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Theoretical stability limit of diamond at ultrahigh pressure

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Based on density-functional total-energy pseudopotential calculations, we find that diamond structure carbon becomes energetically unstable relative to a highly distorted tetrahedrally coordinated structure at pressures above 5.0 Mbar. This distorted phase has a rhombohedral crystal structure containing eight atoms (denoted as the $R8$ structure) and has recently been identified experimentally as a pressure-induced metastable phase of silicon. This result has profound implications for ultrahigh pressure experimentation as it places a substantially lower limit on the maximum pressures attainable with diamond-anvil cell technology than was believed to exist previously.

The field of experimental high-pressure research continues to expand and find relevance in an increasingly diverse range of fields including physics, earth and planetary science, and materials processing. This is largely due to advances and refinements in diamond-anvil cell (DAC) technology.[1] Moreover, the DAC has opened opportunities to perform a vast array of experiments on samples under extreme compressions[2,3] such as x-ray diffraction, vibrational and optical spectroscopy, extended x-ray-absorption fine structure, Mössbauer spectroscopy, and nuclear magnetic resonance. It is now possible to routinely attain static pressures well into the multimegabar regime[4,5] and the highest static pressures ever reached approach 4.5 Mbar.[6] Despite the urge to generate increasingly high pressures in the laboratory, the maximum pressure which can be attained using DAC instrumentation is inherently determined by the pressure at which diamond itself becomes unstable. The importance of this issue has motivated many theoretical attempts to determine accurately this ultimate pressure limit.

A theoretical attempt to determine an upper bound on the stability of diamond-carbon focused on possible transformations to several simple hypothetical high-pressure structures.[7] These included the β-Sn, face-centered-cubic, body-centered-cubic, simple cubic, and hexagonal-close-packed structures. It was found that, among these candidate structures, diamond would first become unstable with respect to the simple cubic phase at a hydrostatic pressure of 23 Mbar with an accompanying 6% volume collapse at the transition. Interest in the ultrahigh pressure properties of diamond also motivated a study of the optical phonons and elasticity of diamond under megabar stresses.[8] The more complex $BC8$ structure (body-centered cubic with eight atoms per primitive cell) which is formed in silicon by decompression from metallic modifications provided a further candidate phase to which diamond might transform under pressure. The $BC8$ structure is fully specified by one lattice parameter and one variable atomic coordinate (x_0) with all atoms occupying equivalent crystallographic sites.[9,10] Theoretical total-energy calculations on carbon indicated that diamond would transform to $BC8$ at a pressure of 11–12 Mbar (Refs. 20 and 21) thus reducing the upper pressure limit on diamond stability by a factor of 2. $BC8$ carbon has been shown in a recent molecular-dynamics study[11] to be mechanically stable with respect to decomposition to lower energy modifications.

It has been very recently reported experimentally that even the metastable $BC8$ phase of silicon actually exists over only a very narrow pressure regime (0 to 20 kbar) and that at higher pressures it transforms to a topologically distinct rhombohedral structure containing odd-membered covalently bonded rings and highly distorted tetrahedral bonding.[12,13] This structure is called $R8$ as it is rhombohedral and contains eight atoms per primitive cell. The $R8$ structure is considerably more complex than $BC8$ as it is characterized by four variable atomic coordinates in addition to a rhombohedral angle. Atoms in the $R8$ structure occupy two inequivalent sites of the $\mathrm{R}\bar{3}$ space group. The greater structural freedom of R8 relative to $BC8$ allows for a greater capacity for volume reduction without energetically unfavorable bond compression. Thus the $R8$ structure represents an attractive candidate for a high-pressure modification of carbon.

In this paper we describe the results of first-principles total-energy pseudopotential calculations of the structural and electronic properties of carbon in the three tetrahedrally coordinated structures: diamond, $BC8$ and $R8$. The details of the calculations can be found elsewhere[14] and we include here only information particular to this application. Nonlocal ionic pseudopotentials were generated by the method described in Ref. 15 and were implemented using the Kleinman-Bylander scheme.[16] The electron wave functions were expanded in plane waves up to a cutoff energy of 408 eV and energy minimization achieved with a conjugate-gradients optimization algorithm. Calculations of energy as a function of volume were performed for each structure considered. For calculations on $BC8$ and $R8$ the internal structure was optimized with respect to atom positions through relaxation under the influence of Hellmann-Feynman forces until no force component exceeded 0.01 eV/Å. For the $R8$ calculations, the rhombohedral angle was also optimized. Calculations were performed using the the generalized gradient approximation (GGA) to exchange and correlation.[17] This has generally yielded more accurate calculated values for binding energies and equilibrium lattice parameters relative to experiment than the local-density approximation (LDA).[18] The number of k points used for each structure was

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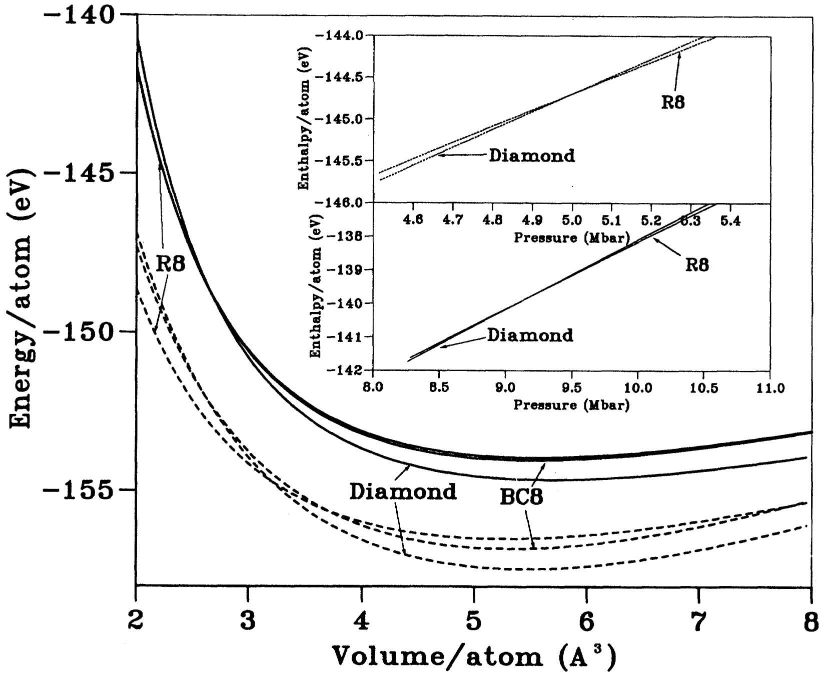

FIG. 1. Total energy vs atomic volume for carbon in the diamond, $BC8$ and $R8$ structures. These calculations were performed using the generalized gradient approximation to exchange and correlation. At pressures above 5.0 Mbar, the diamond structure becomes unstable with respect to $R8$. The inset shows the enthalpy vs pressure for diamond and $R8$ carbon and illustrates the transition to $R8$ at roughly 5 Mbar. The $BC8$ structure is found to be stable relative to diamond at pressures above 8.5 Mbar but unstable with respect to $R8$ at this pressure. By analogy with silicon, it is expected that $R8$ carbon would, upon decompression, transform to $BC8$ as a metastable phase below 2.4 Mbar.

four for diamond, four for $BC8$ and seven for $R8$ which converge energy differences to better than 0.001 eV/atom. It is found that the equilibrium lattice parameter of the diamond structure is 3.55 Å as compared to 3.57 Å from experiment. Otherwise identical *ab initio* calculations on diamond using the LDA gave a lattice parameter of 3.51 Å.[19]

The total energy as a function of atomic volume for the diamond, $BC8$, and $R8$ structures of carbon is shown in Fig. 1. The solid lines are fits to the Murnaghan equation of state for each structure. These results imply that diamond is unstable with respect to transformation to the $R8$ structure at pressures in excess of 5.0 Mbar. The predicted volume collapse at the pressure-induced diamond→$R8$ structural transition is 10%. We also find, in agreement with the earlier LDA calculations,[21,22] that diamond is unstable with respect to $BC8$ at a higher pressure, but our GGA calculations predict this to be 8.5Mbar, at which point R8 carbon is more energetically favorable by 0.8 eV/atom. It has previously been found that LDA overbinding is akin to a spurious pressure,[23] which is corrected in the GGA. Hence our calculations give a lower diamond→$BC8$ transition pressure. These total-energy curves further suggest that if it were possible to achieve the pressure required to form $R8$ carbon, then subsequent decompression might result in the formation of a truly metastable $BC8$ form of carbon at pressures lower than 2.4 Mbar. This is based on analogy with the known behavior of silicon and the relative ease with which $R8$ converts to $BC8$ on decompression.[12]

In the $R8$ structure, two atoms are located at positions (v,v,v), which we refer to as type-I, and the remaining six of type-II are located on equivalent general positions (x,y,z). For special values of the atomic coordinates[13] and a rhombohedral angle of 109.47°, the $R8$ structure reduces to the $BC8$ primitive cell. For $R8$ carbon, the unit-cell dimensions at a pressure of 5.0 Mbar are given by a = 3.13 Å with a rhombohedral angle $\alpha =$ 109.9°. The structural parameters as obtained by fully relaxing the atomic positions under Hellmann-Feynman forces are as follows: $v=0.280(1)$, $x=0.489(1)$, $y=0.993(1)$, and $z=0.290(1)$. The rhombohedral angle is found to be insensitive to applied pressure. We expect that under ambient conditions, the $BC8$ structure will be favored with a lattice parameter of $a=4.45$ Å, and a structural parameter $x=0.094(1)$.

The $R8$ structure allows for four distinct bonds. One of these is associated with bonds between type-I atoms (A bonds), another between atoms of unlike type (B bonds) and there are two distinct bonds (C and C') between type-II atoms. We will arbitrarily define the C bond as the shortest of the type-II contacts. The number of occurrences of each bond type is in the ratio of A:B:C:$C'=1$:6:3:6. An illustration of the $R8$ structure of carbon as obtained from the calculated relaxed structural degrees of freedom is shown in Fig. 2. All atoms are fourfold coordinated with type-I atoms connected to four nearest neighbors by one A bond and three B bonds. Type-II atoms are coordinated via one B bond, one C bond and two C' bonds. The values given for the structural parameters of $R8$ carbon at 5.0 Mbar give the shortest bondlength as 1.278 Å which is the C bond by our labeling convention. The next shortest bond is the B bond and is 1.282 Å in length. The C' bond is slightly longer at 1.294 Å. Thus, the B, C, and C' bonds are within 1% of each other in length while the A bond, between atoms of type-I, is about 5% longer than the average of the other three. These values for the atomic positional parameters also define a unique fifth-nearest-neighbor distance of 1.715 Å which does not correspond to a bond. This occurs between atoms of type-I along the [111] direction of the rhombohedral unit cell. The $BC8$ structure can be obtained from $R8$ by breaking the A bond and rebonding the fifth-neighbor atoms along this direction. This procedure removes five-membered rings. The bond topology and ring statistics of $R8$ carbon are identical

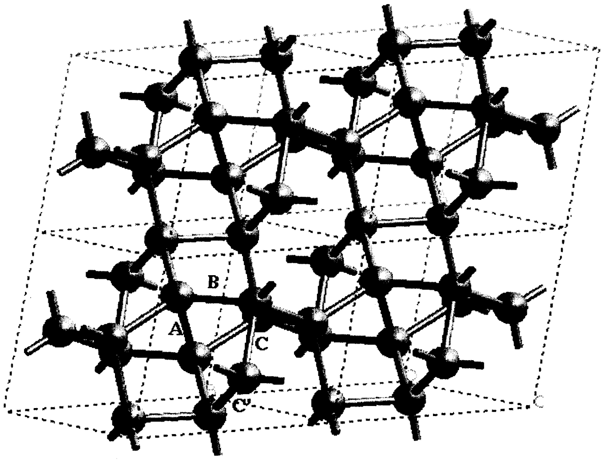

FIG. 2. Illustration of the $R8$ structure of carbon. The crystallographic spacegroup is $R\bar{3}$ and the atomic positions used for this figure are taken from the relaxed structure at 5.0 Mbar and are given in the text. The bonds are labeled according to the types of atoms which they join. Type-I atoms are joined to each other by A bonds, atoms of unlike type are joined by B bonds and type-II atoms are joined by C and C' bonds. The $R8$ structure is comprised of five-, six-, and eight-membered rings of bonds. A bonds are directed along the [111] crystallographic direction. In this figure four rhombohedral unit cells are shown.

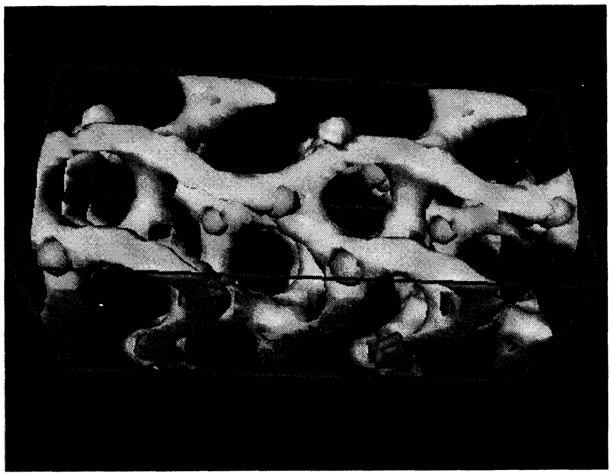

FIG. 3. Valence electron charge distribution for carbon in the $R8$ structure. All atoms in the $R8$ structure of carbon appear to be fourfold coordinated and there is no charge density between next-near-neighbor atoms. Integration of the charge density along the bond direction indicates that the A bond (between type-I) atoms is relatively weaker than the other bonds.

to those found for the metastable $R8$ phase of silicon:[12] all atoms are fourfold coordinated and the structure is comprised of five-, six-, and eight-membered covalent rings. There are no seven-membered rings in the $R8$ structure. Bond angles in the $R8$ structure of carbon are substantially distorted relative to ideal tetrahedral bonding. Specifically, in the five-membered rings bond angles range from 93.11° to 108.1°. The spread of bond angles which comprise the six-membered rings is somewhat larger—they range from 99.4° to 119.7°. The eight-membered rings include bond angles which range from 97.7° to 130.8°.

Some further insight into the nature of the stability and pressure response in $R8$ carbon can be obtained by considering the metastable ambient pressure structure. We find that the spread in bondlengths of the unstable ambient pressure structure is 16% which is considerably larger than the 5% spread found for the stable structure at 5 Mbar. We also note that the length of the B bond at ambient pressure exceeds that of the A bond. Thus pressure appears to have the effect of weakening the A bond with respect to the B bond. We will consider this further in a discussion of the valence charge distribution, below. It is also noted that the bond angles of $R8$ carbon remain relatively unchanged by the application of hydrostatic pressure.

The nature of the bonding in this stable high-pressure form of carbon is most directly examined by studying the valence electron charge distribution. The valence charge density is shown for $R8$ carbon at 5.0 Mbar in Fig. 3. It is evident from this figure that the valence electrons are concentrated in covalent bonds between the atoms and that each atom is clearly fourfold coordinated. A qualitative examination of the valence charge distribution reveals that all atoms are fourfold coordinated via covalent bonds. As expected from the comparison of bond lengths and interatomic separations given earlier, there is negligible electron density between next near-neighbor atoms.

We have attempted to quantify bond strength by numerically integrating the valence charge density contained in each bond. There is no unique procedure by which to achieve this, however an approximation can be made by defining space filling polyhedral regions around the bonds[19,24] and numerically integrating the enclosed discretized charge density. We find that the A and B bonds each contain 1.985 electrons while the C and C' bonds contain 1.919 and 2.057 electrons, respectively. These values are very close to the expected 2.0 electrons per bond in ideal covalent systems.

Self-consistent electronic energy band-structure calculations indicate that $R8$ carbon has a vanishingly small direct

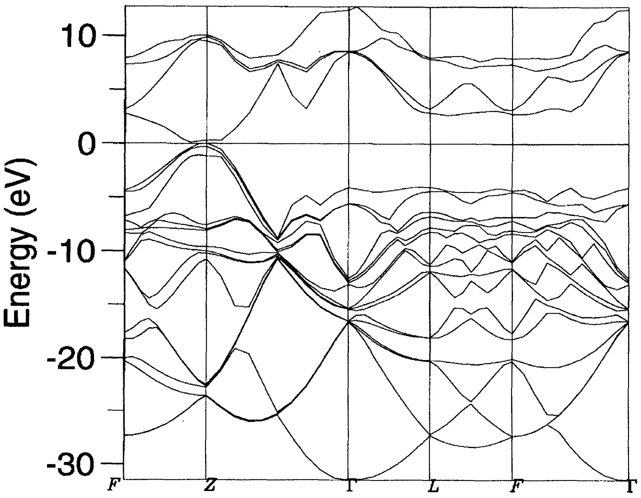

FIG. 4. Valence electron band structure for $R8$ carbon at 5.0 Mbar as calculated using the generalized gradient approximation. At this pressure it is found that the valence and conduction bands are in contact at the Z point of the Brillouin zone.

gap at the Z point of the Brillouin zone. The $R8$ band structure is shown in Fig. 4. The calculated gap of diamond structure carbon at 5.0 Mbar is found to be 6.7 eV. Gap closure in crystalline diamond has been predicted to occur at 9.1 Mbar.[25]

It should be emphasized that pressure-induced structural phase transformations in covalent tetrahedral semiconductors are often characterized by pronounced hysteresis effects. Therefore, in the present case of carbon, it is likely that a diamond-$R8$ transformation will encounter an energy barrier and therefore be inhibited by slow kinetics. This is due to the appreciable difference in bonding topology between the two structures. Thus the diamond-$R8$ pressure-induced transformation is likely to occur experimentally at pressures higher than the theoretical upper limit reported here. Although it is not clear whether such static pressures can actually be obtained in the laboratory, the predicted 5.0 Mbar transition is not far above the maximum pressures already reached.[6] This limit on diamond stability is particularly significant in view of the rapid progress in combined high-pressure/high temperature geophysics research. Under combined pressure/temperature treatment, the kinetics required for diamond to $R8$ conversion could be substantially accelerated.

In summary, we have presented a GGA total-energy study of high-pressure modifications of carbon. We find that diamond is predicted to transform under pressure to a highly distorted tetrahedrally coordinated structure denoted as $R8$ which has recently been identified a pressure-induced metastable modification of silicon. The $BC8$ structure is found to be unstable with respect to either diamond or $R8$ at any given pressure. The transition pressure at which diamond is predicted to transform to $R8$ is approximately 5.0 Mbar under hydrostatic conditions and this therefore represents the theoretical upper bound on diamond stability.

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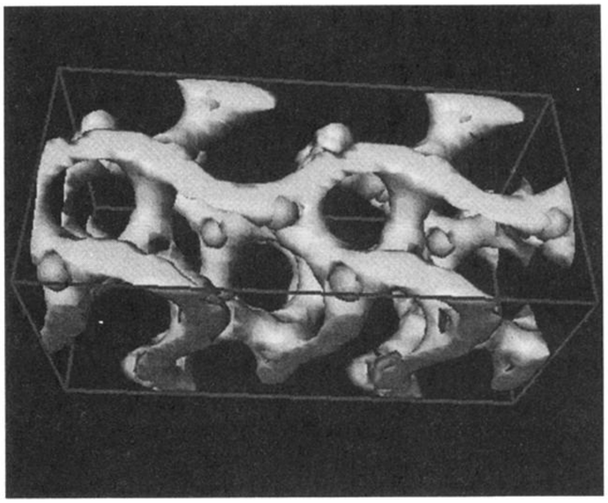

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