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Density-functional calculations for prototype metal-boron nanotubes

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Nanotubular materials inspired by crystalline diborides such as AlB_2 are proposed. The atomic structure, in particular the basic chemical question of where to put Al atoms in order to stabilize nanotubular Al-B systems, is investigated using density-functional calculations for prototype systems. The optimized tubular prototypes are found to be competitive in energy with their bulk crystalline counterparts. All of the tubular Al-B systems investigated are calculated to be metallic.

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I. INTRODUCTION

Soon after the discovery of carbon nanotubes,[1] it was recognized that these compounds can have electronic properties ranging from semiconducting to metallic, depending on the details of their atomic structure (see Chap. 19 in Ref. 2). This has led to much speculation about nanotubular systems becoming the materials of choice for future miniaturizations of electronic devices towards the nanodomain.[3] Some major challenges are the control of the growth mechanism in order to obtain carbon nanotubes with specific electronic properties and the development of techniques to wire together semiconducting and metallic nanotubes in a controlled manner. One approach for connecting carbon nanotube devices could be the use of other metallic nanotubes that function as wires on the same length scale.

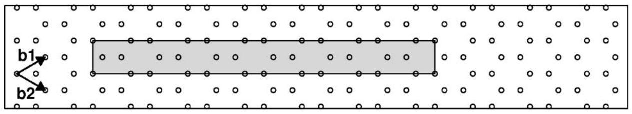
In an earlier publication,[4] we discussed the possible existence of metallic boron nanotubes that could serve such a purpose. Boron nanotubes can be constructed from the so-called *Aufbau principle* for the formation of stable boron compounds formulated in Ref. 5. This Aufbau principle identifies a small set of simple structural features characteristic of the most stable isomers of pure boron clusters and proposes that highly stable boron clusters, surfaces, and networks can be constructed using only these structural elements. Crystalline α-boron has long been the paradigm for boron bonding. It is comprised of B_{12} icosahedra with sixfold inverse-umbrella coordination,[6] a configuration that obeys the Aufbau principle. The coordination in the proposed boron nanotubes is very different—hexagonal pyramidal—but also follows the Aufbau principle. In a recent study of clusters of 96 boron atoms,[7] we showed that the formation of large quasiplanar and tubular systems with sixfold pyramidal bonding is favored over the formation of cluster aggregates typical for crystalline α-boron. We also found that the strain energy of boron nanotubes relative to the corresponding sheets is intermediate between those of the carbon and boron-nitride systems,[4] another favorable condition for the formation of boron nanotubes.

In this paper, the large family of layered metal diborides is used as a starting point for investigating metal-boron nanotubes. Diborides of the AlB_2 lattice type have graphenelike layers of boron atoms, with metal atoms located halfway between the boron layers. These structures are similar to the pure boron surfaces discussed in Ref. 8. In fact, in Ref. 4, the AlB_2 system was used to help elucidate the quasiplanar configurations found for pure boron. Here we extend the analogy to the tubular systems. Density-functional calculations are used to explore the geometry, stability, and electronic structure of some prototype Al-B nanotube materials. The prototype nanotubular systems presented here are found to be energetically competitive with the corresponding bulk counterparts, suggesting that synthesis of such nanotubes might be possible.

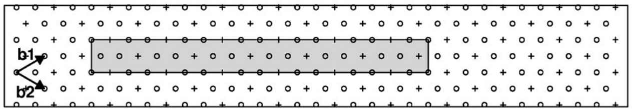
The remainder of this paper is organized as follows. Section II is devoted to the structural properties of the diboride systems. We analyze the AlB_2 lattice type, describe some of the basic physical properties of diborides, and illustrate the geometric construction of metal-boron nanotubes starting from metal-diboride systems. In Sec. III, the technical details of the *ab initio* calculations are given. In Sec. IV, we present some prototypical Al-B nanotubular structures that are calculated to be energetically favorable, and we discuss the bonding and electronic structure of these systems. Conclusions and remarks about future work are given in Sec. V.

II. CONSTRUCTION OF NANOTUBES FROM CRYSTALLINE AlB_2

The typical diboride structure is the AlB_2 lattice, which is composed of two parallel systems of flat layers.[6] One layer contains boron atoms arranged in a honeycomb lattice like a graphene sheet [see Fig. 1(a)]. The Al atoms form a triangular lattice that is located halfway between the graphenelike sheets, positioned so that the Al atoms project down onto the centers of the boron hexagons [see Fig. 1(b)]. The space group is $P6/mmm$, and the primitive cell is hexagonal with one formula unit per cell. Typically, the in-plane lattice constant is around $a = 3.1$ Å.[6] This corresponds to an in-plane B-B distance of about 1.8 Å, which is similar to the B-B bond length in α-boron. The interplanar B-B distance is significantly larger, with typical c/a ratios of about 1.1.[6]



(a) Generating a (6,6) carbon nanotube



(b) Generating a template (6,6) AlB_2 nanotube

FIG. 1. Cut-and-paste construction for (a) (6,6) carbon nanotubes and (b) (6,6) AlB_2 nanotubes. In (a) circles (○) denote C sites; in (b) circles (○) denote B sites and crosses (+) denote the projection of Al sites onto the B plane. In each case, a (6,6) tube is generated by rolling up the shaded strip, the edges of which are defined by the vector $6\mathbf{b}_1+6\mathbf{b}_2$ and the shortest lattice vector perpendicular to this direction.

The family of diborides of the AlB_2 type comprises materials with a wide variety of metal atoms substituting for the Al position. There are at least 22 members of the family,[6] ranging from MnB_2 with an effective metallic diameter of 2.58 Å to GdB_2 with an effective metallic diameter of 3.61 Å. Simple *sp* elements, as well as *d*- and *f*-electron atoms, can be accommodated. The ability of the AlB_2 lattice to incorporate metals that differ so much in size and electronic structure is remarkable, and it raises the possibility of forming alloys between members of this family.

The construction of nanotubular structures from the AlB_2 lattice type is shown in Fig. 1. Ignoring the amplitudes of the Al atoms for the moment [Fig. 1(b)], we see that AlB_2 nanotubes can be generated by the same cut-and-paste procedure used to generate carbon nanotubes from graphene sheets.[2] Nanotubes may be classified by a pair of integers (N,M), which specify a cut along a vector $N\mathbf{b}_1+M\mathbf{b}_2$, where $\mathbf{b}_1$ and $\mathbf{b}_2$ are primitive lattice vectors for the honeycomb lattice. This first cut is followed by a second cut perpendicular to this direction that continues until another atom of the honeycomb lattice is hit. Figure 1 shows the resulting sheet for a (6,6) type of nanotube in both systems. Rolling up a general sheet and pasting it along the perpendicular direction from both ends of the (N,M) cut vector generates the basic unit cell of an (N,M) nanotube. For the purpose of *ab initio* simulations, it is common practice to place these tubes side by side on a hexagonal superlattice,[2,4] thereby approximating the bundles in which these compounds form in nature.

It is interesting to note that if B is substituted for Al in Fig. 1(b), the structure becomes a puckered layer of sixfold-coordinated boron. If the construction described above is applied, we obtain the pure boron nanotubes described in Ref. 4, where we also introduced a different but equivalent construction procedure labeled by a pair of integers that describes cuts along the unit vectors of a triangular lattice. We conjectured that the best way to put boron nanotubes on a hexagonal superlattice would be to arrange them such that pairs of boron atoms meet along the directions of the underlying hexagonal superlattice.[4] Such an arrangement leads to a type of chemical bonding between the tubes that is analogous to what is found for planar forms of pure boron. In the planar systems, pairwise bonds between sevenfold-coordinated boron sticking out of puckered sixfold-coordinated layers of boron were found to be the most favorable arrangement for binding single sheets together to form layered systems.[8]

In earlier studies,[7] we found that tubular boron systems could stand alone; i.e., like carbon nanotubes, they tend to bundle in the form of a hexagonal superlattice, but they do not have to. For the diboride system, the situation may be different. Studies of small boron clusters indicate that neither the honeycomb lattice nor the related carbon-type nanotube structure is stable for boron.[5] In fact, the local atomic structure of the diboride systems suggests that metal atoms are necessary to stabilize honeycomb boron layers and the tubes derived from such layers. The metal atoms themselves have to bind to a sufficient number of boron atoms (12 in the case of the AlB_2 lattice). It is not clear *a priori* whether one could simply bind metal atoms inside or outside of a carbon-type boron tube to stabilize a single tube or whether those tubes are more likely to come in larger bundles of carbon-type boron nanotubes with metal atoms both inside and between the tubes, serving in part to bind the tubes together. For Al-B tubes, our *ab initio* calculations show that the latter arrangement is preferred, as discussed in Sec. IV.

III. TECHNICAL DETAILS

Calculations were carried out using the VASP package,[9,10] a density functional based[11,12] *ab initio* total-energy code using plane-wave basis sets and ultrasoft pseudopotentials.[13,14] The electron-electron interaction was treated within the local density approximation (LDA) with the Ceperley-Alder exchange-correlation functional.[15] When performing structural optimizations, we let *all* degrees of freedom relax, i.e., the complete set of atomic positions as well as the parameters of the unit cell. The optimal configurations as well as the electronic structure for each relaxation step were determined using preconditioned conjugate gradient procedures.[16,17] Starting configurations and relaxed structures are available from the authors.

The kinetic-energy cutoffs used for the plane-wave expansion of electronic wave functions were 358.2 eV for C (which we use as a reference system), 161.5 eV for Al, and 321.4 eV for B and all of the Al-B systems. The Brillouin zone was sampled on grids of $(13\times13\times13)$ $\mathbf{k}$ points in the cases of crystalline AlB_2 and fcc Al, $(8\times8\times8)$ $\mathbf{k}$ points in the case of graphite, $(6\times6\times6)$ $\mathbf{k}$ points in the case of α-boron, and $(5\times5\times5)$ $\mathbf{k}$ points in the case of all tubular systems with the exception of the (6,6) carbon nanotube for which $(4\times4\times4)$ $\mathbf{k}$ points were used. These meshes yield meV accuracy in the binding energies, and their differing sizes reflect differences in unit-cell sizes. Care was taken to include a sufficient number of bands above the Fermi level to avoid numerical problems in the iterative diagonalization scheme.

Although the calculations were well converged with respect to the number of plane waves and $\mathbf{k}$ points, the relative energetics of different phases presented in Sec. IV must be

TABLE I. Number of atoms per unit cell, *n*, and cohesive energies E_{coh} for pure and mixed boron nanotubes and reference structures.

System	*n*	E_{coh} [eV/atom]
(6,6) boron nanotube	36	7.00
Al_3B_{30} nanotube	33	6.88
AlB_2 nanotube	36	6.23
α-boron	12	7.51
fcc Al	1	4.19
AlB_2	3	6.45
Graphite	4	10.16
(6,6) carbon nanotube	24	10.02

interpreted with care. The tendency of the LDA to overbind is problematic in first-row elements like B and C which have very localized atomic orbitals and inhomogeneous charge densities. Since the degree of overbinding varies depending on the nature of the bonding in a solid, LDA estimates for heats of formation can have significant errors. Results for the stability of planar and tubular Al-B compounds with respect to phase separation into covalent inverse-umbrella-bonded α-boron and metallic fcc Al, for example, may not be reliable. Comparisons between phases with similar bonding, like the quasiplanar configuration of boron in the diborides, sheets, and tubes, are more meaningful.

Another potential problem is the fact that the conjugate gradient optimization does not guarantee the detection of a global minimum. Given the reported pathology of the energy hypersurfaces of boron clusters,[5] it is likely that for the large systems discussed below, we relax into local minima rather than global minima. However, as discussed in Ref. 5, it is also likely that the relaxed structures capture the right chemistry, and all we have to worry about is the fact that the total energies of these local minima will be slightly higher than that of the global minimum.

IV. RESULTS AND DISCUSSION

Unlike pure boron and pure carbon nanotubes, the Al-B nanotubes we investigated do not appear to be stable as stand-alone tubes. We were unable to converge structural optimizations of isolated tubes constructed by rolling up puckered sheets of AlB_2. Furthermore, in structural optimizations of Al-B nanotubes on periodic superlattices, the tubes always ended up packed closely together, even if they started out well separated. Hence, for the remainder of this paper, we focus on results for Al-B tubes arranged on a hexagonal superlattice. For comparison, parallel calculations were performed for pure boron and pure carbon nanotubes. In each case, the (6,6) nanotube was used as a prototype.

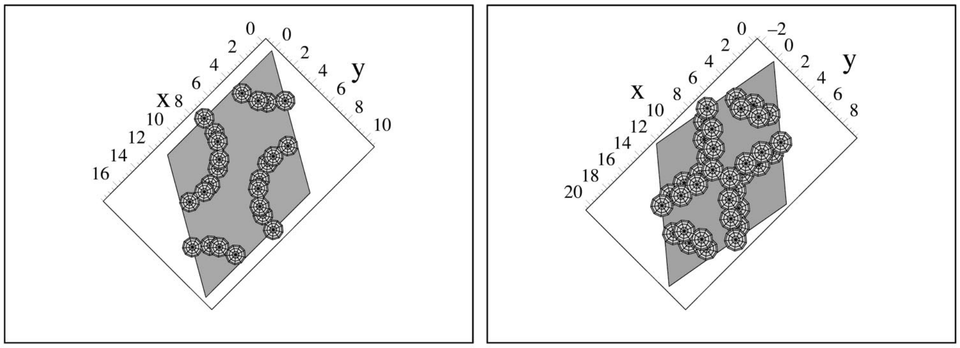
The first step was to generate reference data for atomic structure and cohesive energies. These data are listed in Table I. fcc Al and α-boron serve as basic reference structures for the Al-B systems. The bulk diboride AlB_2 is calculated to be only marginally stable (by about 0.05 eV/atom) against phase separation into fcc Al and α-boron. However, the validity of this result is questionable given the known stability of crystalline AlB_2.[6] While our value for the cohesive energy of α-boron is somewhat higher than previous pseudopotential results,[19,18] the cohesive energies of α-boron, fcc Al, and AlB_2 listed in Table I are all in excellent agreement with recent LDA calculations employing the linearized augmented plane wave method,[20,21] suggesting that the problem lies in the LDA. In particular, the problem of overbinding is likely to be more extreme in covalent α-boron than in the metallic fcc Al and AlB_2 phases, which would lead to an underestimate of the heat of formation of AlB_2. Interestingly, we have found that while the generalized gradient approximation yields smaller cohesive energies for all three solids, it does not significantly stabilize the diboride compared to the elemental systems.

The same considerations apply when we examine the stability of the (6,6) boron nanotube. The results in Table I indicate that the (6,6) boron nanotube is unstable by 0.5 eV/atom compared to crystalline α-boron. On the other hand, our recent all-electron Hartree-Fock study of B_{96} clusters suggests that nanotubular isomers challenge the stability of cluster aggregates found in α-boron.[7] While it is not appropriate to directly compare the cluster results with the present calculations on periodic systems, it is likely the LDA overbinding problems discussed above overestimate the stability of α-boron relative to the nanotube.

The situation looks more promising when we analyze the *chemistry* of the boron nanotubes. The relaxed structure for the (6,6) boron nanotube is shown in Fig. 2(b). Note that the representation of the tubes in Fig. 2 is perhaps unusual in that no tube is shown in its entirety. Instead, this representation is used to emphasize the bonding between nanotubes sitting on the hexagonal superlattice. Prominent boron-to-boron bonding along the direction of the lattice is evident in Fig. 2(b). Further, there is a slight faceting due to undulations from the basic hexagonal lattice of the quasiplanar reference structure. Both of these features are in perfect agreement with the structure and the chemical bonding found in boron sheets.[8] Therefore, it is reasonable to take the relaxed (6,6) boron nanotube as a good starting structure when looking for nanotubes of the Al-B type.

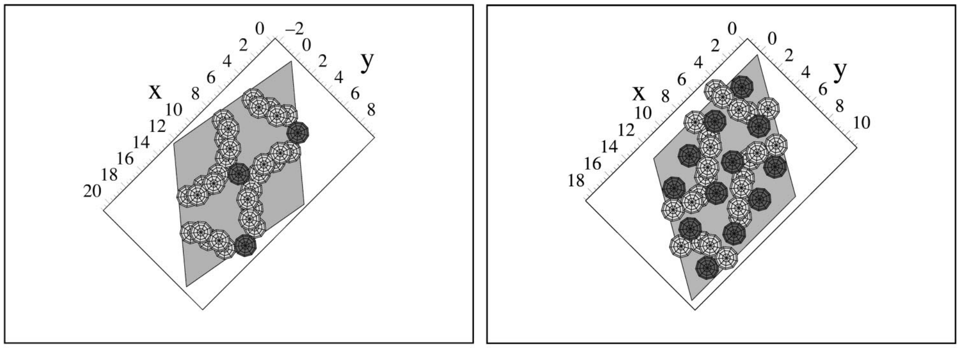
Table I includes an additional set of benchmarks. By comparing graphite and the (6,6) carbon nanotube [Fig. 2(a)], we get a realistic measure for the energetic difference between comparable carbon nanotubes and their layered reference structure. We calculate the (6,6) carbon nanotube to be about 0.14 eV/atom higher in energy than graphite. Tubes with larger radii would have even smaller instabilities.[2]

Among the many variants of Al-B nanotubes that we explored, we focus on the two shown in Figs. 2(c) and 2(d). Our approach was to start with the relaxed B nanotube and substitute Al for B. The structure shown in Fig. 2(c) has composition Al_3B_{30} and was generated from the (6,6) nanotube by removing pairs of boron atoms located along the directions of the hexagonal superlattice and substituting them by single Al atoms. This can happen at three different places within the unit cell. The resulting atomic arrangement near the Al atom is similar to that in AlB_2. Indeed, after full



(a) (6,6) carbon nanotube

(b) (6,6) boron nanotube



(c) Al_3B_{30} nanotube

(d) AlB_2 nanotube

FIG. 2. Comparison of various optimized tubular structures. Each panel shows one unit cell of the hexagonal superlattice on which tubes are arranged. In (c) and (d), the light atoms are B and the dark atoms are Al. Units of the surrounding boxes are given in Å. Note that even after relaxation, the atoms remain stacked in two layers only.

relaxation, the system tends to recreate these local environments, with the tube as a whole becoming less puckered [compare Fig. 2(c) to the puckered B tube in Fig. 2(b) and the unpuckered C tube in Fig. 2(a)]. However, the energetic gain is not substantial: the Al_3B_{30} tubular system is calculated to be about 0.3 eV/atom higher in energy than phase-separated α-boron and fcc Al, so there is only a small improvement in stability as compared to the (6,6) boron tube.

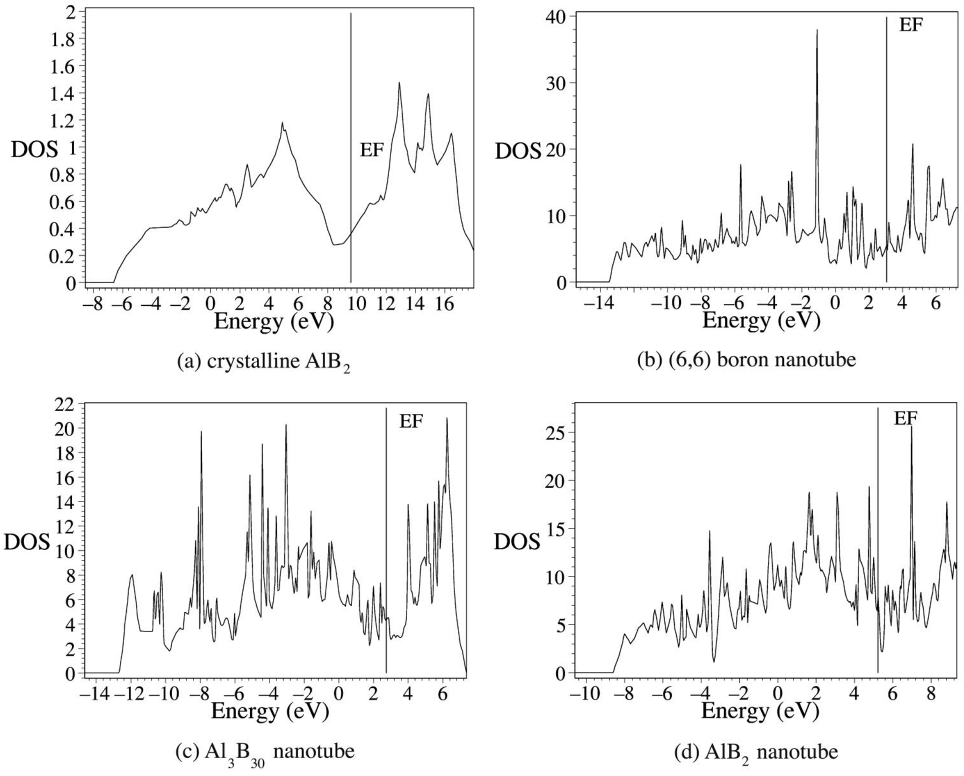
Figure 2(d) shows an Al-B nanotube system with stoichiometry AlB_2. This configuration is calculated to be unstable by only 0.23 eV/atom compared to crystalline AlB_2. While this energy difference is not quite as small as that between the (6,6) carbon tube and graphite, it is close. The structure was generated from the (6,6) boron nanotube by substituting Al for boron at the six positions located along the directions of the hexagonal superlattice, which are on the outside layer of the puckered tube, and at six positions on the inside layer of the tube. In the optimized structure, the tubes are rotated from the orientations they adopt in the superlattice of pure boron nanotubes in such a way that Al atoms sticking out from adjacent tubes do not face each other, but rather sit between boron layers. Such an arrangement locks the tubes together in a gearlike fashion and creates a local environment similar to that in crystalline AlB_2. The inclusion of Al atoms inside the tube is found to be important for stabilizing this structure.

The electronic densities of states (DOS) calculated for crystalline AlB_2 as well as the (6,6) B, Al_3B_{30}, and AlB_2 tubes are plotted in Fig. 3. The DOS curves were obtained with the help of static calculations on relaxed structures using the tetrahedron method for **k**-point sampling. As one can see from Fig. 3, all of the tubes are metallic. This result was predicted in Ref. 4 based on qualitative arguments related to hexagonal tight-binding models,[22] as well as on static *ab initio* calculations. The present results show that these predictions even hold after a complete structural relaxation. The overall shapes of the DOS for crystalline and tubular AlB_2 are similar due to similarities in local atomic environments. The DOS of the AlB_2 nanotube, however, has much more fine structure, which can be understood in terms of a backfolding of the bands of crystalline AlB_2 into the reduced Brillouin zone of the tubular lattice. The DOS of Al_3B_{30} plotted in Fig. 3(c) on the other hand shows some similarity to the DOS of the (6,6) boron nanotube depicted in Fig. 3(b), with some distortion due to the modest content of Al atoms.

V. CONCLUSIONS

We have explored the plausibility of metal-boron nanotubular systems derived from diboride materials. Our data suggest that it may be possible to synthesize such systems. We predict that metal-boron nanotubular materials will likely form in bundles built from rolled up graphenelike sheets of boron, with metal atoms sitting inside and outside the tubes, preserving as much as possible the local atomic environments found in the AlB_2 lattice. *Ab initio* calculations of their basic electronic properties show that such tubular metal-boron systems are metallic.

There are numerous issues of interest for future studies. First, a comparison of the properties expected for nanotubes derived from different diboride compounds—including an assessment of which, if any, form stand-alone tubes—would



(a) crystalline AlB_2 (b) (6,6) boron nanotube

(c) Al_3B_{30} nanotube (d) AlB_2 nanotube

FIG. 3. Densities of state (DOS) in states/eV/cell vs energy in eV for crystalline AlB_2 and various optimized tubular systems. All systems are metallic. Similarities in the DOS arise from similarities in local atomic environments.

be of interest. Continuing along those lines, it may be possible to tune some of the properties of the metal-boron tubes by forming alloys. Alternatively, substitution of boron atoms by carbon is likely to have a serious impact on the electronic structure of the resulting tubular materials, bringing them closer to BN materials.[6] Also, the recent discovery of superconductivity in MgB_2 raises the question of whether some of the diboride-derived tubular materials might superconduct.[23] Finally, and most importantly, we look forward to cooperating with experimental groups that may be able to synthesize tubular metal-boron materials.

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