

Complex tetrahedral structures of silicon and carbon under pressure

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We report self-consistent density-functional calculations of the energy and enthalpy of silicon and carbon in the fully relaxed complex B-8 structure (bcc with 8 atoms per cell). We find B-8 to be unstable in Si, with enthalpy slightly higher than the diamond and β -tin phases. B-8 is found to be a stable phase of C above 12 Mbar, which is a new stability limit for diamond.

The elements Si and Ge are known to exist in complex crystal structures, B-8 (body-centered cubic with 8 atoms per cell) and T-12 (simple tetragonal with 12 atoms per cell), which can be formed under pressure and are metastable at zero pressure.¹⁻³ This family of structures has densities intermediate between diamond and the more closely packed metallic structures, which are achieved by distorted tetrahedral coordination and connectivity topologically different from diamond. The phase diagrams of group-IV elements therefore have a rich variety of possibilities and a complete theoretical study must include these dense, covalent structures. The consequences of such a study of the high-pressure phase diagram of carbon are particularly interesting because little is established experimentally despite many searches and proposals⁴ and because of the importance of the stability of diamond for high-pressure diamond-anvil cells.⁵

In this paper we report results^{6,7} of *ab initio* density-functional calculations for Si and C in the complex structures compared to the diamond and metallic phases considered in previous work.⁸⁻¹² We give extensive results for B-8 and limited results for other structures. In order to predict the properties of such complex structures, we utilize the simultaneous calculation of energy E , forces, pressure P , enthalpy $H = E + PV$, and macroscopic stresses.⁹ These structures are relaxed so that the forces on the ions are zero and, in the case of noncubic structures, the stress is isotropic. The calculations are performed with *ab initio* ionic pseudopotentials,¹³ the local-density approximation (LDA) using the Wigner interpolation form for exchange and correlation, and plane-wave basis sets. These have been shown to lead to properties near equilibrium accurate to within a few percent,⁸⁻¹² and to pressures for the transitions to many simple metallic structures.^{8,10} In particular, Yin and Cohen^{8,10} have

described the diamond-to- β -tin transition in Si (Ref. 8) and also found that diamond carbon is stable with respect to all simple metallic phases tested up to extremely high pressures¹⁰ (23 Mbar, where the volume is compressed to $\frac{1}{3}V_0$).

First, we discuss Si where the existence and many properties of the B-8 phase are established.¹⁻³ In this structure the atoms form sixfold rings with each atom connected to four neighbors by one type- A bond and three type- B bonds with two distorted bond angles ($\approx 99^\circ$ and 117°). Though more dense, the average nearest-neighbor (NN) distances in B-8 are larger than in diamond. The bond angles and the difference between the bond lengths r_A and r_B are determined by the internal parameter of the structure x . The distortion of the angles from tetrahedral is a monotonically increasing function of x , whereas $r_A < r_B$ for $x < 0.1036$, but $r_A > r_B$ for $x > 0.1036$. We have determined the relaxed structure at each volume by finding the value of x where all forces vanish. Although calculations for B-8 are much more difficult than for any of the phases previously considered,⁸⁻¹² we have been able to carry out the calculations with similar accuracy to previous work. Computational details are given in Ref. 14. In Fig. 1 is shown the energy versus volume for Si in the diamond, B-8, and β -tin structures, determined by fitting the Murnaghan equation of state to energies calculated at seven, five, and eight volumes in each phase, respectively. We find the equilibrium B-8 structure at $V/V_0 = 0.903$ ($V_0 = 20.024 \text{ \AA}^3$ is the experimental Si volume) and $x = 0.1022$, in satisfactory agreement with the experimental results,¹ $V/V_0 = 0.912$ and $x = 0.1003 \pm 0.0008$. The calculated minimum energy for B-8 is 0.13 eV/atom higher than for diamond. The common tangent between diamond and B-8 has a pressure of 107 kbar, at which point the enthalpies of B-8 and diamond become equal.

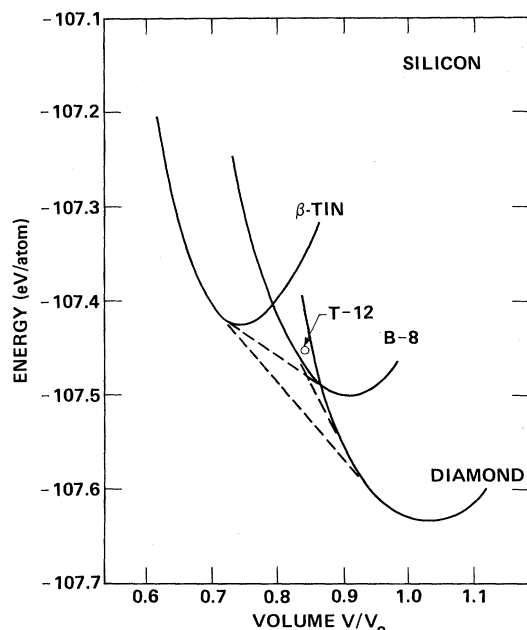


FIG. 1. Energy of silicon in the relaxed B-8, diamond, and β -tin phases as a function of reduced volume. The T-12 energy is shown at one volume. The dashed common tangent lines show that the stable phases under pressure are diamond and β -tin. B-8 and T-12 are at slightly higher enthalpy and may be formed only metastably.

The parameter x increases to 0.105 at the transition point, i.e., the angular distortions increase and the difference $r_A - r_B$ changes sign with pressure. Calculation of the force as a function of the parameter x also leads to a predicted frequency for the Γ_1 Raman mode of 410 cm^{-1} compared to the measured value¹⁵ of $(416 \pm 12) \text{ cm}^{-1}$. From this frequency it is straightforward to show that calculating the relaxed values of x , compared to holding x fixed at the experimental value, lowers the transition pressure by $\sim 15 \text{ kbar}$. The present results find B-8 Si to be a semimetal, within the LDA, with bands touching at the H point in the Brillouin zone (BZ), and a small Fermi surface caused by overlap of $\sim 0.34 \text{ eV}$ of bands between H and F . These results differ from previous empirical pseudopotential calculations³ which found a direct gap. The calculated B-8 energies are insensitive to the Fermi surface, which contains less than 0.2 electrons out of a total of 32 electrons per cell, causing an energy change of $< 0.005 \text{ eV/atom}$.

In order to compare the different structures we have carried out calculations on diamond and β -tin with the same plane-wave cutoffs as for B-8 and with the c/a ratio optimized for β -tin as described in Ref. 16. The results for β -tin give transition volumes very close ($< 2\%$) to those of Yin and Cohen,⁸ and a somewhat lower transition pressure ($\sim 70 \text{ kbar}$). As shown in Fig. 1 the B-8 energy is just above the common tangent for diamond and β -tin, i.e., the enthalpy of the B-8 phase is slightly too high for it to actually be stable at any pressure. The observed formation of the metastable B-8 phase from β -tin as pressure

is released¹ is consistent with our findings. Metastability with respect to diamond can be understood because the different topologies require breaking and reforming many tetrahedral bonds, leading to large energy barriers. On the other hand, consideration of the sixfold coordination of β -tin suggests that barriers are smaller for the transition from β -tin to either B-8 or diamond. Finally, B-8 being more stable than β -tin at low pressures is essential for the growth of a nucleated B-8 phase.

Also shown in Fig. 1 is a calculation at one volume for the more complex T-12 phase where the atoms form five- and seven-member rings. The five free parameters of T-12 were relaxed approximately with the result that the energy is very close to B-8. Thus we find that both structures are nearly stable in silicon. Since the energy is close to that measured¹⁷ [$(0.123 \pm 0.007) \text{ eV/atom}$] for amorphous Si, this suggests the possibility of many structures of different topological connectivity, with similar energies.

We have also investigated the stability of C in diamond, B-8, and the structure of Ref. 19 (MSG). In Fig. 2 is shown energy versus volume for diamond with a very large basis set¹⁸ (curve labeled A) leading to $V/V_0 = 0.982$, $B = 4.94 \text{ Mbar}$, and $dB/dP = 2.6$, in good agreement with previous calculations^{10,11} and experiment ($V_0 = 5.673 \text{ \AA}^3$, $B = 4.42 \text{ Mbar}$, and $dB/dP \sim 4$). A

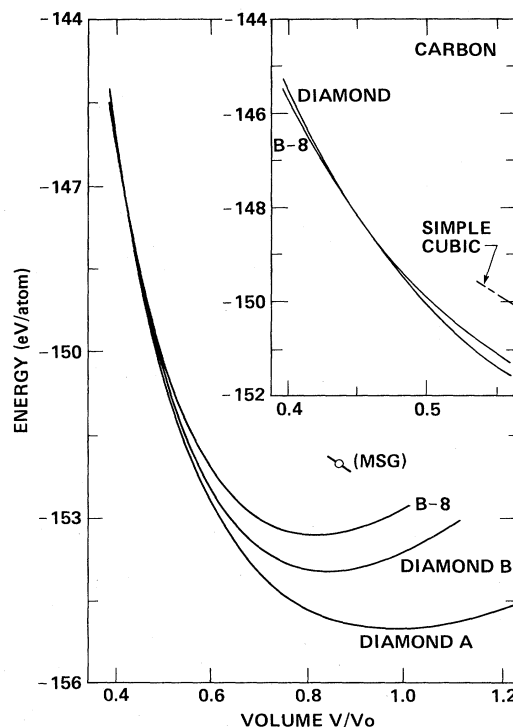


FIG. 2. Energy of carbon in the diamond and B-8 phases as a function of reduced volume. Curves A and B are for larger and smaller basis sets (see Ref. 18) and show that the smaller set used for B and for B-8 are accurate at small volumes near the transition. The inset shows the region where B-8 becomes stable. The energy of the simple-cubic phase from Ref. 10 is shown for comparison. The structure proposed in Ref. 19 (MSG) is high in energy and pressure.

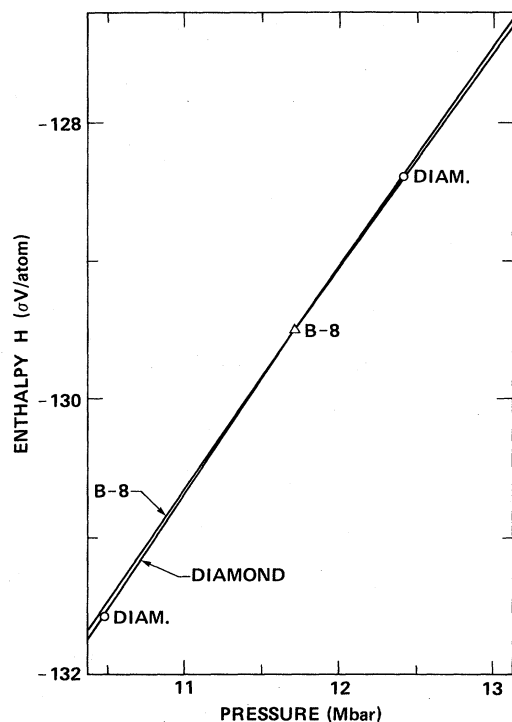


FIG. 3. Enthalpy $H = E + PV$ of carbon in the diamond and B-8 phases as a function of pressure P , showing the transition at 12 Mbar. The points are calculated directly and the curves are fitted equations of state from Fig. 2.

smaller basis set, comparable in size to that for Si,¹⁴ was used for B-8 and for the diamond curves labeled *B*. Comparison of curves *A* and *B* in Fig. 2 shows that, although the larger basis set is needed near the equilibrium volume, the smaller set is sufficient near the predicted transition. The inset shows that B-8 is lower in energy than diamond for $V/V_0 < 0.45$ and well below the simple-cubic phase,

taken from Ref. 10. The calculated x parameter varies from 0.0955 at $V/V_0 = 0.85$ to 0.1030 at $V/V_0 = 0.45$. As in Si, the valence and conduction bands touch at H , so there is no gap within the LDA. Figure 3 shows the enthalpies versus pressure from Fig. 2 and from direct calculations of E and P , which give a transition pressure of 12 Mbar and volume change of $0.011V_0$. Although this is a high pressure, it is much lower than the pressure of 23 Mbar found previously¹⁰ for transitions to simple metallic phases. However, diamond may transform to another structure, not considered so far, at a pressure lower than 12 Mbar. These conclusions on the stability of diamond rest upon the assumptions of the LDA and rigid ionic pseudopotentials at the greatly compressed volumes. The latter could be checked by all-electron calculations.

In conclusion, we have shown that density-functional calculations of energy, force, and stress are powerful tools for predicting properties of complex structures. Calculations for fully relaxed B-8 Si find it to be slightly higher in enthalpy than the diamond and β -tin phases, so that B-8 Si can be formed only as a metastable phase. The B-8 and T-12 structures were found to be close in energy, indicating that their local bonding geometries are candidates for describing distorted structures such as surface reconstructions and amorphous systems. For carbon we find the B-8 phase to be stable above 12 Mbar and to transform only at much higher pressures to the simple metallic phases previously considered.¹⁰ This is a new limit on the stability of diamond.

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¹⁴The basis set for all Si calculations was plane waves up to 12 Ry (~ 84 plane waves per atom near $V/V_0 = 0.9$). Plane waves from 6–12 Ry were treated in a second-order Löwdin Scheme (Ref. 9). The effect of the Löwdin approximation is small, < 2 kbar for the pressure of the diamond-to- β -tin transition. Integrations over the BZ were done with \vec{k} -point sets of one, two, four, and seven \vec{k} points for B-8, two and ten \vec{k} points for diamond, and one and six \vec{k} points for T-12. While the smaller sets were adequate for relative energies within each phase, absolute energies were fixed with the respective seven-, ten-, and six- \vec{k} -point calculations. A large

number of points (40) was used for the metallic β -tin phase.

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¹⁸Diamond *A* was computed with a constant number of ~ 215 exact plane waves per atom (an energy cutoff of ~ 50 Ry at equilibrium and 80 Ry near the transition), while diamond *B*

and B-8 used ~ 85 plane waves per atom ($\sim \frac{1}{2}$ exact, $\frac{1}{2}$ Löwdin). We found one and two \vec{k} points to be sufficiently accurate by comparison to calculations with two and ten \vec{k} points for B-8 and diamond, respectively.

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