STRUCTURAL DEFECTS: ESSENTIAL ELEMENTS OF ICOSAHEDRAL BORON-RICH SOLIDS

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ABSTRACT

Owing to their distinguished outstanding properties, Boron and boron-rich compounds are promising for various technical applications. Icosahedra as their common structural key features suggest that physical characteristics are related. The complex structures of icosahedral boron-rich solids vary from α-rhombohedral boron with ~12 to YB66 –type crystals with ~1584 atoms per elementary cell. Their idealized structures are characterized by considerable electron deficiencies leading to the incorrect theoretical prediction of metallic behavior, opposite to experimental findings. In the real structures, high concentrations of incompletely or even unoccupied regular sites compensate these electron deficiencies, thus making them semiconductors. Hollow spaces between the icosahedra allow accommodation of foreign atoms, thus enabling tailoring individual properties. – In the examples β-rhombohedral boron and boron carbide, structural defects, their determination and the correlation with the electronic properties are described.

INTRODUCTION

Boron and boron-rich compounds are distinguished by outstanding properties like extraordinary high melting points, great hardness, low density and high chemical stability. The 10B isotope, whose share in natB is 19.9 %, exhibits a very high neutron absorption cross section. Typical applications are abrasive materials, high temperature industrial ceramics, lightweight armor, tough coatings and reinforcement of other materials, control rods in nuclear reactors or radioactive shielding. Further unique properties are auspicious for proficient applications. For example, specific electronic properties make boron carbide a highly promising candidate for direct thermoelectric energy conversion, a so far hardly noticed and underestimated method for environmentally friendly reducing the energy problem in the world. For recent reviews on β-rhombohedral boron, see Ogitsu et al.1 and Werheit2, on boron carbide, see Domnich et al.3 and Werheit4,5.

The present paper focuses on the icosahedral boron-rich solids, whose complex structures are based on nearly regular B12 icosahedra, in some cases like boron carbide containing single carbon atoms substituting for boron. These polyhedra form rigid but open networks with rather large hollow spaces in between allowing to accommodate foreign atoms, thus offering a basis for tailoring the individual properties according to technical requirements.

As the inter-icosahedral bonds are stronger than the intra-icosahedral ones, the properties are rather compatible with covalently bonded solids and far from those of molecular structures. Nevertheless,
the structures are complex; they vary from the structure group of the $\alpha$-rhombohedral boron allotrope with $\sim$12 atoms and containing boron carbide with $\sim$15 atoms via the structure group of the $\beta$-rhombohedral allotrope with 106.6 atoms to YB$_{66}$ - type compounds with 1584 atoms per elementary cell. Only few of them like $\beta$-rhombohedral boron and boron carbide have been sufficiently investigated to allow a more or less comprehensive overview. Nevertheless, due to the common structural features, cross-structural similarities of substantial properties are expected.

Such fundamental similarities are evident in the electronic properties of these structures. For decades, the scientific discussions concerned have been determined by fundamental discrepancies between experimental results proving semiconducting character and theoretical calculations predicting metallic behavior. Obviously, general specific relations between the complex structures and the electronic properties of icosahedral boron-rich solids are the reason for these discrepancies and will be discussed below.

Arguments trying to explain these discrepancies by insufficient preparation methods have been rendered obsolete by the preparation of high-quality and high-purity single crystals of sufficient size for reliable experimental investigation at least in representative cases. The substantial agreement of experimental data obtained on high-quality single crystals, samples of laboratory quality or of industrial production demonstrate the fundamental character of unusual properties.

Obviously, there is a not yet understood tendency of these structures to avoid metallic behavior by generating structural defects in concentrations exactly required. These are high, often in the order of 1 to 10 % or even more, thus explaining that theoretical calculations based on idealized undistorted structures and ignoring such high defect concentrations necessarily failed.

These complex structures exhibit largely common electronic properties like similar band gaps, semiconducting behavior in spite of the odd number of valence electrons per unit cell, hopping conduction even in high-purity crystals, p-type conduction, which is difficult to overcompensate to n-type. Apparently one essential reason for this relationship of electronic properties are the icosahedra as common elements of all these structures.

For $\beta$-rhombohedral boron and boron carbide, the best-investigated boron-rich solids, it is shown below that the electronic states in the band gaps are correlated with the structural defects.

**STRUCTURE FAMILIES OF ICOSAHEDRAL BORON-RICH SOLIDS**

Fine-structures of many of these structures are available and allow in the cases of sufficiently investigated electronic properties cross-structural conclusions on correlations between structural defects and electronic properties (for a general survey on experimental data see Refs.6,7).

- **$\alpha$-rhombohedral boron structure group.** The $\alpha$-rhombohedral allotrope of boron is described by the idealized structure formula B$_{12}$. However, IR-active phonons suggests the existence of additional single B atoms in the structure$^8$.
  Compounds in this structure group occur as B$_{12}$X$_2$ or B$_{12}$X$_3$ (X = B or specific non-B atoms in linear arrangements on the main diagonal of the rhombohedral cell). Frequent impurities and defects respectively are C atoms substituting for B in the polar sites of the icosahedra. In boron carbide, B atoms replace C in the end sites of the three-atomic chain; moreover, the central B(3) sites in the chain are incompletely occupied$^{9,10,11,12,13,14,15,16,17}$.

- **$\beta$-rhombohedral boron structure group** (idealized structure (B$_{12}$)$_4$(B$_{28}$)$_2$B or B$_{64}$(B$_{10}$)$_2$B): Incomplete occupancies of sites B(13) (74.5 %) and B(16) - B(20) (3.7 – 27.2 %)$^{18,19,20}$. 
Compounds contain metal atoms accommodated in specific interstitial sites, which are sometimes closely neighbored to or even coincide with partially occupied regular boron sites.

- **α-tetragonal structure group** (idealized structure formula \((B_{12})_4X_2Y_2\)): missing or incomplete occupation of the X, Y sites\(^{21}\),
- **β-tetragonal structure group** (idealized structure formula \((B_{21} \cdot 2B_{12})_4(X_mY_n)\). Real structure with missing or incomplete occupied X, Y sites;
  The compound \(\alpha\text{-AlB}_{12}\) has two missing B sites in \(B_{21}\) double-icosahedra\(^{22}\).
- **Orthorhombic MgAlB\(_{14}\) type compounds** (idealized structure formula \((B_{12})_4Me(1)_4Me(2)_4B_8\). The Me(1) and Me(2) sites are incompletely occupied; possibly, the non-icosahedral B sites are incompletely occupied as well (see Ref.\(^{23}\) and references therein).
- **YB\(_{66}\) type structures** (idealized structure formula \(Y_{48}\cdot ((B_{12})_{13}B_8)\cdot (B_{80})_{18}\). The occupancy of Y sites is \(~55\%) and that of the B sites in the B\(_{80}\) units 22 – 72%\(^{24}\).

In general, the real structures of most icosahedral boron-rich solids contain well-defined defects in the form of incompletely occupied sites or anti-site defects. In contrast, the calculated electronic band structures of the idealized structures exhibit incompletely filled valence bands with the Fermi level close to their upper edges, this way suggesting metallic character. In the real structures, the defects induce the change to semiconductors with completely filled valence bands as follows:

(i) An unoccupied site in the periodic crystal structure splits one electronic site from the valence band and shifts it into the band gap, where it acts as a localized electronic site.

(ii) Carbon substituting for a regular boron atom yields one excess electron, completing one unoccupied site in the valence band.

Peculiarity of the icosahedral boron-rich solids is that the structure generates exactly that number of defects, which is required to avoid metallic behavior. The unoccupied electronic states in the valence band are split-off and form localized states in the gap. The valence band remaining is completely filled, this ways establishing the semiconducting character. The numeric correlation between electron deficiencies and structural defects is shown in Table I.

| Table I. Calculated electron deficiencies of idealized crystal structures and experimentally determined point defects in real structures (Ref.\(^{22}\) and references therein) |
|---|---|---|---|---|---|
| **Valence states** | **Idealized crystal structures** | **Real crystal structures** |
| || valence electrons | electron deficiency | electronic character | electronic character | intrinsic point defects |
| || [(unit cell\(^{-1}\)] | [(unit cell\(^{-1}\)] | [(unit cell\(^{-1}\)] | (theory) | (exp.) | [(cell\(^{-1}\)] |
| *α*-rhombohedral boron\(^{*}\) | 36 | 36 | 0 | Semiconductor | Semiconductor | 0 |
| *β*-rhombohedral boron | 320: | 315 | 5 | metal | Semiconductor | 4.92(20) |
| **Boron carbide** |
| \(B_{13}C_2\) (idealized structure formula \(B_{12}(CBC)\)) | 48 | 47 | 1 | metal | Semiconductor | 0,97(5) |
| \(B_{4.3}C\) (idealized structure formula: \(B_{11}C\) (CBC)) | 48 | 47.83 | 0.17 | metal | Semiconductor | 0,19(1) |
| \(B_{4}C\) (hypothetical, idealized structure formula: \(B_{11}C\) (CBC)) | 48 | 48 | 0 | Semiconductor | --- | --- |

\(^{*}\) recently this structure of *α*-rhombohedral boron has been put in question; additional single B atoms are suggested by IR-phonon spectroscopy \(^{8}\).
Hence, a high concentration of localized states in the band gap between valence and conduction band is a characteristic feature of the electronic band schemes of icosahedral boron-rich solids. Such localized states affect the electronic transport properties considerably. \(\beta\)-rhombohedral boron and boron carbide are the representatives, which have been sufficiently investigated for allowing conclusions on the individual interaction between structural and electronic properties.

**Figure 1.** \(\beta\)-rhombohedral boron, unit cell \(^2\). \(\textbf{a}\), idealized structure \(^25\) consisting of 4 \(\text{B}_{12}\) icosahedra, 2 \(\text{B}_{28}\) units formed by 3 condensed icosahedra and one single B atom in the center; \(\textbf{b}\), additional, partially occupied regular B sites (size of icosahedra reduced) \(^25\). The six B(13) sites in the \(\text{B}_{28}\) units closely neighboured to the central B(15) are partially occupied as well. \(\textbf{c}\), interstitial sites, accommodating transition metal atoms (icosahedra omitted); green, central B(15) atom). 100 % occupied; light grey, \(\text{A}(1)\) sites; yellow, \(\text{A}(2)\) sites; blue, \(\text{D}\) sites; dark grey, \(\text{E}\) sites \(^26\).

### \(\beta\)-Rhombohedral Boron

The lattice parameters of high purity \(\beta\)-rhombohedral boron, symmetry type \(\text{R}_{3}m\), are \(a = 1.09330(5)\) and \(c = 2.38252(17)\) nm (see Refs. \(^{20,27}\)). 105 atoms in the idealized unit cell ((\(\text{B}_{12}\))\(_4\)(\(\text{B}_{28}\))\(_2\)B, see Figure 1a) are accommodated in 15 independent sites. The real structure has 20 sites with the following occupancies \(^{19,20}\) (see Figure 1b):

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1) – B(12)</td>
<td>100.0 %</td>
</tr>
<tr>
<td>B(13)</td>
<td>74.5 %</td>
</tr>
<tr>
<td>B(14), B(15)</td>
<td>100.0 %</td>
</tr>
<tr>
<td>B(16)</td>
<td>27.2 %</td>
</tr>
<tr>
<td>B(17)</td>
<td>8.5 %</td>
</tr>
<tr>
<td>B(18)</td>
<td>6.6 %</td>
</tr>
<tr>
<td>B(17)</td>
<td>6.8 %</td>
</tr>
<tr>
<td>B(20)</td>
<td>3.7 %</td>
</tr>
</tbody>
</table>
Ogitsu et al. explain the partial occupancies of specific regular sites in the β-rhombohedral boron structure by a geometrical frustration originating from the intrinsic instability of the B subunits, using an antiferromagnetic Ising model on an expanded Kagome lattice. However, this description does not answer the question, why the icosahedral boron-rich structures generate spontaneously exactly that concentration of defects, which is required to compensate the unoccupied electronic valence states.

Fig. 1c shows the interstitial sites A(1), D and E, which allow accommodating transition metal atoms. Comparing Figs. 1b and c illustrates that these sites coincide with the regular sites B(16) to B(20) or are at least closely neighboured. In such cases, simultaneous occupation is improbable. The interrelation of occupancies depending on the individual nature of the different interstitial dopants is shown in Table II.

Table II. β-rhombohedral boron doped with 3d transition metals. Averaged occupancies of interstitial sites and partially occupied regular B sites; ZnB

<table>
<thead>
<tr>
<th></th>
<th>A(1) 6c</th>
<th>D 18h</th>
<th>Dd * 36i</th>
<th>E 6c</th>
<th>B(13) 18h</th>
<th>B(17) 18h</th>
<th>B(17d) 36i</th>
<th>B(18) 18h</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-rh. B (pure)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>74.5</td>
<td>8.5</td>
<td>0</td>
<td>4.8</td>
</tr>
<tr>
<td>Sc</td>
<td>0.2</td>
<td>7.7</td>
<td>0</td>
<td>50.3</td>
<td>74.8</td>
<td>11.3</td>
<td>0</td>
<td>4.8</td>
</tr>
<tr>
<td>Ti</td>
<td>14.6</td>
<td>28.4</td>
<td>0</td>
<td>2.5</td>
<td>71.2</td>
<td>4.7</td>
<td>2.8</td>
<td>12.8</td>
</tr>
<tr>
<td>V</td>
<td>49.0</td>
<td>2.5</td>
<td>0</td>
<td>2.5</td>
<td>71.2</td>
<td>4.7</td>
<td>2.8</td>
<td>12.8</td>
</tr>
<tr>
<td>Cr</td>
<td>63.9</td>
<td>1.9</td>
<td>0</td>
<td>2.5</td>
<td>71.2</td>
<td>4.7</td>
<td>2.8</td>
<td>12.8</td>
</tr>
<tr>
<td>Mn</td>
<td>4.9</td>
<td>11.0</td>
<td>0</td>
<td>1.1</td>
<td>69.8</td>
<td>11.7</td>
<td>0</td>
<td>10.3</td>
</tr>
<tr>
<td>Fe</td>
<td>33.4</td>
<td>8.7</td>
<td>0</td>
<td>0</td>
<td>75.3</td>
<td>0</td>
<td>3.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Co</td>
<td>33.5</td>
<td>15.5</td>
<td>0</td>
<td>0</td>
<td>64.1</td>
<td>1.8</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>Ni</td>
<td>13.3</td>
<td>2.4</td>
<td>6.2</td>
<td>0</td>
<td>68.4</td>
<td>4.8</td>
<td>4.6</td>
<td>14.1</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0</td>
<td>4.3</td>
<td>2.1</td>
<td>72.0</td>
<td>0</td>
<td>6.5</td>
<td>14.5</td>
</tr>
<tr>
<td>Zn**</td>
<td>49</td>
<td>34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*) Dd, distorted D sites; for details see Ref. , **) ZnB, additional site G, 13 % occupancy

Figure 2. β-rhombohedral boron; actual band scheme. Full arrows, experimentally determined transitions; dashed arrows, indirectly concluded transitions.
As mentioned, theoretical band structure calculations on β-rhombohedral boron predicted metallic character opposite to experimental findings. The electronic band scheme (Figure 2), which is derived from experimental results, allows consistently describing most of the available experimental results. We have to distinguish between two kinds of gap states:

- Permanent gap states, which are generated by the structural defects mentioned splitting acceptor-like gap states off from the valence band,
- Temporary gap states in the form of electron traps. They are formed after the generation of electron/hole pairs in particular by optical excitation. Excited electrons polarize the icosahedra thus forming local self-trapping binding potentials for electrons.

Some of the experimental results, which are essential for the band scheme in Figure 2, are shown below.

The optical absorption edge in Figure 3 is essentially determined by the energy dependence of the densities of states in valence and conduction band, steeply increasing at the band edges. Theoretical models allow determining energies and characters of interband transitions. Luminescence spectra (insert of Figure 3) are compatible with the absorption. Higher interband transition energies were obtained from dielectric function35 and derivative reflectivity spectra36.

![Figure 3](image)

**Figure 3.** Electronic transitions of β-rhombohedral boron by optical absorption. High-purity31 and carbon doped material32,33, Photoluminescence 34, dielectric function 35 and differential reflectivity ΔR/R 36. Transition energies are indicated by vertical lines.

The electrical conductivity between 140 and 2000 K is displayed in Figure 4 in two versions. Straight-line plot in a specific graphical depiction means agreement with the concerning theory of electronic transport. At high temperatures, the conductivity is thermally activated and the
activation energy corresponds to the optical band gap. At low temperatures, the electrical conductivity varies according to Mott’s theory of variable-range hopping\textsuperscript{82,83,84,85,86}, thus proving the decisive influence of the gap states generated by structural defects.

**Figure 4.** Electrical conductivity of β-rhombohedral boron vs. \(1/T\) and \(T^{-1/4}\) (variable-range hopping)\textsuperscript{37,38}. Insert, Seebeck coefficient of high-purity boron \textsuperscript{37}.

This is compatible with the thermoelectric power (insert of Figure 4). At low temperatures, where hopping is prevailing, the Seebeck coefficient increases with rising temperature, as the mobility of charge carriers increases. Positive sign indicates positively-charged carriers (holes) to be decisive. At high temperatures, in the range of intrinsic conductivity, the Seebeck coefficient decreases with rising temperature. There, negatively-charged electrons contribute progressively to the charge transport and compensate partially the still dominating influence of holes.

The structural defects, responsible for the stationary gap states in β-rhombohedral boron, exhibit a geometrical order described by an antiferromagnetic Ising model on an expanded Kagome lattice (Ogitsu et al.\textsuperscript{28,1}, see above). This description holds for ambient conditions and depends on the atomic potentials at low temperatures. Apparently, these potentials are temperature-dependent, as can be deduced from a weak phase transition near 570 K evidenced by Hoffman and Werheit\textsuperscript{39} (Figure 5). As the main structure parameters change monotonically in this range, the phase transition is obviously limited to structural changes within structural components without affecting
the global structure. Accordingly, partially occupied states are involved, probably by changes of local atomic potentials. Indeed, details remain open.

**Figure 5.** Specific heat capacity of β-rhombohedral boron in dependence on heating rate (heating – above and cooling – below) \(^{39}\). Before these measurements, the used crystal pieces were stored in the laboratory with ambient illumination.

**Figure 6.** Photoconductivity of \(\alpha\)-rhombohedral boron in thermal non-equilibrium at 155 K; electron traps filled after optical excitation across the band gap \(^{40}\) Black, as measured; red, smoothed with the software program ORiGiN.
Few remarks to the temporary gap states in $\beta$-rhombohedral boron: Electrons excited by optical excitation across the band gap are captured in the series of traps shown in the band scheme (Figure 2). Obviously, these are due to self-trapping processes; the excited electrons polarize the icosahedra, this way forming their own capturing binding potential. This polarization distorts the icosahedra along one of the six diagonals of the icosahedron; that is assumed to be the reason of six equidistant trapping levels in the gap.

At sufficiently low temperatures, the thermal energy is not sufficient for fast thermal re-exitation and subsequent recombinination of trapped electrons with holes in the valence band range. Hence a stationary thermal non-equilibrium is established. This has been analyzed by photo-absorption and photo-conductivity measurements including the results of EPR measurements. As an example, Figure 6 shows the photo-conductivity depending on photon energy at 155 K. The sequence of traps is immediately visible from the series of absorption processes starting at specific transition energies each.

As shown in Table II, there is an interdependence between the occupancy of partially occupied regular sites by boron atoms and interstitial doping with metal atoms. In some cases, this has strong impact on the electronic properties. At specific concentrations, interstitial doping with Fe and V atoms changes the p-type character of $\beta$-rhombohedral boron to n-type. This is indicated by the the Seebeck coefficient in Figure 7, changing its sign from plus to minus.

![Figure 7](image)

**Figure 7.** Seebeck coefficient of $\beta$-rhombohedral boron interstitially doped with the $3d$ transition elements V and Fe vs. metal content at ambient conditions. B:V, B:Fe.

Analyzing this transition in the case of vanadium, ~0.15 V atoms per unit cell compensate the electron deficiency of 5 valence electrons (Bullet, see Table I). Assuming charge transfer from the dopant to the basic structure like in classical semiconductors, this means that the vanadium atoms would release ~33 electrons each. As neutral V has 23 electrons only, this interpretation is definitely excluded. Hence a sophisticated interaction between the electronic states of interstitial dopant and partially occupied sites must exist. For a detailed discussion, see Ref.2. The final clarification of this problem is still missing.
Boron Carbide

For general reviews on the properties of boron carbide see Refs. 3, 4, 68; a recent review on the electronic properties of boron carbide was given by Werheit 5.

Compared with β-rhombohedral boron, the structure of boron carbide is more complex in spite of belonging to the less complex α-rhombohedral boron structure group having the same symmetry type $R\bar{3}m$. Initially, a rhombohedral unit cell of boron carbide was assumed to be formed by B$_{12}$ icosahedra at the vertices and a linear CCC chain on the main diagonal parallel to the crystallographic c-axis, leading to the chemical composition B$_{12}$C$_3$ (structure formula (B$_{12}$) CCC). After the central chain atom was proved solely boron, the structure model was modified to (B$_{11}$C) CBC. This is depicted in Fig. 8 using the program VESTA 53.

Figure 8. Structure model of boron carbide. Elementary cell (left) containing differently composed structural elements, B$_{12}$ or B$_{11}$C icosahedra, CBC, CBB and B□B (□, vacancy) linear chains.

The apparently plausible formula B$_4$C is long since proved wrong 54; nevertheless it is still often used as synonym for boron carbide. In reality, the chemical compound B$_4$C or B$_{12}$C$_3$ does not exist, at least not, when common high-temperature preparation methods melting or hot-pressing are applied. The real homogeneity range of boron carbide extends from the carbon-rich limit B$_{4.3}$C 54 to the boron-rich limit B$_{10.8}$C 17. The concentrations of various structure elements depend on the actual chemical composition; their distribution is assumed to be statistical, as no superlattice has been identified so far:

- B$_{12}$ icosahedra
- B$_{11}$C icosahedra with the C atom accommodated in one of the 6 polar sites
- CBC chains
- CBB chains
B□B arrangements (□, vacancy)

Accordingly, boron carbide has no periodic crystal structure with a well-defined unit cell, but exhibits at most an elementary cell with a twelve-atom icosahedron and a mostly three-atom chain, both in varying compositions. Therefore, the prominent methods of structure analysis, x-ray as well as neutron scattering and NMR, fail.

In boron carbide, X-ray and neutron diffraction average large volume with differently composed elementary cells. Hence, these methods yield the atomic sites correctly, but are unable to determine their individual occupancies. This problem is aggravated by the difficulty of these methods to distinguish B and C atoms due to their very similar scattering cross sections.

The NMR spectra contain resonances of $^{11}$B and $^{13}$C isotopes respectively. Their local environments vary in the volume analyzed; thus the general problem in interpreting NMR spectra using more or less arbitrarily chosen structure models for fitting is decisively aggravated in boron carbide. The random mixture of differently composed cells and structural elements makes a reliable analysis of the spectra nearly impossible.

An exception in the boron carbide structure is the central B(3) atom in the elementary cell, which is exclusively occupied by boron atoms, if not unoccupied. Hence, the occupancy of this site can be determined and yields the quantity of chain-free cells or, differently expressed, vacancies of the central B site in the elementary cells by different methods, X-ray and neutron diffraction included.

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As shown in Figure 9, the results of the different methods are consistent: (i) phonon spectroscopy, (ii) neutron powder diffraction, (iii) accommodation of Si atoms, (iv) x-ray scattering.

The problems in determining the structure of boron carbide was overcome by phonon spectroscopy. Figure 10 shows typical spectra of the IR-active phonons. Systematic experimental investigations and theoretical calculations by Shirai et al. and Vast et al. allow attributing some of the phonon modes to specific movements of atoms.

![Figure 10. IR phonon spectra of some $^{10}$B enriched boron carbides (see Ref.17). Attribution of IR-active phonons of boron carbide to movement patterns of specific atoms; arrows indicate moving direction of the central B atom in the particular vibration.](image)

For a detailed description of the numerical evaluation of the different phonon modes of boron carbide, see Ref. The resulting concentrations of different structural components of boron carbide depending on the carbon content are displayed in Figure 11.

In order to determine the concentration of actual defects in boron carbide, which generate localized gap states and their effect on the electronic structure, the energetically most probable structure formula (B$_{12}$)CBC seems appropriate for a reference. Then, according to Schmechel and Werheit, the actual defects in boron carbide are

- B$_{11}$C icosahedra, exhibiting one excess electron compared with B$_{12}$ icosahedra, accordingly generating one donor in the electronic structure,
- CBB chains. Compared with CBC, they have a deficiency of one electron and yield accordingly one acceptor,
- B□B arrangements. Compared with CBC, they have a deficiency of four electrons and yield four acceptors each.
Figure 11. Concentration of structure elements of boron carbide vs. carbon content. 
a, CBC, CBB and B□B (□, vacancy). **Isotopically pure BₓC:** Full squares, CBC chains (derived from the stretching mode); open squares, CBB chains (derived from the stretching mode); triangles, CBC chains (derived from the Eₐ mode); dashed-dotted line, average of chainless elementary cells (see Fig. 4). **natBₓC:** Full diamonds, CBC; open diamonds, CBB.

b. B₁₁C and B₁₂ icosahedra. **Isotopically pure BₓC:** Squares. **natBₓC:** diamonds, this work;. Circles, results obtained from other natB₄.₃C spectra.

Figure 12. Actual electronic band scheme of boron carbide⁶₈.

The electronic band scheme of boron carbide (Figure 12) derived from experimental results reflects the various gap states. There are indirect interband transitions at 2.09 and 2.41 eV¹¹,⁶⁹. These were derived from the optical absorption edge by fitting theoretical models of interband transition to the experimental results (Figure 13). A strong absorption in the edge tail with maximum at 1.5 eV, confirmed by luminescence measurements, has been attributed to an exciton⁷⁰,⁷¹.
Basic electronic transport measurements are presented in Figures 13 – 15. At high temperatures, the electrical conductivity is thermally activated. Different activation energies, depending on temperature, indicate that the Fermi level is subsequently pinned in different high-density gap states. These prevent intrinsic conductivity up to very high temperatures. As shown in Figure 14, up to temperatures considerably higher than 2000 K, the electrical conductivity is determined by several distinct activation energies in limited ranges of temperature, each \( E_a \). The kink at 2300 K in the results of Wood\(^7\)\(^2\)\(^7\)\(^3\) indicates that even at such high temperatures the Fermi level is pinned in gap states, and even close to the melting point there is no intrinsic conductivity.

At lower temperatures, the electrical transport (Figure 15) is determined by variable-range hopping between localized gap states.

The Seebeck coefficient (Fig. 16\(^7\)\(^3\)\(^7\)\(^4\)) underlines the gap state-determined electronic transport at high temperatures. It’s temperature dependence deviates significantly from intrinsic transport in typical semiconductors, where the Seebeck coefficient decreases to small values, as the number of electrons and holes is nearly equal and hence their contributions to the Seebeck coefficient compensate largely each other. In boron carbide, the effect of holes remains prevalent and yields the high Seebeck coefficient up to very high temperatures. This makes boron carbide a promising candidate for thermoelectric energy conversion\(^7\)\(^4\).

In conclusion, the electronic transport is determined by high-density gap states generated by structural defects. The valence band remaining is completely occupied thus bringing out the semiconducting character of boron carbide (see Ref.\(^2\)\(^2\)). Band-type and hopping transport of charge carriers determine the electronic properties. Both mechanisms coexist, but one of them usually prevails depending for example on temperature.
**Figure 14.** High-temperature electrical conductivity of boron carbide$^{4,72,73}$.

**Figure 15.** Electrical conductivity of boron carbide$^{75,68,7}$ plotted vs. $T^{-1/4}$ (Mott’s theory of variable-range hopping).
The qualitative relation between structural defects and electronic properties in boron carbide is meanwhile widely accepted, though it contrasts fundamental with the theoretical band structure calculations determining boron carbide to be metallic. Merely Bylander et al. obtained completely filled valence bands in the case of the likewise hypothetical structure \((\text{B}_{11}\text{C})\text{CBC}\), which is outside the homogeneity range.

The quantitative concentrations of the structural elements, determined by Werheit and Shalamberidze on isotopically pure boron carbides, allow checking the suitability of the hypothetical structure models \((\text{B}_{12})\text{CBC}\) and \((\text{B}_{11}\text{C})\text{CBC}\) determining the related concentrations of donors and acceptors. The results are shown in Figures 17a and b respectively. The chain-free cells
(represented by B□B (□, vacancy) are taken into account alternatively with 3 acceptors each for the missing central B atom and 5 acceptors considering the exchange of the carbon atoms at chain ends by boron additionally. As shown, the results are qualitatively the same:

Taking (B₁₁C)CBC for reference, Figure 17a shows the concentration of acceptors monotonically increasing depending on the carbon content. This is incompatible with the experimentally proved maximum acceptor concentration near the compound B₁₃C₂ (see Figures 17 - 19). With (B₁₂)CBC as reference. Figure 17b indicates that donor prevails near the carbon-rich limit of the homogeneity range in contrast to p-type behavior proved in the whole homogeneity range. Hence, both hypothetical models are individually unsuitable to describe the electronic properties of boron carbide throughout the whole homogeneity range.

Waiving a single reference structure for the whole homogeneity range and taking instead that structure model for reference, which is prevailing in the respective part of the homogeneity range, a composition-dependent defect concentration is obtained, which is compatible with the electronic transport properties. These reference structures are (B₁₁C)CBC prevailing in the carbon-rich and B₁₂CBC prevailing in the boron-rich part of the homogeneity range. Accordingly, B₁₂ icosahedra are defects in the carbon-rich and B₁₁C icosahedra defects in the boron-rich region respectively. In the center of the homogeneity range with 50 % B₁₂ and B₁₁C icosahedra each, both descriptions are equivalent. The results in Figure 1c confirm previous conclusions that the chemical compound B₁₃C₂ has the most-distorted structure in the whole homogeneity range. In this compound, nearly 80% elementary cells exhibit any kind of structural distortion.

The compatibility of the composition-dependent defect concentration (Figure 17c) and the electronic transport properties of boron carbide is proved in Figures 18 - 20. Figure 18 contains dc and ac electrical transport properties at ambient conditions at high temperatures. Figure 18 shows the parameter \( \Pi^2 \) of the dynamical conductivity (FIR reflectivity), where \( \Pi^2 = N/\omega \tau^2 \) is proportional to the density of free charge carriers, assuming that the scattering frequency \( \omega \tau \) is independent or at least largely independent of the carbon content.

![Figure 18](image_url)

**Figure 18.** Transport properties of boron carbide at ambient conditions and high temperatures vs. carbon content. **a.** Dc and ac electrical conductivity and Seebeck coefficient. **b.** Carrier density of the dynamical conductivity. With \( \square \square \square \) assumed to be independent of the carbon content, \( \square \square \square^2 = N/\square \square \square^2 \) is proportional to the density of free carriers. Sum of defects (Figure 16c) for comparison.
In Figure 19, the low-temperature (T = 10K) electrical conductivity is displayed vs. carbon content. According to Mott’s theory of variable-range hopping \(^{82,83,86}\), the hopping probability varies \(\sim \exp (-2\alpha D)\) (\(\alpha\), localization length; \(D\), distance of localized states, immediately related to their density). The accordingly expected exponential correlation with the defect concentration is satisfactorily confirmed.

![Figure 19](image)

**Figure 19.** Low-temperature (10 K) electrical conductivity in logarithmic scaling. vs. carbon content. Sum of defects (Figure 16c) for comparison.

This way, the general correlation between structural defects and electronic properties is established. However, the individual reasons of correlation remain open. Recent results of the specific heat at high temperatures by Werheit et al.\(^{87}\) and pressure-dependent optical properties by Hushur et al.\(^{88}\) provide valuable information on this subject.

![Figure 20](image)

**Figure 20.** Specific heat of B\(_{4.3}\)C boron carbide vs. T \(^{87}\). Open circles, measured; red dashed line, polynomial fit; black line, difference between measured data and fit; dotted line, 1\(^{st}\) derivative.
The specific heat shows a weak phase transition at 712 K. Taking additional results on specific phonons into account\textsuperscript{87}, it seems obvious that this phase transition is closely related to the three-atomic chain. This suggests that the chain-free elementary cells of boron carbide are involved in this phase transition as well.

Transparency photos of a B_{4.3}C single crystal, reported by Hushur et al.\textsuperscript{88} show that this is opaque up to about 37 GPa only. Then it becomes red transparent; meaning that the transparency increases, while the band gap remains largely unchanged. However, the gap increases, when the pressure increases further: The color changes from red via orange to yellow, and at pressures exceeding \sim 60 GPa, B_{4.3}C boron carbide is colorless transparent.

From transparency photos, the pressure-dependent width of the band gap has been estimated. In Figure 21, it is compared with numerous experimental and theoretical results. Initially, with the pressure increasing, obviously the defect-induced gap states vanish, and the transparency in the red spectral range increases accordingly. This changes between \sim 50 and \sim 70 GPa, where the color of the transmitted light varies; indicating that the gap width increases.

Fine structure investigations using synchrotron monochromatic SXD technique depending on pressure\textsuperscript{88} indicate that the structural changes are essentially restricted to the three-atomic chains. Due to the problems of the diffraction measurements in the case of boron carbide discussed above, it seems probable that the chainless cells are involved as well.

Apparently, the atomic potentials of the partially occupied sites are modified by external influences like temperature and pressure, and by internal influences like occupation of nearby interstitial sites with metal atoms. Nevertheless, the basic structure remains largely unchanged.

![Figure 21. Energy gap of B_{4.3}C boron carbide depending on pressure\textsuperscript{88}. Theoretical calculations: Open diamonds, \textsuperscript{52,67,78,89}; pink filled diamond, ordered structure \textsuperscript{90}, pink vertical bar, varying configurational disorder\textsuperscript{90}; red filled circles, pressure dependence\textsuperscript{92}. Experimental results: Blue open squares, ambient conditions\textsuperscript{91,35,32}; blue filled triangles, this work; dash-dotted lines, pressure-dependent decreasing gap based on the results of Dekura et al.\textsuperscript{92} and adapted to results of Werheit et al.\textsuperscript{34}.](https://example.com/figure21.png)
CONCLUSION

As shown by the examples $\beta$-rhombohedral boron and boron carbide, structural defects are essential components in the structures of icosahedral boron-rich solids. Usually, they are regular sites in the structure, which are partially occupied or even completely unoccupied. They are generated in exactly those concentrations, which are required to avoid the metallic character that is expected by theoretical calculations on idealized structures. The driving force for this behavior is still unknown. Apart from this fundamental influence on the electronic structure, the defects determine essentially the character of the electronic transport. At low temperature, hopping processes between localized states in the band gap are decisive. At high temperatures, the densities of states are sufficiently high to pin the Fermi level in limited ranges of temperature.

The concentration of structural defects and the related electronic gap states can be influenced by various parameters, such as temperature and pressure. At ambient conditions, at least in the case of $\beta$-rhombohedral boron, strong interaction with interstitially accommodated metal atoms takes place, even allowing to change the basic p-type character to n-type.

Essential questions on the generation and function of structural defects in the icosahedral boron-rich solids are unsolved and need clarification to prepare the way of further technical application of these solids with extraordinary properties.

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