Face-Centered-Cubic B\textsubscript{80} Metal: Density functional theory calculations

Qing-Bo Yan, Qing-Rong Zheng, and Gang Su
College of Physical Sciences, Graduate University of Chinese Academy of Sciences, P.O. Box 4588, Beijing 100049, China

By means of \textit{ab initio} calculations within the density functional theory, we have found that B\textsubscript{80} fullerenes can condense to form stable face-centered-cubic (fcc) solids. It is shown that when forming a crystal, B\textsubscript{80} cages are geometrically distorted, the $I_\text{h}$ symmetry is lowered to $T_\text{d}$, and four boron-boron chemical bonds are formed between every two nearest neighbor B\textsubscript{80} cages. The cohesive energy of B\textsubscript{80} fcc solid is 0.23 eV/atom with respect to the isolated B\textsubscript{80} fullerene. The calculated electronic structure reveals that the fcc B\textsubscript{80} solid is a metal. The predicted solid phase would constitute a new form of pure boron, and might have diverse implications. In addition, a simple electron counting rule is proposed, which could explain the stability of B\textsubscript{80} fullerene and the recently predicted stable boron sheet.

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Boron and carbon, the neighbors in the periodic table, both possess very rich physical and chemical properties. Carbon forms the backbone of life, as there are millions of organic compounds that contain carbon in nature. Besides the graphite and diamond, carbon also possesses new isomorphics, such as carbon nanotube and fullerenes [1, 2], which have been extensively studied, and may be the fundamental materials for molecular electronics. Boron has a variety of complex isomorphic structures, such as $\alpha$-rhombohedral B\textsubscript{12}, $\beta$-rhombohedral B\textsubscript{105}, and tetragonal B\textsubscript{50}, etc (see e.g. [3] for review). The boron solids are usually band insulators or semiconductors under high pressure [4, 5, 6]. In the past decade, boron sheet, cluster and boron nanotube (BNT) also gain wide attention [7, 8, 9, 10, 11, 12], most of which were shown to be metallic, and they are expected to have broad applications in various circumstances.

Recently, a new allotropic form of boron, B\textsubscript{80}, with a round, monoelemental, and hollow structure, has been predicted [15], which is coined as boron fullerene. It consists of 80 boron atoms, and is very similar in shape to C\textsubscript{60} fullerene except that an additional boron atom sits in the center of each hexagon (Fig. 1(a)). B\textsubscript{80} could be one of the most stable boron cages so far [16], which, if confirmed experimentally, should be the second example of a monoelemental buckyball after C\textsubscript{60} in nature. Our further analyses indicate that B\textsubscript{80} fullerene is probably formed by multi-center deficient-electron bonds, and satisfies a simple electron counting rule. This rule could also apply to explain the outstanding stability of the new class of boron sheets and nanotubes composed of triangles and hexagons predicted recently [17, 18]. On the other hand, recall that soon after discovery of C\textsubscript{60}, people found that C\textsubscript{60} clusters can condense to form solid phases such as simple cubic (sc), face-centered-cubic (fcc) [19], and hexagonal-close-packed (hcp) [20] crystals. As B\textsubscript{80} cluster has a geometrical structure similar to C\textsubscript{60}, and boron and carbon share some similarities in chemistry [21], analogously, it would be natural to anticipate that the boron fullerene could also condense to form solid phases. Here we show that, based on the \textit{ab initio} calculations within the density functional theory (DFT) [22], B\textsubscript{80} clusters can indeed condense to form a stable fcc solid that has a metallic electronic structure, in contrast to either the popular solid phases of pure boron that are usually insulating or semiconducting, or the fcc and hcp C\textsubscript{60} that are band insulators [23]. In addition, we find that, unlike the case of C\textsubscript{60} where the cage structure retains intact and is condensed by van der Walls force in solids [19, 24], when B\textsubscript{80} clusters condense to form the solid phase, the geometrical structure of B\textsubscript{80} is strikingly distorted [Fig. 1(d)], which is resulted from the formation of four boron-boron chemical bonds between every two nearest neighbor B\textsubscript{80} clusters. The total energy of B\textsubscript{80} fcc solid is 0.23 eV/atom lower than the isolated B\textsubscript{80} fullerene, and 0.35 eV/atom higher than $\alpha$-rhombohedral B\textsubscript{12} solid. Therefore, if the fcc B\textsubscript{80} metal is eventually confirmed experimentally, it would compose a new form of pure boron in nature.

Our calculations are mainly performed by means of the ABINIT package [25]. This package is coded within the DFT framework based on pseudopotentials and plane waves, which relies on an efficient fast Fourier transform algorithm [26] for the conversion of wave functions between real and reciprocal spaces, on the adaptation to a fixed potential of the band-by-band conjugate gradient method [27], and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [28, 29, 30]. Troullier-Martins norm conserving pseudopotentials [31] generated by fh98PP code [32] are applied to mimic the electron-ion interaction, and the Perdew-Wang 92 [33] exchange-correlation potential within local density approximation (LDA) [34] is used. The kinetic energy cutoff in the plane-wave basis is taken as 25 Hartree, and the tolerance for absolute differences of the total energy is set as 10$^{-6}$ Hartree.

The structure of the isolated B\textsubscript{80} cluster is optimized in a cubic supercell with a lattice parameter 25 Å by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization [35] with a convergence tolerance of 10$^{-5}$ Hartree/Bohr. As shown in Fig. 1(a), B\textsubscript{80} cluster, bearing $I_\text{h}$ symmetry, is similar in shape to C\textsubscript{60}, but there is an additional B atom centering in each hexagon, in agreement with the early calculation [15]. Apparently, a pure two-center two-electron (2c2e) bonding scheme could not give a proper description of B\textsubscript{80} fullerene, as in which each boron atom has five or six nearest neighbors.
but it only possesses three valence electrons. We believe that
the picture of the multi-center deficient-electron bonding[36]
may apply to the present case. One may note that a hexagon
with an additional boron atom sitting in the center can be
viewed as a group of six triangles. A $\text{B}_{80}$ fullerene consists of
20 such hexagons and 12 pentagon holes, or equivalently,
120 triangles and 12 pentagon holes. Suppose that three boron
atoms on the vertices of a triangle share a three-center two-
electron bond. As there are 120 triangles in $\text{B}_{80}$, we assume that
each triangle consumes two electrons, while pentagon (hexagon)
holes consume no electrons, we would find that the number of total electrons demanded for bondings,
that should be equal to the total number of valence electrons
of the system, is nothing but twice the number of triangles.

This electron counting rule also works for the newly predicted
most stable boron sheet and nanotube[17, 18], which are com-
posed by triangles and hexagon holes. In those cases, 8 boron
atoms form a unit cell, which possess 12 triangles, so according
to the above rule, 24 electrons in total are required for bondings, which just corresponds to the 24 valence electrons
of 8 boron atoms, giving rise to a bonding balance. As illus-
trated in Ref. [17], a pure hexagonal boron sheet is prone to
accepting electrons, while a pure triangular boron sheet has a
surplus of electrons, leading to that a mixture of these two
phases with a proper proportion of triangles and hexagons
would make the structure more stable. Our electron counting
rule may be understood in a similar way. In a boron quasi-
planar structure composed by triangles, a hexagon (pentagon)
hole could be produced by removing the central atom from a
group of six (five) triangles that share the central atom. As dis-
cussed above, according to the multi-center deficient-electron
bonding scheme, each triangle consumes two electrons, such a
removal will reduce one boron atom that has three valence
electrons, and therefore twelve (ten) electrons for bondings.

Consequently, the electron counting rule manifests itself that
a proper proportion of hexagon (pentagon) holes and triangles
are cut down simultaneously. In this way, one may change
the number of hexagon (pentagon) holes to realize the adjust-
ment of the balance of the supplied and demanded electrons.

To seek for stable solid phases of $\text{B}_{80}$, we have attempted
sc and fcc crystal structures, and taken two steps to find the
optimized structures. In the first step, with the atomic posi-
tions in $\text{B}_{80}$ clusters fixed, the total energy of $\text{B}_{80}$ solid with
the presumed lattice, was calculated in every 0.1 Å for the lat-
tice constant (where the data with precision of 0.01 Å are ob-
tained by a spline interpolation from the calculated data with
precision of 0.1 Å). Without loss of generality, in the calcula-
tions a properly fixed orientation of $\text{B}_{80}$ molecules is kept,
namely, the $xy$ plane of $\text{B}_{80}$ molecule is arranged to be along
the (100) plane in the sc and fcc structures, which makes the
system bear a relatively high symmetry. In order to examine
the effect of orientational disorder on the calculated results,
we have rotated $\text{B}_{80}$ clusters randomly to reduce the symmet-
rical orientations, and recalculated the optimized lattice pa-
rameters and the corresponding total energy. The results show
that the total energy increase a lot (several eV per $\text{B}_{80}$ cluster),
suggesting that our presumed geometrical configuration is en-
ergetically more favorable. We therefore get the total energy
as a function of lattice parameters for both sc and fcc struc-
tures, where a single minimum in the curve of energy versus
the lattice constant is found, indicating that a stable structure

FIG. 1: (Color online) (a) Schematic structure of an isolated $\text{B}_{80}$
cluster; (b) is the view of green (dark) parts (a pair of neighbor
hexagons) in (a) after a $\pi/6$ rotation around the x axis; (c) the contour
map of valence electron density in the plane of a hexagon in (b); (d)
the distorted structure of $\text{B}_{80}$ in the fcc solid; (e) is the view of green
(dark) parts in (d) after a $\pi/6$ rotation around the x axis, showing
the distortion of a pair of neighbor hexagons in (b); (f) the contour
map of valence electron density in the plane of the rhombus, which
is composed of the atoms marked by number 1-4 in (e). The red and
blue colors in (c) and (f) represent high and low electron densities,
respectively. (See the color bar in Fig. 2.)
may exist. In the second step, on the basis of the structures obtained in the first step, a full relaxation including the atomic positions, cell shape and volume was conducted by means of the BFGS minimization until the forces acting on atoms are less than a tolerance of $10^{-5}$ Hartree/Bohr. As a result, after relaxation, the shape, lattice parameter, and the total energy are all varied, with the cohesive energies 4.9 eV and 18.2 eV per $B_{80}$ unit, i.e., 0.06 and 0.23 eV/atom, for the sc and fcc $B_{80}$ solids, respectively, which are measured with respect to the isolated $B_{80}$ cluster. As the fcc phase appears to be more stable in energy than the sc phase, we will focus on the fcc phase in the following.

As shown in Fig. 1(d), $B_{80}$ cage is dramatically distorted in fcc solid, where the $I_h$ symmetry of an isolated $B_{80}$ is lowered to $T_h$ symmetry for $B_{80}$ in fcc phase. To check it further, we have relaxed a single distorted $B_{80}$ cage in a supercell, and found that it can indeed revert to the isolated $B_{80}$ cluster [Fig. 1(a)] with a spherical shape. Therefore, the distortion of $B_{80}$ cages in a fcc solid may be mainly owing to the formation of boron-boron chemical bonds between nearest neighbor $B_{80}$ cages. Fig. 1(b) and (e) show the configurations of a pair of hexagons along the $z$ axis before and after distortion, respectively. The sharing arris of the two neighboring hexagons is elongated (from 1.678 $\text{Å}$ to 1.940 $\text{Å}$) and broken, while two central atoms in the hexagons move outward, resulting in a planar rhombus structure composed by atoms denoted by the number 1-4 in Fig. 1(e), where the side length is 1.773 $\text{Å}$ and the angle is 57.87°. The rhombus is surrounded by four skew quadrilaterals, two triangles and two pentagons. Due to the symmetry, there are total six such pairs of hexagons along the $x$, $y$ and $z$ axes in one isolated $B_{80}$ cluster, which evolve into a deformed $B_{80}$ unit with six geometrically equivalent rhombuses. The boron atoms sitting in the centers of the rest eight hexagons in a $B_{80}$ unit all shift inward. Fig. 1(f) presents the valence electron density of the rhombus structure. From the profile, we observe that the boron atoms labeled by 3, 1, 4 and 3, 2, 4 form two B-B-B bridge-type 3c2e bonds, which are very similar to the B-H-B bridge-type 3c2e bond in $B_2H_6$. The valence electron density is rather high between every two of the four boron atoms, and an elliptical high-density area presents in the center of the rhombus. It appears that the two B-B-B bridge-type 3c2e bonds are coupled with each other, which eventually become a new complicated four-center bond. It will be illustrated later that the formation of this four-center rhombus is crucial to the bondings between the nearest neighbor $B_{80}$ units.

As can be seen in Figs. 2(a) and (b), there are four boron-boron chemical bonds between every two nearest neighbor $B_{80}$ units. The two green (dark) bonds are formed between two vertical rhombuses, while the two yellow (grey) bonds connect two parallel pentagons. The lengths of the green and yellow bonds are 1.734 $\text{Å}$ and 1.700 $\text{Å}$, respectively, both falling into the typical boron-boron bond length scales in $B_{80}$ fullerene [15] and other boron materials. In a fcc $B_{80}$ solid, every $B_{80}$ unit has 12 nearest neighbor $B_{80}$ units, and every two nearest neighbor $B_{80}$ units are bonded by four boron-boron chemical bonds, 48 bonds are therefore formed between every $B_{80}$ unit and its 12 neighbors. In this sense, the fcc $B_{80}$ solid can be regarded as a three-dimension network of the distorted $B_{80}$ units. Fig. 2(c) presents the valence electron densities of the fcc $B_{80}$ solid in the (001) plane through the center of $B_{80}$ units. The five big circles indicate the inner hollows of the five $B_{80}$ units in Fig. 2(a). It can be observed that there are high electron densities between neighboring cages, indicating stronger interactions between neighboring $B_{80}$ units. In particular, the densities corresponding to the green bonds are rather high, showing a $\sigma$-like bond character. (The yellow bonds do not lay in this plane and are not shown directly in the density map.) Thus, we may conclude that $B_{80}$ clusters in the fcc phase are connected by strong B-B $\sigma$-like chemical bonds.

In Fig. 2(c), it seems that small spherical-like hollow structures are formed in the space between the neighbor $B_{80}$ units. By looking into it further, we find that it is indeed a $B_{24}$ cage-
like structure composed of 6 rhombuses and 8 hexagons [Fig. 3(a) and (b)]. This structure could be considered as a distorted truncated octahedron or cubo-octahedron, and interestingly, it is also a regular part of the crystal structure of metal-dodecaborites MB₁₂ (M is a metal) [37], in which a metal atom is located at the center of each boron cubo-octahedron. We have also relaxed the B₂₄ cage in a supercell, and seen that it is distorted and becomes more spherical, and every rhombus breaks into two triangles [Fig. 3(c)]. The total energy of the relaxed B₂₄ cage is 0.57 eV/atom larger than the isolated B₈₀ cluster. Thus, this B₂₄ cubo-octahedral structure could exist only in a solid, and cannot appear in an isolated form. Similar to the situation of MB₁₂, the interstitial atoms may be inserted into these hollows to form new boron compounds.

As listed in Table I, the total energy of fcc B₈₀ solid is 0.23 eV/atom lower than the isolated B₈₀. 0.35 eV/atom higher than α-rhomhedral B₁₂ solid. Note that the cohesive energy of the fcc C₆₀ solid is about 1.6 eV per C₆₀ [24], i.e., 0.03 eV/atom. Furthermore, fcc C₆₀ solid and other molecular solids [38, 39, 40] are condensed by van der Walls force, in which no chemical bonds are formed among the neighboring clusters. Our calculations on the inter-cluster bonds, valence electron densities, and the cohesive energies indicate that the condensed mechanism of fcc B₈₀ solid is totally different from the above molecular solids.

The energy bands and the density of states (DOS) for the fcc B₈₀ solid are calculated with the optimized lattice constants, as presented in Fig. 4. The energy bands are quite dispersive, and several bands spread across the Fermi level, as manifested in the left panel of Fig. 4, showing that the fcc B₈₀ solid is a metal. As the most of the BNTs are also observed to have the metallic electronic structures, such a metallic property of the fcc B₈₀ solid is conceivable. Unlike the fcc C₆₀ solid that is a band insulator with a direct energy gap of 1.5 eV [24], the present result shows that the energy gap closes when B₈₀ clusters condense to form a fcc solid. This is understandable, because there are strong interactions between the neighboring B₈₀ clusters in a solid phase, which would inevitably enhance the overlap of the charge densities of electrons, thus broadening the energy bands, and eventually leading to the vanishing of the energy gap. However, albeit the fcc B₈₀ solid shows a metallic behavior, the electronic density at the Fermi surface is not so high, as shown in the right panel of Fig. 4, in which the DOS profile is depicted. The DOS has a minimum slightly above the Fermi level, giving rise to a low electronic density of states. Of particular interest is that the DOS profile of the fcc B₈₀ around the Fermi level look very similar to that of MgB₂, in which the DOS of MgB₂ also exhibits a minimum just above the Fermi level [41, 42]. MgB₂ is a well-known two-gap superconductor with transition temperature T_c ∼ 39 K [43], where it has been established that the energy bands at the Fermi level mainly derive from B orbitals, and is a typical metal that is essentially attributed to metallic boron with covalent B-B and ionic B-Mg bonding [44], whose superconductivity is now well understood within the electron-phonon mechanism. This present analogy between the primary characters of electronic structures of fcc B₈₀ and MgB₂ gives a hint that superconductivity might exist in the fcc B₈₀ crystal.

In conclusion, in terms of the first-principles DFT calculations, we have found that B₈₀ fullerenes can condense to form stable sc and fcc solids. It is also uncovered that B₈₀ cages in fcc solid phase are geometrically distorted, where the I₈₀ symmetry is lowered to Tₖ₈, and four boron-boron chemical bonds are formed between every two nearest neighbor B₈₀ cages. The total energy of B₈₀ fcc solid is 0.23 eV/atom lower than the isolated B₈₀ fullerene. A simple electron counting rule is proposed, which could explain the stability of B₈₀ fullerene and the recently predicted most stable boron sheet. In comparison to the ordinary semiconducting boron crystals that can

### TABLE I: Total energies of the boron sheet, isolated B₈₀ cluster, and B₈₀ fcc solid, with respect to α-rhomhedral boron solid, in eV/atom.

|          | boron sheet | isolated B₈₀ | B₈₀ fcc solid |
|----------|-------------|--------------|--------------|
| Ref. [17]| 0.38        | 0.56         | -            |
| This work| 0.46        | 0.58         | 0.35         |

FIG. 3: (Color online) (a) The cage-like B₂₄ structure between the neighbor B₈₀ units; (b) is the rotational view of (a); (c) is the distorted structure after relaxation in a supercell, where the rhombus breaks into two triangles.

FIG. 4: (Color online) Left panel: Energy bands of the fcc B₈₀ crystal. Right panel: Density of states (DOS) of electrons for the fcc B₈₀ crystal around the Fermi level, which is obtained by means of a smearing technique. The Fermi level is set to zero.
become a metal or superconductor under high pressure, our calculated electronic structures, with some primary features quite similar to those of MgB$_2$ superconductor, show that the fcc B$_{80}$ solid is a metal at ambient pressure, and may be a candidate of new superconductor. As a result, in spite of the popular phases of $\alpha$-, $\beta$- rhombohedral and tetragonal borons, the fcc B$_{80}$ metal may be another novel form for pure boron in nature.

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* Author to whom correspondence should be addressed.

Email: gsu@gucas.ac.cn

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