Diamond-like BC$_3$ as a superhard conductor identified by ideal strength calculations

Jun Yang$^1$, Hong Sun$^{1,4}$, Julong He$^2$, Yongjun Tian$^2$ and Changfeng Chen$^{1,4}$

$^1$ Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, People’s Republic of China
$^2$ State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, People’s Republic of China
$^3$ Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, NV 89154, USA

E-mail: hsun@sjtu.edu.cn and chen@physics.unlv.edu

Received 17 May 2007, in final form 5 July 2007
Published 26 July 2007
Online at stacks.iop.org/JPhysCM/19/346223

Abstract

We present first-principles calculations on the ideal strength of a diamond-like (d-) BC$_3$ phase under tensile and shear deformation. The results show that d-BC$_3$ is comparable in strength to cubic BN, the second (only to diamond) hardest material known. Moreover, the calculated electronic density of states reveal that d-BC$_3$ is metallic not only at equilibrium but also under large tensile and shear deformation, making it the hardest conductor studied to date. We identify a metastable graphitic BC$_3$ precursor that has a low energy barrier to transform into d-BC$_3$.

(Some figures in this article are in colour only in the electronic version)
References

[16] See the web site http://www.nersc.gov/projects/paratec/
First-principles studies of structural and electronic properties of hexagonal BC$_5$

Qianku Hu,$^1$ Qinghua Wu,$^1$ Yaming Ma,$^2$ Lijun Zhang,$^2$ Zhongyuan Liu,$^1$ Jumlong He,$^1$ Hong Sun,$^3$ Hui-Tian Wang,$^4$ and Yongjun Tian$^{1,*}$

$^1$State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
$^2$National Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
$^3$Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, China
$^4$National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

(Received 29 December 2005; revised manuscript received 4 April 2006; published 29 June 2006)

Structural and electronic properties for seven possible stacking configurations in hexagonal BC$_5$ based on hexagonal BN and graphite structures have been studied using the ab initio pseudopotential density functional method within the local density approximation. From the total energies, structural parameters, and electron density of states calculated after full structural relaxation, the configuration BC$_5$-I with AA stacking sequence along the c axis based on the hexagonal BN structure has been shown to be the most stable structure among the seven possible stacking configurations, and both the monolayer and bulk phases of BC$_5$ are expected to show metallicity. The structural stability of BC$_5$-I has been confirmed by calculations of the elastic constants and phonon frequencies.

DOI: 10.1103/PhysRevB.73.214116 PACS number(s): 61.50.Ah, 63.20.Dj, 71.20.—b, 81.05.Zx

I. INTRODUCTION

Due to the improvement of oxidative resistance in boron-substituted carbon compounds known as B$_x$C$_{1-x}$ (0 < x < 0.25), they have been investigated extensively both theoretically and experimentally. Via the solid-state diffusion process between B$_2$C and graphite sheets, it has been shown by Lowell$^1$ that the maximum solubility of boron in carbon is 2.35 at. % at 2350 °C with a random distribution of boron in the lattice. By thermal chemical vapor deposition (CVD) from benzene and boron trichloride at 800 °C, Kouvetakis et al.$^2$ obtained one novel compound BC$_3$, in which the boron concentration reaches 25 at. %. Recently, a BC$_3$ monolayer honeycomb structure with hexagonal symmetry has been obtained experimentally,$^3$ verifying the theoretical expectations.$^4$–$^6$ Sun’s calculations$^7$ have shown that the bulk BC$_3$ phase has two stable stacking structures, different from the previous proposed structures.$^8$ After theoretical studies on the structural stability of B$_x$C$_{1-x}$, solid solutions with different boron content x, Magri$^9$ found that some ordered phases have higher cohesive energies than those with the same composition but random distribution of boron atoms. Thus, she speculated that there should be some ordered structures of B$_x$C$_{1-x}$ with x ranging from 0.15 to 0.25. By varying the ratio between benzene and BC$_3$, B$_x$C$_{1-x}$ compounds with 0 < x < 0.17 have been synthesized at 900 °C by Way et al.$^{10}$ Discontinuity has been observed in the variation of interlayer distance at boron content of about 15–17 at. %, suggesting that there exists an ordered BC$_5$ compound with the possible atomic arrangement of a monolayer. Recently, B$_x$C$_{1-x}$ compounds with x in the range from 0.15 to 0.20 have also been obtained experimentally.$^{11}$–$^{13}$ However, so far in the theoretical studies on the stacking sequences of the hexagonal BC$_5$ compound, only two stacking configurations with graphite structure have been considered, and the structural relaxation has been performed via a step-by-step procedure.$^8$ It has been shown that the most stable configuration of hexagonal layered compounds cannot always be found via the step-by-step structural relaxation procedure.$^7$–$^8$ Up to now, it is unclear how the BC$_3$ layers are stacked up along the c axis.

In this paper, in order to find the most stable structure, seven different stacking sequences of the hexagonal BC$_5$ layered compound have been investigated using the first-principles total energy pseudopotential method. The electron density of states has been calculated after full structural relaxation to explore their electronic properties. Calculations of the elastic constants and phonon frequencies have been performed to check the structural stability of the most energetically preferred BC$_5$ configuration.

II. CALCULATIONAL METHODS AND STRUCTURAL MODELS

Our first-principles calculations were performed using the density functional theory within the local density approximation (LDA) as implemented in the CASTEP code.$^{14}$ The form of Ceperley and Alder$^{15}$ as parametrized by Perdew and Zunger$^{16}$ has been used for the exchange-correlation function. The interactions between the core region and valence electrons were described by ultrasoft pseudopotentials.$^{17}$ The numerical integration of the Brillouin zone (BZ) was performed using $7 \times 7 \times 4$ Monkhorst-Pack$^{18}$ (MP) $k$-point sampling, and the plane-wave cutoff energy was 420 eV. Structural parameters were fully relaxed using the BFGS minimization method,$^{19}$ in which free movement of the atoms in any direction is allowed and no symmetry constraint is imposed. When a finite strain is applied to the optimized structure, the elastic constant is determined from the linear relationship (Hooke’s law) between the resultant stress and the applied strain. In the procedure of calculation, for any distorted structure, the internal atomic coordinates were optimized and the lattice parameters were fixed. The lattice dynamics for the energetically preferred BC$_5$ structure in the unit cell was calculated using the linear-response method.$^{20}$–$^{21}$ An $8 \times 8 \times 10$ MP $k$ mesh was found to yield
impurities such as graphite in synthesized BC$_5$ samples. Both the monolayer and bulk phases of BC$_5$ show metallicity. The features demonstrated in the conduction band of the electron density of states for the most stable BC$_5$-I structure agree well with those in the NEXAFS of the BC$_5$ compound.\textsuperscript{10}

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Grants No. 50225207, No. 50372055, and No. 50532020) and by the National Basic Research Program of China (Grant No. 2005CB724400).
Interlayer stacking and nature of the electronic band gap in graphitic BC$_2$N: First-principles pseudopotential calculations

Zicheng Pan,$^1$ Hong Sun,$^{1,2,*,1}$ and Changfeng Chen$^{2,*,‡}$

$^1$Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, China
$^2$Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, Nevada 89154, USA

(Received 26 January 2006; published 9 May 2006)

Using first-principles calculations we establish the equilibrium structure and resolve the dispute on the nature of the electronic band gap of the layer-structured graphitic BC$_2$N. The calculated results clearly indicate the indirect nature of the band gap and provide a quantitative account for the band gap and the dispersion of the conduction band near the valence band top observed in recent experiments. These results demonstrate the crucial role of the interlayer interaction and the stacking in determining the electronic property of graphitic BC$_2$N.

DOI: 10.1103/PhysRevB.73.193304

PACS number(s): 71.20.–b, 63.20.Dj, 81.05.Zx

The ternary BCN materials have attracted considerable interest in recent years,$^{1–6}$ Among them the layer-structured graphitic BC$_2$N (g-BC$_2$N) has received special attention since it is a $p$-type semiconductor with a particularly reliable composition in the chemical vapor deposited thin film fabrication. Fundamental issues regarding its structural and electronic properties have been explored but remain unresolved. An earlier experiment$^4$ concluded that g-BC$_2$N has a direct band gap. However, it is contradicted by a later experiment under identical synthesis conditions$^6$ that indicated that g-BC$_2$N is an indirect band-gap semiconductor. On the theoretical side, the situation is also unclear. An earlier first-principles calculation$^7$ was performed for a single graphitic BC$_2$N sheet (i.e., a monolayer structure). The calculated electronic band structure is somewhat ambiguous on the nature of the band gap since the lowest conduction band edge cannot be clearly identified. Common wisdom seems to suggest that the interlayer interaction is weak and unlikely to have an impact on the qualitative physics in g-BC$_2$N; as a result, the theoretical work on the monolayer$^7$ has been cited to discuss both direct$^4$ and indirect$^6$ band gap scenarios in bulk g-BC$_2$N. However, the interlayer stacking and its role in determining the electronic properties remain unresolved.

In this paper we report on an $ab$ initio study of the structural and electronic properties of the graphitic BC$_2$N. We conducted an extensive examination of possible stacking options and identified, based on first-principles total-energy and dynamic phonon calculations, several stable structures close in energy but with different stacking positions. The stacking variations lead to significant differences in electronic band structures, particularly in the dispersion of the conduction band near the valence band top. Furthermore, we show that, contrary to previous results, the monolayer g-BC$_2$N is clearly a direct band-gap semiconductor and the interlayer interaction introduces substantial modifications in the dispersion that alter the nature of the band gap.

The total-energy calculations have been carried out using the local-density-approximation (LDA) pseudopotential scheme with a plane-wave basis set$^{8–10}$ and a cut-off energy of 80 Ry. The norm-conserving Troullier-Martins pseudopotentials$^{11}$ were used with a cut-off radii of 1.3, 1.3, 1.5 a.u. for N, C, and B, respectively. The total energy of the structures is minimized by relaxing the structural parameters using a quasi-Newton method.$^{12}$ Phonon modes of the crystal structure were calculated with the linear response theory$^{13}$ using the ABINIT code for the equilibrium structures obtained after the structural relaxation. This approach has been applied to systems containing B, C, and N, including layered graphitic structures, with good accuracies on structural parameters and phonon frequencies.$^{14,15}$ Although LDA cannot describe the van der Waals interactions between the layers, the accurate predictions of the graphitic phases of carbon,$^{16,17}$ boron nitride,$^{18}$ and BC$_3,$$^{15}$ particularly the interlayer distance and the phonon frequency corresponding to the parallel relative motion of the layers, indicate that the short-ranged interactions in these structures are described adequately by LDA. We expect this also to be the case for the layered graphitic BC$_2$N structures given their close similarity in structural and bonding characters.

The unit cell on one g-BC$_2$N layer in Fig. 1(a) is the lowest-energy monolayer structure, in agreement with an earlier calculation.$^7$ To examine the interlayer stacking in ABAB… sequences, we have chosen, within the symmetry constraint of the system, a set of twelve initial positions for the center of the unit cell (CUC) of one layer relative to the adjacent layer before the structural relaxation.

![FIG. 1. (a) The unit cell on one layer of g-BC$_2$N. (b) The initial interlayer stacking positions. The numbered squares indicate the locations of the center of the unit cell of one layer relative to the adjacent layer before the structural relaxation.](image-url)
Prediction of a sandwichlike conducting superhard boron carbide: First-principles calculations

Zhongyuan Liu,1 Julong He,1 Jun Yang,2 Xiaoju Guo,1 Hong Sun,2 Hui-Tian Wang,3 Erdong Wu,4 and Yongjun Tian1,*
1State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
2Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, China
3National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
4Shenyang National Laboratory for Materials Science, Chinese Academy of Sciences, Shenyang 110016, China
(Received 31 March 2006; published 4 May 2006)

Our first principles calculations predict a tetragonal BC3 (t-BC3) phase originating from the cubic diamond structure. The t-BC3 structure is formed by alternately stacking sequence of metallic CBC and insulating CCC blocks, exhibiting a sandwichlike metal and/or insulator layered structure with the anisotropic conductivity on the basal planes formed by the metallic CBC blocks. Its stability has been confirmed by our calculations of the total energy, elastic constants, and phonon frequencies. A low critical pressure of ~4 GPa for a synthesis of the t-BC3 from the graphitelike BC3 (g-BC3) is expected.

DOI: 10.1103/PhysRevB.73.172101
PACS number(s): 62.20.Qp, 81.05.Zx, 71.20.Ps

Superhard materials have very important applications in mechanical machining and semiconductor industries. Both synthetic and hypothetical superhard materials belong to covalent and polar-covalent compounds composed of light elements in periods 2 and 3 of the Periodic Table.1 In the past couple of decades, a lot of interests have focused on the theoretical predictions2-5 and experimental syntheses6-8 of C3N4 and cubic BC2N. One important focus has been the search for novel superhard materials with conductivity.9,10

First-principles calculation is one strong and useful tool to predict the crystal structure and its properties related to the electron configuration of a material before its synthesis. Bond density, bondlength and a degree of covalency are three determinant factors for the hardness estimation. These three parameters can be determined by first-principles calculations and used in a microscopic model of hardness to successfully estimate the hardness of a covalent crystal material,11 making the design of a new superhard material before its synthesis possible. Experimentally, a graphitic BC3 material has been synthesized by the chemical reaction of benzene and boron trichloride.12 The calculated electronic structure13 suggested that the B atoms in the graphitic BC3 lead to a small perturbation on the charge density and structure of the carbon ring, resulting in a slight difference between the C-C bond (1.42 Å) and B-C bond (1.55 Å). It is well known that graphite and hexagonal BN can be transformed into a denser cubic structure in high pressure and high-temperature conditions.14 It may be possible that a new high-pressure BC3 phase could be synthesized from the graphitic BC3 phase with high temperature and high pressure, and it may be the one new candidate of superhard materials. The superhard diamond and cubic BN are insulators with energy gaps of 5.45 eV (Ref. 15) and 6.0 eV,16 respectively. Theoretically predicted superhard materials such as C3N4 (Ref. 2) and cubic BC2N (Ref. 5) with isoelectronic structure are insulators or semiconductors. The boron-doped diamond is a very interesting material due to its hopping conductivity and unusual behavior of the Hall coefficient in a wide temperature region.17 Because of the electronic deficiency in a hypothetic tetragonal B2CN crystal, first-principles calculations revealed certain metallicity in it.18 Therefore, a diamondlike BC3 compound with the electronic structure similar to the tetragonal B2CN crystal is likely to be a conductive and superhard material. In this Brief Report, first-principles calculations have been performed to investigate the stability and conductivity of a tetragonal BC3 (t-BC3) phase derived from the diamond structure. We found that this phase, which is metastable at zero pressure, has a metallicity and hardness of over 40 GPa.

Our calculations were performed using the ab initio plane-wave pseudopotential approach within the framework of the density-functional theory implemented in the CASTEP software.19 The ultrasoft pseudopotentials20 were used in the calculations, and the plane-wave cutoff energy was 310 eV. The exchange-correlation terms were considered by the Perdew-Berke-Ernzerhof form of the generalized gradient approximation.21 The k-points samplings were 7 × 7 × 7 and 6 × 6 × 4 in the Brillouin zone for the t-BC3 and the graphitelike BC3 (g-BC3), respectively, according to the Monkhorst-Pack scheme.22 The elastic constants Cij and bulk modulus B were directly calculated by the CASTEP code. The phonon frequencies of the structure were calculated with a linear response theory using the ABINIT code.

For the cubic diamond and the typical intermetallic structures of B2, B11, B33, C11b, D015, D019, D022, D023, L10, L11, L12, L21, D03, the number of atoms in the unit cell or the super unit cell composed of two unit cells (for only the B2 and L10) is 4n with n being an integer. Based on the above structures, we have constructed a series of different hypothetic configurations of BC3 crystals. After the full geometrical optimization, we have found that except for three hypothetic BC3 structures derived from L12, L21, and diamond, all the other configurations are not able to keep their original structures, indicative of their instability. Among these three probable structures, the one derived from diamond is found to have the lowest total energy per atom. For this structure, only two possible configurations have been found, which are constructed by the boron substitution of two carbon atoms either within or between the two fcc sublattices of the eight carbon atoms in the diamond unit cell.
anisotropically conducting property on the basal planes formed by the CBC blocks. The structural stability has been unambiguously confirmed by our calculations of total energy, elastic constants, and phonon frequencies. A critical pressure of $\sim 4$ GPa is predicted for the synthesis of the $t$-BC$_3$ phase from the $g$-BC$_3$ phase in a high-pressure condition if the proper catalyst is found, much lower than those of diamond and hypothetical cubic C$_3$N$_4$. This unique crystallographic feature of $t$-BC$_3$ is expected to have some potential applications in electronic devices such as the metal-insulator junction and metal-insulator “multiple quantum well” devices and photonic devices based on the surface plasmon polaritons.

This work was supported by National Natural Science Foundation of China (Grant Nos. 50225207, 10325417, 50372055, 50472051, and 50532020) and by National Basic Research Program of China (Grant No. 2005CB724400).

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Ab Initio Study of Structural and Electronic Properties of Hexagonal BC$_2$N

LUO Xiao-Guang(罗晓光)$^1$, LIU Zhong-Yuan(柳忠元)$^1$, GUO Xiao-Ju(郭晓菊)$^1$, HE Ju-Long(何巨龙)$^1$, YU Dong-Li(于栋利)$^1$, TIAN Yong-Jun(田永君)$^{3,3,*}$, SUN Jian(孙建)$^2$, WANG Hui-Tian(王慧田)$^2$

$^1$State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004
$^2$National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093

(Received 29 March 2006)

We investigate hexagonal BC$_2$N in graphite unit cells using the first-principles method and calculate the total energies, lattice parameters, and electronic band structures after full relaxation. It is shown that stable hexagonal BC$_2$N should be stacked sequentially with one graphite layer and one h-BN layer. The density of states indicates that this structure should have metallicity.

PACS: 61.50. Ah, 71. 20. – h, 71. 15. Mb, 81. 05. Zx

Recently, much attention has been paid to ternary B–C–N compounds due to their novel physical and chemical properties. For the cubic B–C–N compounds, their mechanical properties are similar to those of diamond and cubic boron nitride (c-BN), and for the hexagonal B–C–N compounds, their conducting and intercalation properties are expected to be intermediate between those of graphite and hexagonal boron nitride (h-BN). Moreover, the conducting properties of the hexagonal B–C–N compounds could be tailored via not only the composition but also the intralayer atomic configuration and the interlayer stacking sequences. Various methods have been used in the synthesis of the graphite-like B–C–N compounds, such as chemical vapor deposition (CVD), solvothermal method, chemical process, mechanical milling methods, etc. However, most of the synthesized B–C–N compounds have the turbostratic or amorphous structures so far. It has been found that the turbostratic B–C–N phase is formed by alternating layers of graphite and h-BN. The hexagonal BC$_2$N crystals have been reported to be synthesized and they can be formed by ABAB... stacking. To date, for the intralayer distribution of boron, carbon, and nitrogen atoms in the synthesized B–C–N compounds, experimental studies are rare.

Several theoretical investigations have been performed on layered BC$_2$N. Three possible BC$_2$N structures were investigated by Liu et al. It has been shown that the total energy of the BC$_2$N structure can be lowered by maximizing the number of C–C and B–N bonds. This result has been confirmed by Nozaki and Itoh in the investigation of sixteen kinds of BC$_2$N structures using the semi-classical methods, demonstrating that the stable structure of BC$_2$N is formed by increasing the number of both C–C and B–N bonds. Most recently, the first principles calculations by Azevedo et al. and Mazzoni et al. revealed that all the sixteen BC$_2$N monolayer structures have positive formation energy. All the above-mentioned theoretical studies are based on the monolayer structure; namely, the monolayer is constructed of B, C and N atoms. The only theoretical investigation on the stacking sequences of hexagonal BC$_2$N structures was performed by Saalfrank et al. The calculations of the total energies and structural properties of the alternating layer and intralayer substituted BC$_2$N structures show that the alternating layer hybrids are more stable than intralayer substituted structures, even though all the structures have positive formation energy. However, his calculations used the fixed lattice parameters, which were taken as the average of the experimental lattice parameters of graphite and h-BN.

In this Letter, we present the results of the ab initio local-density approximation (LDA) calculations on the hexagonal BC$_2$N structures. Based on the four atom graphite structure, six possible hexagonal BC$_2$N structures are constructed. Full geometry optimizations are performed on all the BC$_2$N structures. The total energy, structural parameters, and electronic band structures are calculated and compared with those in graphite, h-BN, and sixteen-atom intralayer substituted BC$_2$N.

First principles calculations are carried out by using the CASTEP code. The norm-conserving pseudopotentials are selected and the exchange-correlation energy is given by the CA-PZ. A plane-wave cutoff energy of 770 eV is used. Special $k$ points generated according to the Monkhorst–Pack scheme are used for integration over the irreducible part of the Brillouin zone. The $k$ points are chosen at the mesh points in the $k$ space with $11 \times 11 \times 4$. The total energies are minimized by relaxing the structural...

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* Supported by the National Natural Science Foundation of China under Grant Nos 50225207, 10325417, 50372055, 50472051 and 50532020, and the National Basic Research Programme of China under Grant No 2005CB724400.

** Email: hcl@ysu.edu.cn

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and negative formation energies, it is reasonable to expect that its lattice constant \( a \) is larger than that in graphite and smaller than that in \( h \)-BN. This is in agreement with the lattice constant \( a \) in the experimental synthesized the ordered BC\textsubscript{2}N crystals.\textsuperscript{10,11}

![Graph showing density of states](image)

**Fig. 4.** The calculated density of states of structure F. The Fermi level is indicated by the dotted line.

Figure 3 shows the calculated band structures of the structure F, which demonstrate that the conduction bands and the valence bands are superposed at the Fermi level in the range between H and K points. Therefore, the most stable hexagonal BC\textsubscript{2}N should be one conductive material. To further investigate the origin of conductive properties in structure F, the total and partial electronic densities of states of structure F have been calculated and shown in Fig. 4. The partial density of states of the four atoms in the unit cell indicates that the two C atoms make contribution to the conductive properties, while the B and N atoms have no contribution to the conductive properties. The unit cell of structure F consists of two layers, i.e., a graphite layer and a B–N layer. The stacking sequence of these two layers is the same as that of graphite. Thus, in the structure F, the conductive properties are originated from the graphite layer.

In conclusion, hexagonal BC\textsubscript{2}N structures in four-atom graphite structure have been studied by using ab initio pseudopotential LDA calculations methods. Their total energies, lattice parameters, and electronic structures after full relaxation have been calculated and compared with those in graphite, \( h \)-BN, and sixteen-atom intralayer substituted BC\textsubscript{2}N. Our calculation results show that in the LDA, the stable hexagonal BC\textsubscript{2}N structures should be stacked with one graphite layer and one \( h \)-BN layer, implying that the stable hexagonal BC\textsubscript{2}N should be the intercalation products of graphite and \( h \)-BN. The density of states indicates that this structure should be conductive.

**References**

Effects of High Pressure on BC$_3$ *

ZHOU Jin-Ling(周金玲), CUI Tian(崔田)*, MA Yan-Ming(马艳明), LIU Zhi-Ming(刘志明),
LIU Bing-Bing(刘冰冰), ZOU Guang-Tian(邹广田)

National Laboratory of Superhard Materials, Jilin University, Changchun 130012

(Received 3 April 2006)

High-pressure phases of BC$_3$ are studied within the local density approximation under the density functional theory framework. When the pressure reaches 20 GPa, the layered BC$_3$ that is a semiconductor at ambient pressure, becomes metallic. As the pressure increases, the material changes into a network structure at about 35 GPa. To understand the mechanism of phase transitions, band structure and density of states are discussed. With the increase of pressure, the width of bands broadens and the dispersion of bands enlarges. Additionally, the density of states of the network bears great resemblance to that of diamond. Formation of the sp$^3$ bonding in the network is the main reason for the structural transformation at 35 GPa.

PACS: 70.20.-b, 91.60.Gf, 68.18.Jk

Layered BC$_3$ was first synthesized by Kouvetakis et al.[1] about two decades ago. It is of particular interest because of its lighter atomic composition, better electronic conductivity, and less oxidation. Compared to graphite, it can find more applications in industry. Experimentally, the material is identified to be graphite-like with an interlayer spacing between 0.3 nm to 0.4 nm and the basal plane conductivity 10% larger at 800$^\circ$C than the pyrolytic graphite at normal temperature.[1] The electron energy-loss spectrum,[2] electrical transport properties,[3] oxidation,[4] and phonon dispersion curves along the $\Gamma$–$M$ direction[5] all have been studied to explore the properties of this newly synthesized material. Theoretically, many researchers have taken great efforts to predicting possible geometry structures of BC$_3$. Up to now, the single-layer configurations are consistent in the majority, while the packing of the layers is still in controversy.[6–11] The electronic properties[6–11] such as band structure, density of states and charge density distributions are widely investigated for single-layer bulk materials and nanoscale structures at ambient pressure. The monolayer is identified to be of semiconductors and the conductivity of the bulk materials is generally believed to be attributed to the interaction of the layers. The superconducting temperature[15] is also predicted to increase as a function of the hole doping level. Although much work has been carried out on the properties of BC$_3$ under ambient conditions, the theoretical study of its high pressure behaviour is still lacking.

Additionally, from the view of practical applications, the transformation of the graphite-like layered materials to other structures will expand the utility of these materials. High pressure and high temperature technology[16,17] have been used to reach these purposes for a long time. Moreover, an impressive experimental work[18] has shown that a superhard mixture of the composition BC$_3$ can be brought out by high pressure and high temperature technique from a single phase of graphite-like BC$_3$. To understand the dynamics of the high pressure transformation, more theoretical studies are needed to see what is tractable experimentally into the underlying physics of the materials.

In this Letter, we perform ab initio local density approximation (LDA) pseudopotential full relaxation studies on a graphite-like BC$_3$ under different pressures and at zero temperature, in searching for the stable structures of the material. Two phase transitions are found. One is a semiconductor-metal transition at about 20 GPa, signalled by the disappearance of band gap and the other is a structural transformation from the layered configuration to an intertwined network, the symmetry of which is changed from CMCM to C/2C at about 35 GPa. The network phase shows great resemblance to diamond and is predicted to be a possible superhard material.

The starting-up BC$_3$ is based on a model proposed by Sun et al.,[11] which is the most stable one theoretically investigated before. We duplicate it by stacking the pre-optimized single layers as described by Sun et al. for the denoted structure E, a semiconductor in the literature,[11] as shown in Fig.1(a). Full relaxation is then performed on this layered structure under 0K and different pressures step by step up to 45 GPa. We employ the norm-conserving pseudopotentials with the LDA of Ceperley and Alder as

* Supported by the National Natural Science Foundation of China under Grant No 10574053, the Ministry of Education of China under Grant Nos 2004 NCET and 2003 EYTP, and the National Key Basic Research Programme of China under Grant No 2005CB724400.

** Email: cuijian@jlu.edu.cn
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exactly the same configuration. These data are comparable to approximately 442 GPa of diamond according to Refs. [22, 23] and hence indicate a probable superhard property. The hardness of this phase needs further investigation.

In summary, we have theoretically identified two new phases of BC$_3$ under high pressures based on a structure proposed by Sun et al., one is a metallic one with the layered crystal structure, and the other has a network structure with a lower symmetry which is probably a superhard phase. The high pressure network has an $sp^3$ bonding and its density of states is similar to that of diamond except for the lower position of the Fermi level. Pressure-induced formation of $sp^3$ bonding leads to the structural changes.

The authors would like to thank Y. Takada for useful discussion.

References

Ab initio pseudopotential studies of cubic BC$_2$N under high pressure

Zicheng Pan$^1$, Hong Sun$^{1,2}$ and Changfeng Chen$^2$

$^1$ Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, People’s Republic of China
$^2$ Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, NV 89154, USA

Received 13 December 2004, in final form 20 April 2005
Published 13 May 2005
Online at stacks.iop.org/JPhysCM/17/3211

Abstract

We present the results of a systematic study of the structural, electronic, and vibrational properties of various cubic BC$_2$N phases under high pressure. Ab initio pseudopotential total-energy and phonon calculations have been carried out to examine the changes in the structural parameters, bonding behaviours, band structures, and dynamic instabilities caused by phonon softening in these phases. We find that an experimentally synthesized high-density phase of cubic BC$_2$N exhibits outstanding stability in the structural and electronic properties up to very high pressures. On the other hand, another experimentally identified phase with lower density and lower symmetry undergoes a dramatic structural transformation with a volume and bond-length collapse and a concomitant semi-metal to semiconductor transition. A third phase is predicted to be favourable over the above-mentioned lower-density phase by the enthalpy calculations. However, the dynamic phonon calculations reveal that it develops imaginary phonon modes and, therefore, is unstable in the experimental pressure range. The calculations indicate that its synthesis may be achieved at reduced pressures. These results provide a comprehensive understanding for the high-pressure behaviour of the cubic BC$_2$N phases and reveal their interesting properties that can be verified by experiments.

1. Introduction

The synthesis and characterization of ternary B–C–N compounds have attracted considerable interest in recent years due to their outstanding performance properties, such as high melting temperatures, large bulk and shear moduli, and high thermal coefficients, which make them a potential new generation of so-called superhard materials with wide applications in science and technology. Among various ternary B–C–N systems, cubic BC$_2$N phases have received special attention since they are most frequently prepared in experiments and display a wide range of diverse results on structural forms and properties [1–3]. In particular, x-ray diffraction data
Potential super-hard phases and the stability of diamond-like boron-carbon structures

J E Lowther

DST-NRF Centre of Excellence in Strong Materials and School of Physics, University of the Witwatersrand, Johannesburg, South Africa

Received 21 October 2004, in final form 28 February 2005
Published 13 May 2005
Online at stacks.iop.org/JPhysCM/17/3221

Abstract
The properties of some potential super-hard diamond-like boron–carbon phases are examined using ab initio computational modelling. Both the bulk and shear modulus show a steady decrease with boron concentration. Two specific phases, namely BC₃ and BC₇, are singled out and their possible graphitic precursor phases considered. Finally, energies of the graphitic phases are related to the super-hard phases with the same stoichiometry.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As a point defect, boron is an important impurity in diamond, making the material exhibit p-type behaviour with very nearly shallow defect characteristics [1, 2]. It readily occupies substitutional sites in the diamond lattice about which there is very little lattice relaxation. It is effective in enhancing the hardness of diamond and recently it has been suggested [3] that boron atoms located at the surface of diamond form compressed planar sp² bonds with carbon atoms and with a bulk and shear moduli around the surface region increasing over those of the bulk material. Boron itself forms a base for a useful refractory material as is well established by the properties of B₄C and related materials [4–7], although in this material the main building structure relates to boron icosahedra [8, 9] rather than any diamond-related structure.

The maximum concentration of B that can be included into diamond has really not been established to date, although under extreme conditions this content could be significant. Point defect calculations of large concentrations of boron in diamond have indicated that near-neighbour pairing of B atoms is probably unlikely (i.e. the complex is metastable) [10] even though the presence of such near-neighbour defects is suggested from the conductivity of heavily doped boron in diamond [11–13], and even the recent discovery of superconductivity [14] following extreme conditions of high pressure treatment. More recent calculations [15] have suggested that near-neighbour B pairs may be formed in diamond and even act as deep traps for hydrogen. The implication is that large concentrations of boron can indeed be included in diamond, albeit in metastable form. Extreme conditions are apparently
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Diverging synthesis routes and distinct properties of cubic $\text{BC}_2\text{N}$ at high pressure

Zicheng Pan, Hong Sun, and Changfeng Chen

1Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, People’s Republic of China
2Department of Physics and High Pressure Science and Engineering Center, University of Nevada, Las Vegas, Nevada 89154, USA

(Received 26 August 2004; published 29 November 2004)

Using first-principles total-energy and dynamic phonon calculations, we study the structural transformation to and stability of cubic $\text{BC}_2\text{N}$ phases under pressure. We show that different starting material forms lead to distinct synthesis routes, yielding end products with drastically different physical properties. While a high-density phase with no B-B or N-N bonding shows remarkable structural stability at high pressure, a lower-density phase containing a broken covalent N-N bond displays dramatic pressure-induced collapse of bond length and a transition from a semimetal to a semiconductor, first with an indirect band gap and then a direct gap. The present work clarifies a puzzling experimental situation in $\text{BC}_2\text{N}$ synthesis and characterization and provides a coherent picture for their interesting properties.

DOI: 10.1103/PhysRevB.70.174115 PACS number: 61.50.Ah, 61.50.Ks, 81.05.Zx, 71.15.Mb

The human quest for materials with superior mechanical strength or hardness has a long history that predates civilization. The crown jewel of this quest is the discovery of diamond “synthesized” in natural high-temperature and high-pressure environment deep in the Earth’s mantle. To obtain materials with properties comparable to or even exceeding those of diamond in a more controlled way, extensive efforts have been made in the last half century to synthesize strongly covalent, light-element compounds in a laboratory setting for both scientific and industrial applications, with some notable successes such as synthetic diamond and cubic boron nitride (c-BN). In recent years, new ternary BN compounds have attracted considerable interest due to their outstanding performance properties, such as high melting temperature, large bulk and shear moduli, and high thermal coefficients. In particular, cubic $\text{BC}_2\text{N}$ phases have received special attention since they are most frequently prepared in experiments and display a wide range of diverse results on structural forms and properties.\(^1\)\(^-\)\(^3\) It has been suggested\(^4\) that this diversity may result from the fact that these compounds belong to different metastable structures of the material. The most intriguing and controversial result is the observation that cubic $\text{BC}_2\text{N}$ compounds prepared using different starting material forms seem to have very different structural characteristics. Knittle \etal.\(^1\) started from either microcrystalline $\text{BCN}$ or a mechanical mixture of graphite and graphitic boron nitride and applied high static pressure of 30 GPa and laser heating. The resultant $\text{BC}_2\text{N}$ has a bulk modulus of 355 GPa and a lattice constant 0.3% larger than that predicted based on an ideal mixing of diamond and c-BN. These results are confirmed by a more recent experiment\(^2\) that employed similar synthesis conditions using ball-milled graphite and hexagonal boron nitride as the starting materials. On the other hand, Solozhenko \etal.\(^3\) reported synthesis of cubic $\text{BC}_2\text{N}$ from a graphitic $\text{BC}_2\text{N}$ (g-$\text{BC}_2\text{N}$) form under high pressure (25 GPa) and laser heating. They obtained a lower-density phase with a lattice constant 1.4% larger than that of ideal mixing and a low bulk modulus (282 GPa). Previous theoretical work\(^4\) examined the equilibrium structures of cubic $\text{BC}_2\text{N}$ phases at zero pressure but did not offer any insight into the pressure driven synthesis routes that can lead to distinct cubic $\text{BC}_2\text{N}$ phases. There is also a general lack of understanding for their structural transformations under high pressure. From fundamental and practical considerations of cubic $\text{BC}_2\text{N}$ as a new generation of superhard materials,\(^2\)\(^3\) a systematic understanding of their high-pressure behavior is of crucial importance.

In this paper, we report a detailed first principles study of structural transformation toward cubic $\text{BC}_2\text{N}$ phases from different starting material forms. We demonstrate that the use of a mixture of graphite and hexagonal boron nitride or a graphitic form of $\text{BC}_2\text{N}$ as starting material indeed leads to distinct synthesis routes, yielding the two different cubic phases observed in the experiments. Furthermore, we present results of first principles calculations of structural and electronic properties up to 400 GPa and show that variations in local bonding characters in these two cubic $\text{BC}_2\text{N}$ phases result in dramatic differences in their physical properties. Our results provide a comprehensive description for synthesis and characterization of cubic $\text{BC}_2\text{N}$ at high pressure and predict remarkable stability of the high-density phase and dramatic pressure induced collapse of bond length and a semimetal to semiconductor transition in the low-density phase.

The total-energy calculations have been carried out using the local-density-approximation (LDA) pseudopotential scheme with a plane-wave basis set\(^5\)\(^-\)\(^7\) and a cutoff energy of 80 Ry. The norm-conserving Troullier-Martins pseudopotentials\(^5\) were used with cutoff radii of 1.3, 1.3, 1.5 a.u. for N, C, and B, respectively. The exchange-correlation functional of Ceperley and Alder\(^6\) as parametrized by Perdew and Zunger\(^7\) was used. The total energy of the structures is calculated with the linear response theory\(^10\) using the ABINIT code for the equilibrium structures obtained after the structural relaxation. This approach has been applied to systems containing B, C, and N, including layered graphitic structures, with good accuracies on structural parameters and phonon frequencies.\(^4\)\(^,\)\(^12\) In the present work, an eight-atom zinc-blende-structured unit cell is used in the calculations. Out of a total of $8!/(2!2!4!)=420$ different con-
FIG. 4. (Color online) The calculated energy vs volume for three cubic BC$_2$N phases and the ternary analog of fcc, bcc and NaCl structures shown in the upper right part of the figure. Since the enthalpies of BC$_2$N-2, 4, and 6 essentially merge with those of BC$_2$N-1, 5, and 3, respectively, at high pressures (see Fig. 1), they are omitted for clarity. Cubic BC$_2$N-7 is also omitted since our phonon calculations indicate it is unstable. We also examined the four structures with Imma symmetry shown but found they are all unstable. These structures are all pressured from their equilibrium volume up to 400 GPa.

above should not be altered by any moderate quantitative correction of the transition pressure.

Finally, we examine the stability of cubic BC$_2$N at very high pressures and explore possible structural transformations in these ternary zinc-blende-structured covalent materials. Common candidates for high-pressure phases in corresponding binary systems include NaCl, CsCl, and binary analog of $\beta$-Sn phases. Here we examine ternary analog of these phases. Figure 4 shows the calculated energy versus volume results for cubic BC$_2$N phases of interest, together with those for ternary analog of face-centered-cubic (fcc), body-centered-cubic (bcc), and NaCl structures of BC$_2$N. It is seen that both BC$_2$N-1 and BC$_2$N-5 are stable up to the highest pressure calculated (400 GPa), with no sign of a phase transition to each other or to other phases. We also have conducted a careful search for stable BC$_2$N phases with Imma symmetry. The structures of four possible Imma phases are shown in Fig. 4. Our calculations did not find any stable BC$_2$N structure with Imma symmetry. This extends to a ternary system the previous conclusions for binary zinc-blende-structured systems where extensive search for Imma phases did not yield any stable structures.

In summary, our first-principles total-energy and dynamic phonon calculations reveal that different starting material forms lead to diverging synthesis routes and distinct physical properties for cubic BC$_2$N. This may be a general phenomenon in the synthesis of covalently bonded materials with complex compositional and structural characters. The present calculations confirm and explain the experimentally observed variation in structural forms of synthesized cubic BC$_2$N. It is predicted that the high-density BC$_2$N phase will exhibit superb stability to very high pressure and the low-density phase will display a dramatic pressure-induced bond-length (volume) collapse around 44–45 GPa and a concomitant transition from a semiconductor to a semiconductor, with an initial indirect band gap turned into a direct band gap coinciding with the bond length/volume collapse. These results establish a comprehensive understanding for the synthesis routes, structural transformation and stability, and interesting physical properties of cubic BC$_2$N at high pressure. The present work shows that first-principles calculations can be used, in close collaboration with experiments, to clarify how various metastable structures with distinct properties might be synthesized. This approach may be pursued effectively in the study of novel materials in the future.

We thank Yusheng Zhao for discussions on experiments. H.S. acknowledges useful discussions on BC$_2$N at ambient conditions with Marvin L. Cohen and Steven G. Louie. This work was supported in part by the DOE under Cooperative Agreement No. DE-FG52-01NV14049 at UNLV. H.S. was also supported by the NNSF of China under Grant No. 10274050 and computing resources at the High Performance Computing Center at Shanghai Jiao Tong University.

14This example shows that dynamic phonon instability could fundamentally alter the synthesis routes and phase diagram. As a result, phonon calculations should be combined with the usual energy/enthalpy criteria in determining the structural stability.
16Using larger unit cells in the calculation will introduce more structural configurations. However, judging from the excellent
Possible superconductivity in hole-doped BC$_3$

Filipe J. Ribeiro and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720, USA
and Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
(Received 28 January 2004; published 23 June 2004)

In this work the superconducting transition temperature of hole-doped BC$_3$ was studied. The total energy, phonon frequencies, and electron-phonon couplings were calculated for different hole doping levels using the ab initio pseudopotential method within the local density approximation. The harmonic and anharmonic phonon frequencies were calculated by using the frozen-phonon approximation. As in MgB$_2$, the electron-phonon coupling between the electronic states in the $\sigma$ bands and phonon modes associated with bond stretching was found to be very strong. The calculation predicts that the superconducting temperature will increase as a function of doping level.

DOI: 10.1103/PhysRevB.69.212507 PACS number: 74.10.+v, 71.15.Mb, 74.25.Kc, 63.20.Ry

In the past few years a great deal of research has been devoted to the study of superconductivity in MgB$_2$. The relatively high superconducting temperature of 39 K for this material is found to be related to the strong electron-phonon (EP) coupling of the $E_{2g}$ B-B bond stretching phonon modes with the in-plane $\sigma$-bonding electronic states.

The purpose of this work is to demonstrate the possibility of superconductivity in BC$_3$ (Refs. 7–10) which is a graphitelike metallic material related to MgB$_2$. The compound BC$_3$ is synthesized using the chemical reaction of boron trichloride and benzene. As is the case for graphite, BC$_3$ is a layered material where each layer has hexagonal symmetry with eight atoms per unit cell (see Fig. 1). Recent first principle calculations have shown that the stacking of the BC$_3$ layers is not as similar to graphite as one may expect. There are at least two stable equilibrium stackings AB and ABC with 16 and 8 atoms per unit cell, respectively. The AB stacking is the energy minimum of all the studied stackings and electronically it is a semiconductor, while the ABC stacking ranks second in energy with an energy difference of 1.4 meV/atom, and it is a metal. Because of this small energy difference and the fact that experimentally BC$_3$ is a metal, it is expected that the structure, as synthesized experimentally, is a combination of both stackings. In this work the metallic ABC stacking configuration with eight atoms per unit cell is used.

The total energy, phonon frequencies, and EP coupling calculations reported here are based on ab initio pseudopotentials within the local density approximation (LDA). The Ceperley-Alder functional for the exchange and correlation energy was used. The wave functions of the valence electrons were expanded in a plane wave basis with an energy cutoff of 70 Ry, and the interaction with the ionic cores was modeled by separable norm conserving Troullier-Martins pseudopotentials. The total energy is calculated by a numerical integration over the Brillouin zone sampled over a $9 \times 9 \times 6$ $k$-point grid, and the forces are given by the Hellmann-Feynman theorem.

The phonon frequencies were calculated using the frozen-phonon approach. The dynamical matrix was calculated and diagonalized to obtain the 21 optical phonon eigenmodes at the $\Gamma$ point. A calculation of the phonon dispersion and EP coupling for the entire Brillouin zone (BZ) is beyond the scope of this work. Since the BZ in BC$_3$ is roughly $2 \times 2$ smaller than in MgB$_2$, we are assuming that the EP coupling at $\Gamma$ is representative of the full BZ. If the EP coupling is peaked at $\Gamma$, then the superconducting transition temperature $T_c$ can be overestimated.

Anharmonic effects, which play a strong role in the superconductivity of MgB$_2$, are taken into account. The variation of the total energy as a function of a frozen-phonon amplitude was fit to a fourth-order polynomial. The harmonic phonon frequency is obtained from the quadratic coefficient of the fit, while the anharmonic frequency is given by the energy difference between the two lowest quantum-mechanical vibrational states.

The hole-doped calculations have been performed by reducing the total number of electrons in the system when the following figure shows the top views of the BC$_3$ structure with ABC stacking. In (a) two superimposed unit cells are viewed directly from above and in (b) a single layer of atoms is shown. The calculated in-plane lattice constant is 5.13 Å and the interlayer distance is 3.13 Å. Each layer is shifted relatively to the one below by 1.86 Å in the $y$ direction. The layer shift breaks the rotational symmetry of the crystal and the relaxed angle between the in-plane lattice vectors is 60.1°.
monic effects in the doped calculation leads to an overestimation of $T_c$. The undoped results are similar to the doped case, although a sharp decrease in $T_c$ at 0.3 holes/cell is observed. This is connected to the decrease in $\lambda$ at the same doping level.

In conclusion, we have shown that for the metallic $ABC$-stacking BC$_3$ structure, superconductivity at a $T_c$ of about 22 K can be achieved with doping levels of 0.2 to 0.3 holes/cell. The high frequency phonon modes that couple strongly to the electrons are in-plane, bond-stretching modes, very similar to the $E_{2g}$ mode in MgB$_2$. In addition, three out-of-plane modes contribute significantly to $T_c$, mainly due to their very low frequency. The effect of anharmonicity has been taken into account. This leads to an attenuation of the EP coupling constant $\lambda$, and consequently, of $T_c$. However, if anharmonicity is not uniform throughout the Brillouin zone, the attenuation of the EP coupling could be weaker, leading to an underestimation of $T_c$. On the other hand, since only zone-center phonons were calculated, if the EP coupling is peaked at $\Gamma$, $T_c$ could be overestimated. The dependence of the phonon spectrum on doping was calculated and it was shown that the corrections to the frequencies are relatively small.

We would also like to point out that the specific stacking of the BC$_3$ layers should not significantly affect superconductivity. The band structures of all the stackings studied previously$^{11}$ show that the top of the $\sigma$ bands are located very close to the Fermi level. Hole doping BC$_3$ in any of the possible stackings lowers the Fermi level below the top of the $\sigma$ bands. This leads to the strong electron-phonon coupling between the $\sigma$-band electrons at the Fermi surface with the in-plane phonon modes, which is the main contribution to $\lambda$ and $T_c$. Therefore, superconductivity is expected in hole doped BC$_3$ regardless of the layer stacking.

We would like to thank Dr. Hyoung Joon Choi for his valuable comments and interesting discussions. This work was supported by the National Science Foundation under Grant No. DMR-0087088, and by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational Resources were provided by NPACI and by NERSC.

Hydrogen absorption in bulk $\text{BC}_3$: A first-principles study

Changjun Zhang and Ali Alavi

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

(Received 13 December 2006; accepted 3 October 2007; published online 6 December 2007)

We have performed first-principles calculations for H absorption, $\text{H}_2$ dissociation, and H diffusion in bulk $\text{BC}_3$, a graphitelike layered structure. We show that in bulk $\text{BC}_3$, $\text{H}_2$ can dissociatively (and exothermically) absorb at low coverages. Several low-energy pathways have been computed for the dissociation process. The dissociation barriers are on the order of 0.2 eV or less. This presents a striking contrast to the situation in pure graphite and also on monolayer $\text{BC}_3(0001)$, where $\text{H}_2$ dissociative absorption is considerably more difficult. Hydrogen absorption at high coverages has also been investigated; we find that the absorption enthalpy becomes moderately more exothermic at higher coverages. The calculated range of H binding energies is close to the desired value for reversible hydrogen storage. © 2007 American Institute of Physics. [DOI: 10.1063/1.2802338]

I. INTRODUCTION

$\text{BC}_3$ is an interesting material because it has a graphitelike structure yet with improved conductivity with respect to graphite. Since it was first synthesized in 1986 through the reaction between $\text{BCl}_3$ and benzene at 800 °C, extensive studies have been carried out to determine its structural and electronic properties. An ordered structure with hexagonal symmetry was proposed and later confirmed for a layer of $\text{BC}_3$, as shown schematically in Fig. 1(a). Two stable layer stacking structures have also been recently suggested on the basis of theoretical work: $\text{ABAB}$ and $\text{ABCABC}$ layered structures, with the former being slightly more stable than the latter. The interest in the present topic, namely, the nature of the interaction between hydrogen- and boron-containing graphite, originates in fusion research where it has been found that doping with B increases H retention in graphite-based materials used as plasma-facing material in fusion devices. Recently, Ferro et al. have performed first-principles calculations on H adsorption on B-containing graphite surfaces and showed that H binding energy increases upon B substitution of graphite surfaces. However, there has so far been no study of H absorption in the bulk B-containing graphite. We note that a single sheet of $\text{BC}_3$ is semiconducting and it becomes metallic when formed in multiple layers. This, along with the apparent geometrical differences between surface and bulk, may influence the H absorption energetics and mechanism. The study of H in bulk B-containing graphite may also be relevant to the hydrogen storage issues. Carbon-based materials, including graphite layers, are considered to be a promising candidate for hydrogen storage, primarily due to its relatively light mass and large interplanar space, which imply that the desired H weight and volume criteria can be met. Recently, it has been shown that upon B substitution in fullerenes, $\text{H}_2$ binding is significantly enhanced so as to suit hydrogen storage.

In this work, we carried out first-principles calculations based on density-functional theory (DFT) to investigate hydrogen in bulk $\text{BC}_3$. We chose the $\text{ABAB}$ layer stacking structure for the $\text{BC}_3$, which is the same stacking sequence as that in the bulk graphite. Atomic H absorption, $\text{H}_2$ dissociation, and H diffusion have been examined. To make comparisons, similar calculations were performed in pure graphite and on a $\text{BC}_3(0001)$ surface. We also aim to acquire knowledge of H binding energies over a broad range of coverages as an essential first step in assessing the potential of the system as a hydrogen storage material. In our calculations we have also estimated the influence of the zero-point energy of relevant vibrational modes on the absorption enthalpy and have also modeled finite temperature and pressure effects to yield free energies at ambient conditions.

II. CALCULATIONS

Calculations were performed using CASTEP, which is a plane-wave pseudopotential DFT package. Exchange and

FIG. 1. (Color online) Schematic structures of (a) $\text{BC}_3$, (b) and (c) single $\text{H}$ absorption in $\text{BC}_3$ (top and side views), (d) graphite, and (e) and (f) single $\text{H}$ absorption in graphite (top and side views). C atoms are in dark, H in white, and B in purple. For clarity, all top views are shown as a monolayer only. Unit cells are depicted by dotted lines.
absorption energies vary only in a small range with changing coverage, which is important to realize a full absorption/desorption cycle. Finally, it is worth mentioning that for a full account of BC$_3$ as a HSM, one also needs to address issues of the introduction of H or H$_2$ molecules into BC$_3$. As the permeation through layers is difficult, a more likely channel for H or H$_2$ to enter into the interlayer region may be through the edges of BC$_3$ layers, where larger spaces are likely to be available. However, answering this question requires investigation of edge systems and is beyond the scope of this paper. Further studies in this regard will be interesting.

### ACKNOWLEDGMENT

The support of the EPSRC via the TCM/CUC$^3$ Portfolio Award is gratefully acknowledged.

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\mu_{H_2}$</th>
<th>$T\Delta S_e$</th>
<th>$T\Delta S_v$</th>
<th>$\Delta_{ZPE}$</th>
<th>$\Delta G$</th>
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</thead>
<tbody>
<tr>
<td>Low coverage</td>
<td>$-0.48$</td>
<td>$0.41$ to $0.19$</td>
<td>$-0.16$ to $-0.41$</td>
<td>$0.03$ to $0.02$</td>
<td>$0.37$</td>
</tr>
<tr>
<td>High coverage</td>
<td>$-0.83$</td>
<td>$0.41$ to $0.19$</td>
<td>$-0.003$ to $-0.002$</td>
<td>$0.005$ to $0.004$</td>
<td>$0.17$ to $-0.04$</td>
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17. We have optimized lattice parameters of BC$_3$ with GGA and found that the obtained parameter c is rather unreasonable, being $0.7 \AA$ larger than the experimental one.
32. We have also calculated ZPEs in the starting configurations and the transition states and found that the inclusion of ZPEs has only a very small effect on the barrier. In the three dissociation paths, the barriers without ZPEs are 0.07, 0.05, and 0.21 eV and those with ZPEs are 0.06, 0.02, and 0.19 eV, respectively.
33. We have also carried out validation tests in a large cell that contains 48 C and 16 B and found very similar results.