

Si-III (BC-8) crystal phase of Si and C: Structural properties, phase stabilities, and phase transitions

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With use of the pseudopotential local-density-functional approach, the lattice constant, the x parameter for atomic coordinates, and the phonon frequency of the mode Γ_1^+ are calculated for the Si-III (BC-8) crystal phases of Si and C. The results agree well with available experimental data for the BC-8 phases of Si. From the total-energy curves of the diamond and the BC-8 phases of Si, we find that the BC-8 phase of Si is not stable at ambient pressure or at high pressure. The diamond-BC-8 (I-III) transition of Si will not occur quasistatically. Comparing the diamond, the BC-8, and the simple-cubic phases of C, we find that diamond will first transform to the BC-8 phase at 12 Mbar and then to the simple-cubic phase at 27 Mbar under quasistatic conditions.

The Si-III (BC-8) crystal phase is found in Si when the high-pressure β -tin phase (Si-II) is unloaded to ambient pressure.¹ It has a body-centered-cubic structure with eight atoms per primitive cell (Fig. 1). The space group is $Ia\bar{3}$ (T_h^7) and atoms are at 16(c) positions² with an x -parameter value of 0.1003 ± 0.0008 at ambient pressure. It is of interest to study the structural properties, the phase stability, and possible pressure-induced phase transitions associated with this phase from first principles. Furthermore, calculations³ show that the simple metallic phases of C have small cohesive energies and relatively large equilibrium volumes as compared with diamond. This was attributed to its atomic properties that the valence $2p$ electrons of carbon are tightly bound and the orbitals beyond the valence $2s, 2p$ orbitals are loosely bond (having a principal quantum number at least 3). In other words, carbon atoms strongly favor sp^3 bonding. This motivated us to investigate the BC-8 phase of C as a possible phase into which diamond will transform under high pressure because it consists of distorted tetrahedra without large change in interatomic separations and is basically sp^3 bonded.

In this paper, we report calculated results of the equilibrium lattice constants, the x parameters for atomic coordinates, and the phonon frequencies of the Γ_1^+ mode for BC-8 phases of Si and C. These results agree well with available experimental data for the BC-8 phase of Si. We find that the BC-8 phase is metastable at zero pressure for both Si and C. For Si, the diamond-BC-8 transition requires a pressure of 130 kbar. This pressure is higher than that of the diamond- β -tin transition, and thus will not occur quasistatically. In contrast, the BC-8 phase of C is energetically favorable at high pressure. Comparing the BC-8 and the simple cubic (sc) phases of C, we find that diamond will first transform to the BC-8 phase at 12 Mbar and then transform to the sc phase at 27 Mbar under quasistatic conditions (in thermodynamic sense).

The present calculations are performed using the *ab initio* pseudopotential theory⁴ within the local-density-functional (LDF) formalism.⁵ The *ab initio* pseudopotentials

of Si and C are generated using the method proposed by Hamann, Schlüter, and Chiang.⁶ These pseudopotentials have been shown to give accurate results for the structural properties of the diamond phase of Si and C.^{7,8} For a given lattice constant, we solve the pseudopotential Schrödinger equation selfconsistently using a plane-wave basis set with a kinetic-energy cutoff E_{PW} of 11.5 Ry for Si and 35 Ry for C. Eight special \vec{k} points⁹ in the irreducible Brillouin zone are sampled.¹⁰ The total energy is calculated in momentum space¹¹ and the Wigner interpolation formula¹² for the exchange-correlation energy is used.

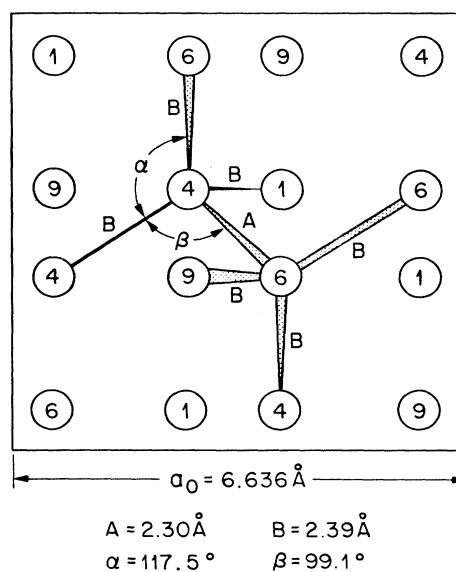


FIG. 1. Projection of the BC-8 (Si-III) structure on (001). Elevations (in $a_0/10$) are given by the numbers inside the circles. (After Wentorf and Kasper, Ref. 1.)

We find that the BC-8 phases of Si and C are poorly conducting semimetals in the present LDF calculations.¹³ There are about 0.01 electrons (per primitive cell) in the occupied conduction band for the BC-8 phase of Si at $a = 6.636 \text{ \AA}$ and 0.007 electrons for C at $a = 3.51 \text{ \AA}$. The conduction-band minimum is below the valence-band maximum (both at point H) by 0.61 eV for Si at $a = 6.636 \text{ \AA}$ and 1.2 eV at $a = 3.51 \text{ \AA}$ for C (Ref. 14). This is consistent with the experimental finding¹ that Si-III is more metallic than ordinary Si-I.

Total energies of the BC-8 phases of Si are calculated at six lattice constants ranging from 6.11 and 7.13 \AA . The x parameter for the atomic coordinates is fixed at the experimental value (0.1003) and the results are least-squares-fit to the Murnaghan equation of state.¹⁵ The derived equilibrium lattice constant a_0 is 6.67 \AA , the bulk modulus is 0.96 Mbar, and the equilibrium total energy E_{\min} is 0.13 eV/atom higher than that of the diamond phase (Si-I).¹⁶ This agrees well with the experimental finding¹ for the BC-8 phase of Si that it is metastable at ambient pressure and a_0 is 6.636 \AA .

We find that the BC-8 phase is unstable even at high pressure as shown in the total-energy plot¹⁷ of the BC-8, the diamond, and the β -tin phases of Si (Fig. 2). Although a tangent can be drawn between the diamond and BC-8 total-energy curves, it has a larger slope than that between diamond and β -tin curves. Quantitatively, the diamond-BC-8 transition requires a higher pressure (130 kbar in the present calculation) than the pressure needed for the diamond- β -tin transition (calculated at 99 kbar, measured¹⁸ at 125 kbar).

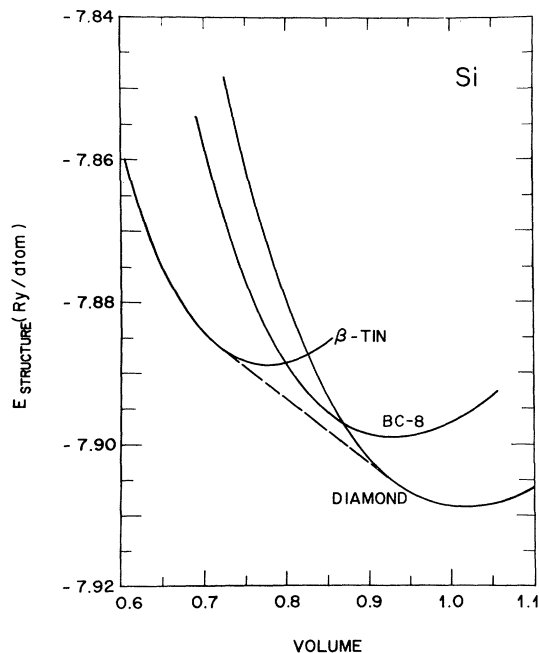


FIG. 2. Total-energy curves of the diamond, the BC-8, and the β -tin phases of Si as a function of volume normalized to measured diamond equilibrium volume. The dashed line is the common tangent of the diamond and the β -tin curves.

If our prediction that Si-III is not stable even at high pressure is true, the fact that Si-III is observed when the pressure is reduced from Si-II implies that the activation energy for the II-III transition is smaller than that of the II-I transition. This implication can be qualitatively understood by structural comparisons among these three phases. A II-I transition can be accomplished by changing the c/a ratio from 0.552 to $\sqrt{2}$. This path is not likely because (i) the activation energy may well be large considering such a large change of c/a and (ii) it takes a coherent motion of the whole lattice. Since all of the three phases have a common feature that they consist of honeycomblike double layers [(111) of Si-I, (101) of Si-II, and (001) of Si-III], we suggest that when the phase transition occurs, atoms do not move into or out of parallel double layers, and bond ruptures and formations occur mainly between parallel double layers. If so, the activation energy of the II-III transition may well be smaller than that of the II-I transition because of the following reasons. The stacking sequence of double layers is of $ABCABC$ type for Si-I, of $ABAB$ type for Si-III, and of $ABA'B' \dots$ type for Si-II. With a slight uniform displacement and simple alternating bond ruptures and formations,¹⁹ A' (B') of Si-II can be made equivalent to A (B). Because of similar type of stacking sequence for Si-II and Si-III, the II-III transition involves bond breaking and atom rearrangement to a lesser extent than the II-I transition. Consequently, the II-III transition rate may be much higher than the II-I transition rate, which facilitates the formation of the metastable Si-III phase as observed in decompression experiments. The present study indicates that the II-III transition will occur at 76 kbar.

We have also done similar calculations²⁰ for the BC-8 phase of C using $E_{\text{PW}} = 35 \text{ Ry}$. The calculated a_0 for the BC-8 phase of C is 4.51 \AA and the bulk modulus is 4.0 Mbar. It is about as dense as diamond with bond lengths within 5% of the measured value of diamond. In addition, the total-energy curves of the diamond and the

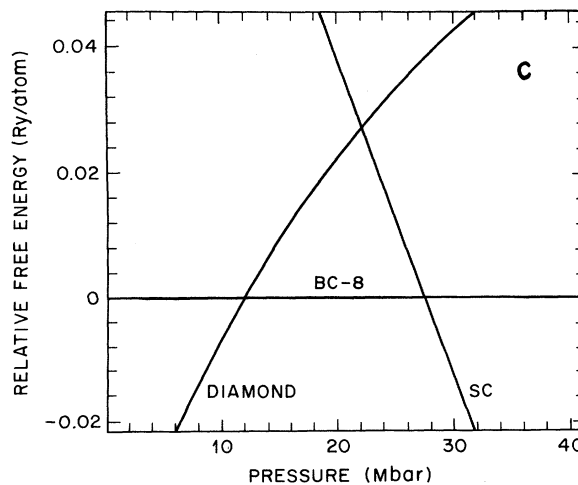


FIG. 3. Relative Gibbs free energy curves of the diamond, the BC-8, and the sc phases of C as functions of pressure.

TABLE I. Transition pressures and volumes for the three pressure-induced phase transition involving the diamond, BC-8, and sc phases of C. Volumes are normalized to the measured diamond equilibrium volume.

	Transition pressure (Mbar)	Initial volume	Final volume
diamond—BC-8	12	0.468	0.456
BC-8—sc	27	0.345	0.326
diamond—sc	22	0.379	0.352

simple-cubic phases of C are also calculated using the same E_{PW} for the phase-stability comparison. It is found that the BC-8 phase has E_{\min} 0.62 eV/atom higher than that of diamond, and thus is metastable at zero pressure. To examine the relative phase stabilities under high pressure, we plot relative free energy versus pressure curves for the diamond, the sc, and the BC-8 phases of C in Fig. 3. (The free energy is relative to the BC-8 phase, i.e., the BC-8 curve is just the x axis.) As shown in Fig. 3, diamond will transform to the BC-8 phase at 12 Mbar and then transform to the sc phase at 27 Mbar under the quasistatic condition. The direct diamond-sc transition at 22 Mbar is not energetically favorable if the BC-8 phase is taken into consideration as in the present study.²¹ The transition pressures and volumes for phase transitions among the three phases of C are given in Table I. We note in passing that since the quasistatic condition is difficult to achieve in an experiment of such high pressure, the activation energies and the nonhomogeneous stress may affect the transitions. Taking into consideration the fact that upon unloading Si-II transforms to Si-III and Si-III persists at ambient pressure, the activation energy may be large for the III-I transition and for the I-III transition as well. Since the directional bonding is even stronger for C, it is possible that the diamond—BC-8 transition in C may be too slow to be observed in a short time interval. As pressure increases, the effect from the activation energy is expected to become smaller because the covalency decreases and the metallicity increases. This suggests that the transition to the sc phase may occur more readily.

We have also tested different functional forms^{22–24} for the exchange-correlation energy. It is found that the re-

sults do not differ significantly from the corresponding results using the Wigner interpolation formula. For example, the diamond—BC-8 transition pressure becomes smaller by less than 5 kbar for Si (0.3 Mbar for C), and the transition volumes change by less than 3%.

Beside volume, the BC-8 phase has another structural degree of freedom with no loss of symmetry, i.e., the x parameter for atomic positions, which we will investigate in the following. The x parameter is varied from 0.098 to 0.1026 in the total-energy and force calculations of the BC-8 phase of Si at the measured lattice constant (6.636 Å). The energy results are then fitted to a third-order polynomial of the x parameter.²⁵ The minimum-energy x parameter x_0 so derived is 0.1015. The variation of the x parameter corresponds to a phonon normal mode. The associated phonon frequency [$\nu(\Gamma_1^+)$] is 12.14 THz derived from the second-order coefficient. These results agree well with the value of 0.1003 ± 0.0008 and 12.48 THz found experimentally.^{1(b),26} The calculated cubic anharmonic force constant (k_3) is $-2.12 \text{ Ry}/\text{Å}^3$. Similar variation of x parameter is also done for the BC-8 phase of C at $a = 3.51 \text{ Å}$.²⁷ The calculated values of x_0 , $\nu(\Gamma_1^+)$, and k_3 are 0.1026, 58.8 THz, and $-40.9 \text{ Ry}/\text{Å}^3$, respectively.²⁸ In these calculations, we find the minimal energy is smaller than the total energy at $x = 0.1003$ by only a small amount: $\sim 0.1 \text{ mRy/atom}$ for Si and $\sim 1 \text{ mRy/atom}$ for C. The fact that the total energy is relatively insensitive to the x parameter justifies our procedure of using a fixed x parameter (0.1003), instead of relaxing the x parameter for each volume, in the phase-stability and phase-transition study. The error in transition pressure caused by such a procedure is less than 5%.

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²*International Tables for X-Ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch, England, 1952), Vol. I, p. 315.

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⁴See, e.g., M. T. Yin and M. L. Cohen, *Phys. Rev. B* **25**, 7403 (1982), and references therein.

⁵P. Hohenber and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

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⁸M. T. Yin and M. L. Cohen, *Phys. Rev. B* **24**, 6121 (1981).

⁹D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5189 (1976).

¹⁰The convergence in crystalline total-energy difference with respect to E_{PW} is estimated to be $\sim 1 \text{ mRy/atom}$ for Si and $\sim 10 \text{ mRy/atom}$ for C. The convergence in total energy with respect to number of sampled \vec{k} points is estimated to be less than 1 mRy/atom.

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¹²E. Wigner, *Tran. Faraday Soc.* **34**, 678 (1938); D. Pines, *Solid State Phys.* **1**, 375 (1955).

¹³We caution that the semiconductor band gaps calculated using the local-density-functional theory do not agree with experiment. (See Ref. 7.) The BC-8 phase of Si was found semicon-

- ducting ($E_g=0.43$ eV) using the empirical pseudopotential approach. [J. D. Joannopoulos and M. L. Cohen, *Phys. Rev. B* **7**, 2644 (1973).]
- ¹⁴Because the fraction of electrons in the occupied conduction band is small, its contribution to total energies and atomic forces is negligible.
- ¹⁵F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).
- ¹⁶The estimated numerical errors for the calculated a_0 and E_{\min} are about 1% and 0.01 eV/atom, respectively.
- ¹⁷The total-energy curves of the diamond and the β -tin phases of Si are quoted from Ref. 7.
- ¹⁸See M. C. Gupta and A. L. Ruoff, *J. Appl. Phys.* **51**, 1072 (1980) for a summary of experimental data.
- ¹⁹The bond ruptures and formations involved in transforming from the Si-II honeycomb layer to the Si-III honeycomb layer do not require large energy because in the process some atoms which were originally 1.25 bond lengths apart come together to form bonds, and some bonds are broken in such a way that end atoms are 1.25 bond lengths apart. The atomic movements are relatively small (i.e., 0.25 bond length) compared with complete bond breaking.
- ²⁰We calculate the total energies of the BC-8 phase of C for eight volumes ranging from $0.33\Omega_0$ to $0.61\Omega_0$ (Ω_0 is the measured volume of diamond). Since the calculated equilibrium volume is $1.011\Omega_0$ (an extrapolation), the errors in the calculation of a_0 and E_{\min} are relative large (about 2% and 0.05 eV/atom, respectively). The final volume of the diamond-BC-8 transition is within the volume range of our calculation.
- ²¹This is to be compared with the value 23 Mbar calculated (Ref. 3) using $E_{\text{PW}}=50$ Ry, which suggest that the convergence error of the transition pressure with respect to E_{PW} is less than 10%.
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- ²⁵Fitting the force results to a second-order polynomial of the x parameter gives almost the same results.
- ²⁶R. J. Kobliska, S. A. Solin, M. Selders, R. K. Chang, R. Alben, M. F. Thorpe, and D. Weaire, *Phys. Rev. Lett.* **29**, 725 (1972).
- ²⁷This is close to the lattice constant of the BC-8 phase of C at the diamond-BC-8 transition.
- ²⁸The Ewald constant as a function of the x parameter of the BC-8 phase has a minimal value -1.7325082 at $x=0.125$. The BC-8 phase is symmetric with respect to $x=0.125$, as is the Ewald constant. As the volume decreases, the system becomes more metallic and x_0 increases toward the value 0.125.