TOPICAL REVIEW — High pressure physics

Theoretical design of diamondlike superhard structures at high pressure*

Quan Li(李全)† and Wei-Tao Zheng(郑伟涛)‡

Department of Materials Science, Key Laboratory of Automobile Materials of MOE and State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, *China*

(Received 20 August 2015; revised manuscript received 4 September 2015; published online 30 May 2016)

Diamond, as the hardest known material, has been widely used in industrial applications as abrasives, coatings, and cutting and polishing tools, but it is restricted by several shortcomings, e.g., its low thermal and chemical stability. Considerable efforts have been devoted to designing or synthesizing the diamond-like B–C–N–O compounds, which exhibit excellent mechanical property. In this paper, we review the recent theoretical design of diamond-like superhard structures at high pressure. In particular, the recently designed high symmetric phase of low-energy cubic BC_3 meets the experimental observation, and clarifies the actual existence of cubic symmetric phase for the compounds formed by B–C–N–O system, besides the classical example of cubic boron nitride.

Keywords: crystal structures, high pressure, superhard materials

PACS: 61.50.–f, 62.20.–x, 71.20.–b, 61.50.Ks **DOI:** 10.1088/1674-1056/25/7/076103

1. Introduction

The ages of stone, bronze and iron in a chronological sequence describe the succession of periods based on the use of stone (and wood), bronze and iron respectively, which are named for their respective tool-making technologies. From the view of mechanical researcher, humans have been searching for new harder materials, and new harder materials have always fascinated them. Natural diamond has long been found and used for making tools; however, it is expensive because it is extremely rare. Since the artificial synthesizing of diamond in the 1950s, its industrial application has been widely developed. Then, the diamond age, in which diamond or other superhard materials with hardness above 40 GPa are used as ideal materials for machine tools and cutting tools, has set in.

Experimentally, diamond is still the hardest known substance with the hardness reaching 100–160 GPa, though over the past decades extensive experimental efforts have been devoted to exploring new materials that could be harder than diamond.[1–4] However, diamond is exceptionally weak for ferrous metal's cutting and is burned into carbon dioxide at 800–900 °C in air, which restricts its applications. Another well-known superhard material is cubic boron nitride (c-BN) with cubic symmetry, which is artificially synthesized and has been considered as the second hardest material for a long time. It possesses fascinating properties, such as high thermal stability (approximately 1650 K) and low chemical reactivity. However, the hardness of c-BN is only in a range of 46–66 GPa, much lower than that of diamond.[5,6] Therefore, the search for new superhard materials with the properties comparable or even superior to those of diamond in hardness and higher resistance to oxidation and ferrous metals, is an intriguing and long-standing job.

Superhard materials are mainly formed by light elements (B, C, N, and O) compounds with short and strong three-dimensional covalent bonds.[6–25] Recently, a new family of materials formed by heavy transition metals and light elements is proposed to be potential superhard since heavy transition metals can basically introduce high valence electron density into the compounds to resist both elastic and plastic deformation.[26–48] Experimentally, these compounds formed by heavy transition metals and light elements have been demonstrated to have high bulk modulus, indicating that those compounds possess excellent ultra-incompressibility. However, the hardness obtained from the asymptotic load-independent region of the hardness as a function of load is not so high as excepted. Drawn from theoretical calculations for these heavy transition metals' compounds is a conclusion that the highly directional bonds between light-element atoms with large electron densities are short and strong; however, most bonds formed between transition-metal and light-element atoms with lower electron densities are long and weak. As is well known, the strong anisotropic bonding behavior is a severe problem for the application. Up to now, it still remains a challenge to obtain superhard materials within the compounds formed by heavy transition metals and light elements.

Diamond and c-BN are transparent crystals with tetrahe-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 51202084, 11474125, and 51372095).

†Corresponding author. E-mail: liquan777@jlu.edu.cn

‡Corresponding author. E-mail: wtzheng@jlu.edu.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

drally bonded atoms in a covalent network lattice (sp^3) that crystallizes into the face centered cubic structure (Fig. 1). The search for new superhard materials has been greatly motivated following the successful synthesis of man-made diamonds and c-BN. Considerable efforts have been devoted to synthesizing various B–C–N compounds with covalent network lattice by sintering various starting materials at high pressure and temperature. The experimental challenge to the synthesis of diamondlike superhard materials still exist, since they can be only synthesized in a narrow temperature and pressure region, which blocks the industrial synthesis in batch. Encouragingly, several sp^3 bonded B–C–N–O compounds have recently been synthesized by high temperature and high pressure method in laboratory and identified as "diamond-like" or "cubic (c-)" compounds. These densely packed, three-dimensional and strongly covalent bonded compounds have short bond length, low ionicity, high bulk modulus and high hardness. The material formed by B, C, N, and O system with 4 valence electrons per atom is classified as isoelectronic compound with diamond, which may possess similar chemical bonds and structural properties to those of isoelectronic compounds of c-BN,[5,6] B_2O,[49] and c-BC_xN ($x = 1$–6),[6,8–11] and asymmetrical and non-isoelectronic compounds of BC_3,[21] BC_5,[13] and B_2CN.[12] As is well known, the crystal structures of materials are the basis for understanding relevant properties. In this paper, the theoretical superhard diamond-like structures for these isoelectronic and non-isoelectronic compounds are reviewed.

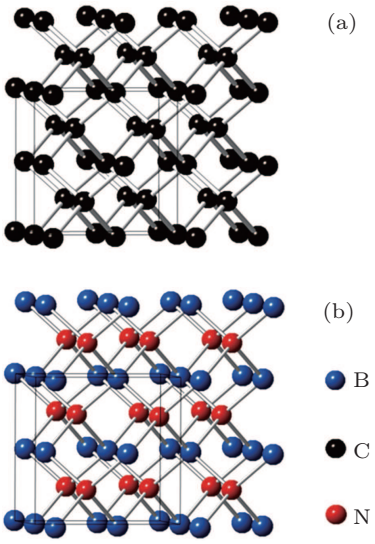


Fig. 1. (color online) Crystal structures of diamond (a) and c-BN (b).

2. Isoelectronic diamondlike compounds

2.1. B_2O

An isoelectronic and asymmetrical compound of diamond, B_2O, was synthesized by Endo *et al.* through the chemical reaction of BP with oxygen[49] under the condition of 2.0–6.0 GPa and 800–1350 °C. The measured Vickers hardness is in a range from 33.5 GPa to 40.5 GPa, which is close to the criterion of superhard materials. From the measured x-ray diffraction data, Endo *et al.* proposed a possible crystal structure consisting of diamond lattice sites with planes of O alternating with two planes of B along the [111] crystallographic direction. Subsequently, Grumbach *et al.*[50] theoretically proposed that the 111 structure be segregated into layers of BO and B and then proposed a 100 structure with stacking the B and O planes in the [100] direction which is energetically more stable than the 111 structure. However, the x-ray diffraction (XRD) peaks of the 111 and 100 structures could not match the experimental data.

Using *ab initio* evolutionary method[51–53] for crystal structure prediction, we have investigated the candidate crystal structures of the synthesized superhard B_2O.[54] We obtained an intriguing monoclinic $C2/m$ structure which is most energetically favorable. The $C2/m$ structure contains four B_2O formula units in one unit cell, in which both B and O atoms occupy the Wyckoff 4*i* ($z1$, 0, $z2$) sites. Interestingly, B atoms possess coordination numbers ranging from 4 to 7. A novel tetragonal $P4_2mc$ contains both sp^3- and sp^2-hybridized boron atoms, in which vertical flat 6-fold rings are linked together by sp^3-hybridized B atoms along *c* axis. The inspection of the crystal structure of hexagonal *P*-62*m* along *c* axis reveals that it can be viewed as distorted graphite with one B atom shifting to the middle of the two flat layers and forming six-coordinated bonds. All O atoms in $C2/m$, $P4_2mc$, and *P*-62*m* structures are three-coordinated (sp^2). The monoclinic *C*2/*m* of B_2O is an excellent potential superhard material with a simulated hardness of 66.7 GPa. However, the XRD of $C2/m$ cannot fit to the experimental XRD data[49] of the synthesized sample.

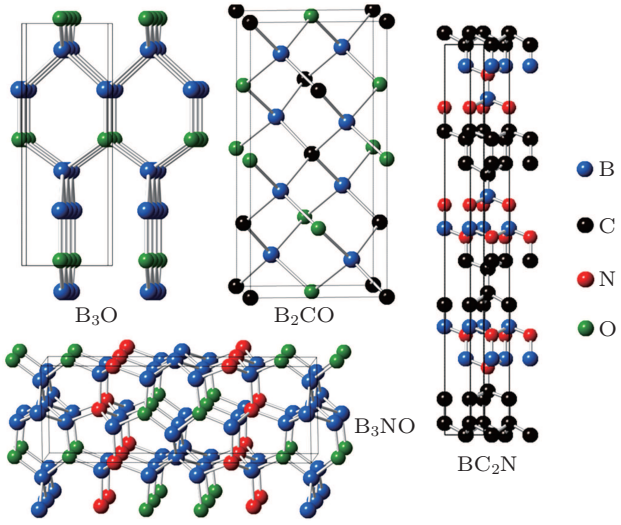


Fig. 2. (color online) Crystal structures of *P*-4*m*2 B_2O,[54] *I*-42*d* B_2CO,[55] *R*3*m*-2*u* BC_2N,[56] and *Imm*2 B_3NO.[57]

From the simulated XRD patterns, the most likely structure for the synthesized superhard B_2O is the *P*-4*m*2 (Fig. 2) or even a mixture of *P*-4*m*2 and $P4_2mc$, which are not diamond-like. The simulated hardness values of $P4_2mc$ and *P*-4*m*2 are 40.5 and 44.8 GPa, respectively, in accordance with the experimental values of 33.5–40.5 GPa.[54]

2.2. B_2CO

Several B–C–O materials have successfully been synthesized at high pressure and high temperature, such as $B_6C_{1.1}O_{0.33}$ to $B_6C_{1.28}O_{0.31}$[58] and $B(C, O)_{0.1555}$,[59] which demonstrate that superhard B–C–O compounds can form typical sp^3 covalent hybridization, which contain B–C, B–O, C–O, and C–C bonds. Therefore, B–C–O materials can be expected to be good candidates for designing new superhard materials. B2CO has 16 valence electrons per formula unit (4 valence electrons per atom) and is thus isoelectronic with diamond.

Using the CALYPSO method[60–62] for predicting the crystal structure, we design a potential superhard ternary material, B_2CO, which is an isoelectronic example in the B–C–O system.[55] We predict two energetically competitive diamondlike structures with space groups of *P*-4*m*2 (*tP*4) and *I*-42*d* (*tI*16), see Fig. 2. The *P*-4*m*2-1*u* structure is isostructural to *t*-B_2CN.[12,63,64] It is found that B atoms in both structures occupy four diagonal positions; while O atoms sit in the vertexes and two opposite surface positions in the *tP*4 structure, and sit on half of the vertexes and surface positions in the *tI*16 structure. Both structures adopt the same sp^3 bonding environment: each B is tetragonally bonded with two C and two O atoms, and C and O atoms are tetragonally bonded with four B atoms, forming B–C and B–O covalent bonds in the diamondlike lattices. The results of total energy calculations at ambient pressure show that *tI*16 structure is 43 meV/f.u. lower than that of *tP*4. The dynamical and mechanical stabilities of *tI*16 and *tP*4 are examined by the calculations of phonon dispersions and elastic constants, respectively. The two structures exhibit similar mechanical properties, such as high bulk modulus (approximately 31 GPa), high shear modulus (approximately 260 GPa), high hardness (approximately 50 GPa), and low Poisson's ratio (approximately 0.17).

2.3. c-BC_2N

In 1994, Nakano *et al.*[11] experimentally observed the formation of c-BC_2N from graphite BC_2N at 7.7 GPa and approximately 2000–2400 K. Later, Knittle *et al.*[8] prepared a c-BC_xN ($x = 0.9$–3.0) solid solution by using even higher static pressure of 30 GPa and laser heating, starting from either the microstalline BCN, or the mechanical mixture of graphitic carbon and boron nitride. The resulting BC_2N has a bulk modulus of 355 GPa. Zhao *et al.*[6] have successfully synthesized millimeter-sized bulk samples of c-BC_2N with the H_v about 62 GPa. Using shock-wave compression, Komatsu *et al.*[10] obtained c-BC_2N with a bulk modulus of 401 GPa, which is larger than that of c-BN. Under high pressure above 18 GPa and high temperature over 2200 K, Solozhenko *et al.*[9] experimentally reported that the bulk modulus 282 GPa of synthesized c-BC_2N is lower than that of c-BN but the measured hardness of 76 GPa is much higher than that of c-BN single crystal and slightly lower than that of diamond. By all the evidence, it is clear that c-BC_2N is a superhard material. Diamond-like BC_2N (c-BC_2N) has gained extensive attention since it has been expected to be thermally and chemically more stable than diamond, and harder than c-BN.

On the theoretical side, much effort has also been made to uncover the crystal structure of the superhard BC_2N.[65–77] As is well known, the stable crystal structure has the lowest Gibbs free energy under the given conditions. Based on this principle, Sun *et al.*[70] proposed seven possible structures (struc-*m*, *m* = 1–7) with different atomic configurations in the eight-atom zinc-blende (ZB) cubic unit cell. They proposed that the struc-1 with *Pmm*2 space group having the lowest energy is the best candidate. While this structure has different appellations in the literature such as BC_2N-1,[66] β-BC_2N,[67] II-BC_2N,[68] and HD1,[68] in fact, they are identical. Sun *et al.*[70] further predicted a chalcopyrite structure (cp-BC_2N) with the tetragonal symmetry (space group, *I*-42*d*). The calculated hardness of cp-BC_2N is 72.2 GPa very close to the experimental value. More recently, Luo *et al.*[78] suggested that the body-centered BC_2N phase (*bc*6-BC_2N) has lower density than ZB BC_2N, wurtzite BC_2N and cp-BC_2N, and they have estimated that the hardness of *bc*6-BC_2N is over 60 GPa. Among the above structures, struc-1 possesses the lowest free energy. Very recently, Zhou *et al.*[72] predicted a *z*-BC_2N structure, which is is comprised of the sixteen-atom supercell of diamond. The simulated XRD spectrum agrees well with the experimental data, and importantly the total energy of *z*-BC_2N is lower than that in struc-1. Luo *et al.*[79] further predicted three structures of wurzite-type BC_2N, among which BC_2N-*w*3 also has lower total energy than struc-1. Very recently, Chen *et al.*[74] proposed a series of short period $(C_2)_n(BN)_n$ (111) superlattices (denoted as $BC_2N_{n\times n}$, with $n = 1, 2, 3, \ldots$). The authors suggested that these superlattices have the lowest energies in those of the previously proposed structures. However, the intense debate is still going on.[76,77] Also, it is worth noting that the crystal structure of superhard c-BC_2N should be unique instead of a structural series.

To clarify the intensive debate on the superhard phase of c-BC_2N, we have extensively explored the crystal structure of BC_2N by using *ab initio* evolutionary method.[56] We have predicted three polytypic structural families: orthorhombic *Pmm*2-*nu*, hexagonal *P*3*m*1-*nu*, and rhombohedral *R*3*m*-*nu*, where *n* refers to that the structure contains *n* BC_2N units

per primitive cell ($n = 1, 2, 4$). Through total energy calculations, it is found that $R3m$ structural series possesses the lowest enthalpy. The structural stability of $R3m$ structural series has been confirmed by the phonon calculations. Analyses of the simulated x-ray diffraction pattern and energy-loss near-edge spectroscopy suggest that our predicted $R3m$-$2u$ [Fig. 2] is the best candidate phase for the observed superhard BC_2N. We have also demonstrated that the previously proposed high density and low density forms might be identical and their x-ray diffraction patterns could be reasonably understood by the single phase of $R3m$-$2u$. The calculated electronic structures show that $R3m$-$2u$ BC_2N is a wide gap semi-conductor with an indirect DFT band gap of 3.8 eV. The calculated bulk modulus of $R3m$-$2u$ BC_2N is 396 GPa, which is in good accordance with the experimental value of 401 GPa by Komatsu *et al.*,[10] but much higher than the measured value of 282 GPa by Solozhenko *et al.*[9] The estimated theoretical Vichers hardness of $R3m$-$2u$ BC_2N is 62 GPa, in agreement with the experimental value of 62–76 GPa.[6,9]

2.4. B_3NO

Previous studies demonstrated that diamond-like superhard c-BN and B_2O compounds can form typical sp^3 covalent network bonds.[54] It is reasonable to explore whether those materials with mixed B–N and B–O bonds may possess high hardness values. We have performed superhard-driven search by using an unbiased structure search method based on CALYPSO method[57] in a ternary B–N–O system, B_3NO, which is also an isoelectronic compound with diamond.[80] Crystal structure is critical to understand the hardness and relevant physical properties of B_3NO. We have predicted various structures for B_3NO under 0–100 GPa.[57] It is in contrast to the traditional ground-state prediction method where the total energy is solely used as the fittness function. We choose hardness as the fittness function in combination with the first-principles method to obtain the hardness versus energy map by seeking a balance between hardness and energy for a better mechanical description of given chemical systems. We predicted a variety of structures with high hardness values and relatively low energies.[80]

A variety of newly structures of B_3NO compound contain short, strong, and three-dimensional covalent bonds, which are responsible for the predicted superior mechanical properties.[57] Two energetically stable B_3NO structures with space groups of $Imm2$ ($oI20$) and $Pmn2_1$($oP20$) are uncovered. The $oI20$ structure (Fig. 2) is the most stable structure which possesses irregular 6-member rings, while $oP20$ is formed by 4-numbered, 6-numbered, and 8-numbered rings. To understand the electronic properties, we perform calculations on the electronic band structures and partial densities of states of $oI20$ and $oP20$. The calculated results reveal the semiconductor features of $oI20$ and $oP20$ structures with indirect band gaps of 0.87 eV and 0.12 eV, respectively. The electronic states near the Fermi level are mainly contributed by B-2p and a few N-2p, and O-2p states. The partial densities of states for B-2p, N-2p, and O-2p are very similar in an energy range from -12 eV to -4 eV, indicating the significant hybridizations between these orbitals and strong covalent interactions in both the B–N and B–O bonds. The calculated electron localization function (ELF) shows that the O atoms in $oI20$ and $oP20$ structures are threefold coordinated with three near-neighbor B atoms and a lone pair of electrons. The results show that $oI20$ and $oP20$ structure may have a broad prospect in industrial applications, such as solar battery, and luminous materials. The two structures exhibit high bulk moduli of 326–332 GPa, significantly higher than that of B_2O (240 GPa),[54] indicating the structures are difficult to compress near their respective equilibrium volumes. The further hardness calculations show the two structures are likely to become superhard materials with Vickers hardness of 45.9 GPa ($oI20$) and 47.4 GPa ($oP20$), respectively, exceeding the criterion of superhard materials (40 GPa).

3. Non-isoelectronic diamond-like compounds

3.1. B_2CN

Eproperties are of considerable demand for the creation of multifunctional device.[81] Since the discovery of superconductivity in boron-doped diamond (4 K),[82] the superconducting behaviors in "covalent metals" (dominated by strong covalent bonds, rather than the metallic bonding) have also been an exotic subject.[83] It is suggested that the strongly directional covalent characteristics in metallic compounds lead to large phonon frequencies and electron–phonon coupling potential, which contribute to the increase of T_c.[84] Thus, metallic B–C–N compound with exclusively covalent bond can thus be expected to simultaneously possess superhard and superconducting properties. Metallicity of ternary B–C–N compounds can be evaluated by the following simple rule: $pZ_V(\mathrm{B}) + mZ_V(\mathrm{C}) + lZ_V(\mathrm{N}) \neq 4n$.[85] The values p, m, l, and n are integers, and $Z_V(\mathrm{B})$, $Z_V(\mathrm{C})$, and $Z_V(\mathrm{N})$ are the atomic valence states (2s and 2p) for B, C, and N, respectively. Recently, diamond-like B_2CN[12,63] and BC_x,[13,21] crystals have been synthesized under the condition of high-pressure and high-temperature (1500–2500 K), which are suggested to be conductors.

We have extensively investigated the crystal structures of B_2CN by using *ab initio* CALYPSO algorithm in a large pressure range of 0–100 GPa.[64] Five competitive structures with clear tetrahedrally sp^3 hybridization are predicted: tetragonal P-$4m2$ (1 f.u. /cell), hexagonal $P3m1$ (1 f.u./cell), rhombohedral $R3m$ (1 f.u./cell), and orthorhombic $Pmm2$ (2 f.u./cell),

and *Pmma* (2 f.u./cell). *P*-4*m*2, *Pmm*2, and *Pmma* can be viewed as a periodic sandwich-like structure formed by stacking CBNB, BNBBCCBN, and CCBNBBNB along the ⟨100⟩ direction of diamond structure, respectively. Instead, the stacking sequences of *P*3*m*1 and *R*3*m* follows the ⟨111⟩ direction. With fixing the numbers of 1 and 2 formula units in the primitive cell, it is found that the energetically best structures are the diamond-[100] structures: *t*-B_2CN and *Pmma*. The C–C and B–N chemical bonds are more favorable than B–B, B–C, and C–N for forming the diamond-like structure with sp^3-hybridized, thus we define C–C and B–N bonds as stable bonds and the other relatively weaker bonds as less stable bonds. In the two most stable structures (*Pmma* [Fig. 3] and *Pmm*2), it is interesting to note that the ratio of the stable chemical bonds to less stable bonds reaches 5:3, which is the largest in the five structures. Further increasing the formula units (3 or 4 f.u./cell) in the simulation cell, we find that the produced structures tend to separate into bulk diamond +c-BN + boron layers. We find that all the B2CN structures have positive formation energies, indicating that these structures tend to phase decomposition. The calculated large bulk modulus (318–333 GPa) and high hardness (56–58 GPa) reveal that they are ultra-incompressible and superhard materials. Therefore, the synthesized B_2CN can be expected to be applied to the high-pressure devices for investigating the electric properties of various materials under extreme conditions.

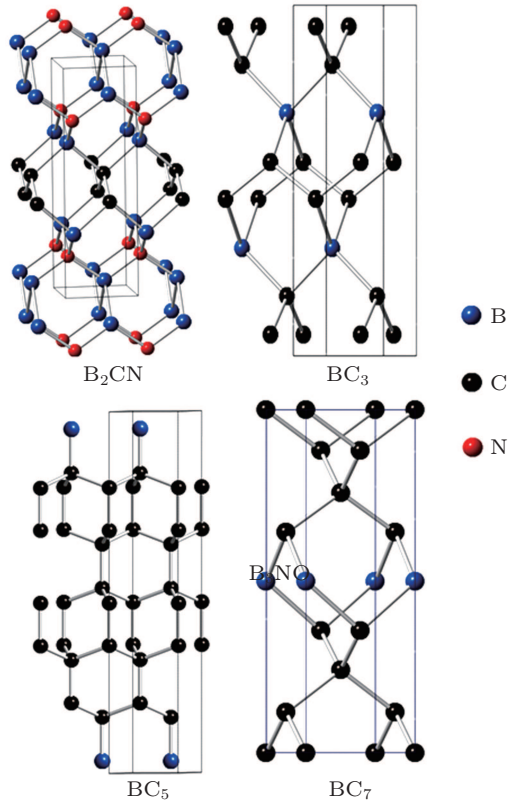


Fig. 3. (color online) Crystal structures of *Pmma* B_2CN,[64] *Pmma-a* BC_3,[86] *P*3*m*1 BC_5,[87] and *P*-4*m*2 BC_7.[88]

Due to the electron deficiency of sp^3 hybridized B_2CN in comparison with that of diamond, the five diamond-like B_2CN structures show metallic with hole nature. Further electron-phonon coupling calculations predict that all the five phases are superconductors. The estimated T_c for diamond-[111] structures (*R*3*m* and *P*-3*m*1) reaches a very high value, 44–53 K, in contrast to the smaller value (2–9 K) in diamond-[100] structures. The large difference in superconductivity of B_2CN is mainly related to the relatively low frequency (< 20 THz). In view of the excellent properties of diamond-like B_2CN, it is necessary to pay much attention to the experimental synthesis and conductivity measurements.

3.2. c-BC_x

Boron-doped diamond has been widely explored as better oxidation and ferrous resistant materials to cover the shortage of diamond and expand the applications to electric devices.[89,90] Electrical measurements demonstrate that Boron-doped diamond becomes metallic and even turns into a superconductor with a transition temperature T_c of 4 K at a higher doping level (2%–3%).[82] Further experimental and theoretical studies indicate a T_c increases with increasing dopant concentrations.[91–93] However, it remains a major challenge to introduce such a large amount of B into diamond in experiments, and the maximum B concentration has been limited up to approximately 5%.[93] An alternative route to achieving high B content is to directly synthesize the B–C compounds. Recently, Solozhenko *et al.*[13] successfully synthesized a diamond-like B–C phase (c-BC_5) with a high B content ever achieved ($\sim$ 16.7%). A subsequent hexagonal structure constructed from a six-atom supercell of diamond for c-BC_5 was proposed[94–96] and a large T_c (45 K) was predicted.[97] The obtained c-BC_5 sample has been measured to possess a large bulk modulus (335 GPa), unusually high fracture toughness (9.5 MPa·$m^{1/2}$), and high thermal stability (up to 1900 K). Remarkably, the indentation experiment has demonstrated an extremely high hardness (71 GPa), harder than cubic BN.[13]

We have uncovered four other low-energy structures: tetragonal *I*-4*m*2 (1 f.u./cell), orthorhombic *Imm*2 (1 f.u./cell), hexagonal *P*-3*m*1 (2 f.u./cell), and orthorhombic Pmma (2 f.u./cell).[98] It is found that except for *Imm*2, other structures are built up by the sandwich-like layers with different stacking sequences. Specifically, *I*-4*m*2 and *Pmma* structures having the atomic packing of ABCABC$\cdots$ along the [100] crystallographic direction of diamond can be viewed as diamond-[100] structure. Instead, *P*3*m*1 and *P*-3*m*1 structures are diamond-[111] structures as the atomic packing follows the [111] direction. Subsequently, a new *P*3*m*1_2*u* [Fig. 3] with slightly lower formation energy was theoretically proposed for the candidate structures for the synthesized BC_5.[87]

All the predicted structures are tetrahedrally bonded with clear sp^3 hybridization. Further increasing the formula units (3 or 4 f.u./cell) in the simulation cell, the produced structures tend to decompose into bulk diamond + boron-carbon layers. This fact is understandable in view of the metastable nature of the synthesized BC_5 compound supported also by the calculated formation energy.

These diamond-like BC_5 possess similar structural and mechanical properties. The calculated bulk modulus is in a range from 373 GPa to 398 GPa, in good accordance with the experimental value of 335 GPa.[98] On the basis of the microscopic hardness model,[99,100] the Vickers hardness of *Pmma* structure is estimated to be 61–74 GPa, in satisfactory agreement with the experimental data (71 GPa). It was previously found that a small metallic component has a strong negative effect on hardness and thus the correction of metallic bonding is necessary to account for the experimental hardness for electron conductors. The underlying mechanism is that those electrons delocalized to contribute to the conduction should be excluded from the hardness calculation. However, for the hole conductors, the major carriers are holes and the valence electrons are mainly localized to form covalent bonds. It is thus unnecessary to include the metallic correction in the hardness calculation. Indeed, if we force to include the correction of metallic bonding, the simulated hardness decreases by about 15 GPa, which is largely deviated from the experimental data.

Using CALYPSO methodology for crystal structure prediction of the potential superhard materials of BC_7, we find four potential superhard structures of tetragonal *P*-4*m*2, hexagonal P3m1, orthorhombic *Pmm*2, and hexagonal *R*3*m*, which are energetically much superior to the previously proposed *P*-43*m* structure.[88] All the predicted structures are tetrahedrally bonded with sp^3 hybridization. The energetically best structure is the tetragonal *P*-4*m*2 (Fig. 3). The calculated Vickers hardness and B_0 of the lowest energy *P*-4*m*2 polymorph reaching very high values (75.2 GPa and 377 GPa) indicate that diamond-like BC_7 is a superhard and ultra-incompressible material. Further phonon and elastic constant calculations imply that these structures are all mechanically stable.

Encouragingly, diamond-like c-BC_3 with high B content is also successfully synthesized under the condition of high pressure and high temperature[21] by using the precursor materials. Numerous structural models have been theoretically proposed to understand the structural nature of diamondlike c-BC_3.[86,87,101] However, none of these proposed sp^3 structural models is consistent with the experimental observation of cubic diamond structure. A lack of accurate structural determination for these materials has severely impeded further study of their properties. We report a novel high symmetric phase of low-energy cubic BC_3 (*I*-43*m* symmetry and 64 atoms per unit cell, d-BC_3) consisting of unique eight B–B bond distributions identified by using an unbiased structure search method based on particle-swarm optimization algorithms in combination with density functional theory calculations.[102] At ambient pressure, the optimized lattice parameter of d-BC_3 is 7.330 Å (Fig. 4), with boron occupying Wyckoff 8*c* (0.89711, 0.89711, 0.10289) and 8*c* (0.24273, 0.24273, 0.75727), and carbon occupying 12*e* (0.26755, 0.0, 0.0), 12*d* (0.0, 0.5, 0.75), and 24*g* (0.61792, 0.87580, 0.87580). A Bader charge analysis reveals that the charge density at the B–B bond critical point is 0.463 electron charges per $Å^3$ with a Laplacian value of −1.14, indicating the covalent nature of the B–B bond in d-BC_3. As shown in Fig. 5, the strong covalent B–B bonding can also be shown in the two-dimensional ELF on the (110) planes passing through the B–B bonds as shown in Fig. 5. The proposed d-BC_3 becomes stable structure with exclusively sp^3 hybridization above 41.3 GPa, in good agreement with the reported synthesis pressure of 39 GPa.[21] The simulated x-ray diffraction pattern and Raman modes of this d-BC_3 phase are in excellent agreement with the experimental data.[21]

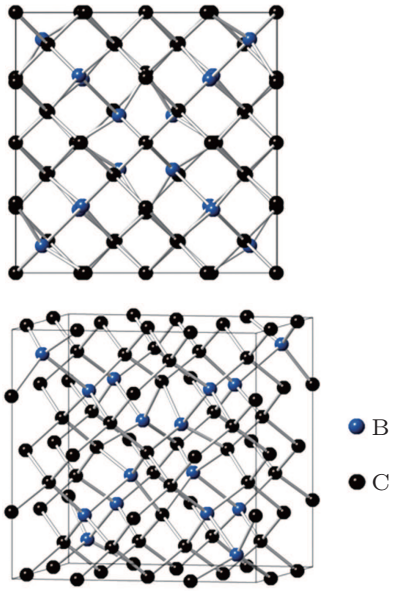


Fig. 4. Crystal structures of d-BC_3.

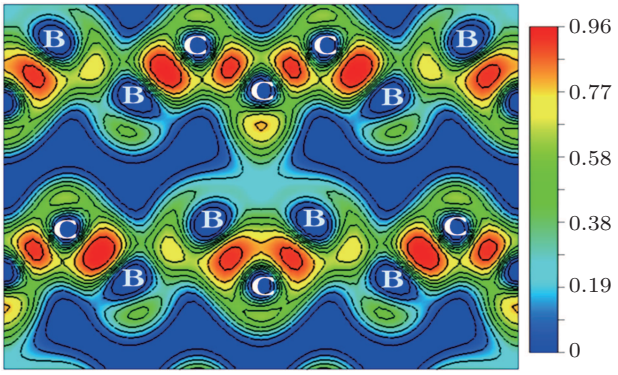


Fig. 5. (color online) The two-dimensional ELF on the (110) planes passing through the B–B bonds.

To deal with the metastable material with a positive formation enthalpy, it is interesting to investigate whether the newly predicted ordered d-BC_3 is more energetically favorable than diamondlike disordered structure. We have used the special quasirandom structure (SQS) approach[103] to randomly distribute B and C in the diamond lattice with different n-atoms ($n = 16$, 32, 64, and 128). The results show that the enthalpies of all the quasirandom diamond-like structures are higher than those of d-BC_3, indicating that the current d-BC_3 is clearly much more stable than the disordered phase at zero temperature. Since the d-BC_3 was synthesized under the condition of high-pressure and high-temperature, the temperature effect on energy should be taken into account. We have calculated the Gibbs free energies with the consideration of the contribution of vibrational and configurational entropy for d-BC_3 and the 128-atom quasirandom BC_3 structure. In any case, our calculations show that with or without the vibrational and configuration entropy contributions, the Gibbs free energy of predicted d-BC_3 are more energetically favorable than that of quasirandom structure below 1166 K (Fig. 6), indicating that our predicted d-BC_3 structure is more favorable for the experimentally recovered sample at atmospheric temperature than the disordered phase.

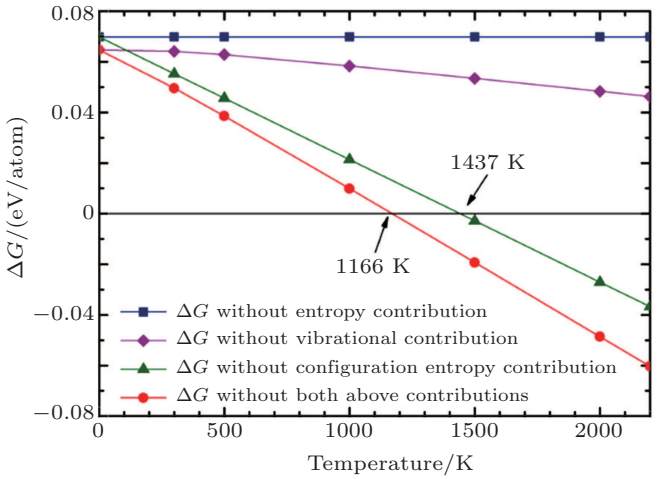


Fig. 6. (color online) Gibbs free energy per atom of quasirandom 128-atom BC_3 structure relative to d-BC_3 at 40 GPa.

The simulated hardness of BC_3 reaches 62 GPa. We have performed first-principles calculations of the stress–strain relations, which provide an insight into the local bond deformation and breaking mechanisms that determine the incipient plasticity in a crystal.[104–106] Its deformation modes under tensile and x shear strains show intriguing bond elongation and sequential bond-breaking processes that lead to remarkable extended ductility and elastic response. The [111] tensile stress decreases very gradually past the peak and the peak-to-valley drop extends over a wide range of tensile strain from 0.08 to 0.18, and the system undergoes a second elastic response regime from tensile strain 0.18 to 0.31. This behavior is highly unusual for a superhard material, and it is in stark contrast to the results for diamond and c-BN where the stress drops precipitously past the peak. The ratio between shear strength and tensile strength (53.0/52.5), which is nearly unity, is the lowest in superhard covalent materials, indicating the superior ductility of d-BC_3 to those of top superhard materials. The results provide a crucial insight into the structural assignment for BC_3 and clarify the actual existence of cubic symmetric phase for other boron carbide.

4. Summary

The review describes the theoretical prediction of the crystal structures for diamond-like covalent compounds formed by B–C–N–O system, which are the ideal targets in search for new superhard phases. Theoretical methods of designing new superhard materials are essential to improve the feasibility and effectiveness of experimental synthesis and/or find some extricable approaches. Material design techniques are greatly desirable to assist experiment, and free energy minimization methods and the recently developed superhard-driven methodology are quite successful for the applications to theoretically design superhard materials.

References

[1] Brazhkin V, Dubrovinskaia N, Nicol M, Novikov N, Riedel R, Solozhenko V and Zhao Y 2004 *Nat. Mater.* **3** 576
[2] Tian Y, Xu B and Zhao Z 2012 *Int. J. Refract. Met. Hard Mater.* **33** 93
[3] Kurakevych O O 2009 *J. Superhard Mater.* **31** 139
[4] Xu B and Tian Y 2015 *Sci. China Math.* **58** 132
[5] Wentorf Jr R H 1957 *J. Chem. Phys.* **26** 956
[6] Zhao Y, He D W, Daemen L L, Shen T D, Schwarz R B, Zhu Y, Bish D L, Huang J, Zhang J, Shen G, Qian J and Zerda T W 2002 *J. Mater. Res.* **17** 3139
[7] Kaner R B, Gilman J J and Tolbert S H 2005 *Science* **308** 1268
[8] Knittle E, Kaner R B, Jeanloz R and Cohen M L 1995 *Phys. Rev. B* **51** 12149
[9] Solozhenko V L, Andrault D, Fiquet G, Mezouar M and Rubie D C 2001 *Appl. Phys. Lett.* **78** 1385
[10] Komatsu T, Nomura M, Kakudate Y and Fujiwara S 1996 *J. Mater. Chem.* **6** 1799
[11] Nakano S, Akaishi M, Sasaki T and Yamaoka S 1994 *Chem. Mater.* **6** 2246
[12] He J L, Tian Y J, Yu D L, Wang T S, Liu S M, Guo L C, Li D C, Jia X P, Chen L X and Zou G T 2001 *Chem. Phys. Lett.* **340** 431
[13] Solozhenko V L, Kurakevych O O, Andrault D, Le Godec Y and Mezouar M 2009 *Phys. Rev. Lett.* **102** 015506
[14] Hubert H, Garvie L A J, Devouard B, Buseck P R, Petuskey W T and McMillan P F 1998 *Chem. Mater* **10** 1530
[15] Oganov A R, Chen J H, Gatti C, Ma Y Z, Ma Y M, Glass C W, Liu Z X, Yu T, Kurakevych O O and Solozhenko V L 2009 *Nature* **457** 863
[16] Solozhenko V L, Kurakevych O O and Oganov A R 2008 *J. Superhard Mater.* **30** 428
[17] Godec Y L, Kurakevych O O, Munsch P, Garbarino G and Solozhenko V L 2009 *Solid State Commun.* **149** 1356
[18] Bullett D W 1982 *J. Phys. C: Solid State Phys.* **15** 415
[19] Kurakevych O O and Solozhenko V L 2007 *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **63** i80
[20] Li Q, Wang H and Ma Y M 2010 *J. Superhard Mater.* **32** 192
[21] Zinin P V, Ming L C, Ishii H A, Jia R, Acosta T and Hellebrand E 2012 *J. Appl. Phys.* **111** 114905
[22] Li Q, Liu H, Zhou D, Zheng W T, Wu Z and Ma Y 2012 *Phys. Chem. Chem. Phys.* **14** 13081

[23] Zhang M, Liu H, Du Y, Zhang X, Wang Y and Li Q 2013 *PCCP* **15** 14120
[24] Li Q, Ma Y M, Oganov A R, Wang H B, Wang H, Xu Y, Cui T, Mao H K and Zou G T 2009 *Phys. Rev. Lett.* **102** 175506
[25] Xia Y, Li Q and Ma Y 2010 *Comput. Mater. Sci.* **49** S76
[26] Crowhurst J C, Goncharov A F, Sadigh B, Evans C L, Morrall P G, Ferreira J L and Nelson A J 2006 *Science* **311** 1275
[27] Gregoryanz E, Sanloup C, Somayazulu M, Badro J, Fiquet G, Mao H and Hemley R J 2004 *Nat. Mater.* **3** 294
[28] Crowhurst J C, Goncharov A, Sadigh B, Zaug J, Aberg D, Meng Y and Prakapenka V B 2008 *J. Mater. Res.* **23** 1
[29] Young A F, Sanloup C, Gregoryanz E, Scandolo S, Hemley R J and Mao H 2006 *Phys. Rev. Lett.* **96** 155501
[30] Jiang C, Lin Z and Zhao Y 2009 *Phys. Rev. Lett.* **103** 185501
[31] Ono S, Kikegawa T and Ohishi Y 2005 *Solid State Commun.* **133** 55
[32] Tolbert S H, Cumberland R W, Clark S M, Gilman J J, Weinberger M B and Kaner R B 2005 *J. Am. Chem. Soc.* **127** 7264
[33] Gu Q, Krauss F and Steurer W 2008 *Adv. Mater.* **20** 3620
[34] Chung H Y, Weinberger M B, Levine J B, Kavner A, Yang J M, Tolbert S H and Kaner R B 2007 *Science* **316** 436
[35] Qin J Q, He D W, Wang J H, Fang L M, Lei L, Li Y J, Hu J, Kou Z L and Bi Y 2008 *Adv. Mater.* **20** 4780
[36] Dubrovinskaia N, Dubrovinsky L and Solozhenko V L 2007 *Science* **318** 1550c
[37] Chung H Y, Yanga J M, Tolbert S H and Kanerb R B 2008 *J. Mater. Res.* **23** 1797
[38] Wang M, Li Y, Cui T, Ma Y and Zou G 2008 *Appl. Phys. Lett.* **93** 101905
[39] Knappschneider A, Litterscheid C, George N C, Brgoch J, Wagner N, Beck J, Kurzman J A, Seshadri R and Albert B 2014 *Angew. Chem. Int. Ed.* **53** 1684
[40] Zhang X, Qin J, Xue Y, Zhang S, Jing Q, Ma M and Liu R 2013 *Phys. Status Solidi-R* **7** 1022
[41] Gou H, Dubrovinskaia N, Bykova E, Tsirlin A A, Kasinathan D, Schnelle W, Richter A, Merlini M, Hanfland M and Abakumov A M 2013 *Phys. Rev. Lett.* **111** 157002
[42] Xie M, Mohammadi R, Mao Z, Armentrout M M, Kavner A, Kaner R B and Tolbert S H 2012 *Phys. Rev. B* **85** 064118
[43] Niu H, Wang J, Chen X Q, Li D, Li Y, Lazar P, Podloucky R and Kolmogorov A N 2012 *Phys. Rev. B* **85** 144116
[44] Wu H, Sun H and Chen C 2014 *Appl. Phys. Lett.* **105** 211901
[45] Chen X Q, Fu C L, Krčmar M and Painter G S 2008 *Phys. Rev. Lett.* **100** 196403
[46] Li Q, Zhou D, Zheng W, Ma Y and Chen C 2013 *Phys. Rev. Lett.* **110** 136403
[47] Wang H, Li Q, Li Y E, Xu Y, Cui T, Oganov A R and Ma Y M 2009 *Phys. Rev. B* **79** 132109
[48] Wang H, Li Q, Wang H, Liu H, Cui T and Ma Y 2010 *The Journal of Physical Chemistry C* **114** 8609
[49] Endo T, Sato T and Shimada M 1987 *J. Mater. Sci. Lett.* **6** 683
[50] Grumbach M P, Sankey O F and McMillan P F 1995 *Phys. Rev. B* **52** 15807
[51] Oganov A R and Glass C W 2006 *J. Chem. Phys.* **124** 244704
[52] Glass C W, Oganov A R and Hansen N 2006 *Comput. Phys. Commun.* **175** 713
[53] Oganov A R, Glass C W and Ono S 2006 *Earth Planet. Sci. Lett.* **241** 95
[54] Li Q, Chen W, Xia Y, Liu Y, Wang H, Wang H and Ma Y 2011 *Diamond Relat. Mater.* **20** 501
[55] Li Y, Li Q and Ma Y 2011 *EPL* **95** 66006
[56] Li Q, Wang M, Oganov A R, Cui T, Ma Y and Zou G 2009 *J. Appl. Phys.* **105** 053514
[57] Zhang X, Wang Y, Lv J, Zhu C, Li Q, Zhang M, Li Q and Ma Y 2013 *J. Chem. Phys.* **138** 114101
[58] Garvie L A J, Hubert H, Petuskey W T, McMillan P F and Buseck P R 1997 *J. Solid State Chem.* **133** 365
[59] Bolotina N B, Dyuzheva T I and Bendeliani N A 2001 *Crystallography Rep.* **46** 734
[60] Wang Y, Lv J, Zhu L and Ma Y 2012 *Comput. Phys. Commun.* **183** 2063
[61] Wang Y, Lv J, Zhu L and Ma Y 2010 *Phys. Rev. B* **82** 094116
[62] Lv J, Wang Y, Zhu L and Ma Y 2011 *Phys. Rev. Lett.* **106** 015503
[63] He J L, Guo L C, Wu E, Luo X G and Tian Y J 2004 *J. Phys.: Conden. Matter* **16** 8131
[64] Li Q, Zhou D, Wang H, Chen W, Wu B, Wu Z and Zheng W 2012 *Solid State Commun.* **152** 71
[65] Sun H, Jhi S H, Roundy D, Cohen M L and Louie S G 2001 *Phys. Rev. B* **64** 094108
[66] Pan Z, Sun H and Chen C 2005 *J. Phys.: Condens. Matter* **17** 3211
[67] Zhang R Q, Chan K S, Cheung H F and Lee S T 1999 *Appl. Phys. Lett.* **75** 2259
[68] Mattesini M and Matar S F 2001 *Int. J. Inorg. Mater.* **3** 943
[69] Kim E, Pang T, Utsumi W, Solozhenko V L and Zhao Y 2007 *Phys. Rev. B* **75** 184115
[70] Sun J, Zhou X F, Qian G R, Chen J, Fan Y X, Wang H T, Guo X J, He J L, Liu Z Y and Tian Y J 2006 *Appl. Phys. Lett.* **89** 151911
[71] Luo X, Guo X, Xu B, Wu Q, Hu Q, Liu Z, He J, Yu D, Tian Y and Wang H T 2007 *Phys. Rev. B* **76** 094103
[72] Zhou X F, Sun J, Fan Y X, Chen J, Wang H T, Guo X, He J and Tian Y 2007 *Phys. Rev. B* **76** 100101
[73] Luo X, Guo X, Liu Z, He J, Yu D, Xu B, Tian Y and Wang H T 2007 *Phys. Rev. B* **76** 092107
[74] Chen S Y, Gong X G and Wei S H 2007 *Phys. Rev. Lett.* **98** 015502
[75] Chen S, Gong X G and Wei S H 2008 *Phys. Rev. B* **77** 014113
[76] Chen C F and Sun H 2007 *Phys. Rev. Lett.* **99** 159601
[77] Chen S, Gong X G and Wei S H 2007 *Phys. Rev. Lett.* **99** 159602
[78] Luo X, Guo X, Xu B, Wu Q, Hu Q, Liu Z, He J, Yu D, Tian Y and Wang H T 2007 *Phys. Rev. B* **76** 94103
[79] Luo X, Guo X, Liu Z, He J, Yu D, Xu B, Tian Y and Wang H T 2007 *Phys. Rev. B* **76** 92107
[80] Li Q, Wang J, Zhang M, Li Q and Ma Y 2015 *RSC Adv.* **5** 35882
[81] Dubitskiy G A, Blank V D, Buga S G, Semenova E E, Kulbachinskii V A, Krechetov A V and Kytin V G 2005 *JETP Lett.* **81** 260
[82] Ekimov E A, Sidorov V A, Bauer E D, Mel'nik N N, Curro N J, Thompson J D and Stishov S M 2004 *Nature* **428** 542
[83] Crespi V H 2003 *Nat. Mater.* **2** 650
[84] Blase X, Bustarret E, Chapelier C, Klein T and Marcenat C 2009 *Nat. Mater.* **8** 375
[85] Matar S F and Mattesini M 2001 *Acad. Sci. Paris* **4** 255
[86] Liu H, Li Q, Zhu L and Ma Y 2010 *Phys. Lett. A* **375** 771
[87] Mikhaylushkin A S, Zhang X and Zunger A 2013 *Phys. Rev. B* **87** 094103
[88] Liu H, Li Q, Zhu L and Ma Y 2011 *Solid State Commun.* **151** 716
[89] Gildenblat G S, Grot S A and Badzian A 1991 *Proc. IEEE* **79** 647
[90] Jones L E and Thrower P A 1991 *Carbon* **29** 251
[91] Ma Y, Tse J S, Cui T, Klug D D, Zhang L, Xie Y, Niu Y and Zou G 2005 *Phys. Rev. B* **72** 014306
[92] Lee K W and Pickett W E 2004 *Phys. Rev. Lett.* **93** 237003
[93] Takano Y, Takenouchi T, Ishii S, Ueda S, Okutsu T, Sakaguchi I, Umezawa H, Kawarada H and Tachiki M 2007 *Diamond Relat. Mater.* **16** 911
[94] Calandra M and Mauri F 2008 *Phys. Rev. Lett.* **101** 016401
[95] Liang Y, Zhang W, Zhao J and Chen L 2009 *Phys. Rev. B* **80** 113401
[96] Lazar P and Podloucky R 2009 *Appl. Phys. Lett.* **94** 251904
[97] Moussa J E and Cohen M L 2008 *Phys. Rev. B* **77** 064518
[98] Li Q, Wang H, Tian Y, Xia Y, Cui T, He J, Ma Y and Zou G 2010 *J. Appl. Phys.* **108** 023507
[99] Gao F, He J, Wu E, Liu S, Yu D, Li D, Zhang S and Tian Y 2003 *Phys. Rev. Lett.* **91** 015502
[100] He J, Wu E, Wang H, Liu R and Tian Y 2005 *Phys. Rev. Lett.* **94** 015504
[101] Liu Z, He J, Yang J, Guo X, Sun H, Wang H T, Wu E and Tian Y 2006 *Phys. Rev. B* **73** 172101
[102] Zhang M, Liu H, Li Q, Gao B, Wang Y, Li H, Chen C and Ma Y 2015 *Phys. Rev. Lett.* **114** 015502
[103] Zunger A, Wei S H, Ferreira L G and Bernard J E 1990 *Phys. Rev. Lett.* **65** 353
[104] Zhang Y, Sun H and Chen C F 2004 *Phys. Rev. Lett.* **93** 195504
[105] Krenn C R, Roundy D, Cohen M L, Chrzan D C and Morris Jr J W 2002 *Phys. Rev. B* **65** 134111
[106] Li J, van Vliet K J, Zhu T, Yip S and Suresh S 2002 *Nature* **418** 307