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Boron Quasicrystals and Boron Nanotubes: *Ab Initio* Study of Various B_{96} Isomers

Ihsan Boustani,*,† Alexander Quandt,‡ and Angel Rubio†

*Gesamthochschule Wuppertal, FB 9, Theoretische Chemie, Bergische Universität, Gaussstrasse 20, D-42097 Wuppertal, Germany;
‡Laboratory of Atomic and Solid State Physics, Cornell University, 530 Clark Hall, Ithaca, New York 14853; and †Departamento de Fı́sica Teorica,
Universidad de Valladolid, E-47011 Valladolid, Spain

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The rhombohedral unit cells of α-boron crystals and of hypothetical α-boron quasicrystals were investigated by applying *ab initio* quantum-chemical methods. The atomic decorations of such unit cells are generally based on a suitable arrangement of eight boron icosahedra, and thus the mechanism of their cohesion was simulated by relaxing a B_{96} supercluster composed of icosahedral boron clusters located at the vertices of the rhombohedral unit cells. Also, several alternative structures of B_{96} clusters were proposed and compared to the rhombohedral phases. To this end, total energies of those structures were computed on the basis of all-electron calculations at the Hartree–Fock self-consistent field level of theory using the standard STO3G basis set. Due to the large number of degrees of freedom, the geometries of all isomers were optimized under reasonable symmetry constraints, but using analytical gradient methods. The resulting total energies show that segments of nanotubes and quasiplanar sheets turn out to be more stable than the unit cells of α-boron (quasi) crystals, indicating new kinds of materials. © 2000 Academic Press

1. INTRODUCTION

The discovery of quasicrystals (1) with unusual 5 and 10-fold symmetries, the detection of fullerenes in the form of carbon spheres (2) and nanotubes (3) opened new horizons in the fields of crystallography, materials science and cluster theory. They also encouraged many researchers to develop new materials by miniaturizing the system sizes down to nanoscale structures, with the hope of possible new applications in the field of microelectronics. Nowadays quasicrystals are obtained by crystallization from suitable intermetallic melts, and the organization of atoms in quasicrystals is thought to form a state lying somewhat between perfect periodic order and complete disorder. Such a state might be characterized by an obvious long-range order, giving rise to diffraction patterns with previously "forbidden" symmetries (e.g., icosahedral symmetry). Quasicrystals still are a challenge concerning the explanation of many of their curious physical properties, as well as concerning their detailed atomic structure, which in large extent is an unsolved problem.

Boron, a light trivalent element, characterized by its short covalent radius and strong directed chemical bonds, seems to be the ideal type of single element to form a quasicrystalline state. Besides various amorphous forms, crystalline rhombohedral α- and β-boron are well known phases of boron. They are composed of quite regular icosahedra attached to each other by direct B–B bonds. By forming such complicated structures, boron is able to solve the problem of its electron deficiency, and the resulting phases possess very important thermal and mechanical properties due to their high melting point 2300°C (about 1000°C higher than silicon) and a hardness similar to that of diamond. Such material properties are very useful in thermoelectrical and nuclear devices (4). Werheit *et al.* (5) experimentally determined many of the properties of β-rhombohedral boron and measured the related band gap to be 1.56 eV.

Besides these well-known crystalline forms of boron, we predicted new phases of boron, which seem to be highly stable. In previous studies we examined pure boron clusters in the form of convex, spherical, quasiplanar, and tubular geometries (6–8). The cluster formation can easily be pictured starting from two basic units only, the pentagonal and hexagonal pyramids (9). Boron sheets and nanotubes then are composed of dovetailed hexagonal pyramids only, and they have been predicted to be metallic-like conductors (10, 11). On the other hand, the convex and spherical clusters are basically composed of a combination of pentagonal (at least one) and hexagonal pyramids (6, 12), and the study of the fusion of two and three B_{12} icosahedral units suggests that closed tubular structures could be formed inside hypothetical α-boron quasicrystals (13, 14). Besides composite boron structures doped with foreign atoms [15], boron and boron–carbon chains as well as boron–hydrogen and boron–carbon–hydrogen chains have been investigated (16, 17).

Due to the fact that one of the most important problems in the field of quasicrystals is the determination of the atomic positions, we begin our considerations by studying the rhombohedral unit cells of real α-boron crystals. From the latter, we are able to derive geometrical models for prolate and oblate unit cells of hypothetical α-boron. We further optimize their geometries and compare the stability of the resulting structures to that of the original crystalline phase. Then we postulate and optimize new boron phases in the form of nanotubes and sheets, and contrast them to the optimized (quasi)crystalline phases. Note that all of these structures are isomers, being composed of 96 boron atoms. Their direct comparison will finally lead us to a couple of interesting conclusions.

2. THEORETICAL DETAILS

The all-electron *ab initio* quantum chemical calculations were carried out using the Hartree–Fock (HF) self-consistent-field (SCF) methods. Due to the size of the system, it was necessary to use the standard STO3G basis set and to consider symmetry constraints in the form of what we think might be the most plausible point group symmetries for all geometries discussed in this work. The linear search of minima on the potential energy surfaces were carried out on the basis of analytical gradients (18). Due to the still overwhelming number of basis functions (five per atom), the calculations were possible only after applying the direct-SCF procedure, which computes integrals at each electronic iteration step. The optimization procedure was done for the ground state of the systems at the restricted Hartree–Fock level of theory, using the program package GAMESS-UK (19). After all, only a reasonably small set of parameters were left to be optimized without breaking the point group symmetry.

Due to the large number of valence electrons within the investigated clusters (480 electrons), we renounced on a determination of correlation contributions and restricted ourselves to the HF-SCF level of theory, which treats the exchange contributions exactly, but neglects correlation completely. Also the determination of the vibrational frequencies of the superclusters was not possible due to their huge size. The electron correlation could of course have some influence on the relative sequence of the isomers. However, the total energies we obtained are well separated from an energetic point of view, such that we can assume that neglecting the correlation would not affect the ordering of the clusters. Also, a previous study of boron clusters at two different levels of theory, namely at the level of HF-SCF (neglecting correlation) and at the level of the local spin density (LSD) approximation of density functional theory (including correlation), shows that the results obtained when including correlation qualitatively turn out to be in very good agreement with results obtained when neglecting correlation, in particular for the ordering of the ground-state energies of the clusters (20).

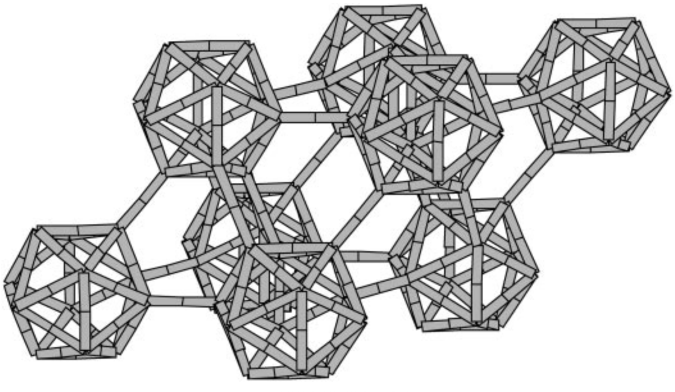
3. RESULTS AND DISCUSSION

The investigated B_{96} isomers can be separated into three groups. The first group contains rhombohedral unit cells of boron (quasi)crystals, the second one consists of a fragment of quasiplanar boron sheets, and the third group comprises segments of nanotubular structures with different diameters.

A. Unit Cells of Boron (Quasi) Crystals

The rhombohedral unit cells of α-boron crystals and hypothetical quasicrystals are characterized by different cell geometries. They basically contain eight icosahedra centered at each vertex of the unit cell. These almost regular icosahedra form a complicated network characterized by multicenter bonds, and a first step during its formation may be described by the aggregation of relatively large B_{96} superclusters. The rhombohedral unit cell of the real α-boron crystals (Fig. 1), has a space group $R3m$, a cell constant of 5.057 Å, a characteristic angle α_{rh} of 58.23°, and a related dihedral angle of 52.93°, as illustrated in Fig. 1. As can be seen, each icosahedron is bonded to six neighboring icosahedra by direct B–B bonds along threefold axes, and each of those coincides almost perfectly with an edge of the rhombohedral cell running through three fivefold axes of the icosahedra. The average bond length lies between 1.67 and 2.10 Å.

The basic unit cells of the hypothetical α-boron quasicrystals are *two* quite different rhombohedral cells. They have the same intericosahedral bond lengths and characteristic bond angles, but their overall geometries differ a lot, which is expressable in terms of the largely different dihedral angle. These two types of unit cells are called prolate and oblate



B_{96} (α-Boron) – C_{2h}

FIG. 1. The rhombohedral unit cell of α-boron crystals. The cluster is indicated by the size and the point group symmetry.

unit cells, and copies of them can be arranged as to fill space in a complete but nonperiodic fashion (21). The prolate unit cell, depicted in Fig. 2, is very similar to that of α-boron crystals. It leads to the same space group and has an intericosahedral bondlength of 4.867 Å, but an icosahedral characteristic bond angle α_{rh} of 63.43° (13) and a corresponding dihedral angle of 58.28° (see Fig. 2). This unit cell might arise during processes that lead to a small deformation of the α-rhombohedral unit cell of boron in such a way that the directions of the fivefold axes of the icosahedra and the intericosahedral bonds still coincide.

The oblate unit cell (Fig. 3) has exactly the same bondlength and the same characteristic bond angle as the prolate unit cell, that is 4.867 Å and 63.43°, respectively. However, its corresponding dihedral angle 31.72° is only half the one related to the prolate unit cell. This oblate unit cell might develop from the unit cell of α boron during a process that will quench the latter considerably. During such a process, the icosahedra lying at a short body diagonal of the rhombohedral unit cell will come extremely close to each other. The only way this can possibly happen without kicking boron atoms out of the system turns out to be the formation of a tubular structure along the short body diagonal of the unit cell (see Fig 4). For fairly weak quenching, the icosahedra along the short body diagonal are starting to connect through six bonds arising from two sets of three interfacing atoms, thus forming an anti-prism. When both sets or atoms approach each other to a distance of about 0.8 Å, a large coulomb repulsion will take place and move the six atoms into positions that form a zig–zag diamond like structure element, and finally leading to a consistent type of binding between atoms of both icosahedra. The resulting closed tubular form is also energetically favored (13).

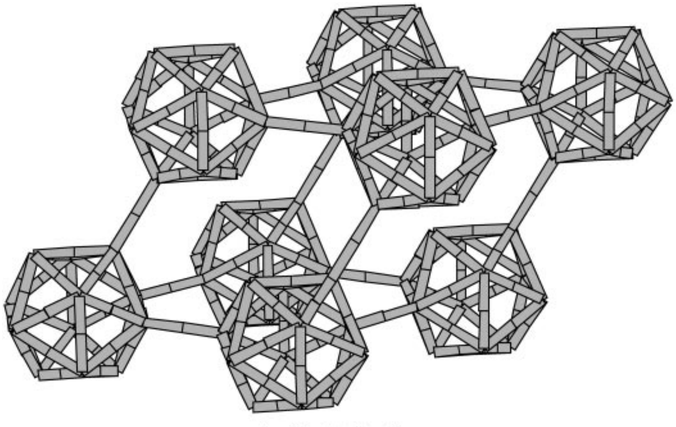


FIG. 2. The prolate rhombohedral unit cell of α-boron quasicrystals. The cluster is indicated by the name and point group symmetry.

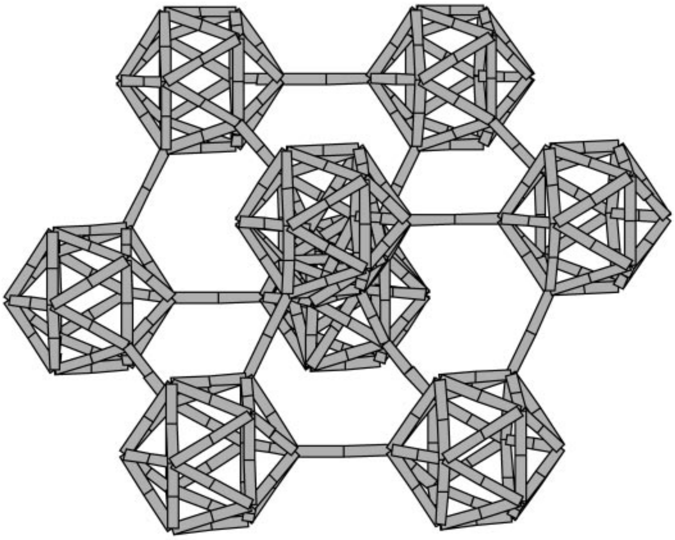


FIG. 3. The oblate rhombohedral unit cell of α-boron quasicrystals. Both icosahedra of the short diagonal are very close to each other. The cluster is indicated by the name and point group symmetry.

B. Boron Sheets

Quasiplanar boron structures were first proposed as small fragments (7), and they were investigated more systematically in a subsequent study (9). These theoretical results were then confirmed by different authors theoretically (22–24), as well as experimentally (25). It becomes more and more obvious that this should be one of the

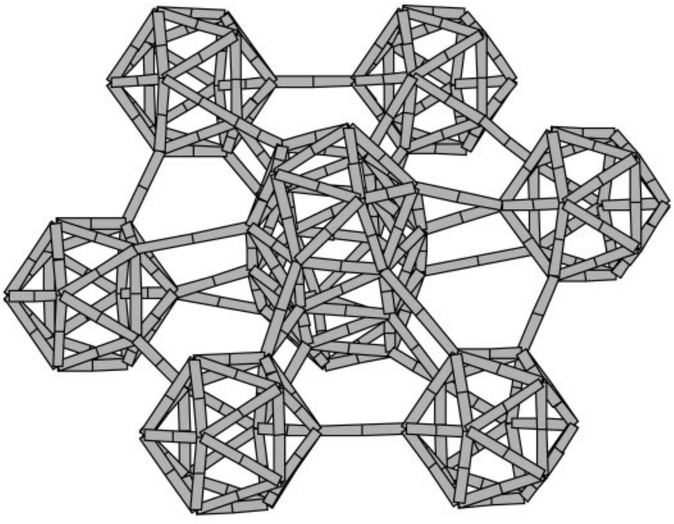


FIG. 4. The optimized oblate rhombohedral unit cell of α-boron quasicrystals. Both icosahedra of the short diagonal are fused to a closed tubular unit. The cluster is indicated the name and point group symmetry.

energetically favored types of bonding within pure boron phases. Here, the atoms are held together by directed sp^2-hybridized σ-type bonds within the plane and further stabilized through p_π orbitals perpendicular to the plane, similar to graphite. In contrast to the empty π-orbital of a single boron (see Fig. 6 in Ref. 7), arises in boron sheets a partial population of π-orbitals, which occurs through sp promotion. That is a decreasing and increasing of s- and p-orbital population, respectively, when the cluster size and coordination numbers increase.

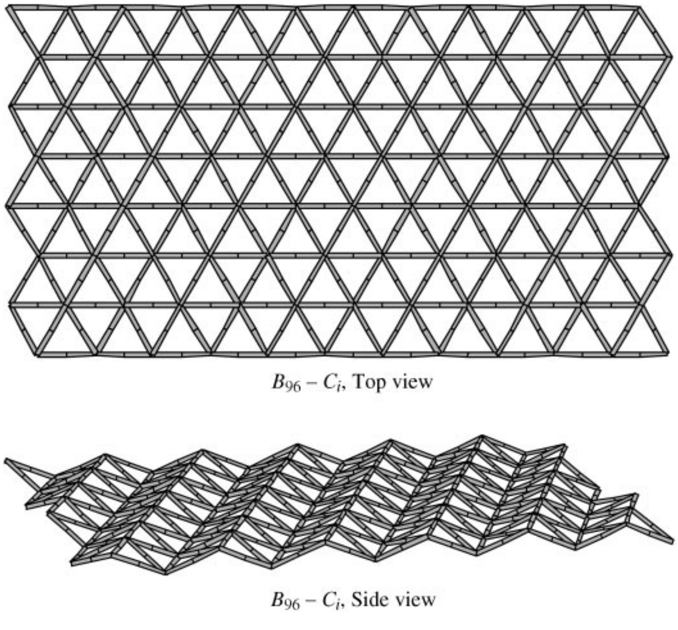
Boron sheets can be generated from a planar hexagonal lattice of boron atoms, being modulated by forcing the atoms out of the plane, up and down, and in a periodic fashion (11). The proposed quasiplanar B_{96} cluster (Fig. 5), has been calculated within the C_i symmetry point group. Of course, there are other possibilities of forming different "buckled" surfaces, but the most important property for the surface is the up–down character of the hexagonal centers, being well represented by the quasiplanar cluster examined in this study.

C. Boron Nanotubes

These new forms of boron can be generated by rolling up boron surfaces over a large energy barrier (8). Nevertheless, the obtained strain energy is still smaller than that of carbon and very close to that of boron-nitride (11). We examined three tubular structures with different diameters, but still comprising the same number of atoms, such that we were able to compare the corresponding total energies directly with those of the rhombohedral ones. These tubular structures are composed of parallel-lying staggered rings with different radii, as illustrated in Fig. 6. The first one consists of two B_{48} rings, the second of three B_{32} rings, and the third of four B_{24} rings. The corresponding diameters are 2.35, 1.56, and 1.23 nanometers, respectively. The corresponding symmetry point groups are D_{24}, D_{16}, and C_{12}.

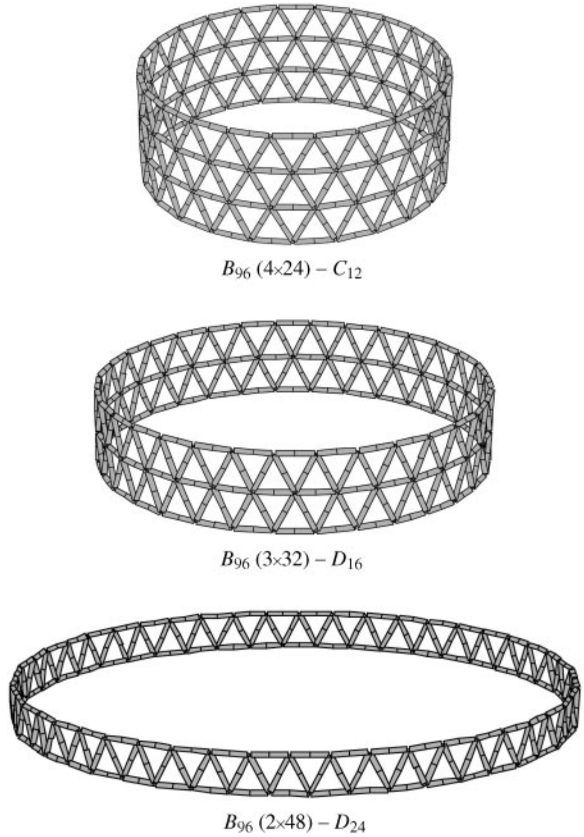
D. Stability of Clusters

The total energies of the rhombohedral superclusters corresponding to the unit cells of α-boron (quasi)crystals, as well as those of the quasiplanar fragments and tubular segments, were determined at the HF-SCF and STO3G level of theory, as listed in Table 1. The ground state energies of the all isomers have closed shell electronic structures with a singlet state. The HF-SCF calculated HOMO-LUMO gap 1.49 eV of the optimized α-boron unit cell (4.808, 58.23, 52.94) is very close to the experimental value 1.56 eV. The corresponding HOMO-LUMO gaps of the other isomers are between 2.8 and 4.8 eV, except for the nanotube B_{96} (4×24), which has a small value of 0.46 eV. As mentioned above, we also give a set of characteristic


$B_{96} - C_i$, Top view

$B_{96} - C_i$, Side view

FIG. 5. A fragment of quasiplanar boron sheets, indicated by the point group symmetry.


B_{96} (4×24) – C_{12}

B_{96} (3×32) – D_{16}

B_{96} (2×48) – D_{24}

FIG. 6. Segments of tubular boron nanotubes with different diameters, indicated by the number of rings and point group symmetry.

TABLE 1
The Total HF-SCF Energies Determined for Different B_{96} Isomers

Group	Geometry	$(R, \alpha, \beta)^a$	$E(STO3G)^b$	$(\Delta E)^c$	$(E_b)^d$
Rhombohedra	Opt. α-boron	(4.808, 58.23, 52.94)	– 2335.108339	—	4.76
	α-Boron	(5.057, 58.23, 52.94)	– 2334.905629	5.52	4.71
	Prolate	(4.867, 63.43, 58.28)	– 2334.876231	6.32	4.70
	Opt. oblate	(4.876, 63.43, 31.20)	– 2333.525272	43.13	4.32
	Oblate	(4.876, 63.43, 31.20)	– 2330.403716	128.2	3.43
Sheets	Quasiplanar	—	– 2335.314635	—	4.82
Tubules	$2 \times B_{48}$-rings	$(2.352)^e$	– 2337.293200	—	5.38
	$3 \times B_{32}$-rings	$(1.557)^e$	– 2336.479271	22.15	5.15
	$4 \times B_{24}$-rings	$(1.231)^e$	– 2335.890420	38.22	4.99
$B\ A(^2P)$	—	—	– 24.14899	—	—

[a] R (Å), α, and β (grad) are the lattice distance and rhombohedral and dihedral angles of the rhombohedral unit cells, respectively.
[b] HF-SCF energies (a.u.) calculated with the standard STO3G basis set.
[c] Energies (eV) relative to the most stable isomer in each cluster group.
[d] Binding energy per atom (eV) calculated after Eq. [1].
[e] The corresponding diameter (nanometers) of the nanotubes.

geometric entities for each structure. These are lattice parameters of different rhombohedral unit cells (lattice distance, rhombohedral angle, and dihedral angle), as well as the corresponding diameters of the tubular boron. The energy differences with respect to the lowest energy in each cluster group has been denoted by ΔE. The binding energy per atom E_b, labeled in the last column, is a suitable measure for the structure stability. It is defined as

$$E_b = (nE_1 - E_n)/n = E_1 - E_n/n, \qquad [1]$$

where E_1 is the atomic energy, E_n is the cluster energy, and n is the cluster size. In the case of $n = 96$ we have $E_b = E_1 - E_{96}/96$.

The first isomer in the rhombohedral group is the real rhombohedral unit cell of α-boron crystals (Fig. 1), with the experimental lattice data (5.057, 58,23, 52.94). The calculated total energy together with the corresponding cohesive energy E_b, 4.71 eV, are labeled in Table 1. Optimizing this unit cell by keeping the rhombohedral and dihedral angles constant and varying the size of the cluster in the sense of a breathing mode, leads to an energy lowering of around 5.52 eV. The resulting energy (labeled in Table 1 as Opt. α-boron), obtained at an optimized lattice distance of 4.808 Å, indicates that an isolated (free) unit cell prefers much compactness, confirming the fact that clusters, as free aggregates, mostly have shorter interatomic distances than solids. This optimized unit cell has the same topology as the one shown in Fig. 1, and with an E_b of 4.77 eV it seems to be the most stable isomer of this group.

The next isomer of this group is the prolate structure (Fig. 2). It is supposed to be a rhombohedral unit cell of the α-boron quasicrystals with the characteristic data (4.867, 63.43, 58.28). This structure was optimized by keeping this set of parameters fixed and varying the radius of the icosahedra only. The lowest energy, obtained at 1.68 Å, is very close to that in α-boron crystals, with an overall energy difference of 0.79 eV only. The related E_b of 4.70 eV is almost identical to that of the optimized free unit cell of α-boron crystals. This is not surprising, as the lattice parameters of both unit cells are quite similar. They deviate in the lattice distance and rhombohedral angle by 1.19 Å and 5.2°, respectively.

The next isomer of this group (Fig. 3) is the nonrelaxed oblate rhombohedral unit cell with the characteristic data (4.867, 63.43, 21.20). The calculated energy, as compared to other obtained energies, is rather high. Its total energy relative to that of the optimized structure of Fig. 1 is 128.2 eV higher than the latter. This can be explained by the large repulsion that results from the way-too-short connections between two sets of three interfacing atoms forming an anti-prism, each belonging to one of the icosahedra lying on the short diagonal of the prolate structure. A geometry relaxation then transfers this anti-prism to a zigzag ring fitting perfectly into the zigzag form of the neighboring atoms within both icosahedra. This results in the formation of a closed tubular structure, located along the short diagonal of the oblate rhombohedral unit cell, being surrounded by six icosahedra, (Fig. 4). This causes an immense energy lowering of about 84.07 eV and might be a prototype for similar kinds of transitions during the formation of intermetallic quasicrystalline compounds.

The next group of isomers is related to boron sheets and contains the B_{96} isomer only, (Fig 5). This two-dimensional isomer is representative for all structures of similar topology. The obtained energy for this structure is lower than the energies of all the rhombohedral supercluster structures, indicating a new form of boron materials. The corresponding E_b is 4.83 eV, lying well beyond that of the most stable structures in the rhombohedral group. This stability can be explained by the above-mentioned type of bonding within such structures: first the directed σ-bonds within the plane with a rather high coordination number of around 6, second by the delocalization of the π-orbitals, which are perpendicular to the plane. Note that the π-orbitals spread over both faces of the sheet, which is a large stabilizing factor.

Finally, one can see that the obtained total energies of the tubular segments, as listed in Table 1, are much lower than those of all other structures. The binding energy per atom E_b of the three isomers B_{96} (4×24), B_{96} (3×32), and B_{96} (2×48) are 5.38, 5.15, and 4.99 eV, respectively. This means that the tubular group is by far more stable than the rhombohedral group, but also more stable than the sheets. It is also obvious that the larger the diameters of the tubes, the higher their stability is. This can once again be explained by the large number of directed sp^2-hybridized σ-bonds within the bent surfaces and by π-orbitals covering the inner and outer faces of the tubes, stabilizing the system even further. The fact that the nanotubular structure B_{96} (2×48) is by 59.45 eV more stable than the rhombohedral unit cell of the α-boron crystals implies that this kind of structure could be the basis of novel boron materials.

4. CONCLUSIONS

A comparison between total energies of various types of superclusters characterizing well-known and plausible new boron materials has been carried out. We have investigated different B_{96} isomers falling into three distinct groups, one being the three-dimensional rhombohedral unit cells of boron (quasi)crystals. The second group comprises quasi two-dimensional boron sheets, and the third group is three-dimensional nanotubular segments. We have shown that there is at least one isomer in the form of a quasiplanar structure, which is more stable than the isolated rhombohedral unit cells of real α-boron crystals, as well as those of the proposed α-boron quasicrystals. The nanotubes in turn are even more stable. We thus conclude that there must be new forms of boron materials in the form of boron sheets and boron nanotubes, which are still waiting to be experimentally observed or synthesized.

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