

Structural and electronic properties of diamond with hypothetical vacancies stabilized by nitrogen or boron atoms

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In an effort to understand the behavior of hard materials in the presence of vacancies or impurities, we study the structural and electronic properties of diamond with specified vacancies. In our model, five carbon atoms in the shape of a centered tetrahedron are missing and 12 carbon atoms surrounding the vacancy are replaced by nitrogen or boron atoms. The bulk modulus of the material with nitrogen substitution is greater than that without substitution around vacancy, although it is still slightly smaller than that of vacancy-free diamond. Boron substitution results in a substantial relaxation of atomic positions and a large reduction in bulk modulus. Born's criterion for mechanical stability is satisfied in both cases. The calculated electronic structures suggest that the doping of N atoms around the vacancy as modeled here fails to generate conduction electrons while that of B atoms successfully produces conducting holes. [S0163-1829(97)02324-2]

I. INTRODUCTION

There has been a great amount of effort to find a "superhard" material on both theoretical and experimental sides. After the original work by Liu and Cohen¹ on the subject, the carbon nitrides with the composition of C_3N_4 have been widely studied as a strong candidate for the superhard material. Recently, a carbon nitride structure with larger bulk modulus than diamond (the experimental bulk modulus of diamond is 443 GPa, the highest among known materials) has been predicted using an *ab initio* calculation.² The short bond length and the strong covalent character of the N-C bond contribute to the low compressibility and large cohesive energy. However, despite the remarkable predictions on the theoretical side, to our knowledge, there has yet been no experiment in which any of the suggested novel structures of the carbon nitride could be identified. A major obstacle here is that the concentration of N is hard to increase in actual crystal growth.^{3,4}

The energetic and mechanical stability of C_3N_4 compounds in the previous calculations suggest that N can be used for the stabilization of structures around vacant sites in diamond. If there is a vacancy (small or large) in diamond, the carbon atoms surrounding the vacancy will have dangling bonds that make the system less stable. The substitution of nitrogens for the unstable carbons might improve the energetic and mechanical stability of the structure near the vacancy. In order to test this idea, we perform a calculation for a vacancy in diamond where five clustered carbons with the shape of the centered tetrahedron are missing. The 12 carbons around the vacancy are replaced by nitrogens in order to stabilize the system and improve the mechanical properties. The reason for choosing a somewhat large vacancy is to magnify the effect of vacancy. (A single carbon atom vacancy is also tested with consistent results as presented below.) For computational convenience, we introduce the periodic arrays of vacancies and employ the supercell method. The resulting material can be thought of as a hypothetical N-doped diamond. We have also performed a calculation in which the 12 carbons are substituted by borons rather than nitrogens since boron has three valence electrons and may

possibly stabilize the vacancy as well. It turns out that the N-C bonds contribute to the reduction of the compressibility and the system remains semiconducting while the B-C bonds make the system more compressible and the material acquires metallic characters. In other words, B atoms do act as *p*-type dopants in the present geometry. Details of our calculation and the comparison between different atomic structures are presented below.

II. MODEL AND CALCULATIONAL METHOD

We consider a vacancy where five clustered C atoms in diamond are absent. Figure 1 shows how the vacancy-N(B) complex is implemented in each supercell. The black circles represent the sites of extracted C atoms. A set of 12 N (or B) atoms replacing C atoms will be called a N_{12} (or B_{12}) shell in the following. The vacancies are assumed to repeat periodically in the diamond structure in order to make the supercell calculation possible. We choose a supercell with the lattice vectors three times longer than those of perfect diamond, hence corresponding to 54 atoms, and implement the above

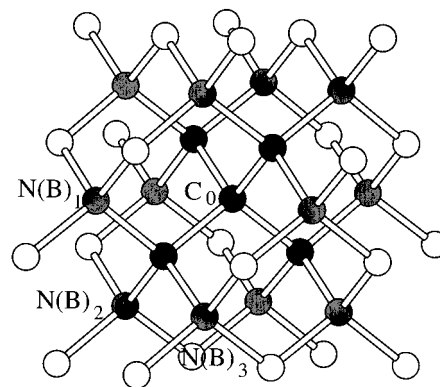


FIG. 1. Central region of the vacancy. Black circles are the sites of five vacant carbons with imaginary bonds, and shaded circles are nitrogens or borons substituting carbons. The blank circles represent carbon sites.

vacancy structure in each supercell. There are 12 N atoms and 37 C atoms in the unit cell and the ratio of the number of the C–C bonds to that of the N–C bonds is 14:9. Within the tetrahedral symmetry, two independent parameters d_1 and d_2 determine the relaxation of the N_{12} shell; d_1 is the distance between C_0 (Fig. 1) and the triangle determined by the three atoms, $N_{1,2,3}$ while d_2 is the distance between the center of the triangle and any one of three atoms, $N_{1,2,3}$. The distortion breaking the tetrahedral symmetry around the vacancy is conceivable. Such a distortion turns out to be energetically unfavorable and does not occur in the test case of $C_{49}N_4$. In other systems considered, we neglect such a symmetry-lowering distortion.

We use the *ab initio* pseudopotential method in the plane-wave basis⁵ and adopt the local density approximation⁶ with the Ceperley-Alder-type exchange correlation.⁷ This method has been known to give accurate results in most carbon compounds.^{8–10} We have generated nonlocal pseudopotentials for *s* and *p* orbitals with the improved Troullier-Martins method¹¹ and set the cutoff energy at 60 Ry. The cutoff radii of C(N,B) are 1.00(1.12,1.00) and 1.54(1.50,1.53) for *s* and *p*, respectively. Five special \mathbf{k} points¹² are used in the irreducible Brillouin zone integration; the convergence in the number of \mathbf{k} points is satisfactory for $C_{37}N_{12}$ since it is semiconducting. As will be shown in the following section, $B_{12}C_{37}$ is metallic and the convergence test is crucial in this case. We have compared the total energy, force, and stress obtained from the special \mathbf{k} point method with those from the linear tetrahedron method, and the differences are less than 1%.

Starting from the ideal atomic positions in diamond, we minimize the atomic forces under a fixed cell volume using the conjugate gradient (CG) method¹³ with the assumption that the Born-Oppenheimer energy surface is quadratic with respect to internal coordinates of atoms. For practical reasons, we choose the internal stress as a criterion of convergence and relax the internal coordinates of all atoms until the stress changes by less than 0.1 GPa with a further CG step. About 5–7 CG steps are needed to reach the desired convergence, reflecting that the initial positions are fairly close to the equilibrium values. In calculating the atomic forces in each CG step, we accelerate the convergence of force in self-consistent loops by including a supplementary term, which partially corrects the error arising from the slightly misconverged potential.¹⁴ The desired accuracy is obtained after 4–5 self-consistent iterations.

Varying the lattice vectors isotropically and relaxing the atomic positions, we calculate the stress and the total energy of the system. Since the compression is isotropic in this calculation, the external pressure corresponds to the minus of a diagonal component in the stress tensor. The symmetry of the crystal is preserved during the relaxation procedures as mentioned above. The equilibrium volume and bulk modulus are obtained by fitting the volume-pressure data sets to the Birch equation of state.¹⁵ The theoretical calculation of the hardness of a material would involve dislocation and plastic deformation as well as the elastic part (bulk modulus) and is beyond the computational capability at present. We only calculate the bulk modulus as commonly practiced. As a reference, we have performed a calculation on C_{49} having the

TABLE I. Relaxed geometry of $C_{37}N_{12}$ and $B_{12}C_{37}$. d_1 is the distance between C_1 and the center of the triangle determined by $X_{1,2,3}$ (Fig. 1), and d_2 is the distance between the center and a vertex of the triangle. Values for diamond are for the ideal unrelaxed geometry.

Structure	d_1 (Å)	d_2 (Å)
Diamond	2.04	1.44
$C_{37}N_{12}$	2.00	1.49
$B_{12}C_{37}$	2.21	1.70

same vacant sites as $C_{37}N_{12}$ but without substitution. The bulk modulus of this reference system is 328 GPa.

III. RESULTS

A. Carbon nitride ($C_{37}N_{12}$)

The relaxation of the nitrogen atoms surrounding the vacancy in $C_{37}N_{12}$ is very small as shown in Table I. Similar observations can be found in pseudocubic C_3N_4 (Ref. 8) and this indicates that the character of the N–C bond is close to that of the C–C bond. The bulk modulus fitted to the volume-pressure relation in Fig. 2 is 388 GPa. This is much larger than 328 GPa for C_{49} , confirming our idea of substituting C by N around the vacancy for a harder material. In order to check the mechanical stability of this material, we have calculated the components of the elastic tensor by deforming the cell shape. According to Born’s criterion, a cubic system is mechanically stable if c_{11} , $c_{11} - c_{12}$, and c_{44} are all positive. A negative sign in any of these components would indicate that the system should collapse or change to a crystal with lower symmetry. We have found that all the relevant constants are positive. In Table II, one can see that the cohesive energy per atom is reduced in comparison with C_{49} , contrary to our initial conjecture. Considering that the electronic distribution along the bonds in $C_{37}N_{12}$ is similar to that of diamond [Fig. 3(a)], we think that the repulsive interactions in the localized lone pairs may raise the total energy of the system slightly.

For comparison, another calculation has been performed on a system where only one C is absent and neighboring four C atoms are replaced by N atoms ($C_{49}N_4$). The results are shown in Table II. The bulk modulus lies between the values

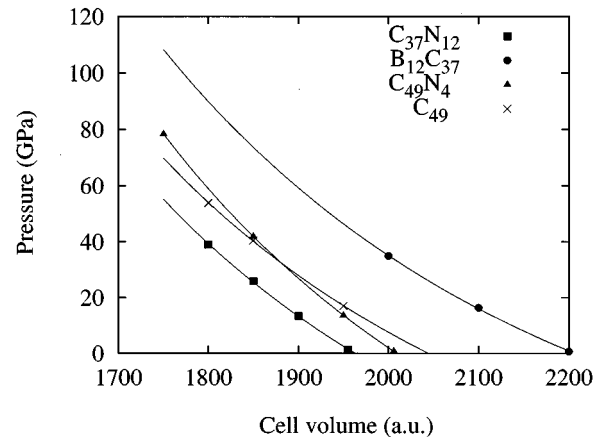


FIG. 2. Volume-pressure curves for the model structures.

TABLE II. Comparison of the calculated equilibrium cell volume V_0 , cohesive energy, and bulk modulus among the model structures.

Structure	V_0 (a.u. ³)	Cohesive energy (eV/atom)	Bulk modulus (GPa)
C_{54} (diamond)	2030	8.70	441
C_{49}	2045	8.38	328
$C_{49}N_4$	2009	8.46	430
$C_{37}N_{12}$	1951	7.85	388
$B_{12}C_{37}$	2202	8.12	301

of diamond and $C_{37}N_{12}$ as expected. From the data on $C_{37}N_{12}$ and $C_{49}N_4$, it is noticeable that the bulk modulus is reduced by about 10 GPa per one vacant site in the unit supercell compared with the intact diamond (i.e., C_{54}).

$C_{37}N_{12}$ is an insulator as shown in the density-of-states plot in Fig. 4(a). This suggests that, if the doping of N atoms in diamond accompanies local vacancy formation as modeled here, we may not effectively create conducting electrons in the material. The band gap of 3.1 eV is smaller than the calculated band gap of diamond, 4.3 eV.¹⁶ (These calculated gaps within the local density approximation are smaller than the experimental gap of diamond, 5.47 eV.) The reduction in the band gap is mainly caused by the nonbonding states in N. (Diamond does not have such states at the top of the valence band and its energy gap is larger.) The total valence electron density on the $(01\bar{1})$ plane containing the center of the vacancy is plotted in Fig. 3(a). A small amount of charge transfer occurs from C to nearby N atoms, but the covalent character is still maintained in each bond. Most of the electrons in the band between -3.6 and -1.5 eV [Fig. 4(a)] are found to be lone pairs from nitrogen atoms and directed toward the vacant sites and they form the top of the valence band. Being localized at the N atom sites and forming a separate band, the excess electrons in N atoms do not disturb charge distributions in the C–C bonds.

B. Boron carbide ($B_{12}C_{37}$)

Similar calculations have been done for boron carbide. The volume-pressure curve is shown in Fig. 2. The bulk modulus is 301 GPa and the equilibrium volume is 2202 a.u.³, which is about 8% larger than the vacancy-free diamond supercell. The charge transfer from B to adjacent C atoms reduces the strength of certain bonds such as the one represented by a thick line in Fig. 3(b) and this is the primary reason for the volume expansion compared to $C_{37}N_{12}$ (the bond length of the thick line is 1.61 Å compared to 1.53 Å of pure diamond). The relaxed geometry of the B_{12} shell (see Table I) is also different from diamond or $C_{37}N_{12}$. Due to the large inward relaxation of B atoms, the C–B–C angle increases to 116.9°, indicating a substantial amount of sp^2 bonding characters. (The ideal sp^2 angle is 120° compared to the ideal sp^3 of 109.47°.) In spite of the large deformation from diamond, this structure is found to meet Born's criterion. The cohesive energy per atom is calculated to be 8.12 eV, which is larger than $C_{37}N_{12}$ but still smaller than C_{49} . This implies that the ionic B–C bonding is weaker than the covalent C–C bonding. The bulk modulus

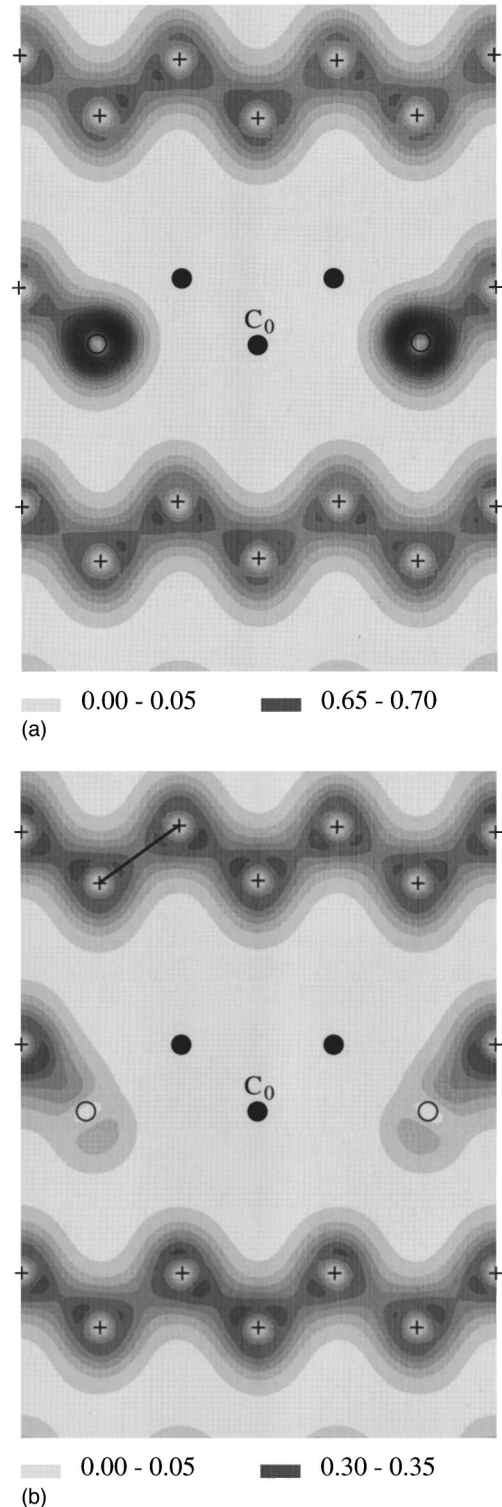


FIG. 3. Total valence charge density of (a) $C_{37}N_{12}$ and (b) $B_{12}C_{37}$ in the $(01\bar{1})$ plane. +, O, and ● denote the sites of C, N, and vacant C, respectively (see Fig. 1). The interval between successive contours is 0.05 electron/a.u.³ The thick line in (b) indicates a weakened bonding between two C atoms.

is far lower than $C_{37}N_{12}$ and this is believed to originate from the weakened C–C bondings and a somewhat ionic character of the B–C bond [Fig. 3(b)]. In general, ionic bonding gives lower bulk modulus than covalent bonding.¹⁷

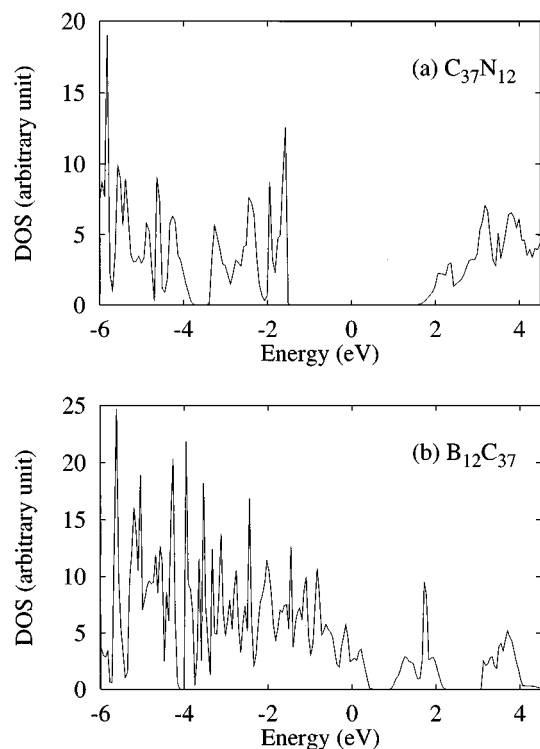


FIG. 4. Density of states (DOS) of (a) $C_{37}N_{12}$ and (b) $B_{12}C_{37}$ near the Fermi level (0 eV).

This material is metallic with hole states as shown in Fig. 4(b). We have found that the states around the Fermi level have the maximum charge density between B and C. Since the electrons in this region have the mixed character of sp^2 and sp^3 type, it is hard to specify the character of hole (valence-band maximum) states. The metallic behavior of $B_{12}C_{37}$ suggests that, if the doping of B atoms in diamond accompanies local vacancy formation, we may still create conducting carriers (holes) successfully in contrast to the case of N atoms. Compositionally, $B_{12}C_{37}$ is similar to the

BC_3 graphitic plane.⁹ All bondings in BC_3 are sp^2 type, which is in marked difference from $B_{12}C_{37}$. The calculated cohesive energy is larger in $B_{12}C_{37}$ by 0.27 eV/atom and this comes from the different ratio in the mixture of B–C and C–C bonds.

IV. CONCLUSIONS

In this work, we have considered hypothetical diamond vacancies with stabilizing N atoms substituting those carbons surrounding the vacancies, and calculated the electronic structure and mechanical properties of the system. Both $C_{37}N_{12}$ and $B_{12}C_{37}$ are found to be mechanically stable in spite of the large vacancies. It turns out that the N substitution in our model system enhances the bulk modulus while the B substitution has the opposite effect. In contrast to $C_{37}N_{12}$, the borons in $B_{12}C_{37}$ form an appreciable, though small, amount of ionic bonding with carbons, and this results in quite different electronic structures and large compressibility compared to diamond. The absence of lone pairs in B allows a significant amount of inward relaxation of B atoms, and this results in partial sp^2 -type bonding between B and C. Cohesive energies of both materials are quite large but they are lower than bare (nonsubstituted) C_{49} . From the purely energetic point of view, this means that C_{49} is easier to generate in experiment than $C_{37}N_{12}$ or $B_{12}C_{37}$. A similar situation may occur in C_3N_4 compounds, i.e., the N sites in C_3N_4 compounds might favor C over N, and this could explain why the concentration of N is hard to increase in the experiment.

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¹A. Y. Liu and M. L. Cohen, Phys. Rev. B **41**, 10 727 (1990).

²D. M. Teter and R. J. Hemley, Science **271**, 53 (1996). We recalculated the bulk modulus of cubic C_3N_4 and obtained 470 GPa, while our method yields 441 GPa for diamond. Our calculated difference from diamond (29 GPa) is in good agreement with their value of 28 GPa. Two special \mathbf{k} points were used for the Brillouin zone integration and cutoff energy was set to 60 Ry. There are slight differences in the relaxed parameters from the above paper. We have compared various components of stress tensor and found that the major contribution to high bulk modulus is the kinetic part of electrons. The electronic structures of pseudocubic and cubic C_3N_4 turn out to be almost the same.

³R. W. Cahn, Nature **380**, 104 (1996).

⁴C. M. Lieber and Z. J. Zhang, J. Adv. Mater. **6**, 497 (1994).

⁵J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

⁶W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

⁷D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978)

⁸A. Y. Liu and R. M. Wentzcovitch, Phys. Rev. B **50**, 10 362 (1994).

⁹D. Tomanek, R. M. Wentzcovitch, S. G. Louie, and M. L. Cohen, Phys. Rev. B **37**, 3134 (1988).

¹⁰A. Y. Liu, R. M. Wentzcovitch, and M. L. Cohen, Phys. Rev. B **39**, 1760 (1989).

¹¹N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

¹²D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

¹³W. H. Press *et al.*, *Numerical Recipe*, 2nd ed. (Cambridge Univ. Press, Cambridge, 1992).

¹⁴C. T. Chan, K. P. Bohnen, and K. M. Ho, Phys. Rev. B **47**, 4771 (1993). This method is efficient especially in the case of carbon nitrides, which are insulators.

¹⁵F. Birch, J. Geophys. Res. **57**, 227 (1952).

¹⁶S. Fahy and S. G. Louie, Phys. Rev. B **36**, 3373 (1987).

¹⁷M. L. Cohen, Solid State Commun. **92**, 45 (1994).