

New boron based nanostructured materials

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Based on a series of *ab initio* studies we have pointed out the remarkable structural stability of nanotubular and quasiplanar boron clusters, and postulated the existence of novel layered, tubular, and quasicrystalline boron solids built from elemental subunits. The present study illustrates and predicts qualitative structural and electronic properties for various models of nanotubular and layered boron solids, and compares them to well-known tubular and layered forms of pure carbon and mixed boron compounds. © 1999 American Institute of Physics. [S0021-9606(99)70205-9]

I. INTRODUCTION

One of the major technological challenges for the next decades is the miniaturization of electronic and mechanical devices down to the atomic scale. This however requires an improved understanding of atomic scaled systems and their physical and chemical properties. The latter two are certainly dominated by a series of very special physical effects typical for systems of mesoscopic size and for systems in effective spatial dimensions lower than 3, which are as yet far from being completely understood. Thus one important task of theoretical investigations in this field is the proposal and construction of suitable theoretical *toy models* which may contribute to our understanding of nanoscaled systems. Another equally important and more practical task should be the modeling of *realistic* mesoscopic systems having virtually the same properties, i.e., by using numerical simulation tools; one should primarily look upon this as some kind of computer modeling, predicting promising real experiments within the “nanodomain.”

During the recent years, high expectations have been placed on carbon systems as possible key materials for future nanotechnologies.¹ These speculations were mainly nurtured by the observation of highly stable carbon clusters in the form of Buckminster fullerenes,² as well as by the subsequent observation of stable carbon nanotubes,³ which could be of outstanding importance for the miniaturization of electronic devices. Many of the recent technological developments in this field are very well described in a comprehensive monography on carbon fullerenes and nanotubes, by Dresselhaus *et al.*¹ The interested reader is directed to this excellent review for more details.

Recent experimental studies on graphitic and $B_xC_yN_z$ nanostructures⁴ confirm that boron is vital for the production

of long carbon nanotubes, and that most carbon nanotubes contain pure carbon along the main body with *boron traces at their tips*. In addition, boron, carbon, and nitrogen appear to form energetically favorable metastable layered structures. These experimentally observed phenomena, in particular the participation and the evident influence of boron on the particle growth, support our theoretical predictions of highly stable convex, spherical, quasiplanar, and tubular nanoscaled boron surfaces, found by systematic investigations described below.

Theoretical results of pure boron, based on accurate *ab initio* quantum-chemical and density functional methods, have led to previously unknown boron structures. Recently studied small cationic⁵ and neutral boron clusters⁶ reveal structures that are fundamentally different from crystal subunits of the well-known α - and β -rhombohedral phases of boron, which consist mainly of B_{12} icosahedra. These novel cluster forms can be classified into four topological groups: convex and spherical,⁷ quasiplanar,⁸ and nanotubular.⁹ The quasiplanar and convex structures can be considered as fragments of planar surfaces and as segments of hollow spheres, respectively. More detail will be illustrated below.

Preliminary experimental results for pure boron systems seem to confirm the existence of boron sheets,¹⁰ and from the theoretical point of view, most of the small boron clusters have already been confirmed by other accurate *ab initio* studies, e.g., Ref. 11. An important finding which may be extracted from the *ab initio* computations is that stable boron structures can be obtained with the help of the so-called *Aufbau principle*, proposed for general boron compounds.¹²

This *Aufbau principle* says that highly stable boron nanoclusters, surfaces, and networks can simply be constructed from two elemental units only, namely pentagonal and hexagonal pyramids, B_6 and B_7 ,⁶ respectively. The construction of any new species can start from a hexagonal pyramid, for example, by adding atoms consecutively forming either hexagonal pyramids only [two-dimensional (2D)

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sheets or nanotubes] or pentagonal and hexagonal pyramids [three-dimensional (3D) sheets or spheres].

Optimized structures of crystalline α -rhombohedral boron, investigated at the same *ab initio* level of theory, obey this *Aufbau Principle* as well. Furthermore, recent new *ab initio* studies on the fusion of two,¹³ as well as three B₁₂ icosahedra,¹⁴ predict the formation of nanotubules inside α -boron quasicrystals.

The present study suggests the existence of new boron materials showing at least the same variety of nanotubular forms as those known for carbon and boron-nitride systems. It may be interesting to point out that *ab initio* studies of BN systems^{15,16} already predicted highly stable BN nanotube, and that they stimulated subsequent experimental work¹⁷ that finally lead to the discovery of stable multiwall BN nanotubes.^{18,19} In contrast to these studies, which primarily oriented themselves on similarities between graphite and layered BN structures on one side, and between *ab initio* results for C and BN nanotubes on the other, the reasoning within the present study is mainly based on *ab initio* calculations of pure boron clusters, pointing out their function as building blocks for nanostructured B materials. The present work is the first one to emphasize these aspects of pure boron compounds, *contrasting* them to the well-known C and BN systems.

In the following sections we will briefly summarize the methods and main results of different calculations on boron compounds, focusing on quasiplanar and tubular clusters, as well as periodic one-dimensional tubules and two-dimensional sheets. From this, simple structure models for layered boron structures, e.g., boron sheets, as well as for tubular boron compounds will be derived. The structure and properties of the former will be contrasted to those of the well-known layered AlB₂ phase. In a special subsection, we will discuss the elastic properties of boron one-dimensional nanotubes, comparing them to those found for C, BN, and other B_xC_yN_z nanotubes. The last section will be devoted to a qualitative comparison of the structural and electronic properties for various nanotubular networks of C, B, and BN type. The nanotubes in each class are composed of six- and 12-membered rings. We close with a discussion of the main results, a prospect for future work and conclusions.

II. THEORETICAL METHODS

Different theoretical methods were applied in order to obtain the various properties of boron, carbon, and boron-nitride species. These methods include *ab initio* quantum-chemical approaches, in the frame of the Hartree-Fock (HF) self-consistent field (SCF), spin-polarized density functional theory (DFT) in form of local spin density (LSD), linearized muffin-tin orbital based band structure methods (LMTO), tight-binding approaches (TB), and finally nonlocal norm-conserving pseudopotential plane-wave (PW) methods. Structural optimizations based on analytical gradient methods as well as calculations of fixed configurations were carried out to determine the final structures and energies.

For calculations of the boron nanotubular segments containing up to 32 atoms, all electrons were considered when applying *ab initio* HF and DFT methods. It is well known

that structural optimizations are generally far from being trivial, as potential energy hyper surfaces are studded with local minima. In order to deal with this problem, one basically has to work with a carefully considered combination of different *ab initio* methods. Consequently, a proper structural optimization should be carried out combining HF-SCF and DFT approximations. Usually the starting point is a geometrically motivated initial guess, which has to be optimized at the HF level using a small STO3G basis set. Then, these optimized structures will be taken as an input for a HF reoptimization using a larger basis set (e.g., 3-21G). In order to properly account for correlation effects, the next step will be a reoptimization of these structures using local spin-polarized DFT methods, followed by a final optimization using nonlocal (gradient corrected) spin-polarized DFT methods. Using the all-electron *ab initio* HF-SCF level of theory with the standard STO3G basis set and structural optimization, was only possible for systems containing up to 60 atoms.

For infinite systems, the structural relaxation was performed within the pseudopotential total-energy scheme^{20,21} using a plane-wave basis set and the LDA approximation. The pseudopotentials were generated following the prescription of Troullier-Martins.²² We have used a plane-wave cut-off energy of 40 Ry to expand the electron wave function. A set of 10 and 64 Monkhorst-Pack²¹ points were used to sample the Brillouin zone of the nanotubes and sheets, respectively. These parameters ensure a good convergence of the total energy for the metallic boron structures. A quasi-Newton method is used to simultaneously relax the internal coordinates and the lattice parameters.²³

In order to calculate the band structure and the density of states (DOS) of periodic unit cells of C, B, and BN surfaces and nanotubes we have used *ab initio* linearized muffin-tin orbital based methods within the atomic-sphere approximation (ASA).²⁴ These methods are based on the local density approximation (LDA) of DFT. The nonspin polarized functionals used here were those proposed by Barth and Hedin.²⁵ The LMTO basis sets provide the method with a reasonable computational speed, as well as with the accuracy necessary to carry out qualitative studies on large systems. Also a minimum of roughly 200 *k* points were considered for each computation. These methods were successfully applied on α -boron type solids and boron sheets, where the input structures for most of the LMTO computations were extrapolated from structural optimization runs for suitable cluster subunits.²⁶

One appropriate approach to calculate large scale of boron systems is the nonself consistent, nonorthogonal TB scheme developed by Porezag *et al.*,²⁷ in which the Hamiltonian and overlap matrix elements are tabulated beforehand on the basis of self-consistent DFT linear combination of atomic orbitals (LCAO) calculations, retaining only two-center contributions to the Hamiltonian matrix elements. The parametrization used for the boron-boron interactions was reported by Widany *et al.*²⁸ These TB methods²⁹ are a good compromise between the sophisticated but much more expensive *ab initio* first principles techniques and the simple empirical potentials, e.g., Tersoff³⁰ potentials. The TB calcu-

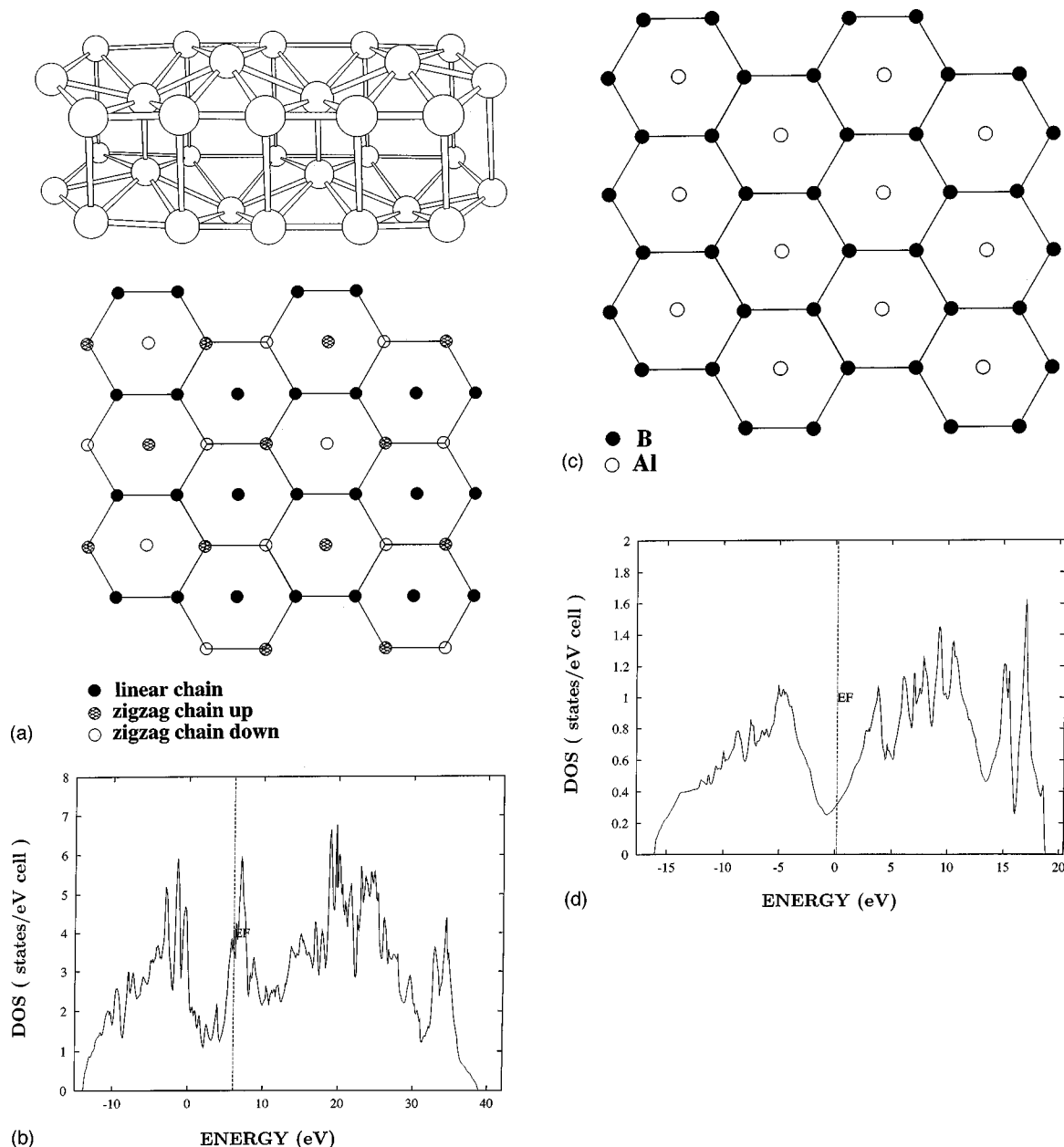


FIG. 1. Comparison of pure boron sheets and AlB₂: (a) Structure of double layered boron cluster (top) (Ref. 8), and structure of monolayer for a model of buckled boron sheets (below). (b) Total density of states for boron sheets. (c) Structure of a monolayer within AlB₂. (d) Total density of states for AlB₂.

lations were performed using Γ -point sampling only, but with periodically repeated cells which were large enough along the axial directions of the boron nanotubes.

III. RESULTS AND DISCUSSION

A. Buckled boron sheets

Before starting a detailed discussion of the layered boron compounds (boron sheets), as suggested in Ref. 8, let us motivate their structures by considering the well-known layered AlB₂ phase,³¹ shown in Fig. 1(c). Obviously, AlB₂ is a puckered hexagonal system, where all Al atoms are situated halfway between two flat honeycomb-shaped layers composed of B atoms. The boron honeycomb sublattice makes a dominant structure element. However, without the presence of the Al atoms, the B sublattice is not saturated. In fact, an

analysis of the electron density of AlB₂ obtained from LMTO band structure calculations, reveals a noticeable charge transfer from the *p* states of B to the *d* states of Al. In the case of pure boron structures, where such charge transfer cannot take place, one would expect the following: first some distortion of the honeycomb sublattice. Second, in virtue of the Aufbau principle, one could regard the pure boron sheets as composed of B₇ hexagonal pyramids, with alternating up-down apex, forming buckled hexagonal sheets. Upon stacking of such layers, bonding between a down apex in the higher layer and an up apex in the lower layer could take place. In fact, the structures for multilayered boron clusters, as described in Ref. 8, show exactly the structure depicted in the upper part of Fig. 1(a). From this one can derive a structure model for planar boron solids as shown in the lower part

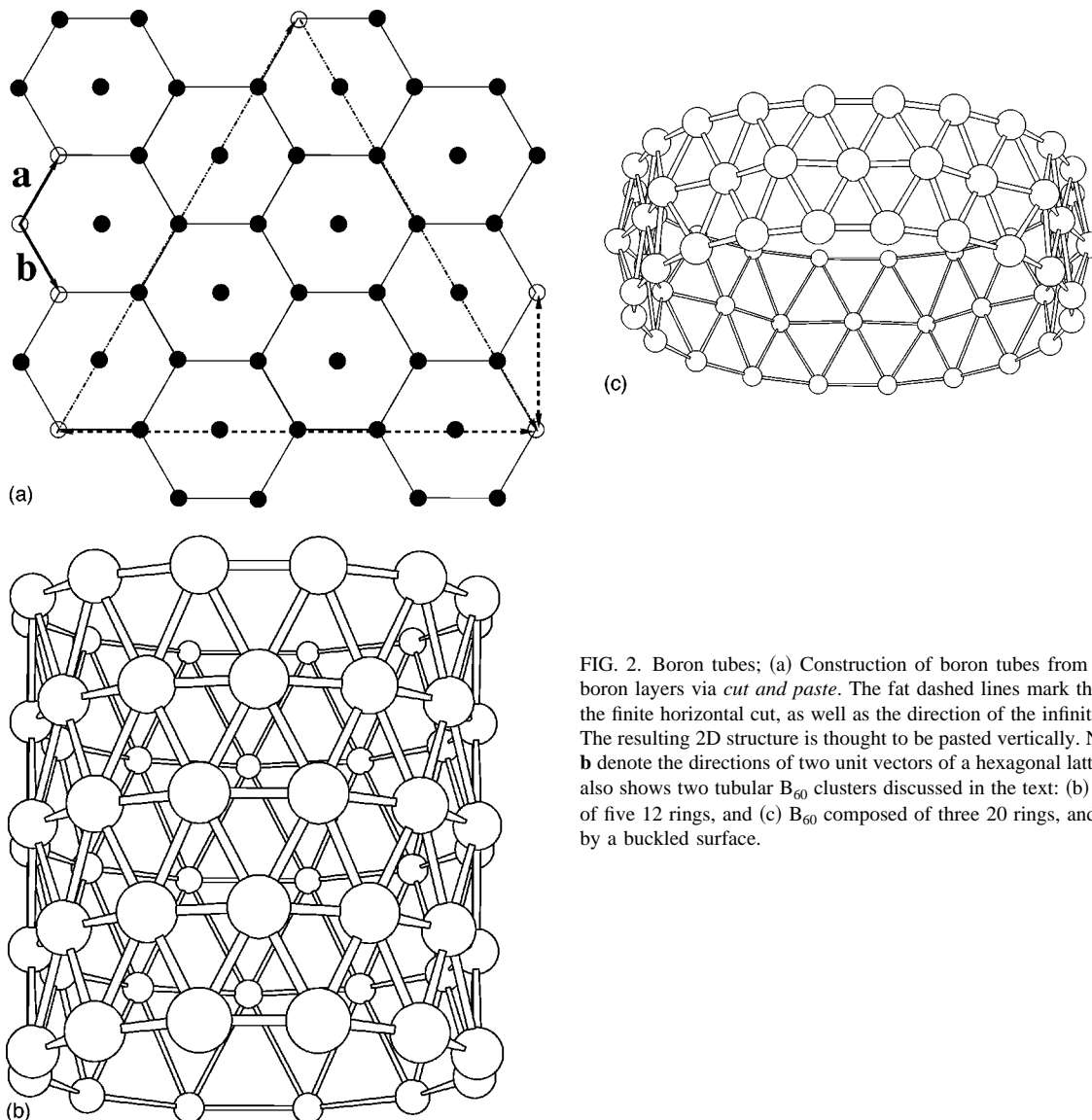


FIG. 2. Boron tubes; (a) Construction of boron tubes from 2D hexagonal boron layers via *cut and paste*. The fat dashed lines mark the directions of the finite horizontal cut, as well as the direction of the infinite vertical cuts. The resulting 2D structure is thought to be pasted vertically. Note that **a** and **b** denote the directions of two unit vectors of a hexagonal lattice. The figure also shows two tubular B_{60} clusters discussed in the text: (b) B_{60} composed of five 12 rings, and (c) B_{60} composed of three 20 rings, and characterized by a buckled surface.

of Fig. 1(a). The structure may be described as a staggered arrangement of infinite zig zag and straight boron chains in 2D, and an AB stacking of layers in the 3rd dimension according to Fig. 1(a). It should be pointed out that the puckering of the model boron sheets is anisotropic compared to AIB_2 .

As described in Ref. 8, one finds an increasing population of the electronic π system between the layers, which favors a strong binding between the different 2D layers, such that the shortest interlayer distances turn out to be around 1.8 Å, an average length for boron bonds. However, the interlayer distance is by far smaller than the usual interlayer distances in graphite or BN, a point which has to be taken into account when setting up model hexagonal tubular networks (see below). More structural details about boron sheets may be found in Refs. 8 and 26. We can distinguish two kinds of covalent bonds in these layered boron compounds. The intralayer bonds exhibit metallic-like character. That can be explained by the electron deficiency forcing the electrons to be shared at the surface, where the apical atoms serve as a bridge for electron transfer within the honeycomb network.

The interlayer bonds resemble covalent bonding which is responsible for a highly stable multilayered ensemble of boron sheets.

Figures 1(b) and 1(d) show the total density of states (DOS) for the model boron sheets as well as for AIB_2 , obtained from LMTO-ASA band structure calculations.²⁴ It should be noted that the DOS for AIB_2 is in a very good agreement with published numerical results (e.g., see Ref. 32, Chap. III). Second, the overall shapes of the DOS are rather similar, which is understandable as both structures are more or less buckled variants of the hexagonal lattice.³³ The differences may be attributed on the one hand to the slight structural changes, and to the fact that Al atoms are replaced by B atoms in the pure boron structures on the other. As a last point, we would like to mention that both structures show a pronounced metallic-like DOS, and therefore they are conducting. We conclude that the boron sheets with their metallic properties have potential technological applications.

Starting from the proposed structural model for pure B sheets described in the previous section, we have used *ab initio* plane-wave calculations to simulate an infinite boron

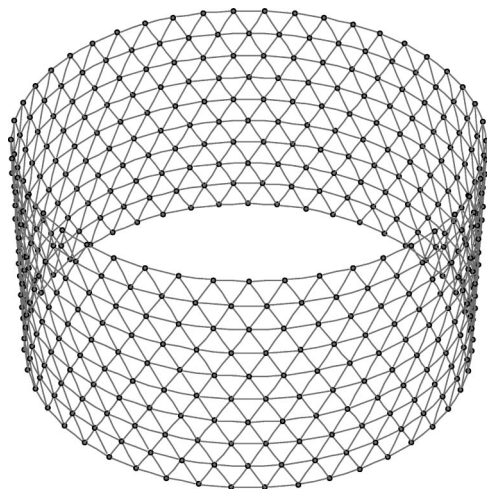


FIG. 3. Boron nanotube; A model for B(15,15) nanotube consisting of 450 boron atoms. This structure, which simulates a segment of an infinite body, is consisting of 10 parallel-lying B_{45} staggered rings.

surface. In addition, we have performed calculations on two other models, namely the unbuckled surface and the hexagonal (graphite isostructural) surface, in order to check the relative stabilities of these candidate structures.

A structural optimization of large unit cells consisting of up to 72 atoms was performed. As expected, the buckled surface was the most stable configuration [see Fig. 1(a)]. The computed gain in binding energy is 0.03 eV/atom with respect to the unbuckled one, and 0.7 eV/atom with respect to the graphite-like honeycomb network. This structure can be described by two parameters: the bond length and the degree of buckling. The optimized bond lengths are 1.68 and 1.76 Å, the first distance corresponding to a hexagonal side, and the second one to the distance between an atom in the hexagon and the apex atom. The instability of the honeycomb boron surface seems to be related to largely unsaturated bonds.

B. From boron sheets to boron nanotubes

The rather lengthy numerical procedure using *ab initio* optimization methods (Sec. II) was first applied to determine the structure of nanotubular and quasiplanar boron clusters with the highest possible accuracy (e.g., see Refs. 8 and 9). It was found that in many cases, nanotubular and quasiplanar boron clusters are almost energetically degenerate, and thus have similar structural stability.⁹ Of course, this depends on the number and size of the rings forming the nanotubules, as well as on the number of layers in the case of quasiplanar surfaces. This behavior is in contrast to what is observed in infinite systems, where flat surfaces are more stable than nanotubular structures. This is the case for carbon and BN,^{34,35} as well as for boron, as will be illustrated below.

The basic procedure of rolling up a boron surface into a nanotube follows the same procedures used in construction carbon tubes from graphene sheets.¹ Nanotubes can be labeled by two indices (n,m) (following Ref. 36) which indicate the way in which the graphene sheet is mapped onto a cylinder. The pair of integers (n,m) defines a Bravais lattice

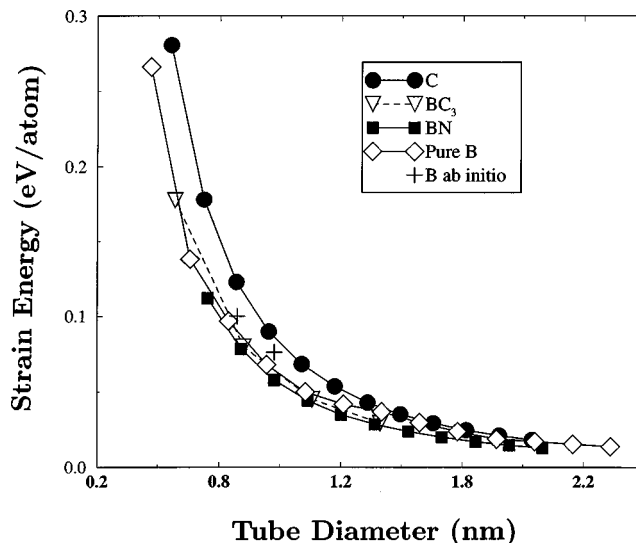


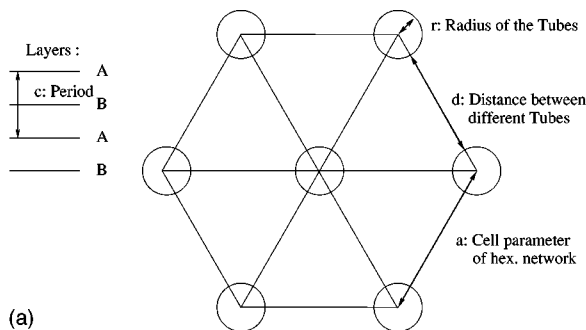
FIG. 4. Strain energy; The strain energy of $B_xC_yN_z$ (n,n) armchair nanotubes for different compositions. We compare pure boron nanotubes with previously reported data on carbon, boron–nitride, and boron–carbide (Ref. 34). The figure shows the strain energy as a function of the tube diameter, as obtained from tight-binding calculations. It also includes *ab initio* pseudopotential calculations for the buckled relaxed structures of B(5,5) and B(6,6) nanotubes, assigned with (+).

vector (in terms of two primitive lattice vectors of the sheet) which determine the tube diameter. The combinations (n,n) and $(n,0)$ are called armchair and zig zag tubes, respectively. They possess a reflection plane perpendicular to the tube axis. All other (n,m) nanotubes will have helical symmetry operators.

We have described how nanotubular boron clusters may be constructed from planar reference structures via a *cut and paste* procedure. The basic building block is a regular 2D honeycomb lattice (for more details of structural data concerning graphite and layered BN the reader should consult Ref. 31), and the finite virtual cut must be carried out along those directions which are integer linear combinations of the unit vectors of the honeycomb lattice (see Ref. 1). In the present study, we will restrict ourselves to discussing those classes of nanotubes which may be created by a cut along the (n,n) directions of the basic sheet (i.e., by going n times along the unit vectors in both unit directions).

In the case of boron, the above mentioned buckling of the layers has been neglected in building the initial tubular geometry, so that the calculations started from a perfectly planar boron nanotube, except for the B(5,5), where the sheet was rolled up from a buckled surface (see below). The boron nanotubes themselves can be constructed by carrying out a hypothetical folding of the planar boron sheets to create boron nanotubes, and the energetics of the entire folding process was studied with the help of *ab initio* methods.⁹

As an example for the resulting nanotubular structures and their remarkable structural stability, we present here two tubular segments of B_{60} [see Figs. 2(b) and 2(c)], obtained at the *ab initio* HF-SCF level. The first one consists of five staggered parallel-lying planar B_{12} rings, and the other one of three staggered parallel-lying planar B_{20} rings. The corresponding HF-SCF energies, calculated with the minimal



type	r (Å)	d (Å)	c (Å)
C (6,6) †	4.125	3.14	2.49
C (3,3) ††	2.105	3.14	2.53
BN (6,6)	4.222	3.3	2.552
BN (3,3)	2.111	3.3	2.552
B (2x12)	3.0	1.8	2.997
B (2x6)	1.67	1.8	3.021

$$\dagger a_{c-c} = 1.44 \text{ \AA}$$

$$\text{(b) } \dagger\dagger a_{c-c} = 1.47 \text{ \AA}$$

Gaussian basis set STO3G, are -1459.75156 and -1460.53425 a.u., respectively. These tubular structures were optimized under the respective point group symmetries C_{12h} and D_{12h} . The corresponding binding energies per atom for each isomer are 4.9 and 5.26 eV, respectively. It must be mentioned that the energy lowering of the tubular B_{60} - D_{12h} [Fig. 2(c)] is related to the buckling behaviour resulting from the geometrical optimization.

Similar puckering behavior was found for a relaxed infinite tubular structure, namely for the B(5,5). Two concentric boron shells were obtained with the corresponding radius of 8.21 and of 8.28 Å. This is consistent with the buckling behavior in boron quasiplanar and tubular clusters, found as well in boron sheets. The degree of buckling seems to be reduced when the nanotubular diameter increases, and it approaches a degree similar to the buckling observed in BN nanotubes.^{16,34}

C. Elasticity of boron nanotubes

A useful way of characterizing the mechanical property and the relative stability of different nanotubular materials is the so called *strain energy*, which is defined as the difference between the energy per atom in a tube of a given diameter and that of the corresponding infinite flat sheet. A low strain energy indicates that nanotubes of the material in question should be easy to obtain. In order to calculate the strain

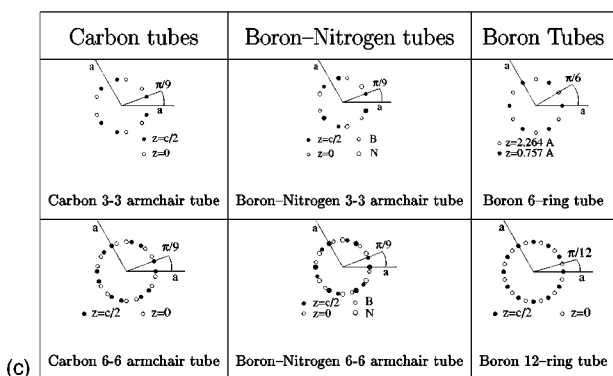


FIG. 5. Hexagonal tubular networks; (a) Global description of the structures for a nanotubular bundle, (b) the values of the global variables for the respective model systems examined. It should be noted that for the carbon tubes, we have used two different values for the interatomic distances a_{c-c} within the reference graphene sheets, where 1.47 Å would lead to the ‘right’ interatomic distance of 1.44 Å within the corresponding tube, and (c) local structures of the various tubular components.

energy of boron nanotubes, tight-binding calculations²⁹ were performed to obtain the energies of infinite sheets and nanotubes of different diameters. We have generated nonbuckled boron nanotubes, with a B–B bond length of 1.65 Å, in the same manner of the *ab initio* obtained tubular B_{60} clusters, shown in Figs. 2(b) and 2(c). They have different diameters with constant length, being of (n,n) type and consisting of 108 up to 540 boron atoms.

One nanotubular model, presented in Fig. 3, is composed of 450 atoms having a diameter of 23.6 Å. This structure can be considered as a segment of a long cylinder formed by ten parallel-lying B_{45} staggered rings. The values of the strain energy are plotted as a function of the tube diameter. For comparison purposes we have also plotted the strain energy for C, BN, and BC_3 nanotubes³⁴ (see Fig. 4). One can recognize that the values of the boron strain energies are below those of the graphite-based carbon nanotubes, having very similar values as the BN and BC_3 tubes. This fact can be interpreted as an indication that boron nanotubes should experimentally be obtainable. Similar arguments have been used in the past to predict the existence of BN and other composite nanotubes.¹⁵ The elastic constants of a boron nanotubular solid are expected to be less anisotropic, as in the case of carbon or BN nanoropes, due to the strong bonds between the B tubes. They are in other nanotubular solids very weak van der Waals-type bonds.

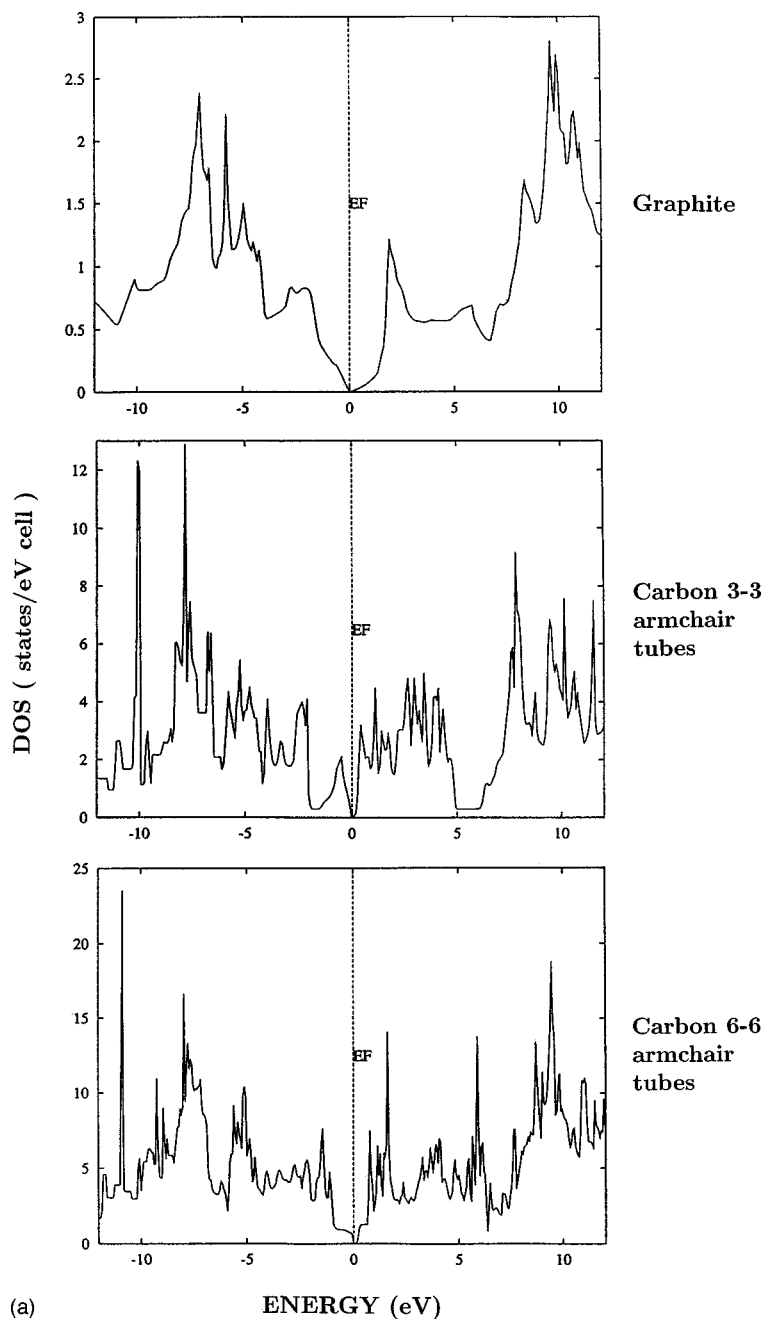


FIG. 6. Total density of states; of (a) carbon, (b) boron–nitrogen, and (c) boron. From top to bottom of each column: Planar reference structures, three-three armchair or six-membered ring systems and six-six armchair or 12-membered ring systems.

D. Hexagonal tubular networks

Let us finally consider the electronic properties of boron nanotubes by means of band structure calculations. We will focus our attention on boron hexagonal tubular networks (see Fig. 5). Our aim here is to compare these systems to the corresponding C and BN structures from the point of view of their electronic structure properties. In order to perform standard band structure calculations for these systems, we arranged the nanotubes on a hexagonal superlattice (*hexagonal tubular network, or nanorope*), such that the tube axes point in a direction perpendicular to the planes which contain the vertices of the hexagonal superlattice [see Fig. 5(a)]. The distances between the tubes are assumed to be the same as the interplane distances within the respective layered reference structures. The corresponding structural data is tabulated in Fig. 5(b) and the variables therein refer to the draw-

ing in Fig. 5(a). The shape and the orientation of the tubes are sketched in Fig. 5(c). Note that for the C and BN tubes, the rings are similarly staggered (armchair tubes), whereas the staggering of the pure B tubes follows the Aufbau principle.

Figure 6 shows the DOS from a series of LMTO band structure calculations on nanoropes of C, BN, and B tubes, and their corresponding 3D layered reference structures. It is obvious that for the (n,n) tubes considered here, the overall shape of the DOS does not dramatically change in comparison to the corresponding 2D sheets. This, of course, is not so surprising, as many of the atoms on the tubes experience a local atomic environment which is very similar to that within the corresponding 3D reference structures, especially when one ignores the curvature of the tubular surfaces. This may also be seen from the fact that the 12-ring tubes, with a

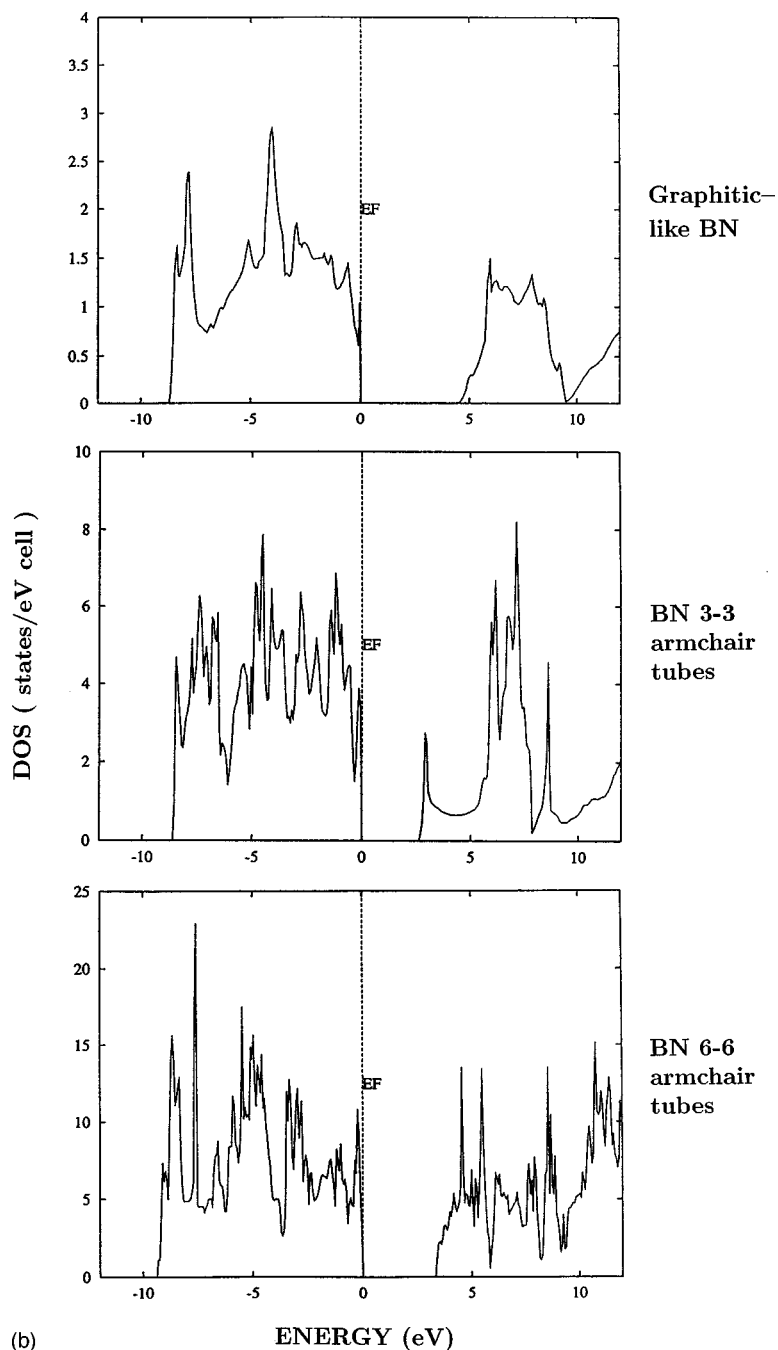


FIG. 6. (Continued.)

somewhat less pronounced curvature, display a DOS closer to the DOS of the reference structures than the highly strained six-ring tubes. As expected from the literature (Ref. 1), the carbon systems are semiconducting or metallic, depending of the chirality, whereas the BN systems are obviously insulating. The boron tubes, however, show a strongly conducting character, just like the boron sheets discussed above.

A final remark concerns the value for the radius of the boron 12-ring tubes: For both six and 12-ring tubes, the structural data was taken from Ref. 9, where the clusters had a somewhat higher symmetry than the one used for the present study [see Fig. 5(c)]. So 3.0 Å is basically an interpolation between two slightly different ring sizes. Of course, there still remain various open questions: So far, we have not

taken into account Peierls distortions, and it is not very likely that these effects might be completely neglected. Also, we did not consider the case of nested tubular boron compounds, which are likely to be formed, as follows from Refs. 8 and 9. Further work along these lines is currently in progress.

IV. CONCLUSIONS

In the preceding sections, we have described several structural models for novel layered and nanotubular boron compounds, and compared their different properties with those of well known C, AlB₂, BN, and more general B_xC_yN_z phases. The experimentally observed accumulation of boron on the tips of graphitic nanotubes, as well as its influence on their growth mechanism, demonstrate the practical impor-

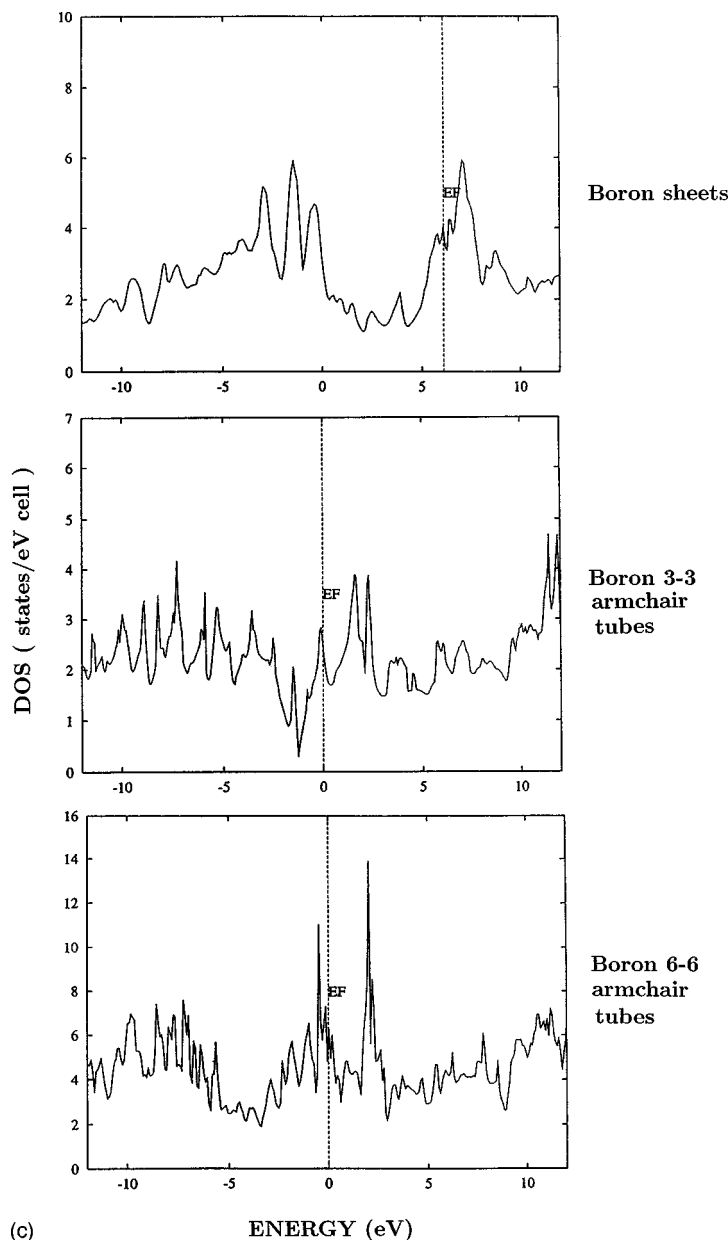


FIG. 6. (Continued.)

tance of boron in nanotube science. In this work we call attention to structural and energetical arguments that indicate that the role of boron is not limited to assisting the formation of C nanotubes; our results show that pure boron nanotubes and other laminar structures may indeed be synthesized in the near future. We have shown that the formation of these novel boron compounds can be derived from (quasi)-hexagonal reference structures, following an Aufbau principle proposed for boron clusters. All the model tubular boron compounds considered in this study showed a metallic-like DOS, and may be expected to be very good conductors, much better than carbon nanotubes with potential applications, e.g., in field emission and high-temperature light materials, and in high-temperature electronic devices.

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¹M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, London, 1996).

²H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* (London) **318**, 162 (1985).

³S. Iijima, *Nature* (London) **354**, 56 (1991).

⁴M. Terrones, W. K. Hsu, S. Ramos, R. Castillo, and H. Terrones, *Fullerene Sci. Technol.* (in press); M. Terrones, A. M. Benito, C. Manteca-Diego, W. K. Hsu, O. I. Osman, J. P. Hare, D. G. Reid, H.

- Terrones, A. K. Cheetham, K. Prassides, H. W. Kroto, and D. R. M. Walton, *Chem. Phys. Lett.* **257**, 576 (1996).
- ⁵I. Boustani, *Int. J. Quantum Chem.* **52**, 1081 (1994).
- ⁶I. Boustani, *Chem. Phys. Lett. *ibid.** **233**, 273 (1995); **240**, 135 (1995).
- ⁷I. Boustani, *J. Solid State Chem.* **133**, 182 (1997).
- ⁸I. Boustani, *Surf. Sci.* **370**, 355 (1997).
- ⁹I. Boustani and A. Quandt, *Europhys. Lett.* **39**, 527 (1997).
- ¹⁰M. Jarrold, Northwestern University (private communication).
- ¹¹A. Ricca and C. W. Bauschlicher, Jr., *Chem. Phys.* **208**, 233 (1996).
- ¹²I. Boustani, *Phys. Rev. B* **55**, 16426 (1997).
- ¹³I. Boustani, A. Quandt, and P. Kramer, *Europhys. Lett.* **36**, 583 (1996).
- ¹⁴I. Boustani and A. Quandt, *Proceedings of the 6th International Conference on Quasicrystals*, Tokyo Japan, Edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998), p. 219.
- ¹⁵A. Rubio, J. L. Corkill, and M. L. Cohen, *Phys. Rev. B* **49**, 5081 (1994).
- ¹⁶X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, *Europhys. Lett.* **28**, 335 (1994); *Phys. Rev. B* **51**, 6868 (1995).
- ¹⁷Ph. Redlich, J. Loeffler, P. M. Ajayan, J. Bill, F. Aldinger, and M. Rühle, *Chem. Phys. Lett.* **260**, 465 (1996).
- ¹⁸N. G. Chopra *et al.*, *Science* **269**, 966 (1996).
- ¹⁹A. Loiseau *et al.*, *Phys. Rev. Lett.* **76**, 4737 (1996).
- ²⁰J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- ²¹M. C. Payne *et al.*, *Rev. Mod. Phys.* **64**, 1045 (1992).
- ²²N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ²³B. Pfrommer, M. Côté, S. G. Louie, and M. L. Cohen, *J. Comput. Phys.* **131**, 233 (1997).
- ²⁴O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
- ²⁵U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ²⁶I. Boustani and A. Quandt, *Comput. Mater. Sci.* **11**, 132 (1998).
- ²⁷D. Porezag *et al.*, *Phys. Rev. B* **51**, 12947 (1995).
- ²⁸J. Widany *et al.*, *Phys. Rev. B* **53**, 4443 (1996).
- ²⁹For a review on tight binding see: C. M. Goringe, D. R. Bowler, and E. Hernández, *Rep. Prog. Phys.* **60**, 1447 (1997).
- ³⁰J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).
- ³¹C. J. Smithells, *Metals Reference Book*, fourth ed. (Butterworths, London, 1967), Vol. 1.
- ³²V. I. Matkovich, *Boron and Refractory Borides* (Springer, Heidelberg, 1997).
- ³³*For comparison, a DOS of model hexagonal lattices composed of s-p-Hybridized elements may be found in: Bonding and Structure of Molecules and Solids*, edited by D. Pettifor (Oxford University Press, Oxford 1995), p. 216.
- ³⁴E. Hernández, C. Goze, P. Bernier, and A. Rubio, *Phys. Rev. Lett.* **80**, 4502 (1998).
- ³⁵A. Rubio, *Condens. Matter News* **6**, 6 (1997).
- ³⁶N. Hamada, S. Sawada, and A. Oshiyama, *Phys. Rev. Lett.* **68**, 1579 (1992).