

A First-Principles Study of Physical Properties of Monatomic Structures of B, C, N, and O

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(Received December 12, 2001)

We have performed a series of studies on the properties of monatomic solid boron (B), carbon (C), nitrogen (N) and oxygen (O) under high pressure with a first-principles method. Four structures with different coordination numbers, i.e., cubic diamond, simple cubic, body center cubic and face center cubic structures, are calculated to investigate the relationship of physical properties and coordination numbers. Our investigation shows that all the four elements under high pressure favor a higher coordination number structure and become more metallic like. The bulk moduli have also been investigated, showing that atomic volume is the most important factor that determines the bulk moduli. The effects of composition and coordination on bulk moduli are secondary for B, C, N, and O. The investigation also reveals that the species having a small atomic volume will have a large bulk modulus. As expected, the bulk modulus of diamond is the largest one we studied. We found that the bulk modulus of carbon in simple cubic structure (3.37 Mbar) is slightly less than that of c-BN (3.67 Mbar), the second hardest material in the world. The bulk moduli of B in fcc structure (2.8 Mbar) and N in simple cubic structure (2.57 Mbar) are larger than that of SiC (2.24 Mbar).

PACS. 64.60.-i – General studies of phase transitions.

PACS. 71.15.Nc – Total energy and cohesive energy calculations.

I. Introduction

The composition and structure of a material are both crucial factors for determining the properties of a material such as hardness, e.g., the extreme difference of hardness and conductance between graphite and diamond [1]. The bonding strength of a crystal structure is manifested as a material's hardness and rigidity, and a convenient measure of such a bonding strength is its bulk modulus, the specific incompressibility of a material. Superhard materials have attracted much attention from industry as they have many superior properties, e.g., the highest compressive strength and thermal conductivity. In forming superhard structures or compounds, the elements boron (B), carbon (C), nitrogen (N) and oxygen (O) are unique in that they are first period elements with p-electrons. As there are no inner p-electrons in the core to push the valence electrons outward, these p-electrons can retreat further inward relative to larger atoms of the same group of elements. Moreover, due to the absence of an inner p orbital in the electron core, the atomic volumes of

these elements are distinctively small. As a result of the high bonding strength and small atoms, many structures and compounds of B, C, N, and O are superhard [2]. Indeed, C forms diamond that is likely the hardest material with a bulk modulus of 4.43 Mbar. B and N are also known to form isostructural cubic boron nitride (c-BN) that may be the second hardest material with a bulk modulus of 3.67 Mbar [2]. Li and Be are elements in the same period but can not form superhard structures as they have too few electrons to form strong bonding between atoms.

The properties and phase transition of a material can be examined as a function of pressure. Due to recent advances in high-pressure technologies such as diamond-anvil cell techniques, experimentally attainable pressures have reached to multi-megabars. High-pressure experiments provide a useful probe for the interactions of varied volumes and lattice constants and this is a manner that can be simulated theoretically. The relative stability of various structures and the properties (e.g., bulk modulus) of these modifications at high pressure can be calculated by a first-principles method. While high-pressure experiments have the capability to reach megabar pressures, it is possible to experimentally verify many hypothetical structures calculated a priori. At low pressures, B forms a rhombohedral structure of icosahedron[®]-phase, C forms a hexagonal structure of graphite. N and O form the strongest diatomic molecules except for H₂ [3]. These low-pressure phases will transform to denser structures under high pressure. A crystal structure with a higher coordinate is denser than that with a lower coordination. Furthermore, monatomic packing is much more efficient, by 1/3 or more, than diatomic grouping. Hence, with increasing pressure, all elements will eventually transform into monatomic structures with increasing coordination number.

Theoretical and experimental studies of N₂ molecules under pressure at a temperature lower than about 30 °K revealed that condensed N₂ solid might undergo several phase transitions [4-6]. For further increases of pressures, theoretical calculations suggest that N₂ molecules may even dissociate to form monatomic metallic phases. The dissociation begins with the formation of a simple cubic structure at a pressure between 0.77 to 0.94 Mbar [6]. Because of the presence of a large activation energy, the dissociation of N₂ molecules to form monatomic structures has not been observed experimentally. Thus, N₂ solid squeezed in diamond anvils at room temperature up to a pressure of 1.3 Mbar [7] and 1.8 Mbar [8], revealed that diatomic N₂ molecules remain stable. However, the vibration modes in Raman scattering indicated that the bonding of N₂ molecules might begin to weaken [9]. At a higher temperature, the large activation energy associated with the dissociation of N₂ molecules may be overcome. Thus, there is evidence that liquid N₂ molecules, when subjected to strong shock waves, may dissociate into monatomic fluid at a pressure of 0.3 Mbar and temperature of 6000 °K [10].

Although some theoretical models of high pressure phases for C and N have been reported [2], there is no systematic comparison of relative stabilities and properties of all four first period elements: B, C, N, and O. In this research, we present the calculated results for the total energies of these elements based on the density functional theory [11] and the local density approximation [12]. In order to scope the effect of pressure on these four elements, calculations are performed on representative structures with increasing coordination numbers (CN). These structures include cubic diamond (cd with CN = 4), simple cubic (sc with CN = 6), body-centered cubic (bcc with CN = 8), and face-centered cubic (fcc with CN = 12) structures. Based on the calculated total energies for these structures, their relative stabilities and bulk moduli are determined. These characteristics of monatomic structures are interpreted with distinctive electron configurations of the atoms for B, C, N, and O. We also investigate the relation between the bulk moduli and the

atomic volume of these different structures.

II. Calculation method

These calculations are based on the density functional theory [11] with the local density approximation (LDA) [12]. The Ceperley-Alder form [13] is used to calculate the exchange-correlation energy in the LDA calculations. The norm-conserving pseudo-potentials for B, C, N and O ions are taken from Bachelet *et al.* [14]. The wavefunctions are expanded with plane waves and the calculations are done in momentum space [15]. The samplings of k points for integration over the first Brillouin zone are chosen by the scheme of Monkhorst-Pack [16]. Convergence is concluded based on a large number of k points: i.e., 256 for cd and sc structures, and 343 for bcc and fcc structures. The energy cutoffs for the calculation are up to 100, 100, 150, and 200 Rydberg for B, C, N, and O, respectively. The error bar of the calculation is estimated to be less than 0.1 eV/atom. The total energies are fitted by the Murnaghan equation [17].

III. Results and discussions

We investigate the material properties of B, C, N and O in the four monatomic solid phases, i.e., cubic diamond (cd), simple cubic (sc), body center cubic (bcc) and face center cubic (fcc) structures. First, the total energies are calculated to study the crystal stability, and then the total energy are fitted to the Murnaghan equation in order to obtain the equilibrium properties of the species mentioned above. The equilibrium properties of the four phases including the minimum total energy (E_0), bulk modulus (K_0), atomic volume (V_0), interatomic distance (d_0) and the average charge density ($n_{av} = Z_v/V_0$, where Z_v is the number of valence electron) will also be discussed. The relations of the equilibrium properties and coordination number are also investigated. The coordination numbers of cd, sc, bcc and fcc structures are 4, 6, 8 and 12, respectively.

The energy curves of B, C, N and O with the four structures, as drawn in Fig. 1, show that the most favored phase of the four structures we calculated are the cd phase for B and C, and the sc phase for N and O. For Boron, the cd phase is the most favored phase of the four structures (cd, sc, bcc and fcc) under ambient conditions and it transforms to the sc phase as the applied pressure is greater than 97 kbar; then transforms to the fcc phase when the pressure is greater than 482 kbar. Among cd, sc, bcc and fcc structures of carbon, the cd phase is the most favorable phase until the pressure is greater than 21.1 Mbar, where the sc phase becomes the most favorable phase. Yin and Cohen (1987) also had a similar prediction that cubic diamond should transform to a sc structure around 23 Mbar [18]. For both N and O, the sc phase is the most favorable phase of the four structures under ambient conditions. N should transform from the sc phase to the bcc phase, if the pressure is greater than 59.1 Mbar. For Oxygen, the sc phase is still the most favorable phase under very high pressures.

We examine the stability of the four phases studied with the equilibrium total energy and the difference between the valence electron number and coordination number ($\mathcal{C} = Z_v - CN$). The equilibrium total energies E_0 (the minimum total energies) vs. different coordination numbers and the relations of total energy and \mathcal{C} are shown in Fig. 2(a) and (b), respectively. We set the minimum total energies of the cd structure $E_0(\text{cd})$ of B, C, N and O to be the reference for

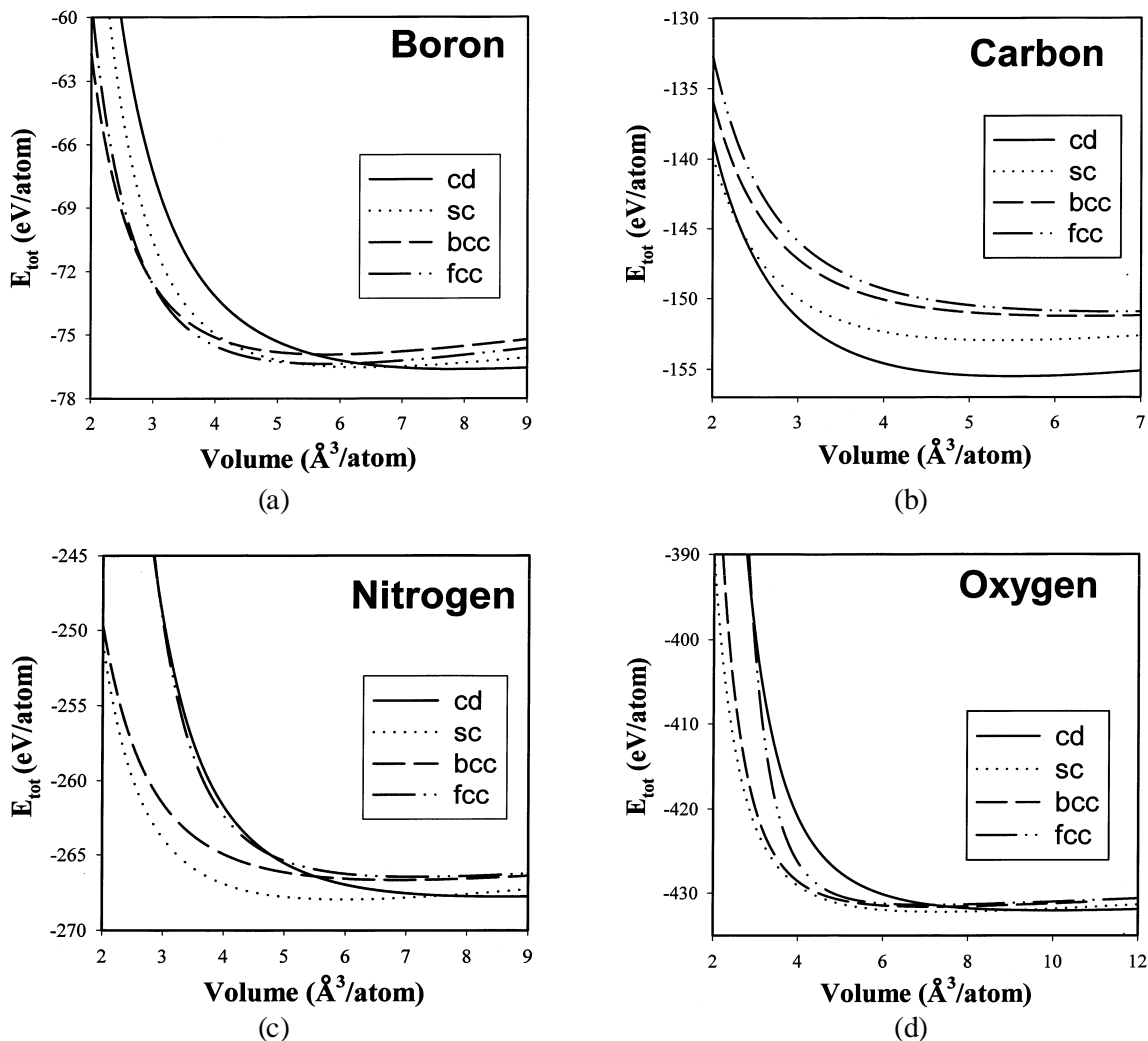


FIG. 1. Volumetric dependence of the total energy for various structures of (a) Boron, (b) Carbon, (c) Nitrogen, and (d) Oxygen.

convenience and the data points are connected with straight lines as a guidance to eyes. The cd structure is the most stable phase and the sc structure is the second stable phase for B and C. That is due to the fact that the valence electrons of B and C are not greater than 4, it is more stable to form a lower coordination number phase (cd phase having CN = 4) than a higher coordination number phase. B has three valence electrons, and it can form a sp^3 atomic configuration with a vacancy. As a result, the cd structure is not stabilized unless the vacancy is filled, such as by the addition of an electron donor, e.g., N in the structure, as in the case of cubic boron nitride. Moreover, a sc structure, due to its orthogonal coordination, would require p^3 -contributions from the valence electrons. As B atoms have only one p-electron, it cannot stabilize a sc structure effectively with two unfilled p-vacancies. Hence, although B still favors forming cd and sc structures, the

preference is not strong. Indeed, at low pressure, B's stable phase is the rhombohedral structure of an icosahedron. In the case of C, it can form bonds other than sp^3 configurations with ease. As a result, both sp^1 (carbyne) and sp^2 (graphite) configurations may become stable at low pressures. Although C can form atomic configuration other than sp^3 , its four valence electrons match perfectly with four coordinated neighbors in a cd structure. As a result of high overlap of valence charges, the bond energy density of C in a cd structure would be very high. With the extra stabilization of this large bond energy, the stability of a cd structure is greatly expanded toward high pressure. C may also form a sc structure. As it has two p-electrons, its sc structure can be more stable than that for B. However, because of the strong stabilization of the cd structure, the sc structure would not be stable until the atomic volume is reduced as shown in Fig. 3(a). This result is consistent with the conclusion that the cd-sc transition for C may occur only when the pressure reaches such a high value, as much as 21.1 or 23 Mbar [18], about that at the center of Jupiter or a small star. When the number of valence electrons is increased, the sc structure becomes more stable than the cd structure, so that the cd structure turns out to be the second stable phase. For N and O elements, the valence electrons are greater than 4, the cd phase cannot provide sufficient neighbors to form stable bonding, thus forming the sc phase (CN = 6) will be more favored than the cd phase. N and O may form a cd structure with extra electrons that may make the structure electrically conducting. Both N and O have sufficient p electrons to align with octahedral coordinated atom; hence, their sc structures are greatly stabilized. The phases with large CN (bcc and fcc) are not favored by the four elements, because forming these high coordination number phases would provide too many holes in the crystal and that would weaken the structure.

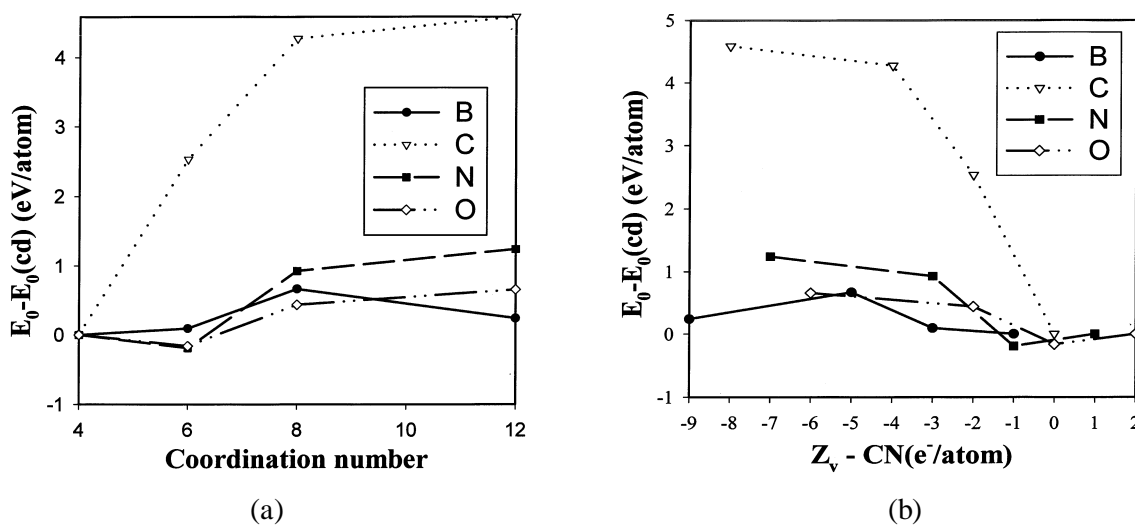


FIG. 2. The equilibrium total energy varies with (a) coordination number and (b) the difference between the valence electron number and coordination number ($\mathcal{C} = Z_v - \text{CN}$). We set the minimum total energies of the cd structure $E_0(\text{cd})$ of B, C, N and O to be the reference for convenience and the data points are connected with straight lines as guidance for the eye.

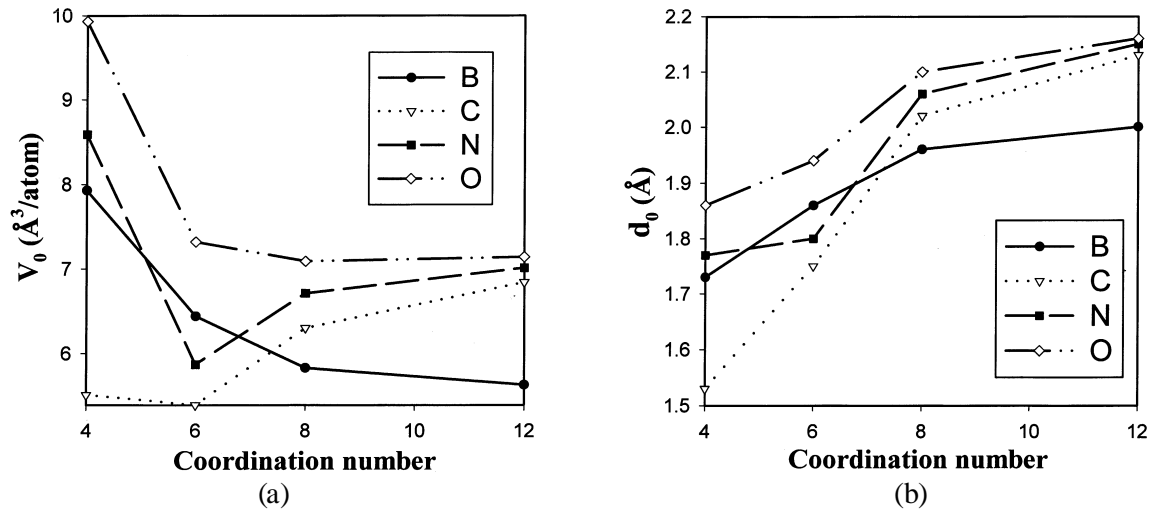


FIG. 3. (a) Atomic volume V_0 and (b) interatomic distance d_0 of B, C, N and O with different coordination numbers.

As $\zeta > 0$ (or $\zeta < 0$), there are extra electrons (or holes) in the crystal that should weaken the structure. The greater the $j\zeta j$, the structure should become less stable. This effect is more significant in the case of carbon and is not significant for the case of boron with bcc and fcc structure, as the value of ζ is too large. When $\zeta = 0$, each valence electron and each neighbor form perfect chemical bonding, no extra electron and hole floating in the crystal and the structure is more stable than the case with $\zeta \neq 0$.

The atomic volume (V_0) and the interatomic distance (d_0) of the four elements with different CN are given in Fig. 3, which shows that the V_0 of the cd structure is the largest one and the V_0 of the phases with large CN are relatively small except for C. Although the valence electrons are closer to the core following the order B, C, N, and O, the atomic volume and the interatomic distance appears to reverse the trend, particularly for structures with coordination number, CN = 8 and 12. Furthermore, except for C, this volume tends to decrease with increasing coordination number. Both trends appear to be contrary to typical elements of the same period, e.g., 3d transition elements: normally, the atomic size tends to shrink with increasing atomic number, and it is likely to expand with increasing coordination number. A notable exception of this reverse trend is C, which shows an increase of atomic size with coordination number. This exception may be due to C's unique ability to withdraw its 2p orbital toward the core. This feature makes the effective size of C atoms exceptionally small when it forms a cd or sc structure. As will be discussed later, the unusual shrinkage of C atoms is responsible for the great increase of bulk moduli for these two structures. As can be seen in Fig. 3, the behaviors of the d_0 -CN curves are different from the V_0 -CN curves. While coordination number increases, the interatomic distance d_0 also increases but not the atomic volume. Except for C, the cd structure has the shortest interatomic distance but has the largest atomic volume; however, it is opposite for the fcc structure. While checking the relation of interatomic distance and atomic volume, we found that the relation is dependent on crystal structure; the fcc structure is a more close-packed phase ($V_0 = 1/2 d_0^3$) than the cd

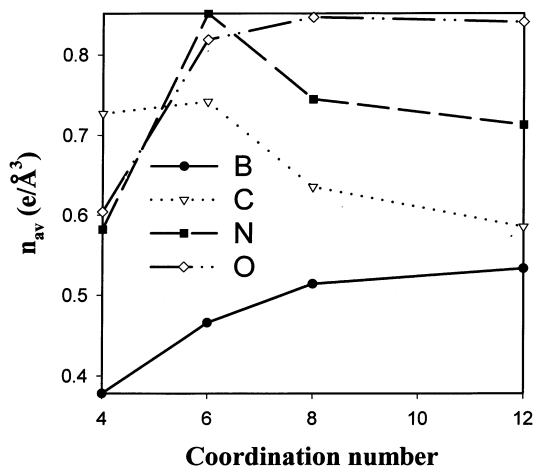


FIG. 4. Average charge density n_{av} of B, C, N and O with different coordination numbers.

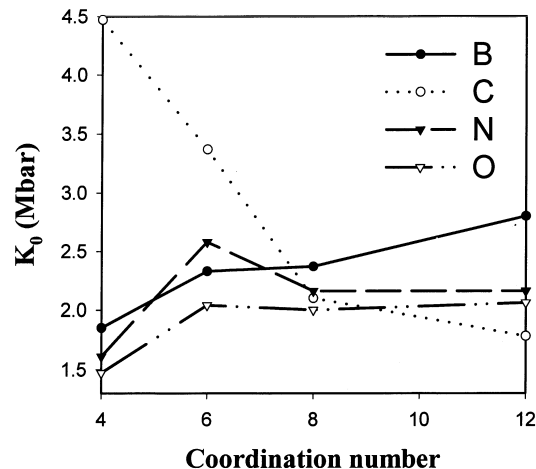


FIG. 5. Bulk modulus K_0 of B, C, N and O with different coordination numbers.

structure ($V_0 = 8 \cdot 3 \frac{D_0}{3d_0^3}$). The fcc structure has a larger interatomic distance but a smaller atomic volume and the cd structure has a smaller interatomic distance but a larger atomic volume. The exception is C, as mentioned above; carbon in the cd phase forms perfect tetrahedral bonding and makes a large shrinkage of volume; the atomic size increases as the coordination number increases.

The average charge density (n_{av}) and bulk modulus (K_0) are shown in Fig. 4 and 5, respectively. For the same element, the n_{av} and K_0 are correlated very well: the smaller n_{av} goes with smaller K_0 , but it is another story for different elements. The n_{av} of B is smaller than the other three elements. As CN increases, n_{av} and K_0 also become larger. Among the four phases of B, C, N and O, the bulk modulus of carbon in the cd phase is the largest one as expected, as diamond can form perfect tetrahedral bonding that is a perfect match of the sp^3 orbitals with tetrahedral coordination and the interatomic bonding is very strong. The carbon atom, lacking the inner p electrons, pushed the valence electron further inward and forms strong bonding between carbon atoms. In the case of C in the sc structure, the bulk modulus drops slightly, because the orientational matching of the four valence electrons with cubic coordination is not as ideal as that in a tetrahedron. However, the sc phase of carbon also has a remarkable K_0 , which is much closer to the K_0 of BN (3.67 Mbar) [19], i.e., probably, the second hardest material in the world. The phase of B with higher coordination number has larger bulk modulus, but the trend of bulk modulus is the opposite for carbon. For nitrogen, the sc phase has the largest K_0 ; K_0 decreases as CN increases and becomes flat from CN = 8 to 12. For oxygen, as CN is greater or equal to 6 the K_0 curve becomes flat. The fcc phase of B (2.8 Mbar) and the sc phase of N (2.58 Mbar) also have large bulk modulus, which are greater than the K_0 of a hard material called SiC (2.24 Mbar).

In Fig. 6 the bulk moduli of all structures considered in this research are plotted against the atomic volume. The first letter and the second number of the label neighboring the symbol represent the kind of atom and CN in various structures, respectively. The relationship of the bulk

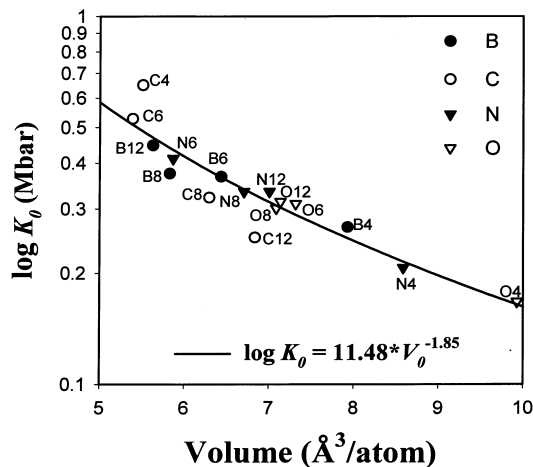


FIG. 6. The relationship between bulk modulus and atomic volume is represented by the solid line with the relation of $\log K_0 = 11.48 V_0^{-1.85}$. The first letter and the second number of the label neighboring the symbol represent the kind of atom and coordination number (CN) in various structures, respectively.

modulus in logarithmic scale and atomic volume appears to be approximately inversely linearly dependent. The relation may be expressed as $\log[\log K_0(\text{Mbar})] = 1.06 + 1.85 \log(V_0(\text{Å}^3))$ or $\log K_0 = 11.48 V_0^{-1.85}$ with a correlation coefficient of 0.998, which is represented by the solid line in Fig. 6. The bulk modulus may reflect the concentration of overlapped electron orbitals in a structure. C has the smallest atomic volume of the four elements studied, so it is uniquely capable of forming high bulk modulus structures. Thus, with all four valence electrons participating in covalent bonding, the cd structure of C has the highest bulk modulus of 4.47 Mbar. Although the p orbitals of carbon are not fully occupied for effective bonding in the octahedral coordination, its sc structure still possesses the second highest bulk modulus (3.37 Mbar) among various phases of the four elements. Thus, the single most important factor that determines the bulk moduli is atomic volume. The effects of composition and coordination on bulk moduli are secondary for B, C, N, and O.

IV. Conclusions

We have carried out a first-principles study for the crystal stability and equilibrium properties of boron, carbon, nitrogen and oxygen under high pressures. Among the cd, sc, bcc and fcc structures, the cd structure is the most stable phase of B and C while the sc structure is the second most stable phase. On the contrary, the sc structure is the most stable phase of N and O, while the cd structure becomes the second most stable phase. For the same element, the average charge density correlates with the bulk modulus very well; the phase with denser charge density usually correlates with larger bulk modulus. The cd phase of carbon has the largest bulk modulus of the four elements in our study, as expected and the sc phase of carbon also has a large bulk modulus (3.37 Mbar), which is lower than that of BN (3.67 Mbar) by 0.3 Mbar. The bulk moduli of B in the fcc structure (2.8 Mbar) and N in the simple cubic structure (2.57 Mbar) are also larger

than that of SiC (2.24 Mbar). From the relation of bulk moduli and atomic volume, we find the single most important factor that determines the bulk moduli is atomic volume and the effects of composition and coordination on bulk moduli are secondary for B, C, N, and O.

Acknowledgments

This work is supported partly by the National Science Council, Taiwan with grant number NSC-89-2112-M-165-002- and partly by the National Center for High-Performance Computing with grant number NCHC-86-01-009, Taiwan. The author (BRW) would like to thank the National Center for High-Performance Computing, Hsin-Chu, Taiwan for computer time on the IBM SP2 Workstations.

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