Present knowledge of electronic properties and charge transport of icosahedral boron-rich solids

Helmut Werheit
Experimental Physics, University Duisburg-Essen, D-47048 Duisburg, Germany
e-mail: helmut.werheit@uni-duisburg-essen.de and helmut.werheit@koeln.de

Abstract. B\textsubscript{12} icosahedra or related structure elements determine the different modifications of elementary boron and numerous boron-rich compounds from \(\alpha\)-rhombohedral boron with 12 to YB\textsubscript{66} type with about 1584 atoms per unit cell. Typical are well-defined high density intrinsic defects: Jahn-Teller distorted icosahedra, vacancies, incomplete occupancies, statistical occupancies and antisite defects. The correlation between intrinsic point defects and electron deficiencies solves the discrepancy between theoretically predicted metal and experimentally proved semiconducting character. The electron deficiencies generate split-off valence states, which are decisive for the electronic transport, a superposition of band-type and hopping-type conduction. Their share depends on actual conditions like temperature or pre-excitation. The theoretical model of bipolaron hopping is incompatible with numerous experiments. Technical application of the typically p-type icosahedral boron-rich solids requires suitable n-type counterparts; doping and other possibilities are discussed.

1. Introduction
B\textsubscript{12} icosahedra or related components determine the crystal structures of the different modifications of elementary boron and of numerous boron-rich compounds extending from \(\alpha\)-rhombohedral boron with 12 to YB\textsubscript{66} type with about 1608 atoms per unit cell. From careful X-ray fine structure investigations (Slack \textit{et al} \cite{1-3}, Lundström (see \cite{4} and references therein), Higashi \textit{et al} \cite{5}) some of these structures are known in detail. At boron carbide these methods failed because the scattering cross section of boron and carbon is very similar, and moreover the carbon atoms are statistically distributed on specific sites. However, this problem was solved by analyzing the phonon spectra (see \cite{6}, \cite{7-10}).

Except \(\alpha\)-rhombohedral boron, the icosahedral boron-rich solids are characterized by high concentrations of well-defined intrinsic structural defects. Apart from the Jahn-Teller distortion of the icosahedra, such defects are missing or incomplete occupation of specific atomic sites, statistical occupation of equivalent sites or antisite defects.

Such high defect concentrations in the icosahedral boron-rich structures exceed negligibly weak disorder by far. This was disregarded in the electronic band structure calculations performed until now. Consequently, qualitative discrepancies arose in contradiction to experimental results. Theoretical calculations predicted metallic character in consequence of high valence electron deficiencies, while experimental results proved semiconducting behavior. This contradiction has been clarified. At \(\alpha\)-rhombohedral boron, \(\beta\)-rhombohedral boron and boron carbide (homogeneity range B\textsubscript{4.3}C to B\textsubscript{11}C), the best-investigated icosahedral boron-rich solids, there is a quantitative correlation between intrinsic point defects and electron deficiencies \cite{11} (table 1).
### Table 1. Icosahedral boron-rich structures: Comparison between theoretical electronic properties, experimental characterization and intrinsic point defects experimentally determined

| Idealized structure | 
|---------------------|
| **structure** | Valence states (unit cell) | Ref. | Valence electrons (unit cell) | Electron deficiency (unit cell) | Electronic character (theoretical) | Real structure | 
| **idealized structure** | **real structure** | **electronic character** (experimental) | **intrinsic point defects** (unit cell) | Ref. |
| α-rhombohedral boron | $B_{12}$ | 36 | [12] | 36 | 0 | semiconductor | semiconductor 0 | [13] |
| β-rhombohedral boron | $(B_{12})_4(B_{28})_2B$ | 320 | [14] | 315 | 5 | metal | semiconductor 4.92(20) | [1-3] |
| boron carbide $B_{12}C_2$ | $B_{12}(CBC)$ | 48 | [15] | 47 | 1 | metal | semiconductor 0.97(5) | [7,8] |
| boron carbide $B_{12}C$ | $B_{12}(CBC)$ | 48 | [15] | 47.83 | 0.17 | metal | semiconductor 0.19(1) | [7,8] |
| boron carbide $B_{12}C$ (hypothetical) | $B_{12}(CBC)$ | 48 | [15] | 48 | 0 | semiconductor | — | — |
| YB$_6$ | $(B_{12})_8(B_{80})_8$ | — | — | — | metal | semiconductor 304* | [5] |

* ~ 42 sites of the $B_{80}$ units are occupied implying a defect concentration of 16.1 % concerning the idealized structure $(B_{12})_8(B_{80})_8$ with 1584 of 1888 sites occupied.

Point defects in semiconductors generate split-off valence states in the band gap. Accordingly, the agreement of the concentration of experimentally proved point defects with calculated electron deficiencies implies that this way the unoccupied valence states of the idealized structures are exactly compensated in the real solids. Hence the real valence bands are completely filled, and the solids are semiconductors in accordance with experiment (see [6,11,16]). This implies that the electron deficiency evokes the generation of compensating intrinsic defects, probably for energetical reasons.

Such high concentrations of gap states attached to the valence band affect the electronic charge transport essentially; in particular they are responsible for the p-type character and the very low electrical conductivity. Aside from the electric conductivity in extended band states, hopping-type conduction in localized gap states must be expected. Their particular share depends on the actual conditions.

#### 2. α-rhombohedral boron

α-rhombohedral boron, the low-temperature modification of elementary crystalline boron can be prepared below about 1500 K. An irreversible transformation into β-rhombohedral boron, the stable modification of crystalline boron, takes place at about 1670, 1890 and 1940 K via three different metastable phases [17]. The preparation of crystals of sufficient size for optical and electrical investigations turned out to be very difficult. Therefore, only few experimental results on α-rhombohedral boron, the only icosahedral boron-rich solid without high concentration of structural defects, have been performed. Some selected results are listed in table 2. For more details, see [16].

### Table 2. α-rhombohedral boron, transition energies

| Theory | Experiment |
|--------|------------|
| eV     | eV         | Method                  | Transition type            | Ref. |
| 1.427  | 0.73(2)    | opt.                    | deep level to band         | [18] |
| ~1.6   | 1.63(2)    | opt.                    | indirect allowed interband | [18] |
| 2.4    | 2.055(2)   | opt.                    | indirect allowed interband | [21] |
|        | 2.0(2)     | el.                     | conductivity               | [22,23] |
The theoretical and experimental interband transitions agree fairly well. The nature of the level in the gap is not yet explained. The effective masses of the charge carriers are estimated to $0.031(2) \, m_0$, the mobility to $100 - 120 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [23,24], and the Seebeck coefficient $400 - 600 \, \mu\text{VK}^{-1}$ [22,23,25]. These data indicate electronic properties comparable to those of classical semiconductors, and confirm that they are not strongly influenced by defects.

These data make $\alpha$-rhombohedral boron a promising candidate for technical application. Certainly, suitable preparation methods for bigger crystals are required.

3. $\beta$-rhombohedral boron

The unit cell of $\beta$-rhombohedral boron contains 106.5 B atoms, while the idealized structure $(B_{12})_4(B_{28})_2B$ describes 15 independent B sites with 100 % occupancy, 105 atoms in total. There are four icosahedra, one at the vertex, three on the edge centres of the unit cell, and two $B_{28}$ units composed of three condensed icosahedra, each, arranged symmetrically to a centred single atom on the main diagonal of the unit cell. In particular group theoretical descriptions the alternative structure formula $B_{84}(B_{10})_2B$ is preferred with a $B_{84}$ unit consisting of the $B_{12}$ icosahedron at the vertex of the unit cell radically surrounded by 12 half-icosahedra completing each other to the $B_{12}$ icosahedra on the edge centres. Two $B_{10}$ units consisting of three condensed caps of icosahedra and the single atom on the diagonal complete this structure description of again the 105 atoms (see [16] and references therein).

In the real structure, 25.5 % of the site B(13) are unoccupied hence forming point defects of the idealized structure. Additional point defects are the sites B(16) to B(20) with 27.2 to 3.7 % occupancy [1,2]. In total their concentration agrees with the electron deficiency calculated for the idealized structure (see table 1).

The great number of atoms per unit cell in $\beta$-rhombohedral boron has prevented the calculation of the complete energy band structure. Only a density of states distribution has been reported [26] exhibiting a band gap of about 2 eV close to the experimentally determined value of about 1.5 eV. Theoretical calculations suggested assigning this gap to the Jahn-Teller distortion of the icosahedra [27]. The gap energies are listed in table 3.

| Natural isotope distribution | $^{10}$B enriched |
|-----------------------------|--------------------|
| $\Delta E_1$ | 1.32(1) | 1.27(2) |
| $\Delta E_2$ | 1.50 | 1.45(2) |

Table 3. Experimentally determined energy gaps of $\beta$-rhombohedral boron (extrapolated to $T = 0 \, \text{K}$)

Numerous experimental investigations yielded the consistent band scheme displayed in figure 1 (see [16] and references therein) [30-34].

Unfortunately, theoretical calculations on defect levels in icosahedral boron-rich solids are missing (apart from bipolaron states in boron carbide, which will be discussed below). Therefore in this respect the actual band schemes depend on experimental results only.

There are six equidistant electron traps attributed to distortions of the icosahedra evoked by electron-phonon interaction [35]. The defect states are attributed to the states separated from the valence band compensating the electron deficiency of the idealized structure. Occupied and unoccupied levels are energetically separated. The recombination of electrons excited from the valence into the conduction band essentially takes place via a cascade-like transition between the different electron traps with the electrons thermally excited from the occupied trap n to the unoccupied trap n+1. This activation energy of about 0.12 eV is the same for all traps.
Electrical transport takes place by free holes generated by thermal excitation of valence electrons into unoccupied gap states and by hopping processes between occupied and unoccupied gap states. The share of both processes depends on the actual conditions like temperature, pre-excitation and antecedent. At low temperatures hopping is prevailing, while at high temperatures the essential electrical conductivity is thermally activated.

Drift experiments with optically generated untrapped electron-hole pairs yielded the ambipolar carrier mobility $\mu_{\text{ambipolar}} = 565(120) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [34]. Long-term drift experiments are dominated by the high probability trapping processes and show a soliton-type propagation of the carriers [36].

![Figure 1](image)

**Figure 1.** Actual Band scheme of $\beta$-rhombohedral boron. Full arrows indicate experimentally determined transitions; broken lines those, whose existence is indirectly concluded.

### 4. Boron carbide

In boron carbide, there is no unit cell representing the whole structure. This is composed of nearly isomorphous elementary cells, whose conformity is merely the 12-atomic, by the Jahn-Teller effect slightly distorted icosahedra at each vertex and the mostly three-atomic linear chains on the main diagonal parallel to the crystallographic $c$-axis. $\text{B}_{12}$ and $\text{B}_{11}\text{C}$ icosahedra, $\text{C-B-C}$, $\text{C-B-B}$, $\text{B□B}$ (□, vacancy), form differently composed elementary cells, statistically distributed over the whole structure (see [6] and references therein, [9,10]). The homogeneity range extends from $\text{B}_{4.3}\text{C}$ at the carbon-rich to $\text{B}_{11}\text{C}$ at the boron-rich limit. Since the carbon-rich limit $\text{B}_{13.5}\text{C}$ was proved by Schwetz and Karduck [37] for the first time, and is meanwhile often confirmed (see e.g., [6], figure 254, and assigned references, [39,40]), the previous designation “$\text{B}_{4}\text{C}$”, based on the hypothetical structure formulas $(\text{B}_{12})\text{C}_3$ or $(\text{B}_{11}\text{C})\text{CBC}$ with uniformly composed unit cells each, is no more acceptable. If this composition occurs, it consists of the compound $\text{B}_{13}\text{C}$ and precipitated graphitic free carbon. Therefore, in particular close to the carbon-rich limit of the homogeneity range, the separate analysis of bonded and free carbon in the structure is indispensable [4]. $\text{B}_{11.2}\text{C}$ synthesized by Gosset and Colin [42] seems to be the boron carbide with the lowest carbon content hitherto obtained.

#### Table 4. Concentration of structural elements in the elementary cell of boron carbide at some selected chemical compositions within the homogeneity range ([6-10,43])

|                  | $\text{B}_{4.3}\text{C}$ | $\text{B}_{13}\text{C}_2$ | $\text{B}_{11}\text{C}$ |
|------------------|--------------------------|---------------------------|-------------------------|
| $\text{B}_{12}$ icosahedra | 0                        | 42                        | 26                      |
| $\text{B}_{11}\text{C}$ icosahedra | 100                      | 58                        | 74                      |
| $\text{C-B-C}$   | 81                       | 62                        | 7                       |
| $\text{C-B-B}$   | 19                       | 19                        | 77                      |
| $\text{B□B}$ (□, vacancy) | 0                        | 19                        | 16                      |
The IR and Raman active phonons yielded the concentrations of the structural elements (see [6], [7-10,43]) leading to the general structure formula \((B_{12})_{1-x}(B_{11}C)_x(CBC)_{1-m-n}(CBB)^m(B\square B)^n\) (some examples in table 4; marginal deviations are discussed in [51]).

A strongly emphasized description of the electronic properties of boron carbide is the bipolaron hopping model developed by Emin and associates [44-50]. However, each theory requires the confirmation by relevant experiments. As shown below, numerous experimentally proved properties of boron carbide are incompatible with (bi)polarons. Therefore, this hypothesis must be taken as definitely disproved [51].

The bipolaron model for boron carbide is essentially based on the discrepancy between a hypothetically assumed high concentration of carriers \(\square 10^{21} \text{ cm}^{-3}\) and the numerous experimental results of different authors (ESR, transport) consistently proving carrier concentrations of the order of \(\square 10^{19} \text{ cm}^{-3}\). As shown above, this high carrier concentration was substantiated by inappropriate assumptions on the microstructure for band structure calculations and does not exist in reality. Accordingly, this basic assumption for the (bi)polaron model is not valid.

The lattice polarizability, an essential requisite for the formation of (bi)polarons, is responsible for the intensity of Raman scattering as well. At icosahedral boron-rich solids the Raman effect is very weak compared with other covalent solids; for boron carbide about three orders of magnitude smaller (see, e.g., references in [6]). Such extremely small polarizabilities make the formation of bipolarons very improbable. This was confirmed by Calandra et al [52] showing that the moderate electron–phonon coupling \(\lambda = 0.81\) is too small for a bipolaronic state in \(B_{13}C_{2}\).

After Emin et al [44-49] the electronic transport in boron carbides proceeds via bipolaron hopping between \(B_{11}C\) icosahedra. However, the densities of hopping states determined according to Mott’s law for dc variable-range hopping, according to the theory of Butcher and Morris [53] for the dynamical conductivity, and corresponding to the Seebeck coefficient \(S\), which is proportional to the reciprocal density of carriers, vary opposite to the concentration of the \(B_{11}C\) icosahedra in the homogeneity range of boron carbide (figure 2). Hence this assumption in the bipolaron hypothesis is disproved as well.

Figure 2. Boron carbide. Densities of hopping sites and \(B_{12}\) icosahedra (see [6,51,63] and references therein). ●, dashed line, derived from DC conductivity after Mott’s law for variable-range hopping; ○, DC results shifted to the carbon-rich limit of the homogeneity range; ■, dash-dotted line, derived from dynamical conductivity results (FIR); ◆, dotted line, \(10^3 S^{-1}\). Seebeck coefficient \(S \sim 1/n\) (\(n\), carrier density) (see [90]); ●, full line, density of \(B_{11}C\) icosahedra (data connected by a spline function).
The problem of the effective mass is a central one in (bi)polaron physics (see e.g., Devreese [54]). Dragging the polarized surrounding with them, the mass of polarons would be considerably higher than the band mass of free holes. Unfortunately, reliable experimental effective mass values as can be obtained by cyclotron resonance experiments are not available for boron carbide. Accordingly, the concerning discussion must be restricted to more or less rough estimations (see table 5).

**Table 5. Estimations of hole masses in boron carbide**

| Band mass of free holes | Effective mass of mobile carriers |
|-------------------------|----------------------------------|
| ~ 10 $m_0$ curvature of valence band [55] | > 3 $m_0$ DC conductivity and ESR [56] |
| ~ 10 $m_0$ luminescence [57,58] | 3…5 $m_0$ IR spectra [59,60] |
| 1…10 $m_0$ Dynamical conductivity [69,70] |

Obviously, there is no indication that the effective mass of the mobile carriers in boron carbide is considerably larger than the band mass of free holes. Hence these results disprove polarons in boron carbide as well.

For supporting his bipolaron model Emin refers to the electrical conductivity of a “typical boron carbide” [44,48,49]. Figure 3 shows the discrepancy to the real conductivity in the high-temperature range consistently measured by different groups [61,62,63] (see also [6]).

![Figure 3. Boron carbide. High-temperature electrical conductivity. Dashed curve, “typical boron carbide”, Emin [44,48,49]; ▽ △ ▼ ●, Wood [62]; ■, Aselage et al [63]; Solid curves, Werheit et al [64,65]; short-dashed curves, fits for determining the activation energies.](image)

It is obvious that at high temperatures the electrical conductivity of boron carbide exhibits well-defined thermal activation energies in different ranges. This interpretation is strongly supported by corresponding gap states determined from the optical absorption edge [66,67,58]. Hence there is no sensible reason for a desperate interpretation within the bipolaron model.

After Emin [68] the coherent motion of bipolarons yields Drude-like optical spectra at low temperatures decreasing with increasing temperatures. The experimental finding for boron carbide and other icosahedral boron-rich solids is opposite to this prediction [69-72], constituting another inconsistency between polaron hypothesis and reality.
The existence of excitons in boron carbide associated to the central B atoms in the three-atomic chains was proved in two independent studies [57,73,74]. Excitons, which are formed by the interaction of free carriers, are incompatible with the existence of polaron.

As shown, there are many discrepancies and even incompatibilities between the (bi)polaron model and the real properties of boron carbide so that this hypothesis must be taken as definitely disproved. This conclusion cannot be put in question by apparently successful descriptions of properties of boron carbide like that of the very low electrical conductivity [44-50], and of the enhanced Seebeck coefficient evoked by carrier-induced vibrational softening (Emin [75] and Aselage et al [76]), because bipolarons, being the fundamental basis of these theories, obviously don’t exist in boron carbide.

The alternative for the interpretation of the electronic properties of boron carbide is the band scheme displayed in figure 4. It allows the largely consistent description of all reliable experimental results, which have become known, and therefore this band scheme seems to be a serious basis for further work.

**Figure 4.** Boron carbide. Energy band scheme based on optical absorption, luminescence, XRS, and transport properties. Left ordinate, energies related to the valence band edge; right ordinate, energies related to the conduction band edge. Arrows indicate the direction of the measured transitions.

**5. Required improvements of the energy band schemes**

The band schemes presented are not intended to be exhaustive. They are essentially based on experimental results obtained more or less close to ambient conditions. However, for β-rhombohedral boron numerous experiments, in particular those on photo-effects show that the electronic properties discontinuously vary at certain temperatures (see [16],[31,77,78]) suggesting that the energetical positions of the gap states depend on temperature. Moreover the photo-effects considerably depend on the antecedent, for example, optical excitation and frozen-in carriers. In particular at lower temperatures, β-rhombohedral boron exhibits long-term memory effects after optical or thermal excitation.

On the other hand, temperature dependent structural modifications are indicated by internal friction maxima at about 150, 250, 340 530, and 570 K (see [16],[79,80]). The last two maxima are correlated with a hysteresis in the thermal expansion curves [81-83,28]. At least some of the internal friction maxima are obviously correlated with critical points of photo-effects. Considerable differences of the electrical conductivity for compression and decompression in high-pressure experiments indicate irreversible or slowly reversible modifications of the structure as well [83].

The correlation between the gap states and the atomic sites B(13), B(16)-B(20) suggests that the energetically most favourable stable positions of these sites in the structure depend on temperature, possibly caused by the anisotropy of the thermal expansion coefficient. The strong influence of
interstitial doping on temperature and height of the internal friction maxima suggests interdependence with the partly occupied B sites. At a pressure of 160 GPa β-rhombohedral boron becomes superconducting [84]. All these aspects require further investigation.

For boron carbide the situation is probably similar. Indeed, there are no corresponding results on electronic properties, however internal friction maxima indicate temperature dependent structural variations for boron carbide as well [85], and their influence on the electronic properties seems natural.

6. Doping of icosahedral boron-rich structures

Doping of semiconductors is important for tailoring their electronic properties for application. The above-described icosahedral boron-rich solids are p-type because of their high concentration of largely unoccupied gap states close to the valence band. Therefore overcompensation to n-type requires high concentrations of doping elements.

Besides doping by the substitution of foreign atoms for boron, the rather open structures allow interstitial doping by the accommodation of foreign atoms in the voids of the structure. Because of its strong affinity to boron, carbon is a hardly avoidable doping element. C atoms typically substitute for B atoms at specific sites in the structures, for example, preferably in polar sites of the icosahedra. However, the expected n-doping resulting from the excess electron of C atom compared with B does not take place. The reason might be that the carbon levels in the gap are rather close to the valence band.

β-rhombohedral boron can be doped by the interstitial accommodation of metal atoms (for details and references see [16]). For Fe, V, Cu, Cr, Li, and Ni n-type behavior was achieved, however in a rather low degree and in limited temperature ranges only. This kind of doping is limited because a destabilization of the structure takes place. In how far the interstitial accommodation of foreign elements affects the occupancy of the sites B(13) and B(16) – B(20) (for details of these sites see ref. [1,2]) has not yet been investigated.

Systematical doping of boron carbide has become known for few elements only (see [16] and references therein). However, n-type conductivity was not realized; but sometimes the Seebeck coefficient became considerably higher. Because of the high concentrations of unoccupied gap states and the limited doping possibility compared with β-rhombohedral boron it is questionable, whether n-doping of boron carbide is possible at all. Systematic investigations on enhancing the p-type character of icosahedral boron-rich structures, e.g., by the substitution of regular B atoms by Be, are missing so far.

Figure 5. Comparison of the phonon spectra of B$_5$C and B$_5$C + Ni (Dowben et al [88] with those of boron carbide (see [6]) and amorphous boron (see [16])
7. Chances for technical application.

Electronic application of the boron-rich solids requires highlighting properties compared with classical semiconductors; such as the high Seebeck coefficient of boron carbide monotonously increasing up to more than 2000 K. Unfortunately, as already mentioned, the high concentrations of unoccupied gap states prevent compensation to n-type in boron carbide. Therefore, n-type counterparts with alternative structures but otherwise similar properties are required. Recently developed candidates are n-type alkaline hexaborides (Takeda et al [86]) or n-type RE boron carbonitrides (Mori et al [87]). A further very promising candidate is a new icosahedral boron-carbon compound (Dowben et al [88-90]). In pure form this compound is p-type, but becomes n-type by addition of Ni. This was proved by the fabrication of homojunction and heterojunction diodes combining both materials [91]. The structure of this compound is different from the boron carbide discussed above. It contains icosahedra as well, but these contain two carbon atoms, while in the icosahedra of boron carbide only one C atom substitute for B in a polar site. Moreover the three-atomic chain characteristic for boron carbide is missing. This becomes obvious by comparing the IR spectra in figure 5, showing that the 1500 cm\(^{-1}\) phonon band representing the stretching mode of the three-atomic chain is absent in this solid.

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