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Will Diamond Transform under Megabar Pressures?

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It is predicted that among the fcc, bcc, hcp, simple cubic, and β-tin phases, diamond will first transform to the simple cubic phase under a hydrostatic pressure of 23 Mbar. The absence of p electrons in the core causes remarkably strong sp^3 bonding in diamond. This stabilizes diamond against the other five phases under high pressures. The study is carried out using *ab initio* pseudopotential theory within the local-density-functional formalism.

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The diamond-anvil-cell technique for generating very high pressures has been widely used in ultrahigh-pressure research.[1] This approach has contributed significantly to discoveries of new states of matter and to our understanding of physical phenomena at ultrahigh pressures. Because of the unique hardness and stability of diamond, pressures as high as 1.7 Mbar have been ingeniously achieved.[2] Since experimentalists are attempting to reach even higher pressures, it becomes important to investigate, on theoretical grounds, the possible phase transformations of diamond at very high pressure and to obtain an estimate of the upper bound of pressures achievable by diamond anvil cells. In this Letter, total energies as a function of volume are calculated for the diamond phase and the following five phases of carbon: β tin, simple cubic (sc), fcc, bcc, and hcp. We predict that among the five phases aforementioned, diamond will first transform to the sc phase under a hydrostatic pressure of 23 Mbar accompanied by a 6% volume change. The relative positions of the total-energy–versus–volume curves of the six solid phases of carbon differ from those of Si and Ge belonging to the same group in the periodic table. In particular, the calculated zero-pressure volume of diamond is either close to or even smaller than those of the other five phases, which seems to defy the common notion that the diamond structure is an open structure and should have a larger atomic volume than those of close-packed structures. This apparent controversy can, however, be understood in light of the atomic properties of carbon that its valence p orbitals are tightly bound and its excited orbitals beyond valence are loosely bound. The surprising finding that diamond is effectively "close packed" inhibits the phase transformation at highly hydrostatic pressures.

The present study is carried out by use of the *ab initio* pseudopotential theory[3] within the local-density-functional formalism.[4] This approach has been shown to yield accurate estimates of the structural properties of solids (see, e.g., Refs. 5–13). In particular, the calculated transition pressures and transition volumes of Si and Ge agree[5] very well with experiment. The *ab initio* pseudopotential of carbon used in the present study is generated[14] by the method proposed by Hamann, Schlüter, and Chiang.[15] Pseudoatomic calculations have been performed for several atomic configurations to assure that the pseudoatomic results agree very well with all-electron atomic results. For a given lattice constant of a phase, we solve[16] the pseudopotential Schrödinger equation self-consistently using the Wigner interpolation formula[17] for the exchange-correlation energy. The total energy is then calculated in momentum space.[18] A plane-wave basis set with a kinetic energy cutoff of 50 Ry is used to represent valence wave functions. By keeping the kinetic energy cutoff the same, the valence charge density is calculated to the same degree of accuracy for different crystal structures. This facilitates an accurate comparison of total energy between different phases.

Total energies at about fifteen lattice constants are calculated for each of the six phases chosen. These data are then least-squares fitted with the Murnaghan equation of state.[19] The resultant total-energy–versus–volume curves are shown

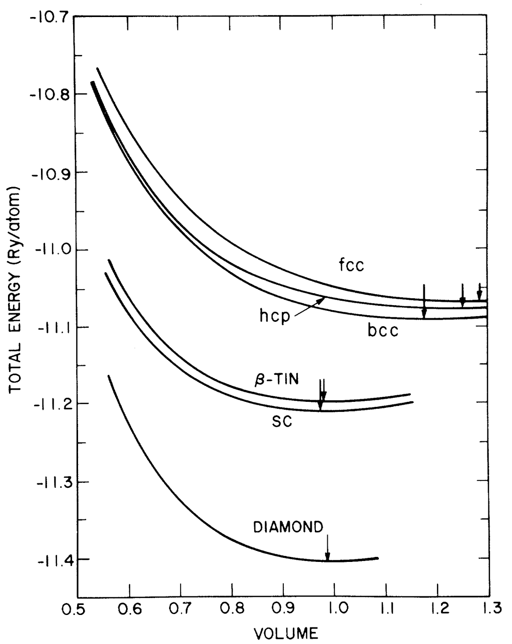

FIG. 1. Total-energy curves of the six phases of carbon as a function of the atomic volume normalized to Ω_0.

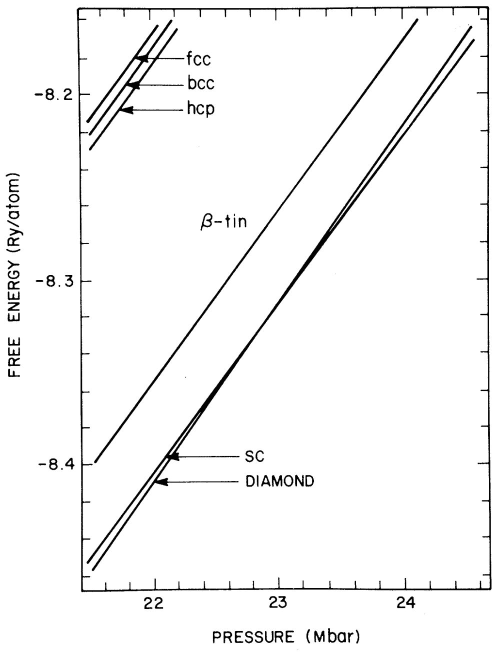

FIG. 2. Zero-temperature free energy of the six phases of carbon as a function of pressure.

in Fig. 1. The minimum total energy per atom ($E_{\rm min}$), the relative total energy difference $\Delta E_{\rm min}$ ($\equiv E_{\rm min} - E_{\rm min}^{\rm diamond}$), and the corresponding atomic volume ($\Omega_{\rm min}$) for each phase of carbon are given in Table I. The insulating diamond phase is found to be more stable than the other five metallic phases. The calculated zero-pressure volume of diamond differs from the experimental value[20] (Ω_0) by less than 2%.

It is clear from Fig. 1 that diamond will not transform to the other five phases within the volume range from Ω_0 to $0.6\Omega_0$, which corresponds to ~5 Mbar. To study the relative stabilities of the six phases under even higher pressure, we have carried out total energy calculations for smaller volumes up to $0.3\Omega_0$. Since the core size is less than $0.1\Omega_0$, the neglect of core relaxation in the pseudopotential frozen-core approximation is still justified. Plotted in Fig. 2 are curves of zero-temperature Gibbs free energy versus pressure [$G(P)$] for the six phases of carbon evaluated with use of a simple Legendre transformation of the total-energy results. The sc curve intersects the diamond curve at 23 Mbar, beyond which pressure the sc phase becomes more stable than diamond. Thus if one assumes that the whole compression process is performed in thermodynamical equilibrium, the theory predicts that within the five metallic phases under investigation, diamond will first transform to the sc phase at 23 Mbar. A small volume change from $0.367\Omega_0$ to $0.347\Omega_0$ is found for this transition. Since it is impossible to examine every possible crystal structure, the present results do not preclude a pressure-induced transition of diamond to another phase not included here or a transition at nonhydrostatic pressures. The calculated pressure for this diamond-to-sc transition should be regarded as an upper bound for pressures achievable by diamond anvil cells.

TABLE I. Volumes at the minimum structural energies ($\Omega_{\rm min}$, normalized to Ω_0), the minimum energies ($E_{\rm min}$), and $\Delta E_{\rm min}$ ($\equiv E_{\rm min} - E_{\rm min}^{\rm diamond}$) for the six phases of carbon.

Phase	$\Omega_{\rm min}$	$E_{\rm min}$ (Ry/atom)	$\Delta E_{\rm min}$ (eV/atom)
Diamond	0.986	−11.406	0
β tin	0.979	−11.199	2.82
sc	0.977	−11.211	2.66
bcc	1.181	−11.092	4.28
hcp	1.252	−11.077	4.48
fcc	1.285	−11.069	4.59

The relative stabilities of the six phases of carbon differ significantly from those of Si and Ge, despite the fact that they are in the same column of the periodic table. In Si and Ge the β-tin phase is calculated[5] to have lower minimal total energy than the sc phase in agreement with experiment.[1] In contrast, the sc phase of carbon has $E_{\min}$ lower than that of the β-tin phase, which makes the sc phase energetically more favorable than the β-tin phase at high pressure for carbon. It is interesting to note that the five metallic phases have their equilibrium volumes, $\Omega_{\min}$, either close to or even larger than that of diamond, while the metallic equilibrium volumes of Si and Ge are about 20% smaller than the equilibrium volumes of their covalent diamond phases. This makes the structural transformation of diamond very difficult. Since the volume is given by the slope of the $G(P)$ curve, a large initial slope in a high-lying $G(P)$ curve causes its possible intersection with the low-lying $G(P)$ curve of diamond to occur at a higher pressure than expected from the behavior in Si and Ge. Here we note that there has been a prediction[21] that diamond will transform to a β-tin phase at 1.7 Mbar and 0 K. That prediction is based on a simple assumption extrapolated from experimental observations in Si and Ge that a ~20% volume change is involved in the pressure-induced transition. As shown above, this simple assumption is not true for diamond.

A physical interpretation of the distinctive properties of the carbon phases can be traced back to its atomic configuration. Because there are no p electrons in the atomic core of carbon, the valence p electrons of the carbon atom are closer to the nucleus (relative to the valence s electrons) than those of Si or Ge (see Table II). The compactness of the valence np electrons of carbon has a larger effect on diamond than on the metallic phases because of the large valence p content in the sp^3 hybridization in diamond. Moreover the orbitals beyond the valence ns, np orbitals (beyond-valence orbitals) have principal quantum number at least $n+1$ in C but n in Si and Ge. The sizes of these orbitals are larger than that of the valence ns, np states by a factor which is significantly larger for C than for Si or Ge (see Table II). Since the metallic phases have larger admixtures of these extended beyond-valence orbitals (mostly d orbitals) than the diamond phase, their atoms tend to be pushed further apart. Both of these mechanisms help to explain why the equilibrium volumes of the five metallic phases of carbon are either close to or even larger than that of diamond. Since the above observations are based on general atomic considerations, we expect that the arguments can be applied to metallic phases of carbon in general. In that case, it suggests that even if diamond will first transform to some other metallic phase not considered here, it will occur at a hydrostatic pressure at least of the order of 10 Mbar because of the large zero-pressure volumes of the metallic phases of carbon.

TABLE II. Radii (in atomic units) for maxima in radial wave functions of atomic C, Si, and Ge. The values r_s and r_p are for valence s,p orbitals of the s^1p^3 atomic configuration. The value r_d is for the d orbital of the $s^1p^2d^1$ atomic configuration.

	r_s	r_p	r_d
C	1.21	1.21	8.51
Si	1.75	2.13	4.89
Ge	1.76	2.14	6.25

In summary, we show that diamond will first transform to the metallic simple-cubic phase under a hydrostatic pressure of 23 Mbar given the choices of fcc, bcc, hcp, simple cubic, and β-tin phases. A small volume change from $0.367\Omega_0$ to $0.347\Omega_0$ occurs at the transition. The unusual compactness of diamond as opposed to close-packed phases stabilizes the diamond phase at high hydrostatic pressures.

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