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Boron and its compounds with nonmetals: chemical bonding and the electronic properties

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Abstract. Theoretical and experimental data on the electronic structure, chemical bonding, and charge distributions in con densed boron and solid-phase boron compounds with a number of *sp*-elements are reviewed. The applicability of quantum chemistry methods to a description of the physicochemical properties of boron and borides of nonmetals, as well as prospects of using computational methods in the theoretical materials science of borides, are discussed. The bibliography includes 452 references.

I. Introduction

Boron and its compounds with *sp*-nonmetals form an important class of chemical substances of great scientific, industrial and commercial importance, due to their unique physicochemical properties. Their well known application fields include synthesis of chemically inert and refractory borides, abrasives, dopants to heat-resistant alloys, components of multi-purposes ceramic materials, nuclear energy (boron), elements of cutting tools, composites, abrasives (boron carbides), high-temperature ware, semiconducting devices, chemical engineering (nitrides, phosphides, and arsenides), important precursors for the preparation of other numerous boron compounds (oxides).

Here lies the main reason for an intense development of the synthesis of novel, more complex boron-containing phases and materials, as well as for studies of their crystallography, thermodynamics, and other physicochemical properties, like electromagnetic, thermal, *etc*. Extensive experimental data obtained in these studies are presented in numerous original publications and summarised in a number of fundamental reviews and monographs.[1–41]

Recently, substantial progress in the investigations of the electronic structure and chemical bonding in the compounds under discussion was achieved using advanced computational quantum chemistry methods. The aim of these studies was to gain insight into the particular properties of different borides on a microscopic level, including interpretation of experimental physical chemistry data, and direct theoretical modelling of structures and properties of the novel boron-containing compounds and materials.

In this paper, we have attempted to discuss the state-of-the-art and some prospects for computational solid state quantum chemistry studies of the fundamental electronic properties of boron and its compounds with nonmetals. Emphasis was placed on the most widely studied boron compounds such as carbides, nitrides, carbonitrides, B-containing nanostructures, as well as on boron phosphides, arsenides, and oxides.

Results of quantum chemistry calculations are discussed with the use of experimental (mainly spectroscopic) data that give additional information on the electronic structure of these phases.

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II. Chemical bonding and electronic structure of condensed boron

1. Crystalline boron

Among few other elements, boron forms a wide range of various phases in solid state. More than 10 polymorphous crystal modifications of boron may be prepared under specific conditions (temperature, pressure, various impurities, *etc*.).[1–8, 17, 22–25, 32, 36–42]

Up to now, three most stable forms of solid boron with the known crystal structures were obtained unequivocally: α-rhombohedral B_{12}, α-tetragonal B_{50}, and β-rhombohedral B_{105}. There are several indications of other forms, such as β-tetragonal B_{192} and orthorhombic phases detected at high temperatures ($T \sim 1500$ K).[37–42] Crystal structures of these phases differ in the arrangement of B_{12} icosahedra, which are the fundamental building blocks of boron phases.

According to [1, 8, 28, 32, 36, 43], the crystallographic and physicochemical properties of crystalline boron are defined by electronic structure of isolated boron atom, which has s^2p^1 valence electron configuration. This configuration is unfavourable, and it should transform to the more stable s^1p^2 when the solid state is formed (the transformation proceeds as a one-electron transition $s^2p^1 \rightarrow s^1p^2$). For the latter configuration further transition can occur according to the scheme: $s^1p^2 + s^1p^2 \rightarrow s^1p^3 + s^1p^1$. Therefore, in the real modifications of crystalline boron a number of s^xp^y electron configurations due to electronic exchange between

boron atoms is possible. Since the relatively stable electron configurations in multi-particle system can be achieved in many ways, a variety of crystal structures with different properties might be formed.

Below we consider the results of quantum chemistry computations of electron energy spectra for the different forms of solid boron.

Rhombohedral α-B_{12}. The unit cell of α-rhombohedral boron (α-B_{12}) with parameters $a = 5.057$ Å and $\beta = 58.10°$ consists of 12 boron atoms.[44–48] The basic polyhedron is an icosahedron conjugated with the neighbouring icosahedra (Fig. 1*a*). High precision structural studies of α-B_{12} indicate slight distortions of ideal B_{12} polyhedra due to the Jahn–Teller effect, which lowers its symmetry from I_h to D_{3d}.

The problem of interatomic interactions and stability of the B_{12} icosahedron, the main building block of crystalline boron, was considered for the first time by Longuet–Higgins and Roberts[49] in terms of molecular orbital (MO) theory. Using theoretical group analysis orbitals of B_{12} were classified into irreducible representations. Two main blocks of MOs were defined depending on their spatial orientation. The first block consists of hybrid *sp*-MOs that are responsible for the 'intracluster' bonding. The second block includes B 2*p*-like orbitals oriented outside the cluster moiety that in turn are subdivided into bonding and nonbonding ones. The sequence of filling of the MO system in the overall B_{12} spectrum places only 2 electrons on 'outer' bonding orbitals. In terms of the common theory of covalency, this fact attests to the instability of the isolated icosahedron hindering formation (under normal conditions) of boron crystal structures of high symmetry with low coordination number (*n*). According to the estimates,[49] the electronic configuration of boron atoms in the icosahedron is close to the s^1p^2 in contrast to s^2p^1 configuration for the isolated boron atom.

The assumptions made in Ref. 49 were confirmed in later studies,[50] where a qualitative scheme of orbital configurations and interparticle interactions in solid α-B_{12} is compared to that in isoelectronic Al metal.

Quantitative estimates of MO energies and compositions for isolated B_{12} fragments were performed using cluster quantum-chemical approaches. The scattered waves X_α method (X_α SW) was applied to the studies of the electron energy spectrum (EES) of the icosahedral B_{12}.[51] In the calculations interatomic B–B distances were varied in the range of 1.75–2.05 Å. The equilibrium value of 1.96 Å [51] was determined using the total one-electron energy of the fragment, which exceeds the experimental value for α-boron by 10%.[44–48, 52] This inconsistency may be due to the fact that the model cluster has an open outer shell, which is in agreement with its chemical instability.

Chemical bonding in crystalline boron has a delocalized and electron deficient nature.[53] Taking this into account, an empirical '$3n+2$' rule (where $n = 12$) was formulated [53] stating that two additional electrons are needed for a closed electron shell to stabilise the crystalline boron and the higher borides containing B_{12} icosahedra as the structural elements.

The calculated MO diagram [51] (Fig. 2) is in good agreement with a qualitative scheme.[49] The cluster states may be subdivided into bonding (oriented to the neighbouring centres) and non-bonding (directed to the outer parts) states. The energy gap between the T_{2u} HOMO and the H_g LUMO ('forbidden zone') obtained with transition state formalism [54] is 1.6 eV. It is close enough to the experimental estimate of this value in α-B_{12}.[55]

The MO system of B_{12} group, similar to that obtained in study [51], was reproduced under the tight binding (TB) approximation.[56] The probable interactions between bonding and non-bonding states were neglected.[57, 58] The calculated values of equilibrium interatomic distances and bonding energies are 1.85 Å and 5.7 eV atom^{-1}, respectively. Electron energy spectra for a number of isolated atomic polyhedra B_4, B_6, and B_{12} were also simulated using extended Hückel (EH)[59] and Hartree–Fock (HF) methods.[60]

The dependence of EES transformations for boron microparticles on their geometry and dimensionality was studied by X_a

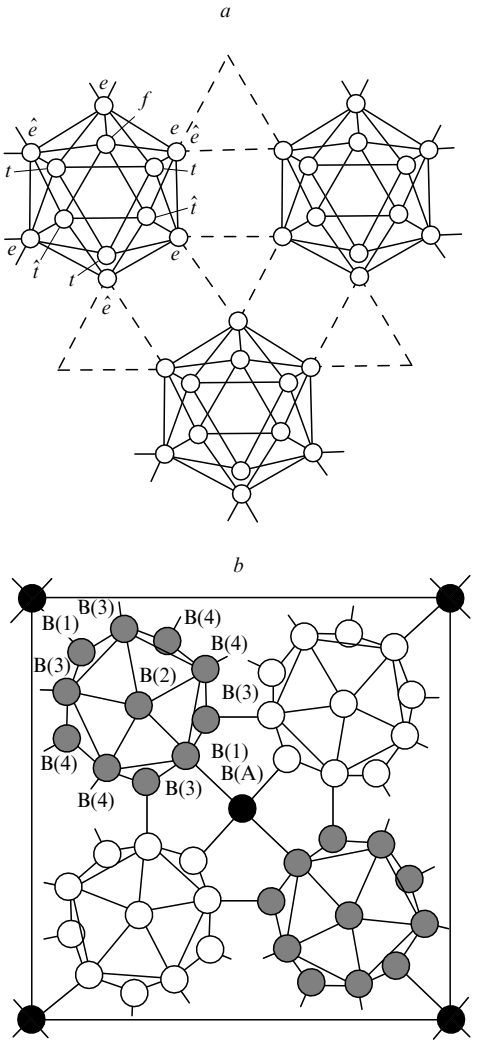


Figure 1. Fragments of crystal structures for (*a*) α-B_{12} and (*b*) α-B_{50}.

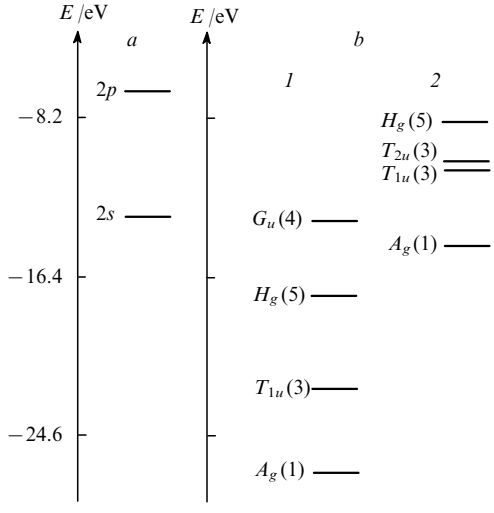


Figure 2. Energy levels (E /eV) of (*a*) boron atom and (*b*) B_{12} icosahedron; (*1*) — bonding, (*2*) — antibonding orbitals; the values in brackets are degeneracies of the corresponding MOs.

SW method [clusters with nuclearity $n = 0, 1, 2, 3, 4, 6$; *i.e.* B(0), B_2 (D_∞), B_3 (D_{3h}), B_4 (T_d), and B_6 (I_h) that contain only structurally identical centres were considered].[61] The touching spheres approximation was applied; the exchange correlation parameters were taken from the published tables.[62] The results of calculations indicate the presence of vacant *p*-states in the MOs system of the clusters, so they should have a prominent acceptor character and require introduction of additional electrons to achieve a stable configuration.

As it was pointed out,[61] an increase in the n and valence electron concentration (VEC) results in an increase in the width of the occupied band. During this process, redistribution and delocalisation of atomic *s*- and *p*-states occur (since delocalized chemical bonds are formed), and the average one-electron energy (per boron atom) changes

$$\varepsilon \simeq \frac{1}{N}\sum_i n_i\,\varepsilon_i\,,$$

where N is a number of atoms in the cluster, n_i is occupancy and ε_i is the energy of the ith orbital. For instance, energy values for B_2 and B_6 are 25.6 and 33.8 eV, respectively. These results indirectly support higher stability of high-coordinated structures of boron [61] and its compounds.[63]

The instability of the ideal B_{12} icosahedron was explained [65] by possible Jahn-Teller distortions due to a partial filling of degenerate higher orbitals.[64] In the calculations, a molecular dynamics method using the non-empirical Car-Parrinello scheme [66] under local electron density approximation (LDA)[67] was applied. The simplest version of this scheme was applied [68] to the reduction of icosahedral symmetry $I_h \rightarrow D_{3d}$.

Basic concepts of the method are given in Refs 69–73. The existence of a local minimum of $E(\varphi,R)$ (where φ is a wave function and R are atomic coordinates) for a polyhedron of C_i symmetry typical of boron crystalline compounds was established by the total energy minimisation method.[65] The maximum stability corresponded to the 'open' cluster framework B_{12} with C_i symmetry (Fig. 3), that possesses the minimum energy $\Delta E = E(C_i) - E(C_s) = 0.62$ eV. In the latter case, despite the decrease in the number of interatomic bonds from 30 (C_i) to 27 (C_s), the stability of the C_i form of B_{12} is higher due to the absence of the 'outer' nonbonding cluster orbitals (Fig. 4).

The first band theory calculation of crystalline α-B_{12} was performed by Perrot [74] using the muffin-tin orbitals (MTO) method [74] and Cohn–Sham potential parameters.[76] The calculations were done for 14 k-points in the irreducible part of the Brillouin zone (IPBZ) (Fig. 5). Bands energy dispersion in the direction $G \rightarrow Z$ is shown in Fig. 6. According to calculations,[74] 18 low energy bands are filled and separated from the lowest unoccupied bands by a forbidden gap (FG) with an energy of indirect transition $\Delta E_g = 2.88$ eV. This value is in accordance with experimentally proved non-metallic behaviour of α-boron.[37–41]

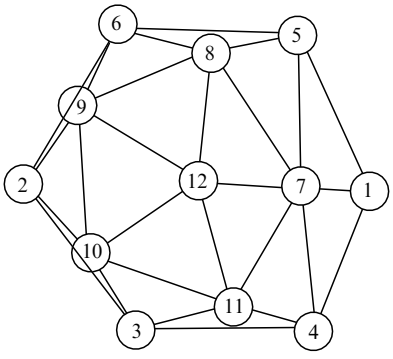


Figure 3. Optimised structure of B_{12} polyhedron in α-boron structure with atom numbers (1–12).

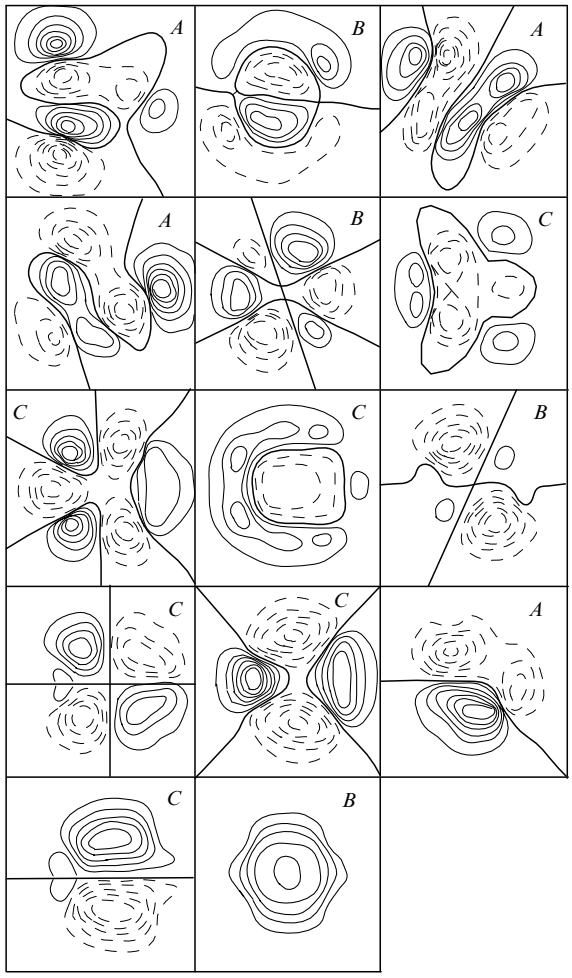


Figure 4. Wave function profiles of the optimised B_{12} structure [lower left part of the polyhedron; planes going through the atoms 1, 7, 12, 2 (*A*); 3, 6, 8, 11 (*B*); 4, 5, 9, 10 (*C*) as in the Fig. 3].

It is noteworthy, that the width of the filled band *d* (9.87 eV)[74] is significantly lower than the value 15.5 eV obtained from X-ray emission spectroscopy (XES) measurements.[77] The reason for this inconsistency lies in the application of the touching spheres model to loosely packed structures like *a*-B_{12} (in this case, it is necessary to take into account non-muffin-tin corrections) and also in the neglected correlation effects, which, as it is known,[78] may strongly

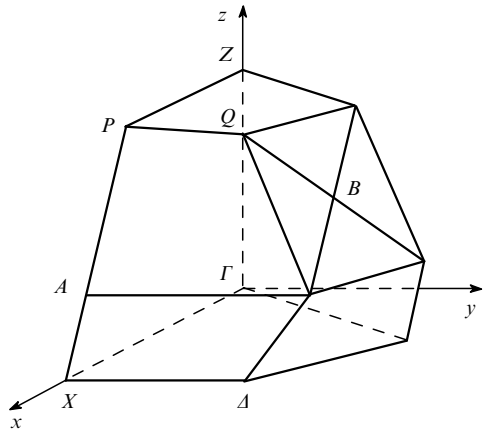


Figure 5. Irreducible part of the Brillouin zone for α-B_{12}.

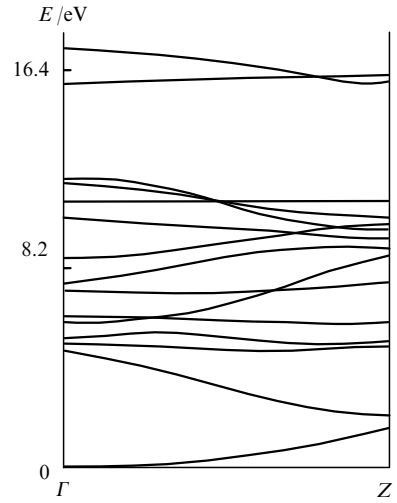


Figure 6. Energy bands for α-B_{12} (E, eV).

influence the width of the forbidden zone. Minimisation of the intersphere region (structural factor S was varied in the range of 1.25 – 1.50 R_{MT}, where R_{MT} is muffin-tin radius) has lead [74] to a noticeable increase in both FG (5.33 eV) and the valence zone width (16.13 eV): the latter appeared to be substantially closer to the experimental values.

According to the data of non-SCF calculations using augmented plane waves method (APW)[79], α-B_{12} should exhibit semiconducting properties. A qualitative scheme of interatomic bonds in α-boron based on the analysis of the energy dispersion was proposed. This scheme includes bonds of a boron atom with five nearest neighbours in the B_{12} fragment and two- and three-centre bonding interactions with boron atoms of the neighbouring polyhedra.

The energy band structure of α-rhombohedral boron was also calculated by the pseudopotential method [80] with Bassani and Brust parameters.[81] Initial calculations gave the value $\Delta E_g = 5.0$ eV, which is noticeably higher than the experimental value 2.0 eV (see Refs 82, 83) obtained from optical absorption data. Further fitting was performed by cutting of the potential $y(q)$ at $q = 3.2$ (a.u.)$^{-1}$, and satisfactory agreement with experimental data was achieved for $q = 3\ k_F$ [where $k_F = 1.2$ (a.u.)$^{-1}$ (see Ref. 84)]. A more precise *ab initio* calculation of a crystal built of B_{12} fragments was done using a basis set of 2870 plane waves.[85] Both energy functions $E(\vec{k})$ and equilibrium interatomic distances were obtained. Analysis of the dispersion curves $E(\vec{k})$ lead to the values of 1.427 eV for indirect transition across a forbidden zone (between the top of valence zone X and the bottom of the conduction zone Γ), and -1.780 eV for the direct forbidden zone (in Γ point).

Charge distribution patterns in the planes defined by centres of icosahedra and by three independent faces of B_{12} (Fig. 7) are quite informative. Additional charge density is concentrated on the atoms along the z axis indicating larger contribution of these atoms to chemical bonding in the icosahedron compared to the atoms in the (100) plane. It was concluded [85] that intracluster bonding in B_{12} crystals as well as bonding between icosahedra situated in different planes are the most substantial, while the

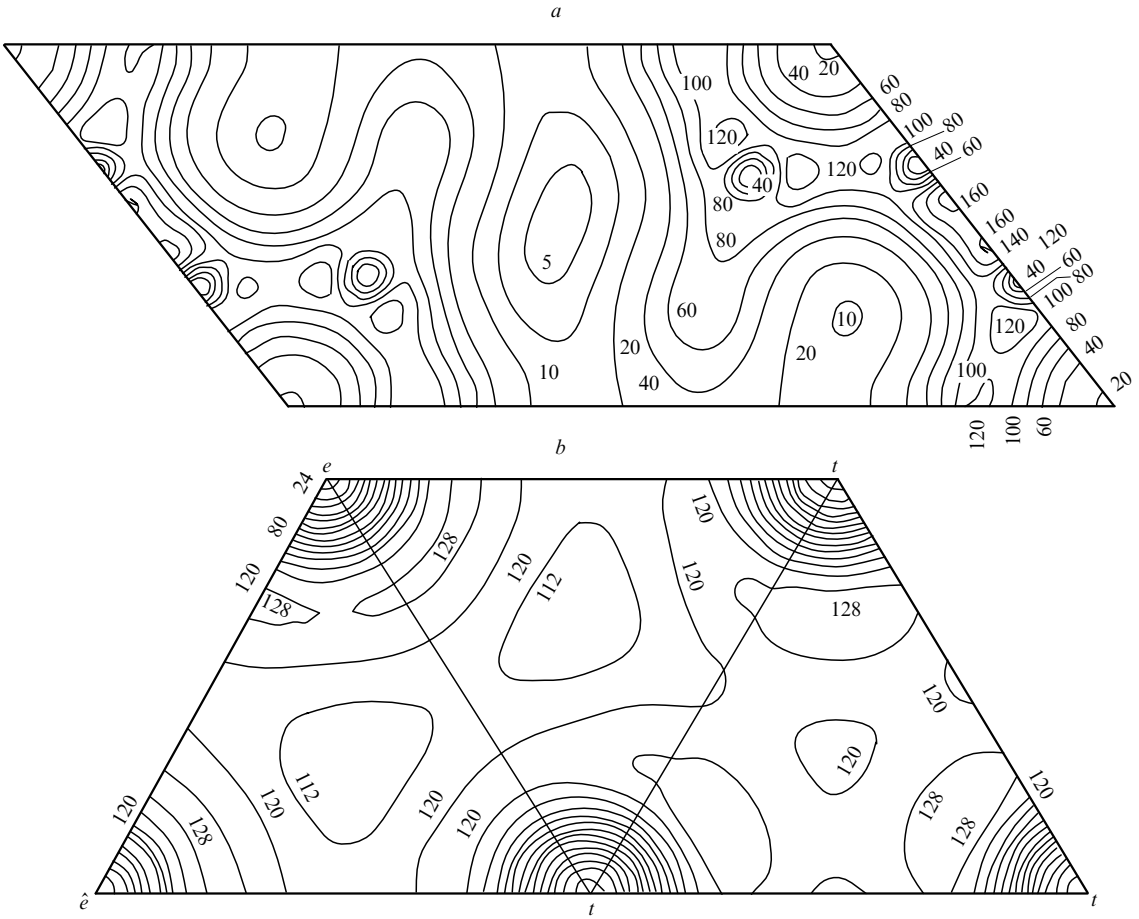


Figure 7. Charge density profiles inside α-B_{12} crystal.
(*a*) Pattern vertices are at the centres of neighbouring icosahedra; (*b*) charge density in three faces of the B_{12} icosahedron with boron atoms in *t*, *e* and *ê* positions. Numbers at contours are charge density values in millielectrons per atomic unit.

Table 1. Energy spectra parameters for α-B_{12} and α-B_{50}.[86]

Parameter	α-B_{12}	α-B_{50}
FG /eV		
indirect FG	1.70 ($Z \rightarrow \Gamma$)	—
direct FG	2.17 (Γ)	2.16 (Γ)
	4.12 (X)	3.20 (X)
	2.79 (Z)	3.95 (S)
	3.53 (A)	2.90 (Z)
	4.12 (D)	—
experiment [83]	1.19	—
calculations		
(indirect FG /eV)	1.43 (see [85])	—
	1.70 (see [79])	—
	2.40 (see [110])	—
Subband width [a] /eV		
C	10.00	10.67 (filled)
		1.37 (above E_F)
B	2.57	2.03
A	0.82	0.33

[a] For subbands $A-C$, see Fig. 8.

bonds between clusters lying in the same plane are much weaker. Another electron band calculation of α-B_{12} using the orthogonalised linear combination AO method (OLCAO),[86,87] was done with the set of 1s, 2s...3p orbitals.[86] The form of the dispersion function $E(\vec{k})$ allowed one to assign [86] α-B_{12} to semiconductors with an indirect FG of 1.8 eV. Table 1 lists the corresponding experimental data along with the values of ΔE_g obtained in other calculation schemes. The observed differences between the calculated FG values are mostly the result of different correlation exchange formalism and different basis sets.

Figure 8 shows the total and local densities of states (TDOS and LDOS respectively) in α-B_{12}.[86] The 'A' band (with occupation number, ON = 8 e) is composed mainly of B 2s AOs and is separated from the 'B' and 'C' bands (ON = 12 and 16 electrons, respectively) by a narrow (~0.5 eV) gap. The 'B' band has a mixed $p-s$-character, while the 'C' band corresponds mainly to boron 2p- AOs. The calculated optical characteristics of α-B_{12} [86] are in reasonable agreement with the experimental data,[88,89] which makes it possible to reproduce the general shape of the optical absorption spectrum and to explain the positions of its major maxima.

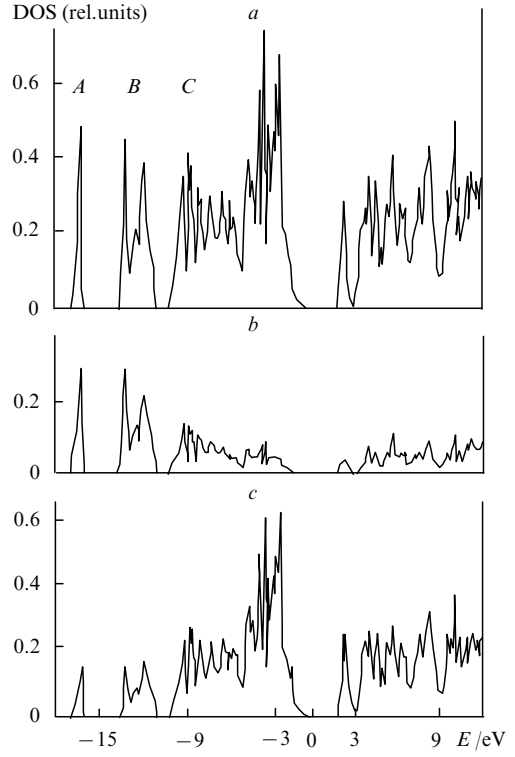


Figure 8. Total density (*a*) and local density of B 2s (*b*) and B 2p states (*c*) in α-B_{12}.[86]

Finally, the paper [90] aimed at the theoretical modelling of probable structural transformations of α-boron under high pressures (P), has to be mentioned. The model assumed that the kinetic energy (E_k) of the electron subsystem increases at the expense of its potential energy (E_p). This assumption is well known for condensed phases with covalent interactions, where substantial localisation of electron density on interatomic bonds is observed. Since E_p and E_k are proportional to $V^{-1/3}$ and $V^{-2/3}$ respectively (where V is a cell volume), an increase of pressure associated with a decrease in V, will probably result in a faster increase in E_k. So, it will lead to a more uniform distribution of the electron density and in a closer packing as a consequence. This tendency was confirmed in many experimental [91–97] and theoretical [98–103] solid state studies.

The analysis of this effect was based [90] on calculations of boron crystal total energy (E_{tot}) as a function of volume. The calculations were performed using a non-empirical pseudo-potential (PP) method in LDA approximation [104–107] and the linearised MTO method (LMTO).[108]

As possible boron allotropes, α-B_{12}, diamond-like, simple cubic (c), face-centred cubic (fcc), body-centred cubic (bcc), and hexagonal closely packed (hcp) structures were considered. Probable distortions of boron structure from bcc to body-centred tetragonal (bct) form were also taken into account.

The dependence of the total energy on volume [E_{tot}(V)] obtained in the LMTO calculations [90] is shown in Fig. 9. A similar correlation was found in PP calculations. Table 2 summarises the equilibrium volume, bulk modulus, and the corresponding minimum values $E_{tot}(V_0)$ from PP and LMTO calculations for all structures along with the experimental data.[109] These data demonstrate that α-B_{12} is the most stable structure at normal pressures, whilst on a pressure increase (and volume decrease), a structural phase transition α-B_{12} – bct (at P ~210 GPa) should occur followed by a stabilisation of the bcc form (at P ~360 GPa).

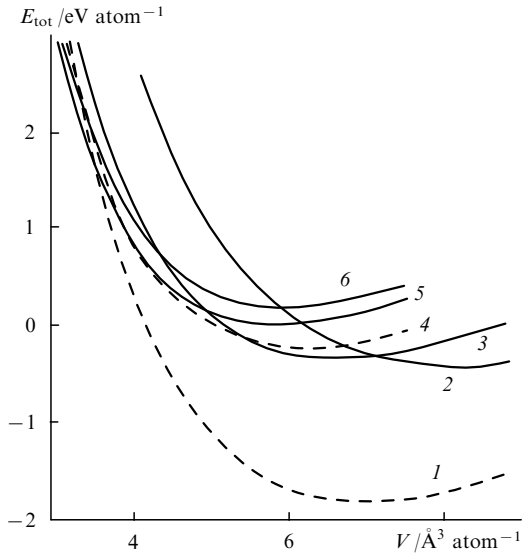


Figure 9. Total energy *vs.* volume for α-B_{12} (*1*), boron with diamond structure (*2*), simple cubic (*3*), body-centred cubic (*4*), face-centred cubic (*5*), and hexagonal closely packed (*6*) boron sublattice.
LMTO calculations.[90]

Table 2. Equilibrium volume (V_0), bulk modulus (B_0), and total energy [$E_{tot}(V_0)$] for different boron crystalline structures (see text).

Structure	V_0 /Å^3		B_0 /Mbar		$-E_{tot}$ /eV atom^{-1}	
	PP	LMTO	PP	LMTO	PP	LMTO
Calculations						
α-B_{12}	7.05	6.93	2.49	2.66	1.43	1.83
Diamond-like B	7.93	8.23	1.86	1.86	0.32	0.42
Simple cubic B	6.43	6.65	2.41	2.43	0.24	0.35
fcc	5.65	5.91	2.69	2.66	0.00	0.00
hcp	5.72	5.99	2.68	2.55	−0.19	−0.18
bcc	5.88	6.12	2.37	2.32	−0.38	−0.29
Experiment [109]						
	7.28		2.0		–	

This transitions should be accompanied by a weakening of certain localised covalent B−B bonds, a decrease in the forbidden zone, and a transition of bcc structure to a metallic-like state as observed in aluminium.[110]

Tetragonal α-B_{50}. The crystal structure of α-B_{50} has been described.[111–116] The tetragonal cell with the parameters $a = 8.75$, $c = 5.06$ Å includes 4 ideal icosahedra and 2 boron atoms [B(A)] with 4-fold coordination. Boron atoms composing icosahedra can be subdivided into 4 types [B(1)...B(4)] depending on their position relative to other B_{12} polyhedra and B(A) atoms (see Fig. 1*b*). Only one type of boron atom that does not belong to the icosahedron may be present.

Quantum-chemical calculation of α-B_{50} by simple LCAO method [79] allowed one to describe a general structure of its electron energy spectrum. It includes partially filled valence band formed by boron 2*s* and 2*p* AOs, which determines metal-like properties of the tetragonal α-B_{50}. This band is separated from the lowest unoccupied band by FG of ∼1.43 eV. To fill the valence band during the corresponding transition from the tetragonal phase into the more stable semiconducting phase, 10 additional electrons per unit cell are needed. This explains a known tendency of α-B_{50} to form stable compounds with electron-rich *p*-elements (C, N).

To date the best of the most rigorous calculations of α-B_{50} was performed by OLCAO method.[86] Analysis of TDOS shapes for α-B_{50} demonstrated the metallic character of the phase with the FG of about 2.16 eV width lying above the Fermi level by 1.38 eV. The spectrum of the filled states consists of three main subbands with the occupation numbers of 8, 24, and 128 e, respectively. The main differences in EES parameters for α-B_{12} and α-B_{50} are clearly seen in Table 1. The decomposition of TDOS onto partial components [corresponding to atom types B(A), B(1)...B(4), see Fig. 1*b*] shows that the electronic states of B(A) and B(1) that form local bonding orbitals of the [B(A)$B(1)_4$] tetrahedron make the main contribution to the Fermi level (*i.e.* are responsible for the metal character of α-B_{50}).

Analogies between atomic structures of α-B_{50} and fullerene C_{60} as well as electronic structures of α-B_{50} and $YBa_2Cu_3O_7$ were observed.[86]

In the latter case, both α-B_{50} and the superconducting oxide possess a subband of hole states near the Fermi level separated from the higher virtual states by a semiconductor gap.[117–119] The analogy allows one to suggest that α-B_{50} may exhibit superconductivity.[86]

The relative instability of α-B_{50} may be explained by the presence of unfilled states between E_F and the bottom of the forbidden zone. The tetragonal α-B_{50} structure can be stabilised by doping with electron-rich nonmetals to form phases like $B_{48}B_2C_2$ or $B_{48}B_2N_2$[120, 121] or with *d*,*f*-elements to form higher borides. Calculations of E_{tot} *vs.* volume dependence, estimates of

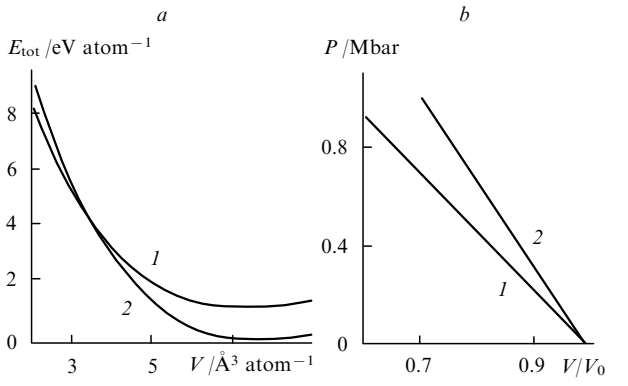


Figure 10. Total energy *vs.* volume (*a*) and pressure *vs.* volume (*b*) for α-B_{12} (*1*) and α-B_{50} (*2*), V_0 is the equilibrium volume.

V_0, B_0, and $P(V/V_0)$ for α-B_{50} showed that B_0(α-B_{50}) > B_0(α-B_{12}) (Fig. 10). This fact indicates higher hardness of the tetragonal phase. The $P(V/V_0)$ function indicates a higher thermodynamical stability of α-B_{50} (at 0 K), although a phase transition α-B_{50}→α-B_{12} is possible when the external pressure is increased up to ∼360 GPa. This high pressures can result in substantial structural distortions of both phases and does not exclude a possibility of formation of alternative structural modifications,[86] similar to those discussed elsewhere.[90]

Figure 11 shows the calculated optical characteristics of α-B_{50}:[86] the interband absorption (σ), real (ε_1) and imaginary (ε_2) parts of dielectric functions, and energy loss function (ELF) in the range of 0–10 eV. The $\sigma(E)$ function contains peaks at the energies ∼1.1 and 1.5 eV related to the transitions from the filled band to the unoccupied band near the Fermi level. The minimum

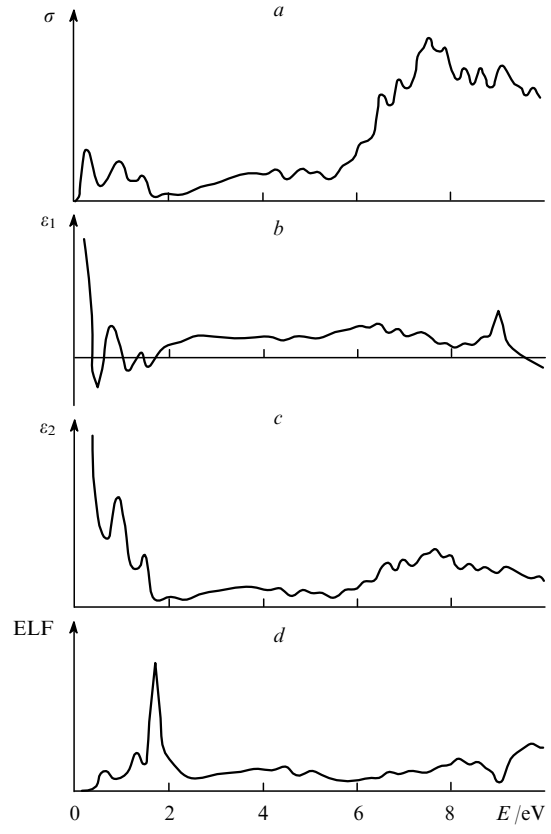


Figure 11. Changes of σ (*a*), ε_1 (*b*), ε_2 (*c*), and ELF (*d*) for α-B_{50} in the photon energy range 0–10 eV (for notations see text).

of $\sigma(E)$ in the region 2.0–5.5 eV corresponds to the forbidden zone in the energy spectrum. Above 5.5 eV, the absorption intensity increases abruptly (due to transitions to unoccupied states above the forbidden zone), and the structure of $\sigma(E)$ in this region becomes similar to that of α-B_{12}.[90]

Rhombohedral β-B_{105}. The crystal structure of β-B_{105} has been determined.[122–125] The main building block of the structure is a B_{84} polyhedron (Fig. 12) that includes a central icosahedron coordinated by 12 pentagonal pyramids B_6. The unit cell of β-B_{105} contains 15 structurally non-equivalent positions occupied by boron atoms.

The complexity of the β-B_{105} structure hampers strict non-empirical quantum chemistry calculations of its EES. Thus, the energy spectrum of β-B_{105} was calculated only using a simplified LCAO approach under the two-centre approximation.[79] The TDOS histogram obtained (Fig. 13) exhibits fine structure. However, assignment of its peaks to structurally non-equivalent groups of boron atoms was not performed.[79] Complete filling of the valence band requires 320 electrons while unit cell contains only 315 e. Therefore, β-B_{105}, like α-B_{50}, should exhibit metal-like properties. The width of the forbidden zone (in the region of unoccupied states) in β-B_{105} is estimated as ~2.7 eV.

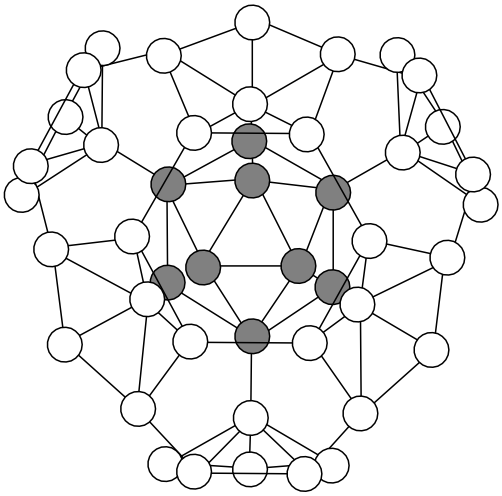


Figure 12. The structure of the central part of 84-atomic polyhedron, which is the principal building block in β-B_{105} crystal lattice.

Numerous experimental data (see, for example, a review [126]) demonstrate that filling of cell cavities in β-B_{105} by transition metal atoms results in certain cases in the increase in microhardness of the phase and dramatically changes its conductivity.[127–129]

It should be generally noted that experimental studies of β-B_{105} [using XES,[130–134] XPS,[135,136] optical absorption,[137–143] Raman spectroscopy,[144–146] Auger electron spectroscopy (AES),[135] and ESR [147–151]] lead to inconsistent conclusions as to its conductivity. For instance, according to optical absorption and XPS data,[136,138–143] β-boron is a semiconductor with an indirect FG equal to 0.65–1.73 eV. However, according to ESR data,[147–151] the forbidden zone of β-B_{105} contains a system of 'trap' levels composed of different states of non-equivalent B atomic groups, which causes several types of jumping conductivity. An empirical scheme of β-B_{105} band structure reflecting this feature has been proposed [152] (Fig. 14). Werheit [153] confirmed and developed this model based on the recently obtained experimental results [154–159] (mainly from visible, IR, and Raman spectra, conductivity measurements and magnetic parameters) both for pure and doped β-boron.

The correct interpretation of all experimental data on β-B_{105} (see also Refs 160, 161) definitely requires further detailed calculations of its spectral fine features.

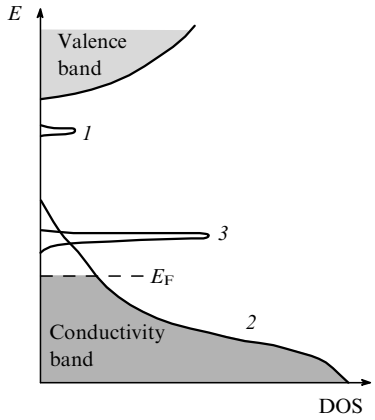


Figure 14. Energy bands scheme for the rhombohedral β-boron; (*1–3*) are states localised near the Fermi level determining possible types of jumping conductivity. Valence band and conductivity band dashed.

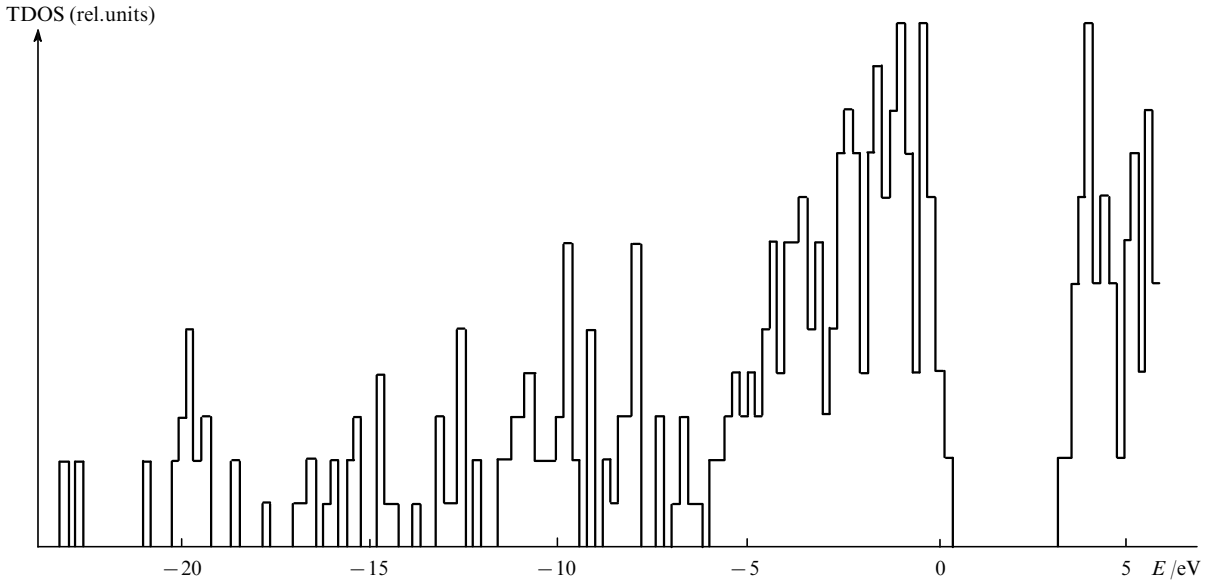


Figure 13. Total density of states of β-B_{105}. LCAO calculations.

2. Amorphous boron

The electronic factors that determine the relative instability of crystalline forms of boron are responsible for the existence of its amorphous state. Amorphous boron usually exists as films deposited on certain supports. Numerous studies were devoted to the formation conditions and the properties of amorphous boron [2, 5, 25, 37–41] though most technological and scientific interest lies in its amorphous alloys with metals (like $M_{80}B_{20}$, *etc*). In the experimental studies dedicated to amorphous boron (AB), the main attention has been paid to the investigation of the mechanism of its transition into the crystalline state.[162–165] According to conductivity measurements, AB is an amorphous semiconductor.[151, 166, 167] The structure of AB may be described as a conglomerate of atomic clusters composed of B_{12} polyhedra [168–176] with a size in the range 2–5 nm.[177]

Data on EES of AB are rather scarce and in most cases are based on XES.[130–132, 177, 178] According to literature data,[130, 177, 178] the boron K_α-spectrum in AB is similar to that of β-B_{105} except for a shoulder at 179 eV that is more intense for β-boron.

The combination of XES and extrinsic photoeffect quantum yield spectrum on a common scale allowed one to estimate a FG for AB as 1.2±0.2 eV,[131] which is in a reasonable agreement with the photoconductivity data (1.27±0.05 eV [179]) and estimations from measurements of high-temperature conductivity of AB films (~1.00 eV [142]). The analogy of the optical properties of AB and β-B_{105} was also observed,[166] the study of optical absorption and photoeffect for AB gives indirect FG value equal to 0.56±0.03 eV.

III. Boron carbides

Boron carbides (B_xC_y) exhibit very interesting properties.[1, 7, 11, 15, 25, 28, 32–41, 180] Phase relations in B–C systems were investigated in much detail, and the existence of a number of individual phases as well as interstitial solid solutions (for example, of boron or carbon in $B_{12}C_3$, see [37–39, 41]) was clearly demonstrated. According to recent data,[38, 39, 41, 180–186] structures of carbides with lower carbon content (from 9 at.% to 20 at.%, *i.e*. from $B_{10}C$ to $B_{12}C_3$) are connected with the parent structures of solid boron. The main building blocks of these structures are B_{12}-like icosahedral clusters.

In a number of studies,[187–189] the synthesis of carbon-rich carbides $BC_{3\pm x}$ with layered graphite-like structure was reported. In addition to the phases mentioned above, numerous heterogeneous boron carbide phases ($B_{13}C_2$ + C), non-stoichiometric boron-carbon compounds $B_{1-x}C_x$,[183–186, 190] and B_xC_y-based composites [191] are also known. The electromagnetic,[192–196] spectroscopic,[197–199] and thermal [200] properties of B_xC_y phases as well as their behaviour in reactions with metals,[201] oxides,[202] ferroalloys,[203] *etc*. have been thoroughly investigated.

A phenomenological model of chemical bonding in boron carbides containing B_{12} polyhedra ($B_{13}C_2$, $B_{12}C_3$)[180] describes these polyhedra as electron-deficient systems with 'delocalised' covalent bonding. A possibility of different electronic configurations (sp^2 and sp^3) for carbon atoms is suggested. Using atomic-term energies for B and C, the heat of boron carbide formation and atomisation of boron and carbon, the degree of metallicity, covalency, and ionicity has been estimated to be 0.58, 0.93, and 0.35 respectively.[180] In fact, the qualitative character of these estimates cannot be a serious basis for the micro-level description (and, moreover, predictions) of the fundamental electronic properties of B_xC_y phases.

Three ordered phases, *viz*. $B_{13}C_2$, $B_{12}C_3$, and BC_3, were the subject of several studies using advanced computational methods of quantum chemistry. Special attention has been paid to the calculation of EES parameters and to the problem of reliable determination of crystal structures. The relative stability of the possible icosahedra (B_{12} and $B_{11}C$) composing the $B_{13}C_2$ and $B_{12}C_3$ carbides is still under discussion. The composition of triatomic 'intercluster' linking chains also remains obscure (the suggested variants are CBC, CCC, BBC).

Boron carbide $B_{13}C_2$. The structure of $B_{13}C_2$ is still a subject of lively discussions. $B_{11}C$ clusters and (BBC) chains were suggested as main building blocks of the structure.[194, 195, 197] On the other hand, an alternative variant of B_{12} clusters and CBC chains (Fig. 15) was discussed [204–206] on the basis of X-ray diffraction data. Experimental difference electron density maps dr were also obtained.[204–206] Analysis of these maps lead to a conclusion that B(3)–C σ-bonds dominate within C–B(3)–C chains, between these chains and icosahedron [C–B(1)] and between atoms of the icosahedron [B(2)–B(2)].

A structural model [203–207] was used for the band structure and cluster calculations of the electronic properties of $B_{13}C_2$.[208] It was found that the dispersion $E(k)$ in all symmetrical directions of the

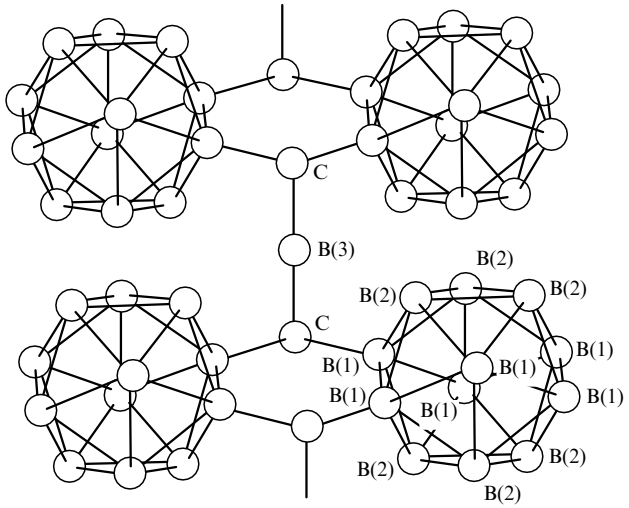


Figure 15. Structure of $B_{13}C_2$.[204]

Brillouin zone (BZ) does not exceed ~3 eV, the carbide VZ is filled only partially and is separated from the forbidden zone (ΔE_g ~4 eV) by a subband of unfilled states. According to data,[208] $B_{13}C_2$ should exhibit metal-like properties. It was concluded [208] that the conductivity of the carbide phase will decrease as the content of carbon increases (in the row $B_{13}C_2 \rightarrow B_{12}C_3$, *i.e*. on filling of unoccupied upper region of the VZ). It agrees generally with an empirical interpretation of changes in conductivity of B_xC_y.[209]

Pseudomolecular calculations [210] with Born–Karman boundary conditions were performed in order to determine bond and charge state parameters for $B_{13}C_2$ (Table 3). It is clearly seen that bond populations in icosahedra are noticeably lower than for the 'chain' bonds. Relative charges on different atoms (B or C) are in accordance with their electronegativities. This conclusion also

Table 3. Bond populations (I) and effective charges (q) of atoms and groups of atoms in $B_{13}C_2$ phase.[210]

Bond [a]	I /e	Atom [a]	q /e
B(1)–B(1)	0.50	B(1)	0.20
B(1)–B(2)	0.49	B(2)	−0.16
B(2)–B(2)	0.52	B(3)	0.81
B(3)–C	1.05	C	−0.57
B(1)–C	0.83	I[b]	0.33
		II[c]	−0.33

[a] For atom notations, see Fig. 15. [b] I is a B_{12} icosahedron. [c] II is a CBC chain.

holds for atomic groups of the elements considered. The general tendency of charge density polarisation (in the direction B→C) agrees with dr experimental data.[204–206]

In the most rigorous non-empirical calculations of the energy band structure for $B_{13}C_2$,[211] two alternative structures of the carbide B_{12}(CBC) and B_{11}C(BBC) were considered. For the latter, three possible arrangements of carbon atoms in the icosahedron and in the chain were taken into account.[212] In two cases (α and γ), the carbon atoms occupied the terminal positions of the chain, and the 'icosahedral' carbon lay in the equatorial plane of the polyhedron near the chain carbon atom (α) or far from it (γ). The case β implies that a carbon atom is situated in the lowest vertex with no direct C–C bonds.

The relative stabilities of the above structural types were compared based on their bonding energies (Table 4). The B_{12}(CBC) form appeared to be the most stable. This conclusion is supported by comparison of the free energy values F; for B_{11}C(BBC), taking account of the number of possible configurations (α, β, γ) is given by a formula:

$$F[B_{11}C(BBC)] = -kT\ln\left[6\exp\left(-\frac{15E_\alpha}{kT}\right) + 12\exp\left(-\frac{15E_\beta}{kT}\right) + 6\exp\left(-\frac{15E_\gamma}{kT}\right)\right],$$

and for B_{12}(CBC), by

$$F[B_{12}(CBC)] = -15E[B_{12}(CBC)].$$

Bonding energy values (see Table 4) give $F[B_{12}(CBC)] - F[B_{11}C(BBC)] = -1.669$ eV per unit cell.

Along with the energetic characteristics, the lattice constants, the equilibrium cell volume, bond lengths, and bond angles were calculated.[211] The result for the B_{12}(CBC) structure are in the best agreement with experimental data.[204–207]

Table 4. Cohesion energy (E_{coh} /eV atom^{-1}) for different $B_{13}C_2$ structures and diamond.[211]

Structure [a]	E_{coh}	Structure [a]	E_{coh}
B_{12}(CBC)	7.1408	B_{12}(BBC)	6.9312
B_{11}C(BBC)		B_{11}C(CBC)	7.2592
α	7.0013	B_{12}	6.8402
β	6.9926	Diamond	8.3895
γ	6.9482		

[a] For notations of B_{11}C (BBC) α–γ, see text.

Thus, rigorous quantum chemistry calculations of energies for different structural models proposed for $B_{13}C_2$ give a convincing argument for a B_{12}(CBC) form and allow one to reject all alternative variants.[194, 195, 197]

Boron carbide $B_{12}C_3$. General information on the properties and structural features of the $B_{12}C_3$ phase has been summarised.[37, 39, 41]

One of the first studies devoted to the qualitative description of the nature of chemical bonding in $B_{12}C_3$ [50] stated that bonding of terminal and central carbon atoms in the C–C–C chain involves only four electrons. This fact may cause the instability of the carbide and opens broad prospects for variations of the carbon content (from 4 at.% to 26 at.% of C).[213, 214]

The first simplified band theory calculation of $B_{12}C_3$ [B_{12}(CCC) structure] was accomplished [79] using a basis of the valence 2*s*, 2*p* AOs of boron and carbon; a crystal potential was approximated by superposition of the atomic potentials. The results of the calculation showed a typical semiconducting structure of the VZ including a FG of ~3.8 eV. Semi-quantitative estimates of the effective atomic charges gave a transfer of two electrons from the central (in the CCC chain) carbon atom to C–B_{12} bonds.

The features of the band spectra for B_{12}(CCC) and B_{11}C(CBC) were compared using the so-called 'universal form' of matrix elements within the pseudopotential scheme.[56] Estimates of one-electron bonding energies in the icosahedra composing the structures mentioned demonstrated that the corresponding value for B_{11}C polyhedron exceeds that for B_{12} by ~3 eV. This may be considered as a qualitative confirmation of the CBC preferable chain configuration in $B_{12}C_3$.

A pseudopotential method was used [208] to compare three possible structural forms of $B_{12}C_3$. The following structures were analysed: (1) B_{11}C(CBC), where B(1) atom was replaced by carbon (Fig. 15); (2) B_{11}C(CBC), where B(2) atom was replaced, and (3) B_{12}(CCC), where B(3) atom was replaced. The E_{tot} values (Table 5) point to the instability of (3). IR data [215] and ^{13}C, ^{11}B NMR spectra [216, 217] also indicate the most probable formation of CBC chains oriented along the [111] direction in the structure of $B_{12}C_3$.

The cohesion energy for $B_{12}C_3$ [structure (2)] was estimated by the non-empirical self-consistent pseudopotential method [218] together with the equilibrium value of the lattice parameter. Calculated data conformed with the experimental value with the accuracy of 0.5%.

The most stable structure for $B_{12}C_3$ has been modelled [219] by the cluster Hartree–Fock method. The structure of boron carbide was approximated by a $B_{12}C_3H_6$ molecule, hydrogen atoms being introduced to compensate the 'cleaved' bonds. The analysis of E_{tot} for clusters with different configurations of the intericosahedral chains lead to a conclusion that the formation of the C–B–C chains is preferable as compared to the C–C–C chains.

The most comprehensive of the reported calculations for $B_{12}C_3$ [B_{11}C(CBC) configuration] has been performed [220] with the basis set of 3580 plane waves for 32 points of the IPBZ. Parameters of the energy band structure, equilibrium lattice constants, the value of (indirect) FG (2.781 eV), and effective atomic charges have been determined. Comparison of the cohesion energies (E_{coh}) for B_{11}C(CBC) and alternative B_{12}(CCC) configuration indicates that the former is more probable.

'Devolution' of the electron density maps for the faces of B_{11}C icosahedron allows one to trace the charge distribution therein (Fig.16). This analysis demonstrated that the character of B–B and B–C bonds is mostly covalent.

Table 5. Energy positions of the valence zone (E_{VZ}), conductivity zone (E_{CZ}), value of the forbidden gap ΔE_g, charges (q) on atoms B(1), B(2) and on icosahedra (q_n), and total energy per unit cell (E_{tot}) for different $B_{12}C_3$ structures.[208]

Structure [a]	$-E_{VZ}$/eV	$-E_{CZ}$/eV	ΔE_g/eV	$-E_{tot}$/eV	q[B(1)]/e	q[B(2)]/e	q_n/e
1	6.8	2.8	3.0	710.59	+0.12; +0.22	−0.22; −0.11	0.16
2	6.7	3.0	3.7	711.92	+0.22; +0.11	−0.12; −0.22	0.30
3	7.1	4.2	2.9	704.49	+0.16	−0.21	−0.33

[a] For structures 1–3, see text.

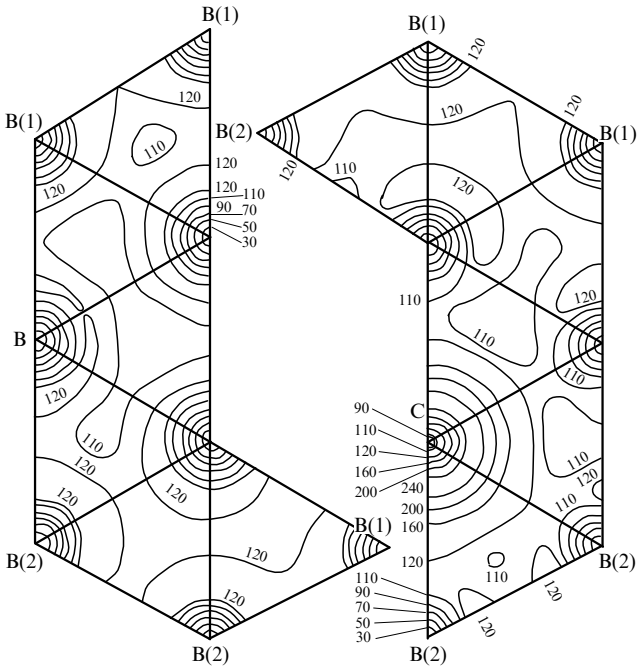


Figure 16. Charge density distribution in the faces of the $B_{11}C$ polyhedron in $B_{12}C_3$ [$B_{11}C(CBC)$ ordering type]. B(1) and B(2) atoms have, respectively, one and two carbon atoms in their closest environment. Numbers correspond to ρ values in 10^{-3} electrons per atomic unit.

The known [220] value of E_{coh} for $B_{12}C_3$ was [85] used to calculate the heat of formation (ΔH) of the carbide according to the scheme:

$$\Delta H(B_{12}C_3) = 15E_{coh}(B_{12}C_3) - 3E_{coh}(C) - 12E_{coh}(B_{12}).$$

$E_{coh}(B_{12})$ was found in Ref. 85. The final calculated value of $\Delta H(B_{12}C_3)$ was 1.632 eV per unit cell, which is close to the experimental estimates of 1.795 and 1.940 eV per unit cell (see Refs 221 and 222, respectively). The somewhat smaller theoretical value of ΔH is probably due to the use of the valence approximation in this study.[220]

Boron carbide BC_3. Synthesis of a layered boron carbide BC_3 *via* a reaction

$$2BCl_3 + C_6H_6 \xrightarrow{800\,^\circ C} 2BC_3 + 6HCl,$$

has been reported.[187–189]

It was pointed out, that partial B→C substitution in the graphite-like structure proceeds in a regular way with B_6 hexagons surrounding C_6 rings (Fig. 17). The density of the thus produced material is lower (since interatomic B–C distances are longer than C–C distances by *ca.* 10%) and its conductivity is higher than that of graphite.[188]

The higher conductivity of the BC_3 may be caused by the lack of electrons in the carbide (as compared to graphite), which favours the appearance of a certain concentration of holes at Fermi level. In order to check this suggestion and to determine the nature of chemical bonding in BC_3, a number of quantum-chemical calculations were performed.[188,223–225] According to estimates using the Hückel method,[188] the value of the forbidden gap in BC_3 is close to 1.8 eV and the Fermi level is located near the bottom of the π-band.

More rigorous *ab initio* calculations [224] were performed using the pseudopotential LCAO method with a basis set of *s*- and *p*-AOs.[226] Since interlayer separation in BC_3 (3.35 Å) is substantially larger than bond distances in the layer, calculations for a single layer of the carbide structure were carried out as the first step. Comparison of the electron density distribution in BC_3 monolayers (Fig. 18*c*) and graphite (Fig. 19) leads to a conclusion that the lesser electron density is concentrated on boron

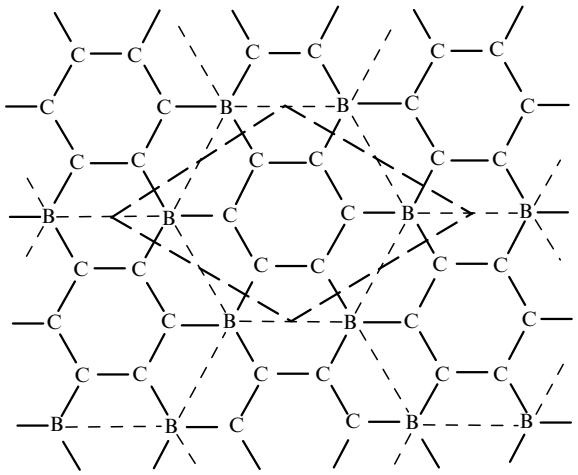


Figure 17. Structure of layered BC_3 (unit cell is shown).

atoms. However, electron distribution within C_6 rings is rather unperturbed, since the C–C interatomic distances in graphite and BC_3 are close.

The distribution of the density of states (DOS) for BC_3 single layers is shown in Fig. 18 and for graphite (Fig. 19). There is a FG between filled and unfilled states with the value of indirect transition ~0.66 eV. Account for interlayer interactions [224] (with AA and AB possible relative orientations of neighbouring layers) results in a disappearance of the FG; the material acquires the properties of a metal with higher conductivity for the AA packing.

The conductivity of BC_3 carbide, therefore, is defined by interlayer interactions.[224] However, the energy of these interactions is relatively small (according to some estimates,[224] not higher

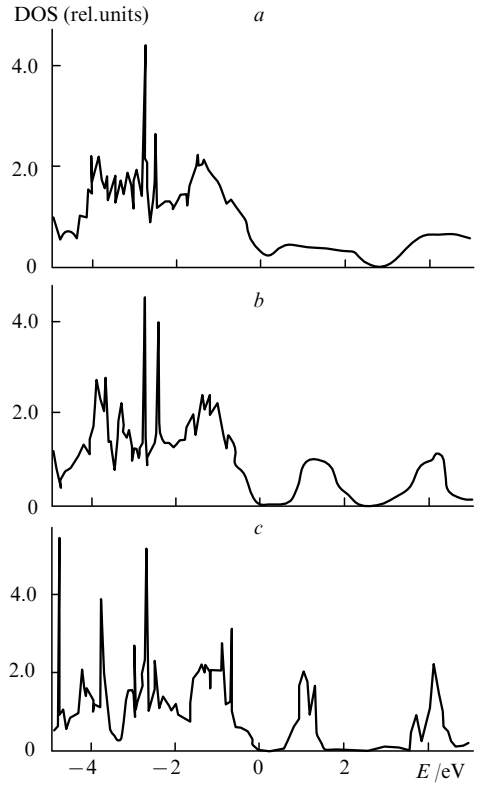


Figure 18. Density of states in BC_3 with (*a*) AA layers arrangement, (*b*) AB layers arrangement, (*c*) single layer.[224]

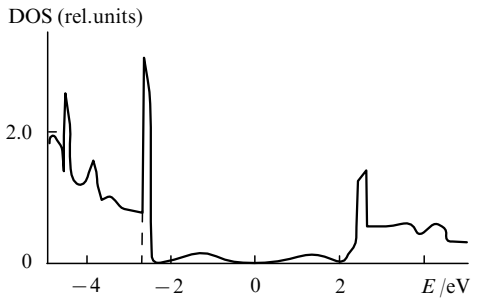


Figure 19. Density of states in graphite.[224]

than ~0.1 eV), although the total cohesion energy is about 7.8 eV.

The detailed analysis of changes in composition of states near the Fermi level for BC_3 compared to graphite was done [225] using energy band calculations for single layers of graphite and BC_3 (Fig. 20). The analysis of the energy band distribution shows that the former σ-like bands are rather remote from the Fermi level and cannot take part in conductivity processes. However in the carbide the Fermi level (situated lower due to a decrease in general electron concentration) intersects the σ-band in the Γ point.

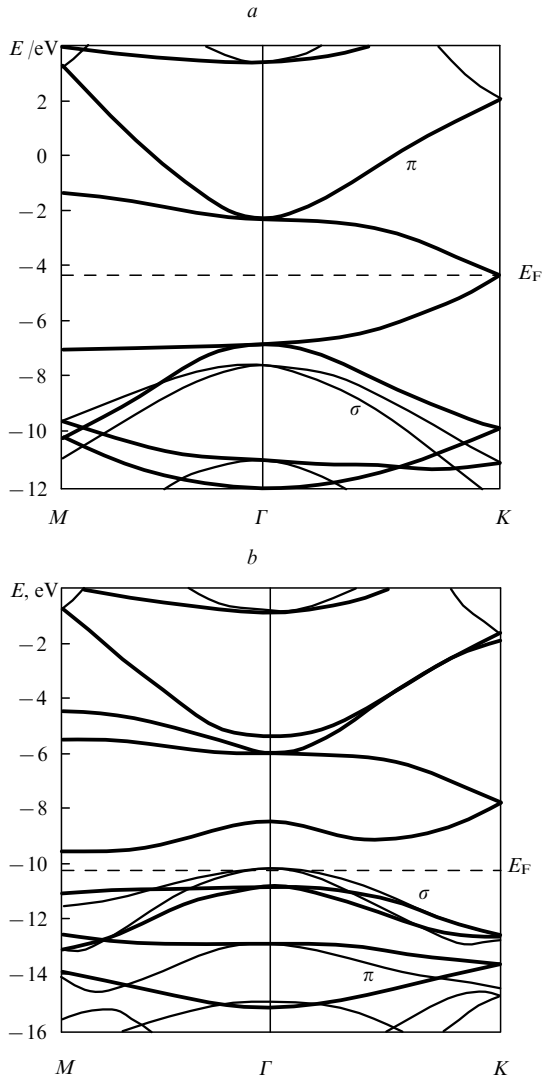


Figure 20. Energy band dispersion for single layers of (*a*) graphite and (*b*) BC_3. The states with σ- and π- symmetry are marked, upper numbers denote a degeneracy.[225]

These bonds, along with π-like states, govern the conductivity properties of BC_3 (hole conductivity).

The above considerations were applied to a description of the electronic properties of boron carbides with a definite stoichiometry. However, along with such phases, a number of solid solutions (SS) with a variable composition are formed.

Recently,[227] model calculations of electronic and structural parameters for one of these solid solutions, B_xC_{1-x}, with graphite-like structure have been carried out using the pseudopotential method under a local electron density approximation.[227]

It should be noted that the layered boron-carbon SS are usually prepared as films.[189] SS with a boron content less than 4% (intercalated graphites) can also be attributed to this type.[228]

The main goal of a study (Ref. 227) was to determine the most probable type of ordering for boron atoms in the graphite lattice. To this end, the total energy values for ordered and disordered structures of B_xC_{1-x} were compared. It was pointed out that intercluster interactions promote segregation of boron atoms and long-order formation in the case of SS with low boron content ($x \leqslant 0.25$). It was suggested [227] that the increase in boron content should violate the ordered atomic arrangement with a transformation of the initial graphite-like crystal structure. This effect is primarily caused by the substantial difference in the atomic radii of boron and carbon.[227]

IV. Boron nitrides

Crystalline boron nitride BN, due to its unique properties and exceptional technological importance,[15, 20, 26, 28–34, 36] is one of the best studied compounds of boron with *p*-elements. There are three known structural modifications of BN: hexagonal (graphite-like h-BN), cubic (sphalerite-like c-BN), and wurtzite-like (w-BN). The latter can be prepared from the h-BN as a result of a phase transition under high temperature/pressure treatment.

Synthetic methods, crystal structures, conditions of phase transitions (including the influence of lattice defects, admixtures, *etc*.) for boron nitrides were discussed in detail.[26, 229–237]

Extensive experimental data obtained using XES, AES, XPS, absorption spectroscopy [238–244] allow one to determine general features of EES of boron nitrides. The anisotropy of band dispersion for the layered BN was investigated [243] using the polarised XES technique. This effect was also discussed in studies of Compton profiles in h-BN[245] and of the electron inelastic scattering.[246]

Infrared and VIS-UV spectroscopies are widely used for characterisation of dielectric properties of nitrides.[247–257] Their detailed comparison with the results of quantum chemistry calculations published before 1987 has been made.[258] Electron energy loss spectroscopy has been used [259–262] in order to obtain the EES parameters. The luminescence properties of BN were considered in Refs 263–267.

Theoretical studies of the fundamental properties of BN are also rather extensive. The first band theory calculation of the c-BN, which is a semiconductor of III–V type, in simplified TB approximation was performed in 1952.[268] Since then, theoretical calculations of EES and many other properties have been carried out using almost all of the known band and cluster schemes for h-BN,[269–286] c-BN,[287–325] and w-BN.[325–332]

Without going into discussion of the results of theoretical studies and some inconsistencies between the particular results (unavoidable because of different computational schemes, basis sets, potential parameters, *etc*.), we shall consider general electronic properties for all three modifications of BN calculated within the same approaches.[324, 325]

The results of OLCAO band structure calculations for h-BN and w-BN are shown in Fig. 21*a*,*b*. Low energy bands of h-BN are composed mainly of (N,B)2*s*-states separated from the main hybrid (N*p*–B)2*p* band by an energy gap. The band structures for c-BN and w-BN are similar (Fig. 21*c*). Principal differences in the electronic structure parameters for the nitrides are clearly seen

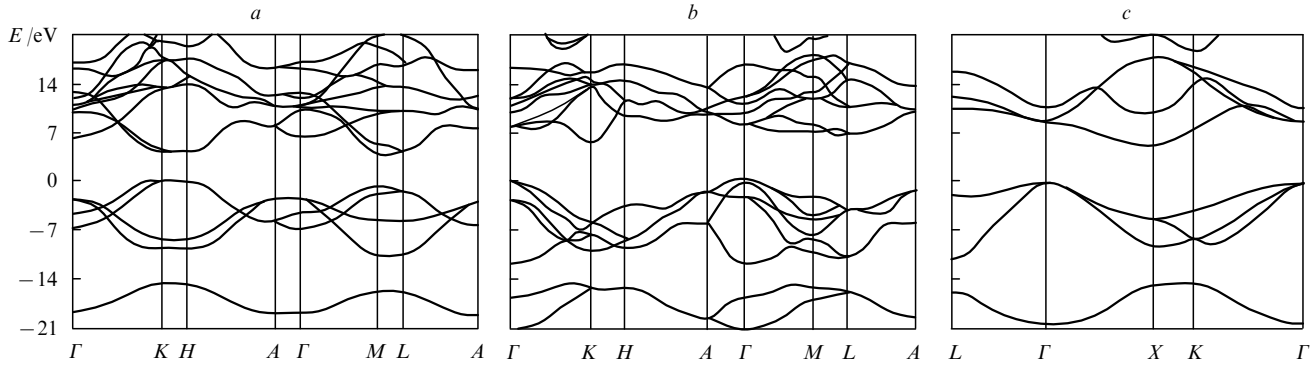


Figure 21. Energy bands of (*a*) h-BN, (*b*) w-BN, and (*c*) c-BN.

from Table 6. For the layered nitride, energy dispersion $E(\vec{k})$ along the direction k_z is relatively small. All BN modifications have indirect FG. For h-BN, the width of the VZ is minimum; in c-BN and w-BN it has comparable values due to a similarity of their atomic environments. This points to the local character of interatomic interactions that have a heteropolar nature in boron nitrides, determined, for instance, by B→N charge transfer (Table 6).

Recently, greater attention was paid to studies of EES in boron nitride crystals containing various structural defects. Investigations of complex systems (ceramics, composite materials based on boron nitrides, *etc*.) at the micro level will probably result in a substantial progress in the nearest future. However, only a few studies have been performed in this field to date. The most interesting results are the following.

Table 6. Electronic and optical characteristics of boron nitrides.[325]

Parameter	h-BN	c-BN	w-BN
FG /eV			
indirect	4.07 ($H \to M$)	5.18 ($G \to X$)	5.81 ($G \to X$)
direct	8.9 (G)	8.7 (G)	8.0 (G)
	4.6 (M)	10.3 (X)	9.3 (X)
	5.6 (L)	12.4 (L)	10.7 (L)
	10.5 (A)	11.8 (K)	10.6 (A)
	4.2 (H)	—	12.8 (H)
	4.5 (K)	—	11.7 (K)
Band widths /eV			
upper VZ	10.40	10.94	11.76
gap between VZs	4.42	3.28	2.93
lower VZ	4.02	6.92	6.28
Effective charges on atoms /e			
B	2.70	2.80	2.99
N	5.30	5.20	5.01
Total energy /a.u. per molecule	−12.7638	−12.7123	−12.7011
Pressure of electron-nucleus system/MBar	3.35	3.70	3.90
Dielectric constant			
$\varepsilon(0)$	3.61	3.86	4.17
$\varepsilon_1(0)$	4.32	—	4.16
$\varepsilon_{11}(0)$	2.21	—	4.18
Main plasmon peaks /eV	11.6	27.3	26.4
	23.7	32.5	32.0
	36.3	38.5	

Studies of h-BN films [326–329, 331] (promising as inhibitory dielectric films and X-ray membranes) revealed a substantial dependence of their optical properties on stoichiometry (B/N ratio). To explain this fact, calculations were performed [330] using TB approximation. A two-dimensional graphite-like structure was used as a model; variations in the composition of h-B_xN_y (with assumption of random B→N substitution) were taken into account in coherent potential approximation.[331]

The distribution of the π-type states indicates the absence of the FG in contrast to the experimental data [329] that give decrease of the ΔE_g for h-BN from 5.0 to 2.5 eV when the B/N ratio changes from 1 to 5.1.

Accounting for a partial ordering of atomic configurations leads to appearance of the FG (Fig. 22) linked with the emerging of additional subband of the boron p-states, whose width is proportional to B/N ratio.[330] Therefore, thin films of h-B_xN_y should exhibit regular spatial distribution of the atomic components similar to that in the crystalline h-BN.

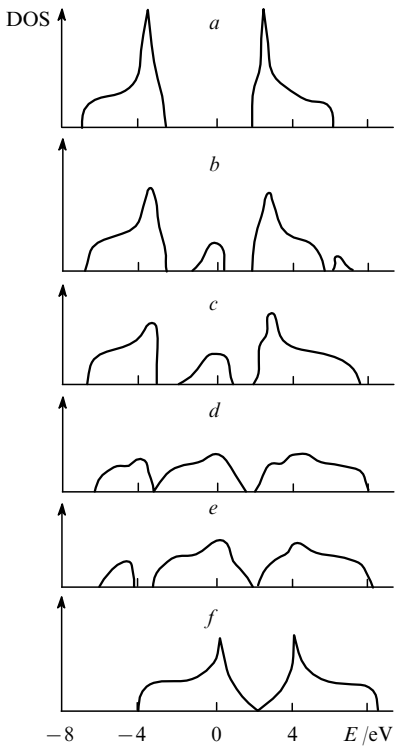


Figure 22. π-DOS distribution in the 2D-layer of boron nitride.[330] The B/N ratio is 1 (*a*), 1.25 (*b*), 2 (*c*), 5 (*d*), 8 (*e*); (*f*) pure boron.

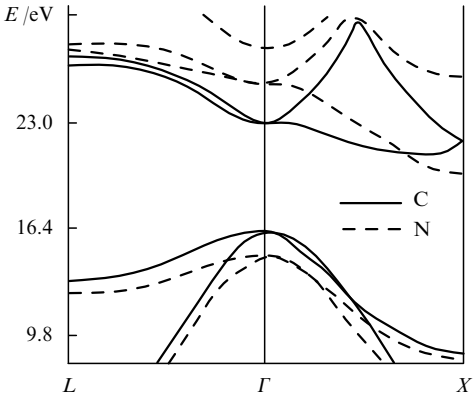


Figure 23. Energy bands of the heterogeneous phase system (110) diamond – boron nitride.

The features of the energy states, typical of the heterogenous system diamond/(boron nitride), have been analysed using the linearised method of augmented plane waves (LAPW).[332] A supercell that models the atomic geometry of the interface region including N/N layers ($N = 1;3;5$) of the C/BN (100) plane was used. It was found that energies of the internal layers and atomic charges for the central layer of each component become close to the corresponding values for the ideal C and BN crystals already for $N = 3$. Band distribution near the Fermi level for the 5/5 layered system is shown in Fig. 23. It should be noted that, though the bottom of the conductivity zone is composed of BN bands (a gap between zones at the X point is about 0.7 eV), the top of the VZ relates to the 'diamond' states. The magnitude of the gap between zones is about 1.42 eV.

In Ref. 333, the method of an effective Hamiltonian [334, 335] (in Del Re parametrisation [336]) has been used as a theoretical basis for optimisation of the carbamide technology for h-BN preparation. In particular, carbamide $(NH_2)_2CO$ (1) was replaced in the technological process by cyanuric acid $H_3C_3N_3O_3$ (2) or melamine $(NH_2)_3C_3N_3$ (3). Atomic charges and energies of bonding states for the molecules (1) – (3) as well as for orthoboric acid and boric anhydride were estimated.[333]

Taking into account the electronic structure of the initial reagents and reaction products, it was pointed out [333] that formation of h-BN in the interaction of carbamide, cyanuric acid, and melamine with H_3BO_3 may be considered as electrophilic substitution. In this mechanism, the boron and carbon atoms in H_3BO_3, boric anhydride, and initial compounds 1 – 3 may be ranged in the order of decreasing activity towards orthoboric acid: $(NH_2)_3C_3N_3 > H_3C_3N_3O_3 > (NH_2)_2CO$. This has lead to a conclusion [333] that the replacement of $(NH_2)_2CO$ by melamine in the multi-stage carbamide technology provides (due to its higher activity) a decrease in a number of stages. Replacement of carbamide by cyanuric acid results in a decrease in NH_3 output, *i.e.* in the increase of the environmental safety of the process.

V. Boron carbonitrides

Synthesis of a series of layered SS based on graphite and h-BN[188, 337, 338] led to studies of their electronic spectra. Theoretical modelling of atomic ordering character in these systems was also carried out.[339 – 341]

The electronic structure of a cluster composed of three hexagons of the h-BN single layer, where a central nitrogen atom is replaced by C, was calculated [339] using the Gaussian orbitals LCAO (GO LCAO) method.[342] It was assumed that the carbon atom is situated 0.76 Å above the h-BN plane. Using the value of the constant of hyperfine interaction with ^{13}C nucleus (~ 1.8 Gs), it was possible to qualitatively explain the ESR splitting in a boron nitride enriched by carbon.[343, 344]

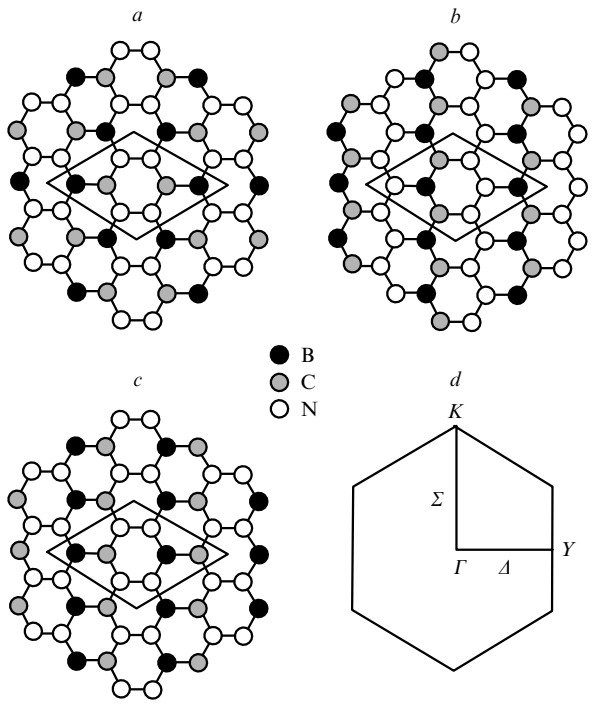


Figure 24. Models of atom ordering in boron carbonitride single layer ($a - c$) and Brillouin zone used for BC_2N calculations (d). Atomic ordering type: (a) *I*; (b) *II*; (c) *III*. Unit cell boundaries are shown.

Boron carbonitride BC_2N was considered as a two-dimensional crystal, and Extended Hückel (EH) band calculations of the BC_2N single layers were accomplished for three different atomic arrangements of the atomic in 8-atomic planar unit cell (Fig. 24).[340] Interlayer interactions were not considered. It was found that the conductivity properties of the system depend strongly on the ordering type. For instance, the energy diagram for π-like band of BC_2N with the structure *I* (see Fig. 24 *a*) does not contain a forbidden gap, but for the ordered structures *II* and *III* (Fig. 24 *b,c*) ΔE_g is equal to ~ 1.8 and 2.9 eV, respectively. According to photoemission data and conductivity experiments,[341] the SS of BC_2N exhibits the metallic properties; therefore, the structure *I* was considered as the most probable for the BC_2N.[340]

The problem of atomic ordering and its influence on the electronic properties of BC_2N were also analysed using the pseudopotential method.[341] The same three models of structural ordering in the single layer were discussed (Fig. 24 $a - c$). According to the values of the adhesion and chemical bonding energies (Table 7), form *II* should be the most stable. According to the FG values obtained (Table 7), the phase *I* should exhibit the metallic properties, while the phases *II* and *III* are semiconductors (Fig. 25). It is noteworthy that the two-dimensional structural model (neglecting interlayer interactions) can substantially affect

Table 7. Chemical bonding energies (E_b), cohesion energies (E_{coh}), and forbidden gap values (ΔE_g) for boron carbonitride BC_2N with different structures of single layers.[341]

Structure[a]	E_b	E_{coh}	ΔE_g /eV
	eV per molecule		
I	23.7	20.0	—
II	24.7	21.2	1.6
III	23.7	18.5	0.5

[a] see Fig. 24

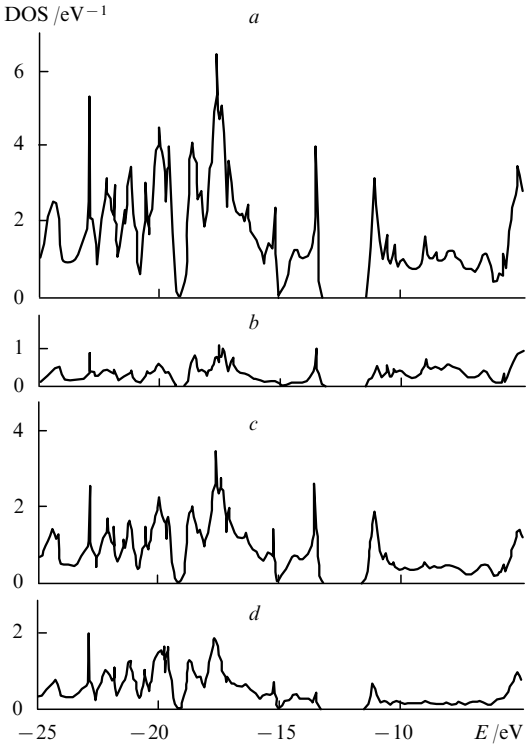


Figure 25. Total (*a*) and partial (*b*–*d*) density of states in BC_2N for the atomic ordering model *II* (see Fig. 24). Partial densities of states: (*b*) B; (*c*) C; (*d*) N.

the results of calculations. It was demonstrated,[224, 307] that the interlayer interactions (in the c direction for h-BN and BC_3) increase the energy dispersion of π-bands which determine the conductivity properties of solid solutions. Further calculations that will take it into consideration are therefore required for a reliable theoretical description of conductivity.

VI. Nanostructures based on boron, boron carbides, and boron nitrides

The term 'nanostructure materials' usually refers to metastable cluster structures, *viz*., nanospheres, nanoclusters, nanotubes. Rapid development of chemistry and technology of nanostructure materials is stimulated by a search for new substances without analogues in nature possessing unique topological, superconducting, catalytic and other properties.[345–349] Most progress in the field recently is related to the synthesis and studies of carbon nanospheres, fullerenes.[348, 350–356]

In the first attempt to prove theoretically the existence of polyhedral carbon C_n or hydrocarbon C_mH_m clusters, the Hückel model of the π-electron system has been used.[357] MOs and resonance energies for the unsaturated carbododecahedron C_{20} and carbo-*s*-icosahedron C_{60} were calculated. Later, features of the electronic structures of buckminsterfullerene C_{60}, its isomers, and higher fullerenes were discussed in numerous publications;[358–370] their structure and properties were extensively studied theoretically (see review 371). For spheroid fullerenes with a higher number of carbon atoms C_n ($n > 78$, giant fullerenes) a series of rather complicated structures were proposed (barrellenes, capsullenes, torrenes, *etc*.).[372–375] The properties of cylindrical carbon macromolecules (tubulenes) and thread-like crystals formed on the base of the nanotubes have been discussed.[376–378]

Recently, along with development of the technology for the preparation of new nanomaterials, a noticeable progress was achieved in the quantum chemistry of nanostructures formed in part on the basis of boron and/or its compounds with non-metals.

Direct modifications of the properties (including superconductivity) of the solid fullerenes C_n were carried out by including doping components into their structures, for instance, alkali metals, which act as electron donors.[364, 379–382] An opposite effect (doping fullerenes with holes) may be achieved by partial substitution B→C,[383] or by an inclusion of halogen admixtures.[384]

The role of boron as a hole donor in the formation of the electronic properties of crystalline BC_{59} was examined by non-empirical band theory.[385] Calculations of equilibrium lattice parameters (a_0) demonstrated that the B→C substitution results in a contraction of the BC_{59} polyhedron (as compared to the C_{60}) and a decrease in a_0 from 14.2 Å for C_{60} (see Ref. 386) to 13.5 Å for BC_{59}. DOS distributions in the valence zone region for C_{60} [380] and BC_{59} are similar. The only difference consists in an additional partially filled peak near the Fermi level (Fig. 26 *a*) composed of the boron states with the admixtures of the π-type C 2*p* states of the neighbouring carbon atoms. The formation of these states (similar to the formation of the acceptor levels in a usual semiconductor) are clearly seen in the map of total charge density (Fig. 26 *b*). Therefore, the result of the inclusion of boron into the solid-state C_{60} will be that fullerene will acquire more metallic character due to an appearance of dopant acceptor states in its valence spectrum. Estimates made of the energy [285] showed that the above mentioned process is exothermic; the most probable product of the synthesis is a mixed C_{60}/BC_{59} fullerene.

The B→C substitution leads to a decrease in the electron concentration (per C_{60} molecule), BC_{59} MO system has an open electron shell. The increase in electron deficiency as the boron content increases will create progressive difficulties in the preparation of boron-rich fullerenes B_xC_{60-x}.

The electronic properties of mixed polyhedral clusters $B_nC_mN_k$ were discussed in a number of papers.[387–396] Heats of formation of B_2C_{58}, $C_{58}N_2$, $BC_{58}N$, $B_{24}C_{12}N_{25}$, and $B_{30}N_{30}$ were calculated and used for a discussion of stabilities of these molecules relative to C_{60}.[387]

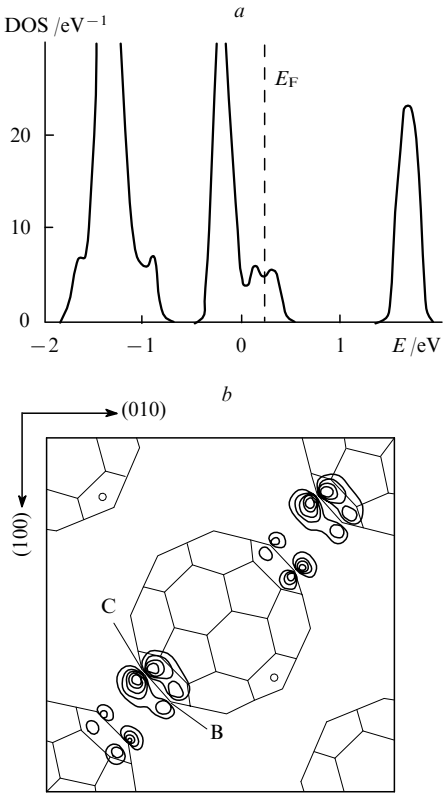


Figure 26. Total density of states for BC_{59} (*a*) and isoelectronic contours of charge density in the energy range $E_F - 0.1$ eV (*b*).

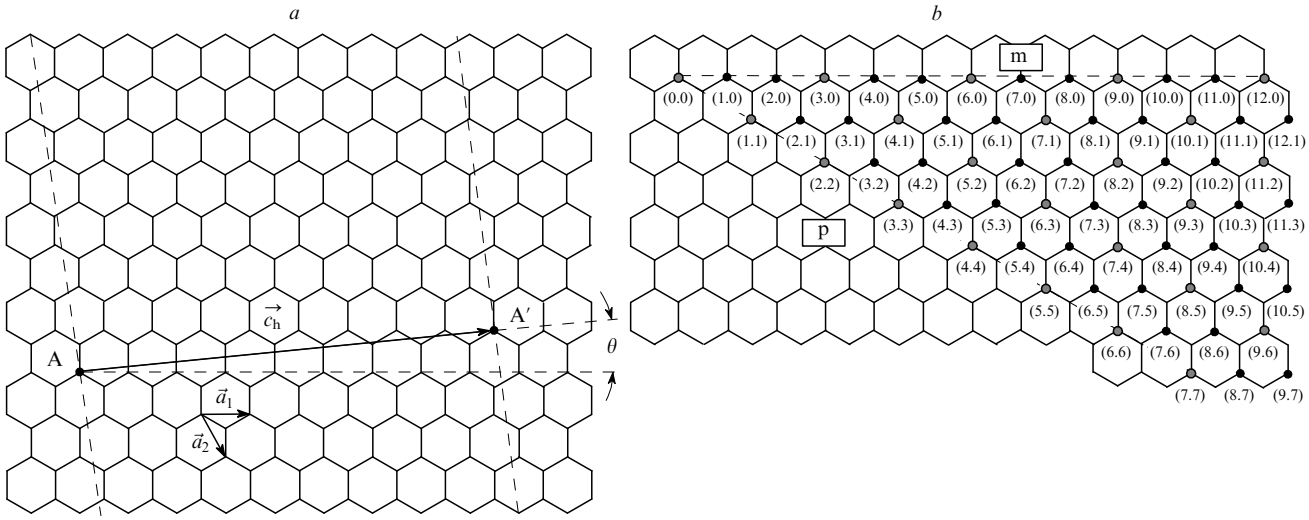


Figure 27. Illustration of the $\vec{c}_h$ vector selection that defines diameter and chirality of nanotubes formed by rolling single layers (point A conforms with A′) (*a*) and possible vectors for chiral graphite nanotubes (*b*); m is metallic character of the nanotube, p is a semiconducting character.[401]

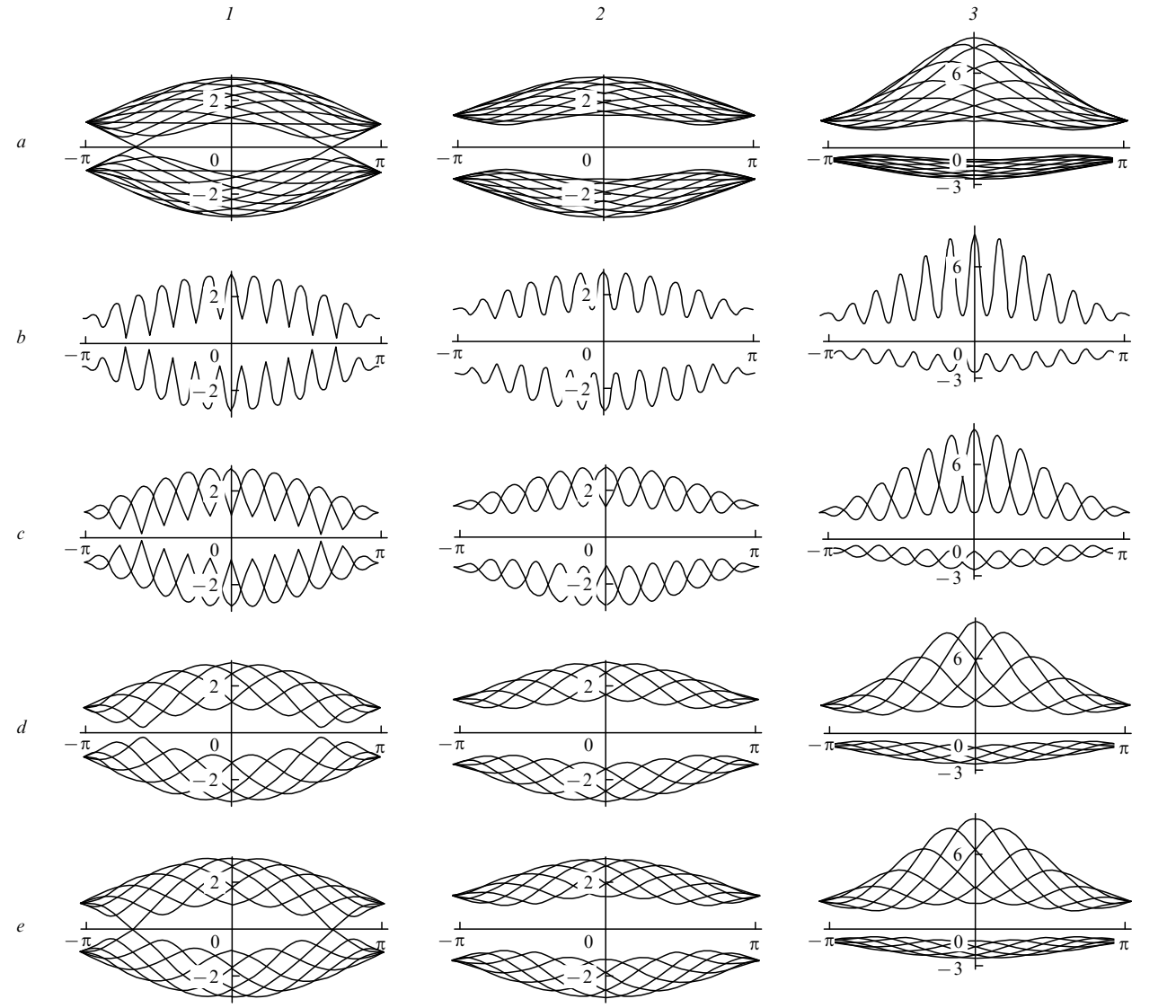


Figure 28. Energy bands for carbon (*1*) and BN (*2,3*) nanotubes with structural indexes (*n,m*); (*n,m*): (*a*) (12,0); (*b*) (12,1); (*c*) (12,2); (*d*) (6,5); (*e*) (6,6); (*1,2*) Hückel calculations; (*3*) EHM calculations.

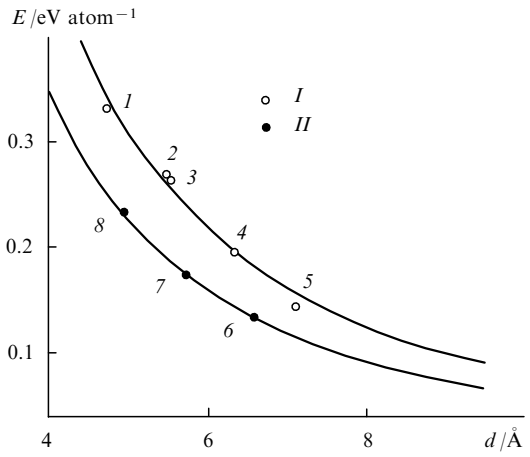


Figure 29. Deformation energies for nanotubes based on BC_3 (*I*) and graphite (*II*). (*n*,*m*): (*1*), (6,0); (*2*), (7,0); (*3*), (4,4); (*4*), (8,0); (*5*), (9,0); (*6*), (4,0); (*7*), (2,2); (*8*), (3,0).

Taking into account the isoelectronic nature of a BH unit and the C atom, the existence of BH-formed nanospheres, which may be structural analogues of C_{60}, was predicted.[397] For the synthesis of these species, laser ablation of layered graphite-like borides of alkali-earth metals in hydrogen atmosphere was suggested. It is noteworthy that the idea of the synthesis of stable boron-carbon clusters comes from the early works of Longuet–Higgins and Roberts,[49] in which the so-called '$n+1$' rule was proposed on the basis of MO theory. This rule gives electron concentrations of stable borohydrides with composition $B_nH_n^{2-}$ as in systems with close electron shells.

Table 8. Cohesion energies for clusters based on BH and C.[389]

Cluster	$-E_{coh}$ /eV	Cluster	$-E_{coh}$/eV
$B_{12}H_{12}$	9.37	$B_{12}H_{12}^{2-}$	9.98
$B_{32}H_{32}$	9.29	$B_{32}H_{32}^{2-}$	9.44
$B_{60}H_{60}$	8.82	$B_{60}H_{60}^{2-}$	8.86
C_{60}	8.50		

In order to examine the validity of the hypothesis proposed (*cf*. Ref. 397), the relative stability of $(BH)_{60}$, an analogue of C_{60}, as well as those of $(BH)_{32}$, $(BH)_{12}$, and some other homologues, were estimated using local electron density functional theory.[398] The analysis shows that borohydride nanocomplexes are more stable in ionic form. Their stability also increases as the average cross-section radius of the group decreases (Table 8).

Along with nanospheres, nanotubes, *i.e*. coaxially oriented fibres forming needle-like crystals, also attract considerable attention due to their unusual mechanical properties and conductivity.

These systems can be considered theoretically as a set of nanotubes (NT) with diameter of several nanometers. Each NT is formed by rolling up the corresponding planar atomic net and is characterised by a diameter and by the type of helicoidal ordering (chirality). If an NT is designed in this way, its diameter (d) and chirality may be described by a vector $\vec{c}_h = n\vec{a}_1 + m\vec{a}_2$ [the so-called (n,m)-NT] (Fig. 27). Then

$$d = \frac{|c_h|}{\pi} = a\frac{[3(n^2 + m^2 + nm)]^{1/2}}{\pi},$$

where a is a bond distance in the planar network.

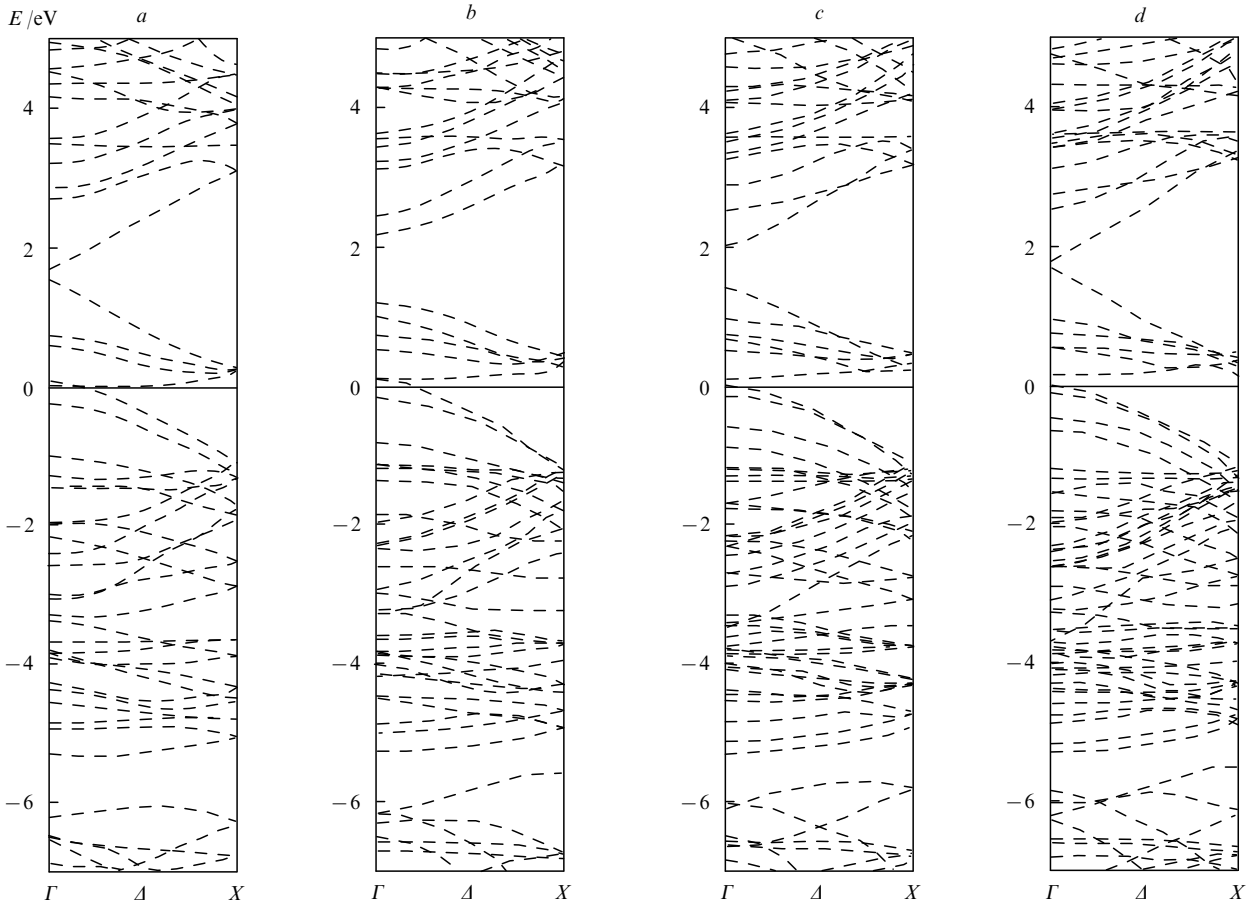


Figure 30. Band structure in achiral BC_3 nanotubes depending on their diameter. (*n*,*m*): (*a*), (3,0); (*b*), (4,0); (*c*), (5,0); (*d*), (6,0).

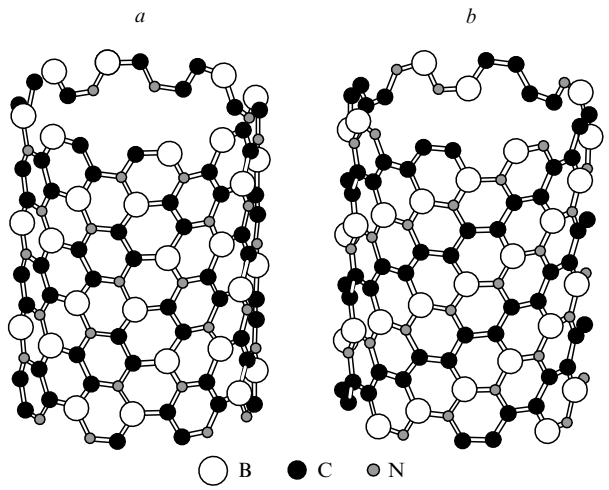


Figure 31. Possible atomic geometries of the nanotubes based on hexagonal boron carbonitride. Conductivity type: (*a*) *I*; (*b*) *II*.

Structures of graphite NT[372, 399–406] revealed the dependence of their electronic properties on the diameter and chirality. For instance, depending on *d*, the conductivity type changes from semiconducting to metallic.

Attempts to forecast the electronic properties of a number of nanosized tubular structures have been made.[407–409] These might be formed on the basis of the known layered boron-containing phases with a hexagonal lattice: h-BN, BC_2N, and BC_3.

The electronic structure of boronitride nanotubes[407] was considered in terms of the Slater–Coster TB method.[410] It was assumed that taking into account the specific type of chemical bonding in h-BN (noticeable contribution of the ionic component), the electronic properties of NTs based on h-BN should be less sensitive to the size and structure compared to the graphite-based NT. This is of great technological importance for the preparation of nanomaterials with desired properties. As it was demonstrated,[407] all NT considered are semiconductors with FG varying in the range from 4.5 to 1.0 eV with the decrease in the tube diameter. This change is related to the change in ΔE_g of h-BN under external pressure (see chapter IV). In contrast to (*n*,0)-NT, chiral (*n*,*m*)-NT are less sensitive to variations of the diameter. Besides, (*n*,0)-NT are semiconductors with direct FG (transition $\Gamma-\Gamma$), while (*n*,*m*)-NT have indirect FG (transition $\Delta-\Gamma$). The change in chiral angle θ (see Fig. 27) is more critical for tubes with a smaller diameter, while NT with a $d > 12$ Å possess broad FG with weak dependence on chirality. This may be qualitatively explained by the fact that the distance between the diametrically opposite boron and nitrogen atoms on the surface of NT with small radius is comparable with the interlayer separation in h-BN, so its change [depending on chirality: $d(4.0) = 6.4$ Å and $d(4.4) = 10.6$ Å] should strongly influence direct interactions between these atoms.

The above discussed energy band transformation for nanotubes of h-BN depending on their structure is illustrated in Fig. 28, where the results of a Hückel calculation for NT a h-BN[411] are compared with the band states of isostructural carbon quasi-one-dimensional systems.

The electronic structure of NT based on the highest boron carbide BC_3, has been studied.[409] In order to estimate the mechanical properties of BC_3 nanotubes, calculations of elastic deformation energies were performed that gave smaller values in comparison with graphite-like NT (Fig. 29). This may indicate higher stability of BC_3 nanotubes.[409]

Band structures of BC_3 (*n*,0)-NT ($n = 3$, 4, 5, and 6) are shown in Fig. 30. The conductivity type unequivocally changes from metallic to semiconducting as the diameter increases. This effect is associated with noticeable deviations of bond angles (for NT of small size) from 120°. As a consequence, both sp^2- and sp^3-hybridised atoms are involved in s-interactions. The sp^3 type determines energies of borders for valence and conductivity zones, *i.e.* the magnitude of FG. With the increase in the NT diameter, the interbond angles approach the limiting value in the planar net (120°), and ΔE_g for NT approaches the FG value in BC_3 single layers. More adequate studies of BC_3 nanotubes should take into consideration not only single NT, but a system of coaxial NT as well[409] that can be formed by the rolling of several boron carbide nets. This is due to the fact that an account of interlayer interactions plays a decisive role in simulations of the conductivity properties of boron carbide.[224]

It is well established that planar nets of boron carbonitride BC_2N can manifest either the metallic or semiconducting properties depending on the ordering type of atoms therein.[341] Thus, one may expect that rolling a BC_2N single layer of the types *I* and *II* (see Fig. 24 *a,b*) into cylinders will result in NT with distinctly different properties. Geometry of BC_2N (*n*,*n*)-NT of types *I* and *II* for $n = 4$ is shown in Fig. 31. Band structure calculations by TB method[408] indicate that NT with a small diameter ($n = 2$) maintain the conductivity properties typical of parent single layers. However, for (*n*,*m*)-NT of type *I* the change in the conductivity type from metallic to semiconducting, depending on diameter and chirality, is possible (like for graphite NT). Presumably, (*n*,*n*)-NT of the type *II* should be the most stable (see Fig. 31), since their atomic configuration provides the maximum number of strong C–C and B–N bonds.[408]

Anisotropy of conductivity in BC_2N single layers allowed one to suggest that chiral NTs can conduct helicoidal current, and therefore act as nanocoils.[408] Many questions that require deep theoretical considerations are related to the capillary effect in boron-containing nanotubes. Microlevel modelling of the influence of various impurities and structural defects that can appear during synthesis on their properties is also of great significance.

One of the examples of deviations from the 'ideal' structure for BC_2N has been discussed.[408] In the experiment, carbon atoms as an admixture substituted boron or nitrogen atoms. It was pointed out that the C→N substitution gives rise to the appearance of an acceptor level above the top of VZ by 0.03 eV, and the C→B substitution generates a donor level lower than the bottom of the conductivity zone. As a consequence, a conductivity type for semiconducting carbonitride nanotubes (*n*- or *p*-type) may be regulated by changing their stoichiometry, since the electron or hole concentration can increase in $B_{1-x}C_{2+x}N$ or $BC_{2+x}N_{1-x}$, respectively.

A number of papers devoted to the synthesis of tubular carbon nanostructures containing admixtures (boron, nitrogen)[412, 413] have been published recently.[414–417] In particular, the topology of terminal groups in NT has been discussed.[417]

VII. Boron phosphides and arsenides

Among the known boron phosphides and arsenides,[5, 7, 10, 22, 32] the sphalerite-like BP and BAs attributed to semiconductor type *III–V*, are the best studied.[258, 293, 295, 297, 302, 306, 418–423] Band structures of BP and BAs calculated by the APW method (Fig. 32) are typical of this type of semiconductors. The valence zone includes a low energy subband mainly of *s*-states that is separated from the zone of hybrid *p–p* states by an energy gap, and the dispersion $E(k)$ is much larger for BAs than for BP. Most attention in the papers mentioned was paid to the estimations of the FG. Data shown in Table 9 allows one to judge the order of these values. It is clearly seen that on going from BP to BAs, ΔE_g for indirect FG decreases by ~1.1 eV and for direct FG increases by ~0.2 eV.

Calculations of the optical properties[258, 295, 297, 302, 306, 418–423] allow reliable interpretation of the experimental results. The most intense peak $\varepsilon_2(w)$ for BP ($E = 6.8$ eV) is caused by the interband transition $X_{5v} \rightarrow X_{3c}$, and the next (as regards intensity), ($E = 7.6$ eV) is caused by the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transition.[423] The

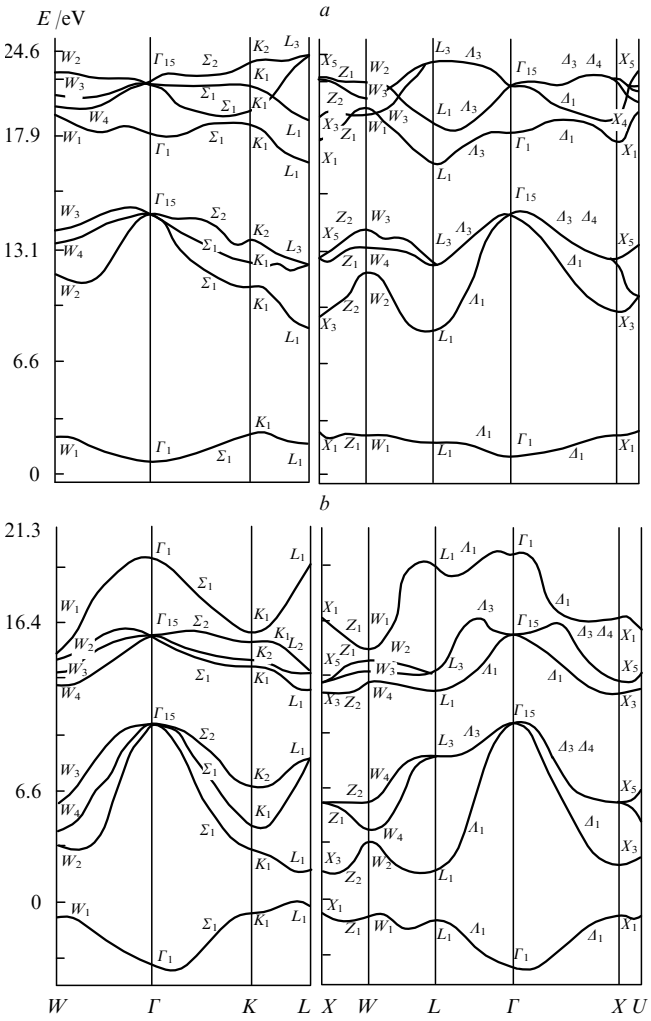


Figure 32. Valence bands of sphalerite-like BP (*a*) and BAs (*b*). APW calculations.[423]

Table 9. Calculated results and experimental values of direct (ΔE_g^d) and indirect (ΔE_g^i) forbidden gap, lattice constant (*a*), and volume modulus (B_i) for BP and BAs.

Parameter	Calculation	Experiment	Ref.
Results for BP			
ΔE_g^d /eV	5.0	—	297
	4.0	—	423
ΔE_g^i /eV	6.2	2.0	424, 426
	6.0	2.1	425, 427
	4.2	2.0	418, 230
	2.2	2.4	297, 428
	2.4	—	423
a /Å	4.60	4.54	315, 431
B_0 /GPa	171	173	315, 431
Results for BAs			
ΔE_g^d /eV	3.6	—	421
	4.2	—	423
ΔE_g^i /eV	1.6	1.5	421, 429
	1.3	1.4	423, 430
a /Å	4.83	4.78	315, 431
B_0 /GPa	149	—	315

maximum at the energy 5.7 eV is attributed to the $L_{3v} \rightarrow L_{1c}$ transition. For BAs, the main peak $\varepsilon_2(\omega)$ can be attributed[423] to the $L_{3v} \rightarrow L_{1c}$ transition and the next one (the same as for BP) is associated with the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ transition.

Band calculations of the bulk modulus and lattice constants for BP and BAs have been performed,[423] the divergence with experiment did not exceed $\sim 1.5\%$ (see Table 9).

To our knowledge, only one XES study of a more complex system BP_xAs_{1-x} has been carried out.[432] Comparison of parameters of P $L_{2,3}$, P K_β, and B K_α spectra for the SS with the corresponding XES data for BP and BAs (see Refs 81, 433–436) leads to the conclusion that,[432] along with XES peaks that reflect P 3*s*,3*p*–B 2*p*, P 3*s*,3*p*–B 2*s*, and P 3*p*–B 2*p* interactions, P $L_{2,3}$, P K_β, and B K_α bands of a quasi-binary system BP-BAs constitute an additional substructure that can be attributed[432] to the formation of direct P–As interactions.

Data on the electronic structure of other phases that are formed in a B–(P,As) system involve only XES results for $B_{12}P_2$ (see Refs 81, 436) and calculations for $B_{12}P_2$ and $B_{12}As_2$ performed by the APW,[53] TB,[110] and pseudopotential[437] methods. According to,[110] the electronic structure of $B_{12}P_2$ and $B_{12}As_2$ is close to that of α-B_{12}. These phases have a flat valence zone with indirect FG equal to ~ 2.5 ($B_{12}P_2$) and ~ 2.3 eV ($B_{12}As_2$).

VIII. Boron oxides

In a rather numerous group of boron oxides and other more complex oxygen-containing compounds described in the literature,[5, 7, 14, 32, 34] the EES of boron trioxide B_2O_3 [131, 238, 241, 438–443] and boric acid H_3BO_3 [131, 241, 438, 444] were extensively studied with XES, AES, and XPS. These two substances that play an important role, for instance, in the technology of boron-containing glasses, have similar crystallographic characteristics.

Preliminary studies of B K_α emission and absorption spectra for B_2O_3 [131, 238, 438–441] revealed a number of spectral maxima that reflect [399–402] mixing of boron states with O 2*s* states (high wavelength satellites in XES) and O 2*p* subbands. Selective maxima in the absorption spectra can be explained by an exciton mechanism of their formation. This interpretation was qualitatively confirmed by semiempirical CNDO cluster calculations for a minimal group that model B_2O_3 (BO_3^{3-} and BO_3B clusters) and H_3BO_3 (cluster H_3BO_3).[445] In particular, a low-energy absorption peak is due to an excitation of B 1*s*-electrons and their transition to vacant $2a_2$ MOs (in the MO system of BO_3^{3-}) composed of $2p_z$-orbitals of the boron.[445] The broad absorption subbands that follow in energy may be assigned to subbands of B $2p_{x,y}$-states.

A detailed study of B_2O_3 and H_3BO_3 was carried out[241] using XES, AES, and XPS spectroscopy. Comparison of measured binding energies for B 1*s* levels in the diboron trioxide with MO calculation data[445] allowed one to evaluate the effective charge on the B atoms (+0.6 e). Figure 33 illustrates the structure of the B_2O_3 valence band. XPS and (O,B) K_α X-ray emission spectra contain two distinct filled subbands. O 2*s* and B 2*s* states contribute to the lower subband, and the higher corresponds to a mixed B 2*s*–O 2*p*–B 2*p* type. The Fermi level coincides with a short-wavelength maximum in the B K_α spectrum.

It should be mentioned that the X-ray photoelectron spectrum reflects virtually no contribution of B 2*p* states to the VZ due to low magnitude of the photoionisation cross-section of B 2*p* states (0.0002) as compared to the others: 0.0193 (O 2*p*), 0.022 (B 2*s*), and 0.1405 (O 2*s*).[446] Two peaks in the XPS spectrum with the energies of 10.7 and 6.9 eV correspond to the peaks (11.5 and 7.2 eV) in O K_α-XES spectrum and form the *II* doublet band (see Fig. 33) that overlaps the broad subband with a maximum at 14.4 eV (peak *I*). Taking into account the values of photoionisation cross-sections, the latter can be attributed to B 2*s* states. Comparison of experimental intensities for peaks *I* and *II* with theoretical values obtained under assumption of atomic and hybrid sp^2-configuration of the atomic components allows one to suggest the presence of covalent bonds in the planar layers

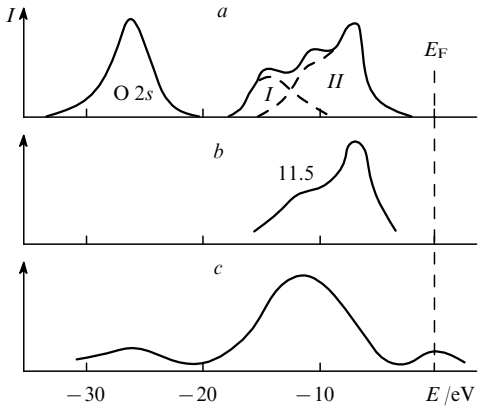


Figure 33. XPS (*a*) and X-ray emission O K_α (*b*) and B K_α (*c*) spectra of B_2O_3.

composed of atomic triangles (the crystal structure of B_2O_3 is described, for example, in Refs 447–449) and formed mainly due to the B (2*p*)–O (2*p*)–B (2*s*) overlap.

Results of B_2O_3 and H_3BO_3 studies by secondary ion mass spectrometry [241] indicate a weakening of several B—O bonds in boric acid in comparison with diboron trioxide. It may be attributed to the formation of additional O—H interactions in H_3BO_3.

Auger electron spectra for B_2O_3 and H_3BO_3 (Fig. 34) consist of six distinct peaks.[241, 450] Calculations of the possible *KLL* Auger transitions, including interatomic ones, were performed [241] using binding energy values for core and valence states. It was demonstrated that peaks *5* and *6* are due to several probable transitions of the *KLL* series, and the low energy peaks *1–4* probably have a plasmon nature. More narrow peaks for H_3BO_3 might indicate the simpler structure of the VZ for boric acid in comparison with that of B_2O_3.[241]

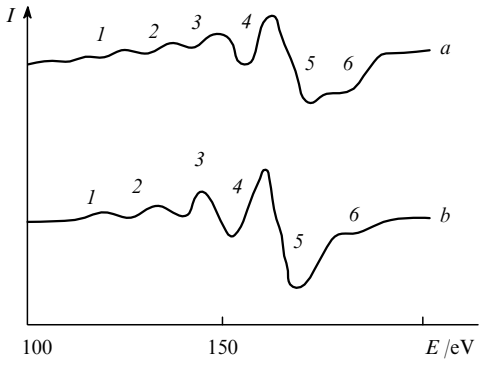


Figure 34. Derivative AES spectra of B_2O_3 (*a*) and H_3BO_3 (*b*). *1* to *6* see text.

Further studies of B K_α-XES for B_2O_3 [443, 444] have confirmed a typical three-peak structure of the spectrum; its interpretation has been proposed. A low-energy maximum ($K_{\alpha'}$ satellite separated by ~14.5 eV from the main peak) is formed due to a contribution of p-states of the emitting centre to the O (2*s*) subband. High-energy substructure of K_α spectrum near the absorption edge have a resonance nature.[444] It is formed with participation of orbitals attributed to virtual levels with π* symmetry (in the non-excited state). In order to confirm it, B K_α bands for a number of minerals {$AlBO_3$, $Be_2(BO_3)OH$, $Mg[(OH)_3BOB(OH)_3]$, $CaB_2Si_2O_8$, BPO_3}, where the first two species contain boron in trigonal coordination and the other — in tetragonal coordination, were compared.[444] B K_α XES spectra contain a prominent high-energy satellite (for trigonal coordination the lowest unoccupied states have σ* and π* symmetry), although for the tetragonal coordination (with unoccupied states of only σ* symmetry) this spectral maximum is virtually absent.

B K_α spectrum of boron suboxide $B_{13}O_2$ was also studied.[77] Oxygen atoms in this structure form O—B—O chains between B_{12} icosahedra.[451] Therefore, the emission line of the sesquioxide appears to be very similar to that in α-B_{12}. However, the width of the B K_α band for $B_{13}O_2$ is ~0.3 eV less than in the crystalline α-boron.

The detailed description of the chemical bonding nature and EES features for the boron oxides definitely requires quantum chemistry calculations.

IX. Conclusion

This paper reviews data on several classes of solid state compounds of boron with nonmetals most frequently studied by quantum chemistry methods. Fundamental and technological properties of other borides of nonmetals either in the crystalline or molecular state, *i.e.* boron hydrides (boranes), halogenides, silicides, *etc.* are also of great interest.

Studies of properties of the borides considered above, and their application in the search for new high-technology materials are developing intensively. This can be judged, in particular, by the range of problems discussed at the International Symposium on boron and borides: investigations in the field of the amorphous state of boron; boron doped with different dopants (including transition and rare-earth metals); amorphous alloys of boron; the role of nonmetallic borides in thin-film technology; problems of deposition and functionality of boron-containing coatings; polytypism among borides; factors which determine polytypes formation; ultradispersed and single crystal borides and their properties; design of supersolid materials, multi-purpose ceramics (B_4C–TiB_2, Al—B—C, Al—B—Ti, *etc.*), bi- and multi-layer composite materials with borides.

These trends in the investigation of material science of borides, in our opinion, will determine the principal directions in the development of theoretical quantum chemistry models, methods for the description and prediction of properties of borides.

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