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, it was recognized that these compounds can have electronic properties ranging from semiconducting to metallic, depending on the details of their atomic structure (see chapter 19 in Ref. 1). This has led to much speculation about nanotubular systems becoming the materials of choice for future miniaturizations of electronic devices towards the nanodomain. 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, 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. 2. 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 six-fold inverse-umbrella coordination – 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, we showed that the formation of large quasi–planar and tubular systems with six-fold 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, 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 graphene-like 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. 3. In fact, in Ref. 4, the AlB$_2$ system was used to help elucidate the quasi-planar 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 prototypical 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. Sec. 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. The present study proposes a new class of nanotubular materials and opens the door to a range of interesting problems for future studies.
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. 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 graphene-like 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. 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.

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 ranging from MnB$_2$ with an effective metallic radius of 1.29 Å to GdB$_2$ with an effective metallic radius of 1.81 Å. Simple sp$_2$ 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. Nanotubes may be classified by a pair of integers ($N$, $M$), that 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, 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 six-fold coordinated boron. If the construction described above is applied, we obtain the pure boron nanotubes described in Ref. 1, 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 lattice. 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 7-fold coordinated boron sticking out of puckered 6-fold coordinated layers of boron were found to be the most favorable arrangement for binding single sheets together to form layered systems.

In earlier studies, we found that tubular boron systems could stand alone, i.e., like carbon nanotubes, they like 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. In fact, the local atomic structure of the diboride systems suggests that metal atoms are necessary to stabilize honeycomb boron layers or 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 13, a density functional 14,15 based ab initio total-energy code using plane-wave basis sets and ultrasoft pseudopotentials. 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.

The kinetic-energy cutoffs used for the plane-wave expansion of electronic wavefunctions 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 (13x13x13) k-points in the case of crystalline AlB$_2$ and fcc Al, (8x8x8) k-points in the case of graphite, and (5x5x5) k-points in the case of all tubular systems with the exception of the (6,6) carbon nanotube for which (4x4x4) 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 re-
spect to the number of plane waves and k-points, the results presented in Sec. IV have to be interpreted with care. In particular, the ultrasoft pseudopotential for boron seems to overbind α-boron by about 0.7 eV/atom as compared to results for the same system obtained with harder norm-conserving pseudopotentials. On the other hand, the cohesive energy we calculate for the diboride system is calculated to be 6.38 eV/atom. As can be seen in Table I, crystalline AlB$_2$ is calculated to be only slightly stable against phase separation. However, the validity of this result is questionable in light of the known stability of crystalline AlB$_2$. As we did a full relaxation on all systems, with high plane-wave cutoffs and many k-points, we attribute the problem to the overbinding of α-boron discussed in Sec. III. As already mentioned, the cohesive energy of AlB$_2$ obtained in a recent all-electron calculation is in excellent agreement with our value listed in Table I.

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. This is in contrast to our recent all-electron ab initio calculations, which found that for B$_{60}$ clusters, the nanotubular isomers challenge or exceed the stability of cluster aggregates found in α-boron. Again, we attribute this discrepancy to the overbinding of α-boron by the ultrasoft pseudopotential used.

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 chemical 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). Furthermore, 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. 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.

Among the many variants of Al-B nanotubes that we explored, we focus on the two shown in Figs. (c) and (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$_3$B$_9$ and was generated from the (6,6) nanotube by removing pairs of boron atoms located along the directions of the hexagonal lattice, and substituting them by single Al atoms. This can happen at three different places within the unit cell, and the Al atom then sees a local atomic environment similar to AlB$_2$. Indeed, after full relaxation, the system tends to recreate these local environments, and the tube as a whole becomes 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 cohesive energy of phase-separated Al$_3$B$_9$ is about 7.2 eV/atom, 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 gear-like 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$_3$B$_{30}$, and AlB$_2$ tubes are plotted in 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, as well as on static ab initio calculations. The present results show that these predictions even hold after a complete structural relaxation. The overall shape 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$_3$B$_{30}$ 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 suggests 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 graphene-like 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 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. Also, the recent discovery of superconductivity in MgB$_2$ raises the question of whether some of the diboride-derived tubular materials might superconduct. 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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TABLE I: Number of atoms per unit cell \( n \), and cohesive energies \( E_{\text{coh}} \), for pure and mixed boron nanotubes and several reference structures.

| System                  | \( n \) | \( E_{\text{coh}} \) [eV/atom] |
|-------------------------|--------|-------------------------------|
| (6,6) boron nanotube    | 36     | 7.001                         |
| Al\(_2\)B\(_3\) nanotube | 33     | 6.884                         |
| AlB\(_2\) nanotube      | 36     | 6.227                         |
| \( \alpha \)-boron       | 12     | 7.399                         |
| fcc Al                  | 1      | 4.119                         |
| AlB\(_2\)               | 3      | 6.451                         |
| graphite                | 4      | 10.156                        |
| (6,6) carbon nanotube   | 24     | 10.019                        |

FIG. 1: Cut-and-paste construction for (a) (6,6) carbon nanotubes and (b) template (6,6) AlB\(_2\) nanotubes. In (a) circles \[\circ\] denote C sites; in (b) circles \[\circ\] 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.
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.
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.