a description as $(M^{2+})_2(B_2)^{2-}(B_6)^{2-}$, and the B–B distance within the dumbbells is at about 167 pm rather shorter than that found in γ-B_{28} (173 pm). The ThB_4 structural type displays octahedral units as known from the hexaborides, which form seven-link rings with the B_2 dumbbells. This is known from the tetraborides of several transition metals, lanthanoids, and actinoids as well as magnesium. MgB_4, however, was described orthorhombically in space group *Pnma* (no. 62, $a = 546.4$ pm, $b = 442.8$ pm, $c = 747.2$ pm),[291,292] whilst the name-giver crystallizes tetragonally (space group *P4/mbm*, no. 127). It may be assumed that a revision of the structure of MgB_4 would result in isotypy with the other tetraborides, but it has not so far been possible to reproduce the synthesis of crystalline magnesium tetraboride.

$CaB_{4-x}C_x$, which was recently described as a tetraboride,[293] crystallizes in the same type of structure; it is not, however, a binary compound. The incorporation of carbon into the samples described was detected experimentally,[294] and theoretical work has shown that the compound would be electronically unstable without incorporation of a third element.[295] In combination with other borides, “CaB_4” was announced as a very light and stable metal-matrix composite.[296]

5.4. Layered Structures: MgB_2, LiBC, MgB_2C_2, BeB_2C_2, CaB_2C_2, $Al_{0.9}B_2$

The exciting discovery in 2001 that the well-known compound MgB_2 is a metallic superconductor with a transition temperature of $T_c = 39$ K was mentioned in the introduction.[13] Several authors believe the mechanism of superconductivity to be a phonon-mediated pairing of the charge carriers. MgB_2 crystallizes in the AlB_2 type, which has been known since 1935.[297] The crystal structure was published by Jones and Marsh in 1954 (space group *P6/mmm*, no. 191, $a = 308.34$ pm, $c = 352.13$ pm).[298] The unit cell exhibits its metal atoms on the corners, and in between there are planar layers of condensed six-rings of boron atoms (6^3 nets). It is a filled variant of the tungsten carbide (WC) structure type. The boron atoms are situated in trigonal prismatic gaps of the hexagonal primitive metal atom arrangement and the metal atom prisms are triply capped by boron atoms; prisms with only two of the rectangles capped with boron atoms would result in a zigzag chain (as in FeB[299]). Capping of all three rectangles with metal atoms would give us the cementite structure type (Fe_3C, Fe_3B). Formally, one could consider a 2e charge transfer from one magnesium to two boron atoms (“$Mg^{2+}B^-{}_2$”) for MgB_2, namely the ${}^2_\infty[(B^-)_{6/3}]$ arrangement, analogous to graphite. However, the compound shows metallic conductivity, so the transfer of electrons is not at all complete in the sense of an ionic compound. There also exists AlB_2, which would anagously then have to be described as “$Al^{3+}B^-{}_2(e^-)$”. A modern electron density analysis indicates that for MgB_2 one would be talking about a transfer of 1.5 to 1.6 electrons per magnesium atom.[300]

Surprisingly, Burckhardt et al. discovered that aluminum diboride always has a 10% underoccupation of the metal atom site, and should thus be called $Al_{0.9}B_2$.[301] Finally, there are two interesting mixed aluminum magnesium diborides $Mg_{1-x}Al_xB_2$ with x close to 0.5, which have a superstructure and exhibit superconductivity (T_C ca. 4–6 K).[302]

Following the discovery of the superconducting properties of MgB_2, much experimental, theoretical, and conceptual studies on this compound were published (> 5000). The latest experimental efforts seek better characterization[303] and to partially replace the Mg (by Li) and B (by C) atoms in MgB_2[304–306] in the hope of improving its superconducting properties. So far, however, only transition temperatures below 39 K have been found for C-substituted samples.[305]

LiBC is an electronically precise substitution variant of MgB_2, whose structure differs from the one described above in that the positions in the layers of condensed six-rings are occupied by alternating boron and carbon atoms.[307] The B/C alternation is also preserved perpendicular to the layers, so that the *c* axis is twice the length of that in MgB_2. This, too, is formally $Li^+{}_2(CB^-)_2$ in a ${}^2_\infty[C_{3/3}(B^-)_{3/3}]$ arrangement, analogous to graphite (“heterographite”). A comparison with hexagonal boron nitride BN works even better, since this also exhibits layers of condensed six-rings which are arranged directly above each other with B/N alternation perpendicular to the layers. LiBC can be synthesized from the elements at 1770 K in niobium ampoules closed by welding and the excess lithium afterwards distilled; it has a bright golden color (transparent red in thin crystals) and is soft. According to INDO calculations,[308] it is a semiconductor with a band gap of about 4.2 eV. Measurements on powder compacts show much fluctuation in the values of electrical conductivity. The B–C distance is 158.9 pm.

Fogg et al. recently published the results of a synthetically engineered underoccupation of the Li position in Li_xBC, in which a range of $0.4 < x < 0.95$ was examined.[309] The authors discuss the question as to why such compounds are not, in contradiction to theoretical predictions,[310,311] superconducting.

MgB_2C_2 is another variant of MgB_2, again an electronically precise substituted compound, in which every other Mg position is left unoccupied. The B/C six-ring layers, however, are somewhat distorted, which results in a slight corrugation. Its structure has been described in the orthorhombic crystal system.[312]

The third known structural variant of MB_2 is realized in beryllium diboride dicarbide. Its structure was first described in 1966,[313] but has only recently been definitively resolved and described.[152] This was achieved by a combination of X-ray powder diffractometry on the basis of synchrotron data, and experimental as well as theoretical determination of the ELNES. DFT calculations confirm the proposed structural model. BeB_2C_2 is dark gray and crystallizes in space group *Pmmn* (no. 59 $a = 613.42$ pm, $b = 542.20$ pm, $c = 469.28$ pm). The observed $\eta^1\eta^6$-Be coordination by B and C atoms (Figure 12) is reminiscent of the $\eta^1\eta^6$ coordination of the metal-organic compound $[BeCp_2]$ ($Cp = C_5H_5$). [314] The planar ${}^2_\infty[C_{3/3}(B^-)_{3/3}]$ layers in BeB_2C_2 are indeed displaced from each other as in graphite, so that this is the first example

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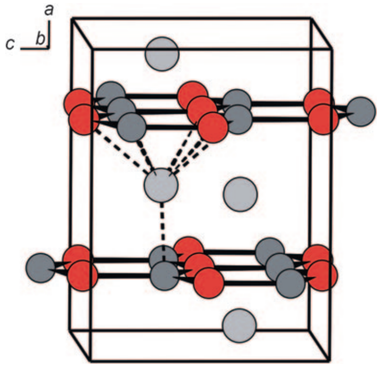

Figure 12. $\eta^1\eta^6$ coordination of Be in BeB_2C_2.

of a real graphite analogue. Superconducting properties could not be detected up to a temperature of 4.2 K.[315] However, a recently published study predicts superconductivity for $Be_xB_2C_2$ with $x < 1$, similar to the Li compound discussed above.[316]

All the borides and boride carbides with two-dimensional nonmetal arrangements described here are based on the six-ring as the smallest structural unit. Only one of the main group element compounds of boron known so far diverges from this structural principle: calcium diboride dicarbide, CaB_2C_2, which has layers of four- and eight-rings, so-called 4.8^2 nets. The crystal structure of this red substance, which is highly sensitive to air and was originally believed to be isotypic with LaB_2C_2 and $Ce_2B_2C_2$,[317] was determined on the basis of X-ray powder diffractograms in 1998 (space group $I4/mcm$, no. 140 $a = 537.3$ pm, $c = 741.6$ pm)[318] and confirmed by EELS and DFT calculations a little later.[319,320] It had been the subject of intense debate even before that, because the arrangement of the C and B atoms—the so-called "coloring",[319,320]—had not been established beyond doubt. Theoretical (Hückel) calculations showed that the stability and the physical properties (electrical conductivity) of the compound varied greatly depending on the "coloring". Having been established that the B and C atoms in the layers and perpendicular to the layers are alternately arranged—that is, in other words, the compound does not crystallize isotypically with the rare-earth diboride dicarbides (for example, neutron diffraction examinations of CeB_2C_2, space group $P4/mbm$[321])—and that CaB_2C_2 is a semiconductor, a conclusive picture finally emerges. The crystal structure of CaB_2C_2 can be derived from that of CaB_6 by two group-subgroup transitions. This requires a "translationengleiche" transition of the index 3 from $Pm\bar{3}m$ to $P4/mmm$ and a "klassengleiche" transition to $F4/mmc$ (nonstandard setting of $I4/mcm$).[318]

One thing that cannot be explained, however, is the unexpected ferromagnetic behavior that has been observed in CaB_2C_2 up to an estimated high Curie temperature of 770 K.[322] The authors compared this observation with $Ca_{1-x}La_xB_6$, but it is highly likely that it is due to undetected contamination (CaO and CaB_6 are proven contaminants), since samples synthesized from highly pure starting substances (for example, distilled calcium) do not have such properties.[323,324]

There are no further boridecarbides of main group elements, with the exception of Al_3BC_3 and Al_3BC. Al_3BC_3, the first carbide carboborate, contains single carbon atoms and C-B-C chains, well-known from boride carbide and $LiB_{13}C_2$.[325] Al_3BC_3 is an important phase in the system of "B_4C"/Al, which has been intensively investigated in the quest for highly strong composite materials, for example, for aeroplane construction.[49] It was obtained from the elements by high-temperature synthesis with an excess of aluminum (metal melt) in the form of light yellow, transparent crystals. Linear, complex anions $(C{=}B{=}C)^{5-}$ isoelectronic with CO_2 were postulated and observed by vibrational spectroscopy. The C–B distance is 144 pm, which is comparable with the distance of 143 pm in the C-B-C chains of $B_{13}C_2$. The compound is very hard: high-pressure examinations of the lattice parameters resulted in a compression module B_0 of 153 GPa,[326] the microhardness is 28 GPa.

Aluminum boridecarbide, Al_3BC, is an aluminum-rich phase which is also important for the investigation of composite materials "B_4C"/Al. It was synthesized as bluish-black crystals by high-temperature synthesis from the elements in an excess of aluminum (metal flux).[327] The boron atoms in Al_3BC are located in octahedral gaps, which is unusual. Metal borides normally have trigonal prismatic gaps in which the boron atoms are located (for example, FeB; exception: Fe_2B,[299] where the boron atom is situated in a square antiprismatic gap of metal atoms). Al_3BC is almost unique in yet another way: it is (with the exception of Mo_2BC[328,329] and boride carbides of niobium[320]) the only boride carbide known without B–C bonds.

5.5. A Boron Atom Chain: LiB_{1-x}

LiB_{1-x} ($0.82 < x < 1.0$) was obtained by reaction of the elements in niobium ampoules at 723 K. X-ray diffraction studies at room temperature showed a unique structure with a linear chain of boron atoms which is both disordered (with respect to other B chains) and incommensurable (with respect to the arrangement of the lithium atoms). After simulation of the diffuse scattering fractions, an electronic state similar to that of isoelectronic polyethyne (carbyne) was assumed for this chain.[331] Neutron diffraction studies of isotopically pure samples below 150 K,[332] however, contradict the image of alternating triple and single bonds, and instead show equidistant boron atoms in the linear chain in an ordered, but still incommensurable phase; this suggests a comparison with cumulene, in which only double bonds occur. The structure was refined in a (3+1)-dimensional periodic lattice (supergroup $P\bar{1}$; αβγ). $LiB_{0.88}$ is metallic.

5.6. Other Boron Compounds of Main Group Elements

The existence of further lithium borides that were published earlier is unconfirmed and doubtful: $LiB_{10.85}$, LiB, Li_2B, Li_5B_4, Li_3B, Li_7B_6, LiB_2, LiB_{10}, LiB_3.[333–339]

It can be stated that despite intense efforts, it has not so far been possible to produce binary borides of rubidium,

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cesium,[340] gallium, indium, thallium, tin, lead, antimony, bismuth, or tellurium.[341]

A variety of ternary, boron-poor phases are known in combination with transition metals. Compounds with gallium, indium, and tin (for example, Ga_8Ir_4B, In_3Ir_3B, $Ni_{21}In_2B_6$, $Ni_{21}Sn_2B_6$) were recently described by Adelsberger and Jansen, Klünter and Jung, as well as Ade.[342–345] Ternary borides in the system Ni/Al/B are representative of the surprises one may encounter in the field of borides.[346] Starting with the ideal composition of $Ni_{20}Al_3B_6$, two different types of aluminum atoms which are differently coordinated can be substituted differently. Besides nickel-rich phases $Ni_{20}Al_{3-x}Ni_xB_6$ $(0 < x < 1)$, there exist boron-rich phases $Ni_{20}Al_{3-y}B_{6+4y}$, $(0 < y < 2)$, where B_4 tetrahedra replace Al. Upon heating, the boron-rich phase transforms into $Ni_{12}AlB_8$, which contains single boron atoms and fragments of zigzag chains of five boron atoms.[347]

The first borosilicide with a clathrate I structure, $K_7B_7Si_{39}$, also stirred excitement when it was recently discovered. Boron atoms occupy some of the positions of silicon atoms in the clathrate framework, as determined by EELS and other methods.[348] Borosilicides with clathrate frameworks are promising candidates for good thermoelectric properties.

6. Summary and Outlook

The existence of the two modifications of boron that are obtained at ambient pressure, usually named α-rhombohedral boron or B_{12} (here: α-B) and β-rhombohedral boron or B_{105} (here: β-B) seems proven beyond doubt—even if the last successful growth of a single crystal of α-B was achieved about 40 years ago, and despite the fact that the actual number of interstial and partially occupied positions of boron atoms in β-B is uncertain. The ground-state energies of the two modifications are very similar. α-B is slightly denser, harder, and only stable at temperatures below about 1300 K. β-B is obtained from the melt. Under pressure, a phase named as γ-B_{28} is obtained which has a structure that can be derived from α-B. It is also similar in structure to boron subcompounds, for which at least $B_{4.3+x}C$, B_6O_{1-x} and B_6P can be considered as largely confirmed formulas. Variants with Si, N, As, S, and Se have also been described. These hard substances are extremely interesting compounds which are in urgent need of further characterization. The structure of binary boron compounds with main group elements can also be derived from the β-B structure. Recent studies have been concentrated in particular on $LiB_{\approx 10}$ und $MgB_{17.4}$. They lead to the conclusion that one of the boron atom positions of the so-called B_{28} unit is only two-thirds occupied, which suggests that it would be better described as a B_{27} unit. A similar claim has been made for the structure of the elemental modification. According to this, the central boron atom in the β-B structure has a distorted tetrahedral coordination, which is vaguely reminiscent of the coordination of boron or foreign atoms in the t-I structure. The t-I and t-II structures do not yet seem to be sufficiently supported by evidence for elemental modifications, but metal borides and boride carbides are known whose crystal structures have analogous boron polyhedral frameworks, which could serve as reference systems with respect to the electronic situation.

The identity and crystal structures of further boron-rich borides have been described and evaluated. For boron-rich compounds of the main group elements, linked octahedra, pentagonal bipyramids, (trigon) dodecahedra, doubly capped antiprisms and, of course, icosahedra exist, but layered structures of condensed six-rings, eight-rings, and four-rings also occur, as well as one compound with a linear chain of boron atoms. Generally speaking, boron-rich borides clearly tend towards an electron-precise composition.

The electronic structure of boron-rich compounds, their bonding situation and—resulting from this—their physical properties such as electric conductivity, Seebeck coefficients, magnetism etc., are currently being intensely studied and often initiate controversial discussion. Not all postulates advanced to explain them stand up to critical examination, as the discussion of the "model of free electron gas" has shown. It should also be stressed that a critical examination of the fundamentals on which conclusions are based would often be desirable, be it the quality of samples in experimental investigations or the quality of the structural models used for calculations. Much remains to be done. The solid-state chemistry of the element boron is full of booby traps at all levels, none of which detract from its charms.

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