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Structural properties of a three-dimensional all-sp^2 phase of carbon

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We have studied the structural properties of a recently proposed, hypothetical, all-sp^2 phase of carbon, using the first-principles pseudopotential total-energy method. Our results are compared with those of an earlier tight-binding calculation. While the two calculations yield equilibrium volumes and bond lengths that are in excellent agreement, there are discrepancies in the cohesive energy, elastic constants, and predicted stability of this phase.

A hypothetical structure for carbon was proposed in a recent paper.[1] The structure, called *H*-6 carbon, consists of a three-dimensional network of sp^2-bonded carbon atoms situated in such a way that the structure can be continuously deformed to diamond without breaking any bonds. Because of this relationship to diamond, it was speculated that *H*-6 carbon might play a role in the chemical vapor deposition of diamond films. An initial study[1] of its properties based on the tight-binding method indicates that *H*-6 carbon is metallic and metastable with respect to diamond. The tight-binding results also suggest that the bulk modulus of this hypothetical solid could be larger than that of any existing material.

The *H*-6 structure is illustrated in Fig. 1. It consists of layers of carbon chains joined by bonds parallel to the *c* axis. The orientation of the chains rotates by 60° about the *c* axis from layer to layer. The Bravais lattice is hexagonal, and the primitive cell contains six atoms with positions (in Cartesian coordinates) $(0,0,0)$, $(a/2,0,ch)$, $(a/2,0,c/3)$, $(a/4,-a\sqrt{3}/4,c(h+1/3))$, $(a/4,-a\sqrt{3}/4,c2/3)$, and $(0,0,c(h+2/3))$, where a and c are the hexagonal lattice constants and h is a free parameter. Ideal sp^2 geometry, where all bonds are equal in length and all bond angles are 120°, corresponds to $c/a=9/(2\sqrt{3})$ and $h=\frac{1}{9}$. When c/a and h deviate from these values, the bonds oriented parallel to the *c* axis (interchain) can differ in length from those contained within the carbon chains (intrachain).

In this work, we investigate the structural properties of *H*-6 carbon using the *ab initio* pseudopotential total-energy approach.[2] This first-principles approach based on density-functional theory is known to be much more accurate than the tight-binding method used in Ref. 1, particularly for cohesive energies and elastic properties. Tight-binding predictions for a structure such as *H*-6 carbon involve large uncertainties because of problems associated with the transfer of empirical parameters between different bonding configurations. In contrast, the method used in this paper has been very successful in describing the structural properties of carbon in a wide range of crystal structures.[3] We expect that the present description of *H*-6 carbon should be equally accurate.

The total energy of the solid is calculated using the momentum-space formalism[4] within the local-density approximation. *Ab initio* pseudopotentials[5] are used to represent the electron-ion interaction, and the Hedin-Lundqvist function[6] is used for the exchange and correlation potential. Because of the strongly attractive nature of the carbon $2p$ potential, we have used a localized-orbital formalism,[7] where the electronic wave functions are expanded in linear combinations of Bloch sums of Gaussian orbitals centered on the atomic sites. The potential is iterated to self-consistency with plane-wave components up to an energy cutoff of 64 Ry. For integrations over the Brillouin zone, a uniform grid of 40 $\mathbf{k}$ points in an irreducible wedge of the Brillouin zone is used.

Static properties such as equilibrium volume (V_0), isothermal bulk modulus, and its pressure derivative are estimated by calculating the total energy of *H*-6 carbon at different volumes, ranging from about $0.8V_0$ to $1.2V_0$. At each volume, the total energy is minimized with respect to both c/a and h. The Birch-Murnaghan equation of state[8] is then used to fit the calculated total-energy–versus–volume curve.

Figure 2 shows the total energy as a function of volume for carbon in the *H*-6 and diamond structures. The calculated structural properties of *H*-6 carbon are summarized in Table I. The structure is found to have an equilibrium volume of 6.29 Å^3/atom, which corresponds to a density of 3.17 g/cm^3. At equilibrium the intrachain and interchain bond lengths are found to be 1.47 and 1.45 Å, respectively. These values are in excellent agreement with the earlier tight-binding calculation.[1] For comparison, the carbon-carbon bond length in graphite is 1.42 Å and that in diamond is 1.54 Å. The interchain bonds are longer than the bonds in graphite because the 60° rotation of carbon chains between layers weakens the π bonding along the *c* direction. As for the intrachain bonds, although there is π bonding along the chains, the repulsion

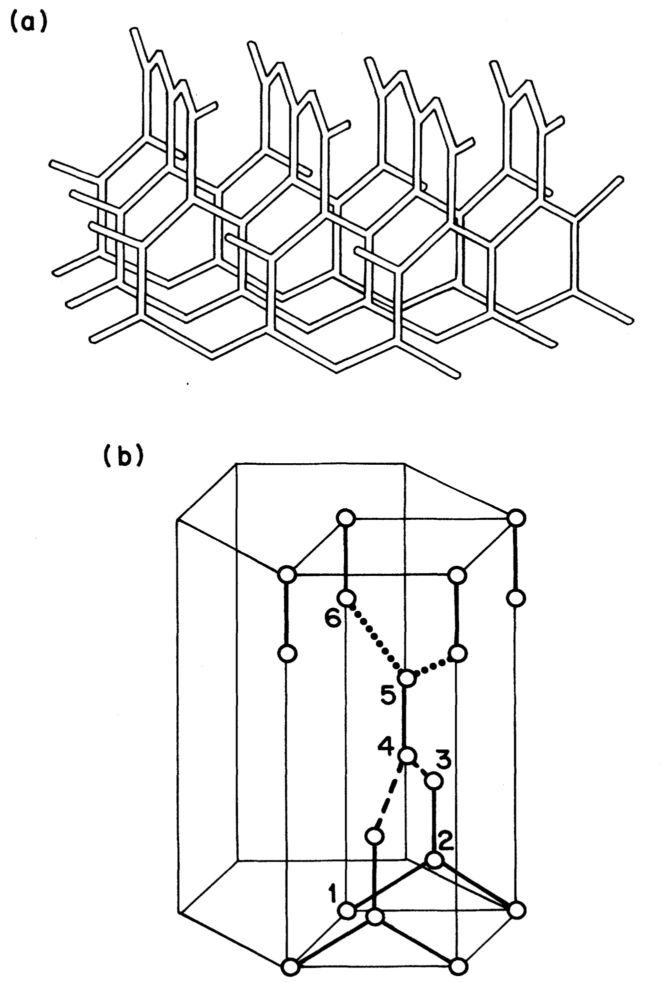

FIG. 1. (a) Perspective view of the H-6 lattice showing only the sp^2 σ bonds between nearest-neighbor atoms. The atoms lie at the threefold vertices. (b) Unit cell of the H-6 structure. One choice for the basis is indicated by the atoms numbered 1 through 6.

between π orbitals on parallel chains in the same layer results in the intrachain bonds being even longer than the interchain bonds.

The fit of the calculated total energies of H-6 carbon to the Birch-Murnaghan equation of state yields a bulk modulus of 372 GPa. This can be compared to the results of a simple semiempirical model for the bulk modulus of covalent solids.[9] Originally formulated for semiconductors with the diamond or zinc-blende structure, the model has been modified to allow for deviations from tetrahedral coordination.[10] The resulting expression for the bulk modulus of a homopolar covalent solid is

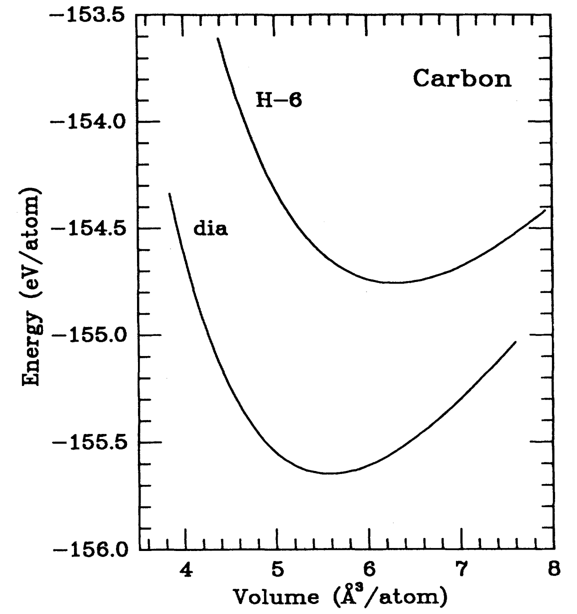

FIG. 2. Total energy vs volume for H-6 carbon and diamond. The curves are fits of the calculated points to the Birch-Murnaghan equation of state.

$$B=\frac{1971}{d^{3.5}}\frac{\langle N_c\rangle}{4}, \tag{1}$$

where B is the bulk modulus in GPa, d is the bond length in Å, and $\langle N_c\rangle$ is the average atomic coordination. Although the bonds in H-6 carbon are shorter than the bonds in diamond, the lower coordination number of the H-6 structure reduces its bulk modulus compared with that of diamond. Using $d=1.463$ Å, which is a weighted average of the calculated interchain and intrachain bond lengths of H-6 carbon, and $\langle N_c\rangle=3$, we obtain a bulk modulus of 390 GPa, which is within 5% of the value calculated from first principles. In contrast, the tight-binding calculation[1] indicated that the bulk modulus of H-6 carbon could be significantly larger than that of diamond (443 GPa). As noted in the initial study,[1] there are considerable uncertainties associated with the transfer of tight-binding parameters between different structures, and a significant error in elastic constants calculated with

TABLE I. Calculated equilibrium volume, bond lengths, bulk modulus, and cohesive energy of H-6 carbon. The difference in cohesive energy between the diamond and H-6 phases of carbon is also listed. The tight-binding results are from Ref. 1.

	V_0 (Å^3/atom)	d_{intra} (Å)	d_{inter} (Å)	B_0 (GPa)	E_{coh} (eV/atom)	$E_{\text{coh}}^{\text{dia}}-E_{\text{coh}}^{H\text{-}6}$ (eV/atom)
Present calc.	6.29	1.47	1.45	372	7.53	0.89
Tight-binding	6.25	1.47	1.45	690	6.94	0.40

this method is not uncommon.

Even though the present calculation indicates that the bulk modulus of *H*-6 carbon is smaller than that of diamond, the predicted value of 372 GPa is still among the largest of all materials. Only a handful of *metals* have bulk moduli greater than 350 GPa. These include a few transition metals[11] and transition-metal carbides,[12] in which the bonding is very different from that in *H*-6 carbon. As a high bulk modulus *covalent* solid, *H*-6 carbon is also unusual in that it does not contain tetrahedrally coordinated sites. It is known, of course, that the in-plane elastic constants of sp^2-bonded graphite are very large; prior to Ref. 1, however, the elastic constants of a more isotropic threefold-coordinated system had not been examined.

The cohesive energy of *H*-6 carbon is estimated by evaluating the difference between the total energy of the crystal at the minimum in Fig. 1 and the energy of the separated carbon atoms in their ground state. Calculations based on the local-density approximation tend to overestimate the cohesiveness of solids, but the relative energies of different structures are usually reliable. The present calculation yields a cohesive energy of 7.53 eV/atom for *H*-6 carbon, which is about 0.89 eV/atom lower than the value obtained for diamond using the same calculational method. An earlier study[3] of possible structures of carbon employing the same methods used in this work found that at low pressure the structures of carbon group together in energy according to coordination number. The threefold- and fourfold-coordinated structures such as graphite and diamond lie lowest in energy and are well separated from sixfold-coordinated structures, which in turn are separated from the highly coordinated close-packed structures. Not surprisingly, we find that *H*-6 carbon, which is a threefold-coordinated structure, lies within the lowest-energy group.

As discussed in Ref. 1, the *H*-6 and diamond structures are topologically related in that there is a high-symmetry transition path along which one can be continuously deformed into the other. In this transformation, new bonds are formed between parallel chains, while π bonds along the chains are disrupted. The initial study of *H*-6 carbon using the tight-binding approach indicated that although *H*-6 carbon lies higher than diamond in energy, there is a barrier along the *H*-6 to diamond transition path which stabilizes the *H*-6 phase. The present first-principles investigation of the transition yields a qualitatively different result. The total energies of several intermediate structures along the transition path have been calculated and the energy is found to decrease monotonically in going from *H*-6 carbon to diamond. Hence *H*-6 carbon is found to be unstable with respect to the transformation to diamond.

The instability of *H*-6 carbon is probably related to the short distance between carbon chains in the *H*-6 structure. At the unstable equilibrium position, carbon atoms on neighboring chains are separated by only 2.36 Å. This distance is comparable to the interlayer bond length at which covalent bonding between layers becomes significant in the graphite-to-diamond transition.[13] As soon as the symmetry is broken in *H*-6 carbon, new localized bonds between neighboring chains begin to form at the expense of π bonds within chains. This is accompanied by a decrease in the exchange-correlation energy. Other components of the total energy change as well, but because the exchange-correlation contribution favors inhomogeneity in the charge distribution, it is a good measure of changes in the bonding configuration. The incorrect prediction of an energy barrier in the earlier tight-binding study is indicative of the uncertainties involved in describing both strong (intrachain) and weak (interchain) interactions simultaneously using semiempirical techniques. The present first-principles results for *H*-6 carbon may therefore provide an important addition to the data base available for developing such techniques.

In summary, we have examined the structural properties of the recently proposed *H*-6 phase of carbon using a first-principles calculation based on density-functional theory. The present results confirm earlier tight-binding predictions for the equilibrium volume and bond lengths, but find significant differences in the bulk modulus, cohesive energy, and stability of *H*-6 carbon. Even though the *H*-6 structure is found to be unstable for carbon, it is an interesting example of a three-dimensional, all-sp^2 network. Studies of related structures such as the carbon phase proposed by Hoffman *et al.*,[14] or boron or boron nitride in the *H*-6 structure, would be of interest.

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