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Correlation between structural defects and electronic properties of icosahedral boron-rich solids

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Abstract. From fine-structure investigations it is well known that in many icosahedral boron-rich solids the occupation densities of specific atomic sites are considerably reduced. Investigations of the electronic properties have proved that the electronic properties of these semiconductors are strongly influenced by high densities of intrinsic states in the band gaps. For β-rhombohedral boron and boron carbide, the best investigated icosahedral boron-rich solids, it is shown that the concentrations of structural defects and electronic gap states are quantitatively correlated, and that this way the electron deficiencies theoretically calculated for the valence bands of corresponding idealized structures are compensated. Obviously, the structural defects in these crystals are the necessary consequence of the valence electron deficiency. It is suggested that this correlation holds for the icosahedral boron-rich solids in general.

1. Introduction

The structures of icosahedral boron-rich solids extend from α-rhombohedral boron with 12 to YB_{66} type crystals with approximately 1608 atoms per unit cell. Irrespective of the structural diversity they are related by B_{12} icosahedra forming the basic elements of all these structures. Careful fine-structure investigations of many of these crystals are available and indicate that apart from α-rhombohedral boron, whose structure is formed by one B_{12} icosahedron on the vertex of the rhombohedral unit cell, the structures of all the other icosahedral boron-rich solids are more or less characterized by the existence of well defined defects in the form of incomplete occupations of specific sites or of antisite defects. At least in many cases, insufficient preparation methods can be excluded as the reason for these structural defects. This suggests that they are fundamental peculiarities of icosahedral boron-rich structures.

Examples of such defects (for a general survey see [1] and [2]) are

- *α-rhombohedral boron structure group* (idealized structure formulas $B_{12}X_2$ or $B_{12}X_3$ ($X = B$ or specific non-B atoms in two-atom or three-atom arrangements on the main diagonal of the rhombohedral unit cell)): incompletely occupied sites in the chains [3–10].
- *β-rhombohedral boron structure group* (idealized structure formula $(B_{12})_4(B_{28})_2B$ or $B_{84}(B_{10})_2B$): considerably reduced occupation densities of B(13) (74.5%) and of B(16) to B(20) (3.7–27.2%) [11–13].
- *α-tetragonal structure group* (idealized structure formula $(B_{12})_4X_2Y_2$): missing or incomplete occupation of the X, Y sites [14].

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- *β-tetragonal structure group* (idealized structure formula $(B_{21} \cdot 2B_{12})_4(X_mY_n)$: missing or incomplete occupation of X, Y sites, two missing B sites in B_{21} double icosahedra (B_{19} in α-AlB_{12}) [14].
- *Orthorhombic $MgAlB_{14}$ type compounds* (idealized structure formula $(B_{12})_4Me(1)_4$ $Me(2)_4B_8$): incomplete occupation of the Me(1) and Me(2) sites, possibly incomplete occupation of the non-icosahedral B sites (see [15] and references therein).
- *YB_{66} type structures* (idealized structure formula $Y_{48}\cdot((B_{12})_{13})_8\cdot((B_{80})_8)$: reduced occupation of the Y sites ($\sim$55%) and of all the B sites in the B_{80} units (22–72%) [16].

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

Franz and Werheit [17, 18] pointed out the role of the Jahn–Teller distortion of the B_{12} icosahedra leading to a separation of occupied and unoccupied electronic states and thus explaining the semiconducting behaviour. They assumed the experimentally proved electronic level 190 meV above the actual valence band [19] in β-rhombohedral boron to result from the Jahn–Teller splitting. However, there remained the inconsistency that the optical interband transitions seemed to indicate band type behaviour of this split-off band implying extended states, while the interpretation of the transport properties required localized states in this electronic level [20]. Since the static Jahn–Teller effect distorts the B_{12} icosahedra of the structure in the same way, the resulting electronic states have the translation symmetry of the crystal and should be delocalized.

The CI (configuration interaction) calculation by Fujimori and Kimura [21] on the icosahedral $B_{12}H_{12}$ cluster, well representing the bonding of B_{12} icosahedra in β-rhombohedral boron and boron carbide, proved that the Jahn–Teller effect distorting the regular icosahedron to the D_{3d} symmetry of the α- and β-rhombohedral boron structure groups leads to a separation between ground and first excited state of about 1.5 eV. This value is close to the typical band gaps of many icosahedral boron-rich solids, which seem to be accordingly explained; however it considerably exceeds the distance between the actual valence band and the split-off band. Hence its attribution to the Jahn–Teller effect cannot be maintained and its identification requires new considerations.

Band structure calculations have been restricted to idealized structures. This means that structural defects are neglected or hypothetical structure models were used, which are not in agreement with the real structures. The results are characterized by deficiencies of valence electrons implicating metallic behaviour in contrast to the experimental results and by the absence of the high-density gap states which are experimentally proved to strongly influence the electronic properties of these solids.

For β-rhombohedral boron and boron carbide, the best investigated boron-rich solids, it is subsequently shown that the densities of specific electronic states in the band gaps can be quantitatively correlated with the densities of structural defects.

2. Relation between electron deficiencies and structural defects

Band structure calculations of the complex icosahedral boron rich solids are impeded by the large number of atoms per unit cell and have become only available for α-rhombohedral boron [22–26], β-rhombohedral boron [27] and boron carbide (B_4C and $B_{13}C_2$) [28–31]. They are

based on idealized structures without defects but use the real atomic positions known from fine structure investigations, and thus the Jahn–Teller distortion of the B_{12} icosahedra can be assumed to be implicitly considered. While the band structures calculated by different authors slightly differ in energies and symmetry properties, the densities of valence states are largely consistent and, apart from α-rhombohedral boron, small deficiencies of valence electrons result ($\sim$1.5% for β-rhombohedral boron and $\sim$2% for boron carbide $B_{13}C_2$). A compensation of these deficiencies by structural defects is suggested in [27] and [29], and Bullett [32] assumes that the numerous intrinsic defects in the structure could have an electronic origin. However, these aspects have not yet been discussed in detail. The experimentally proved high densities of electronic states in the band gaps of the icosahedral boron-rich solids are missing in all calculated band structures.

The concentration of intrinsic structural defects can be determined from the occupation densities determined by x-ray fine structure investigations:

- In α-rhombohedral boron the two different atomic sites B(1) and B(2) are completely occupied, and hence the defect concentration is zero.
- In β-rhombohedral boron the regular B(13) position is occupied by 74.5(6)% [11] and the sites B(16)–B(20) by 27.2%, 8.5%, 6.6%, 6.8% and 3.7% (in total 1.7 B atoms per unit cell) respectively [12, 13]. This leads to an intrinsic point defect density of about 4.9 defects per unit cell ($\sim$4.7 at.%).
- In boron carbide the defect concentration is already high when only the considerable variation of the carbon content within the homogeneity range is taken into account. Moreover, the concentrations of B_{12} and $B_{11}C$ icosahedra, CBB and CBC chains vary and chainless unit cells occur when the composition deviates from the carbon-rich limit $B_{4.3}C$ of the homogeneity range [5]. According to Kleinman *et al* [29] $B_{13}C_2$ with the structure formula B_{12}(CBC) is the energetically most favourable structure, and, therefore, it will be taken for reference. Then, based on the 42% B_{12} icosahedra 58% $B_{11}C$ icosahedra, 62% CBC chains, 20% CBB chains and $\sim$19% missing chains experimentally determined by Kuhlmann *et al* from phonon spectroscopy [5, 6], the defect concentration in $B_{13}C_2$ is about 9.3 at.%.
- According to Higashi *et al* [16] the occupancies of the sites B(10)–B(13) in the non-icosahedral B_{80} unit of YB_{66} are 72, 65, 31 and 22% respectively leading to an actual number of $\sim$42 B atoms in this B_{80} unit and to an average defect concentration of 17 at.%.

For some structures the calculated deficiencies of electrons in the valence bands and the concentrations of structural defect are compared in table 1. Obviously, there is a strong correlation between them, hence suggesting the valence electron deficiency to be the driving force for the generation of structural defects in icosahedral boron-rich solids.

3. Electronic properties of point defects

Since theoretical calculations on the electronic properties of point defects in icosahedral boron-rich solids are lacking, the following considerations are only qualitative. At first, the different kinds of possible point defect must be distinguished concerning their varying effect on the electronic structure:

For an *interstitial* site, the electronic states of the atom are localized due to the lack of translation symmetry. Hence the number of valence band states remains unchanged, while the number of valence electrons increases, when the interstitial atom is ionized.

Table 1. Calculated electron deficiencies for the valence bands of idealized crystal structures and experimentally determined point defect concentrations in the real crystals.

Idealized crystal structure					Real crystal structure		
Valance states [per unit cell]		Valence electrons [(unit cell)$^{-1}$]	Electron deficiency [(unit cell)$^{-1}$]	Electronic character (theoretical)	Electronic character (experimental)	Intrinsic point defects [per unit cell]	
α-rhombohedral boron							
36	[22]	36	0	semicond.	semicond.	0	[3]
β-rhombohedral boron							
320	[27]	315	5	metal	semicond.	4.92(20)	[12]
boron carbide							
$B_{13}C_2$ (idealized structure formula B_{12}(CBC))							
48	[28]	47	1	metal	semicond.	0.97(5)	[5, 6]
$B_{4.3}C$ (idealized structure formula: B_{11}C(CBC))							
48	[28]	47.83	0.17	metal	semicond.	0.19(1)	[5, 6]
hypothetical B_4C (idealized structure formula: B_{11}C(CBC))							
48	[28]	48	0	semicond.	—	—	—

In a covalent crystal every regular bond between neighbouring atoms contributes to the total number of valence band states. In a *vacancy* these regular bonds are broken. The reconstructed bonds have no translation symmetry and hence the related unoccupied electronic states are localized and energetically separated from the valence band. Accordingly, vacancies reduce the number of valence band states.

In binary A_nB_m compounds like boron carbide *antisite defects* occur, when A substitutes for B or *vice versa*. If, as in boron carbide, the number of electrons of the atoms differs by only one, an antisite defect generates a donor and an acceptor state respectively. The acceptor removes one electron from the lattice and reduces the number of valence band states by one. This occurs as an unoccupied localized state, which is shifted into the band gap. The donor supplies an additional electron to the lattice, but does not change the number of valence band states.

Based on these considerations, the number of electronic states generated by the above-mentioned structural defects can be estimated for β-rhombohedral boron and boron carbide:

3.1. β-rhombohedral boron

In the rhombohedral unit cell, there are 1.52 vacancies (six partially occupied crystallographically equivalent B(13) sites) and 3.38 interstitial atoms (weakly occupied sites B(16)–B(20)). Bullett [27] calculated for the idealized structure (sites B(1)–B(15) fully occupied, B(16)–B(20) unoccupied) 320 valence band states occupied by $3 \times 105 = 315$ valence electrons.

The B(13) site has the coordination number 6 like the surrounding B sites as well, and hence half of the three valence electrons can be attributed to each regular bond. For each B(13) vacancy there are three electronic states and three electrons are removed from the valence band. Moreover, $6 \times 1/2 = 3$ occupied localized electronic states from the surrounding B atoms additionally reduce the number of regular valence states by three. In total, for each vacancy six electronic states and six electrons are removed from the valence band. However, the three electrons in the localized states may fall down into the energetically more favourable unoccupied valence band states. Hence, from the 1.52 B(13) vacancies per unit cell $3 \times 1.52 = 4.56$ unoccupied localized states are generated, which are energetically separated from the valence band. Compared with the calculated deficiency of five valence electrons this would satisfactorily explain the semiconducting character of β-rhombohedral boron.

Additional electrons come from the B(16)–B(20) sites assumed as interstitial, while the number of states in the valence band remains unchanged. Hence, in total there are $3 \times 1.52 + 3 \times 3.38 = 14.70$ electrons per unit cell available compared with the valence electron deficiency of 5. Assigning an error of only 2% to the occupation densities obtained from literature, the completely occupied valence band leaves 10 electrons per unit cell to be distributed on localized gap states originating from the B(13) vacancies or from interstitial B(16)–B(20) states. If one assumes that the B(13) vacancy generates a gap state, which can be occupied by two paired electrons, similar to the vacancy V^{2+} state in silicon [33, 34], the number of interstitial B(16)–B(20) atoms exactly corresponds to the number of unoccupied sites in this orbital. If single ionization of the interstitial B atoms is assumed, the valence band and the B(13) vacancy orbitals are exactly filled up.

That assumption easily explains the ESR results. The density of paramagnetic centres (about 10^{15} cm^{-3} [35]) is very low compared with the defect concentration (about 10^{20} cm^{-3}) and can only be appreciably enhanced by heating or optical excitation [36, 37]. Moreover, it is consistent with the charge transport in β-rhombohedral boron preferably due to hopping processes but with a certain contribution of delocalized carriers (see [1]). Hence it seems evident that the experimentally proved electronic level 0.19 eV above the actual valence band (see [1]) is formed by orbitals of the B(13) vacancy and occupied by paired localized electrons originating from the intrinsic structural defects.

This rough estimation demonstrates that the concentration of intrinsic structural defects in β-rhombohedral boron is able to exactly compensate the electron deficiency calculated for the valence band of the idealized structure. Indeed, further investigations, in particular on the molecular orbitals of the intrinsic defects in β-rhombohedral boron, are necessary to confirm this model.

3.2. Boron carbide

As mentioned above, the idealized, according to theoretical calculations [30, 31], energetically most favourable structure of boron carbide $B_{13}C_2$ (structure formula B_{12}(CBC)) is taken for reference to determine the concentration of structural defects. These are antisite defects in the form of $B_{11}C$ icosahedra (donors) and CBB chains (acceptors) and vacancies in the unit cells with missing chains (alternatively α-rhombohedral-boron-like or B□B arrangements with two separated B atoms and a vacant B(3) site based on phonon spectroscopy [5, 6], B□B arrangements according to the calculation of reaction kinetics [38], vacancy of B(3), no specification of the chain end atoms, derived from neutron scattering [7]). Interstitial atoms in boron carbide have not become known, possibly except for Al, which occupies sites sideways shifted from the main diagonal in chainless unit cells [39].

The valence band of boron carbide contains 48 electronic states per unit cell, while the number of valence electrons depends on the carbon content. For $B_{13}C_2$ 47 and for $B_{12}C_3$ (structure formula B_{11}C(CBC)) 48 valence electrons per unit cell are available [26].

In an antisite defect the C→ B substitution acts as a donor and the B→ C exchange as an acceptor. For each pair of these substitutions the total number of valence electrons remains the same, but every acceptor state reduces the valence band states by one. To compensate the electron deficiency of one per unit cell by antisite defects, one acceptor state per unit cell is necessary. This would require us to transform the idealized structure B_{12}(CBC) completely to B_{11}C(CBB) in contrast to the real structure, which however offers the vacancies in ∼19% chainless unit cells [5–7] as further defects to compensate the valence electron deficiency.

In principle, according to the hitherto available results the following chain configurations in chainless cells seem possible: C□C, B□B, □□□(□, vacancy). Based on the experimentally

Table 2. Calculated concentrations of structure elements in boron carbide ($B_{13}C_2$) for different configurations of the 19% chain-free unit cell.

	Concentration of structure elements				
	Assumed configuration (□ = vacancy)				
Structure element	C□C	B□B	□□□	Experimental	
Chain-free cells (exp.)	19%	19%	19%	19%	[5, 6, 7]
B_{12} icosahedra	31%	42%	70%	42%	[5, 6]
$B_{11}C$ icosahedra	69%	58%	30%	58%	[5, 6]
CBC chains	9%	62%	81%	62%	[5, 6]
CBB chains	72%	19%	0%	19%	[5, 6]

proved 81% occupation probability of the B(3) position, the concentrations of the different structure elements were calculated, assuming that the remaining valence electron deficiency is compensated by antisite defects (table 2): the concentration of CBB chains is calculated according to the requirement to compensate the valence electron deficiency, while subsequently the concentrations of B_{12} and $B_{11}C$ icosahedra result from the stoichiometry of the compound. In the C□C configuration, due to the broken bonds two electronic states around the vacancy become localized reducing the number of states in the regular valence band. The remaining valence electron deficiency can be compensated by antisite defects B→ C. One vacancy and two antisite defects are attributed to the B□B configuration. In the □□□ configuration the structural defects would be sufficient to compensate the electron deficiency by six broken bonds at the chain ends reducing the valence band states by $6 \times 0.2 = 1.2$ per unit cell, but it is known from α-rhombohedral boron that this configuration is not very stable.

For the B□B configuration the calculated concentrations of the structure elements excellently agree with the results experimentally determined by Kuhlmann and Werheit [5, 6] and make this structure assumption the most probable, and exclude also for chain-free unit cells the occupation of the end position of the chain by carbon atoms.

With increasing carbon content the concentration of $B_{11}C$ icosahedra increases with the carbon atoms acting as donors. The accordingly increasing number of valence electrons reduces the probability of vacancies assumed to be formed to compensate the electron deficiency. Idealized B_4C has 48 valence electrons and should be able to form a crystal without vacancies. Indeed, $B_{4.3}C$ boron carbide at the experimentally determined carbon rich limit of the homogeneity range [40, 41] is known to have no chain-free unit cells [5, 6].

If the carbon content is lower than in $B_{13}C_2$, the electron deficiency increases, and additional vacancies generating acceptor states by transforming B_{12}(CBC) to $B_{11}C$(CBB) are to be expected. Accordingly, compared with $B_{13}C_2$ more $B_{11}C$ icosahedra should be formed in spite of the lower carbon content, and the concentrations of CBB chains and chain-free unit cells should increase.

Based on this qualitative consideration the concentration of the different elements of the boron carbide structure was calculated with the following assumptions:

(i) The electron deficiency D is compensated by B□B and CBB generating four and one acceptor sites respectively. $D = 4c(\text{B}\square\text{B}) + c(\text{CBB})$.

(ii) The relation $R = c(\text{CBB})/c(\text{CBC})$ is taken from the oscillator strengths of the stretching mode of CBB and CBC chains respectively (see figure 7 in [6]). In this quotient the not excludable influence of experimental error in determining the absolute oscillator strengths of the chains is largely eliminated.

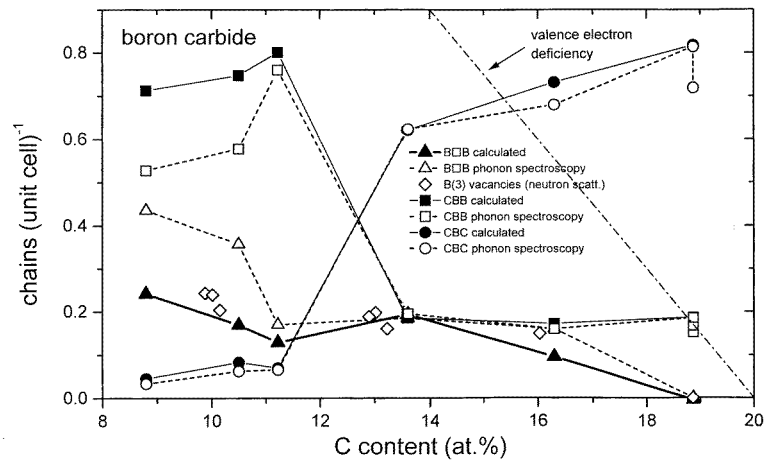

Figure 1. Density of atom arrangements on the trigonal axis of the rhombohedral unit cell of boron carbide (CBC and CBB chains, B□B arrangements); solid symbols, this work, open symbols, determined by phonon spectroscopy [5, 6]; diamonds, B(3) vacancies (centre of the three-atom chain) determined by neutron scattering [7]. The reason for the considerable difference close to the boron rich limit of the homogeneity range is that in the phonon spectroscopy the absolute oscillator strengths were used, while in the present work their relation is taken and thus experimental error by light scattering at non-ideal surfaces is largely eliminated. Calculated valence electron deficiency for comparison.

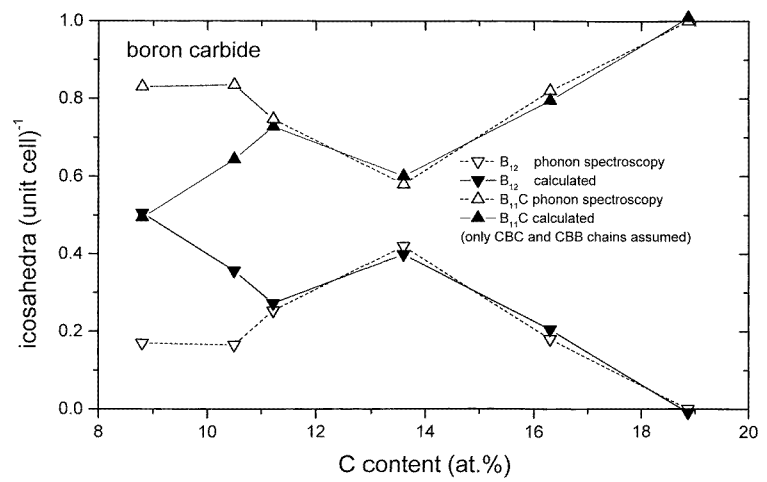

Figure 2. Density of B_{12} and $B_{11}C$ icosahedra calculated from the densities of the atoms on the trigonal axis (figure 1) and the stoichiometry of the samples (for details see table 1 in [6]); solid symbols, this work, open symbols, determined by phonon spectroscopy [5, 6]. For the differences close to the carbon rich limit of the homogeneity range see figure 1.

(iii) Each rhombohedral unit cell has any arrangement on the main diagonal, accordingly $c(\mathrm{B\square B}) + c(\mathrm{CBB}) + c(\mathrm{CBC}) = 1$.
This leads to

$$c(\mathrm{B\square B}) = (R(D-1) + D)/(3R+4).$$

After the concentrations of CBB and CBC chains are accordingly calculated, the numbers of B_{12} and $B_{11}C$ icosahedra immediately result from the compound stoichiometry. In figures 1 and 2 the accordingly calculated concentrations of the different structural elements are compared with those derived from phonon spectroscopy [5, 6] (recalculated for the B□B arrangement). Between about $B_{11}C$ and the carbon rich limit of the homogeneity range $B_{4.3}C$ the agreement is excellent. Moreover the calculated B□B concentration is well confirmed by the B(3) vacancies determined by neutron scattering [7]. There remains some uncertainty with respect to the quantity of B□B configurations close to the boron rich limit of the homogeneity range. Probably, there the direct attribution of the CBB and CBC densities to the experimentally determined oscillator strength [5, 6] gives too small results because of the strong damping of the oscillators, which are therefore not clearly enough separated from the background absorption.

4. Conclusion

The valence electron deficiency of β-rhombohedral boron and boron carbide is obviously the driving force for the generation of vacancies and antisite defects. Those are responsible for high-density intrinsic electronic states in the band gaps of these semiconductors. It seems that this correlation between structural defects and electronic gap states is a general property of icosahedral boron rich solids and is only missing when accidentally the electron deficiency is zero as in α-rhombohedral boron. This result strongly supports the conception that the basic electronic band structures of the icosahedral boron rich solids are typical for crystals (see [1] and references therein), in contrast to Golikova's 'amorphous concept' (see [42] and references therein), which attributes to these semiconductors a degree of amorphization depending on the number of atoms per unit cell. As shown, the localized states come from well defined structural defects, which on the other hand depend on the electron deficiency.

In β-rhombohedral boron, these localized states form the well known electronic level, which is 190 meV above the valence band edge and responsible for the hopping processes prevailing in the electronic transport. The contribution of non-localized carriers presumes the thermal activation of electrons from the valence band (see [1] and references therein). The mentioned inconsistency of the optical interband absorption attributed to indirect allowed transitions [19] can easily be solved by the attribution to non-direct transitions having the same dependence on photon energy [43].

For boron carbide at the carbon rich limit of the homogeneity range, the ∼17% concentration of the CBB chains exactly coincides with the electron deficiency. If one concludes from the CBB concentration, which is largely independent of the C content down to about 13.5%, that this CBB concentration is intrinsic, this easily explains that $B_{4.3}C$ is indeed the limit of the homogeneity range as experimentally determined [40, 41]. Since the boron carbide samples were prepared from the melt ($T_m \sim 2750$ K) or by hot-pressing ($T_{hp} \sim 2300$–2400 K), the intrinsic concentration of CBB chains may be thermally generated at these temperatures. The accordingly calculated activation energies are 0.42 and 0.36 eV respectively, which are of the order of magnitude for point defects. One can expect that boron carbide with higher carbon content than $B_{4.3}C$ can only be obtained, if a chemical reaction of the elements is possible at low temperatures e.g. in some degree by a magnesiothermal reaction ($T \sim 2000$ K).

The maximum electrical conductivity of boron carbide was found at about 13.5% C, where the B_{12} icosahedra have their maximum and the $B_{11}C$ icosahedra their minimum concentration (see [44] and references therein). Based on the results in the present paper, figure 3 shows that the density of states determined from the electrical conductivity (see [44]) is inversely correlated with the total density of point defects ($B_{11}C$ icosahedra, CBB chains and B□B arrangements).

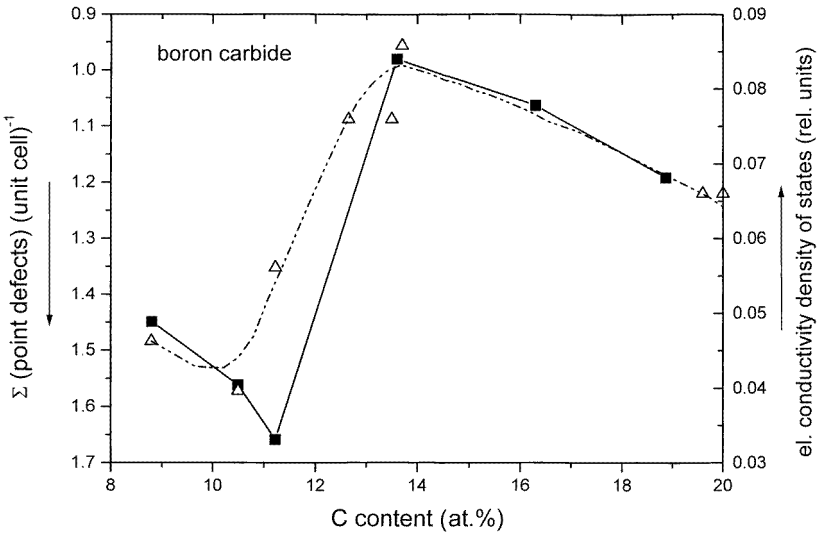

Figure 3. Total density of point defects ($B_{11}C$ icosahedra, CBC, CBB, B□B) (this work) compared with the density of states derived from the electrical conductivity using Mott's law for variable-range hopping (see [44] and references therein) against carbon content.

This is an unequivocal contradiction to the hole bipolaron hypothesis, which attributes the electrical conductivity to hole bipolaron hopping between $B_{11}C$ icosahedra [45–48].

As shown in the YB_{66} type crystals the defect concentration of about 17% exceeds that in the other icosahedral boron rich solids by far. There are at least four well defined defect sites leading to a corresponding variety of electronic levels in the band gap. Therefore it is not surprising that the low energy tail of the optical absorption [49, 50] edge is much stronger than for the other boron rich solids.

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