New Model for Icosahedral Carbon Clusters and the Structure of Collapsed Fullerite

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We propose a new class of structures consisting of compact carbon clusters with surface threefold coordination and bulk fourfold coordination. These clusters are the diamond analogs of fullerenes, maintaining icosahedral symmetry and almost perfectly tetrahedral bonding. Two potentially stable forms are investigated: molecules with hydrogenated surfaces and solid close-packed arrangements of the carbon clusters. The latter form may account for several recent experimental observations of collapsed fullerite, a new form of carbon produced by compression of C_{60} crystals.

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The remarkable stability of the recently discovered [1] C_{60} molecule and its derivatives (fullerenes) has motivated extensive searches for new forms of solid carbon. Some new forms have been experimentally realized, including van der Waals bonded crystals of C_{60} units [2] and concentric graphitic tubules [3], while others, such as negative curvature surfaces containing hexagons and higher polygons [4,5] remain interesting theoretical predictions. Recent attempts to compress the van der Waals C_{60} crystals seem to have produced yet a new form of carbon [6], dubbed collapsed fullerite (CF), which exhibits intriguing structural and electronic properties.

The purpose of this Letter is to propose a novel carbon structural unit which can be assembled into compact solid forms, or form the core of dense, stable molecules. In analogy to the C_{60} molecule, which is derived from the open graphitic form of solid carbon, our model is based on diamond, the more compact and dense form of solid carbon. Thus, bonding in our model is very close to tetrahedral, while the overall symmetry is that of the icosahedral group, as in C_{60}. Since diamond can be obtained from graphite by compression, it is not unlikely that the CF phase, produced by compressing C_{60} crystals, will exhibit structural features related to our model.

Before discussing the forms in which these new structures may be realized experimentally, we describe the features of our model. Its core, a dodecahedron of 20 threefold coordinated carbon atoms (C_{20}), is comprised of pentagons with bond angles of 108° which are very close to tetrahedral bond angles (109.4°) (see Fig. 1). Thus, the valence electrons of C_{20} form sp^3 bonding orbitals, leaving one sp^3 electron per atom unbonded. These dangling bonds render C_{20} unstable as an isolated molecule. However, the hydrogenated form ($C_{20}H_{20}$ [7]), as well as distorted dodecahedral clusters composed of metal and carbon atoms (e.g., Ti_8C_{12} [8]), have been found experimentally. Just as hydrogenation saturates $C_{20}H_{20}$, each dangling bond of an isolated C_{20} can lower its energy by bonding to a carbon atom placed radially outward from it in a second shell. The singly coordinated carbon atoms of the second shell are stabilized by the addition of a third shell of 60 carbon atoms (see Fig. 1), which renders the atoms in the second shell fourfold coordinated, while the third shell atoms are threefold coordinated. Accretion of successive shells of carbon atoms in this manner can be continued in accordance with the icosahedral point group symmetry. The most stable structures built this way have all inner (bulk) atoms fourfold coordinated, and all outer

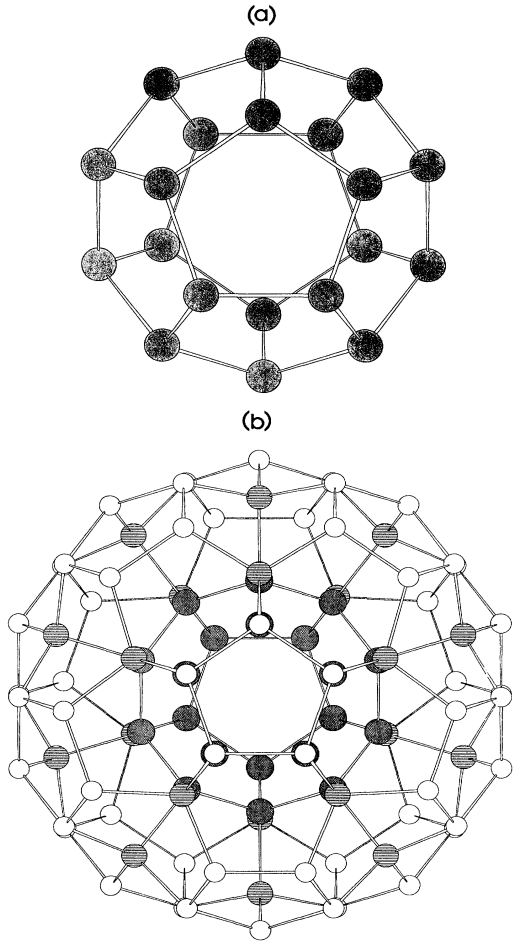

FIG. 1. Structure of (a) C_{20}, the core of the icosahedral tetrahedrally bonded structures, and (b) C_{100}, the smallest such structure with fourfold coordinated inner atoms. In (b) the dark circles are the 20 atoms of the core, the shaded ones are the atoms of the second fourfold shell, and the white ones are the 60 surface atoms.

TABLE I. Structure of the smallest icosahedral carbon clusters with tetrahedral bonding, containing fourfold coordinated inner (bulk) atoms and threefold coordinated outer (surface) atoms.

Atoms	Shells	Surface atoms	Energy (eV/atom)	Diameter (Å)	Bond lengths (Å)
20	1	20	−5.78	4.29	1.53
100	3	60	−6.57	8.66	1.51–1.60
300	7	140	−6.54	15.54	1.51–1.63
650	13	180	−6.64	19.88	1.50–1.72

(surface) atoms threefold coordinated. The 20 atom (first shell) and 100 atom (first three shells) structures shown in Fig. 1 are the smallest examples, while successive sizes contain 300 atoms (first seven shells) and 650 atoms (first thirteen shells). Table I displays structural properties of the optimized geometries for these four sizes. For these structural studies we used Tersoff's empirical potential [9] to determine the approximate positions of atoms in each shell through Monte Carlo minimization of the energy. This potential gives a reasonably accurate description of bonding in graphite and diamondlike structures of carbon [9]. For example, it predicts the bond lengths of C_{60} to about 3% of the experimental values.

The four icosahedral carbon clusters considered thus far may be unstable as isolated molecules because their tetrahedral bonding leaves numerous dangling bonds at their surfaces. However, it is quite possible that under proper experimental conditions, the C_{100} cluster and its larger counterparts (C_{300},C_{650}, etc.) may be rather stable in hydrogenated form. Specifically, one might expect $C_{100}H_{60}$, $C_{300}H_{140}$, $C_{650}H_{180}$, to exist as stable molecules, in analogy to $C_{20}H_{20}$. These molecules, as well as others of intermediate size, may be formed under high pressure in a hydrogen-rich atmosphere. In order to investigate this possibility, we constructed a series of molecules starting from the $C_{20}H_{20}$ structure and partially filling the second through seventh shells (up to C_{300}) of the icosahedral structure with carbon atoms. Each surface atom of these clusters is saturated with the proper number (between 1 and 3) of hydrogen atoms to render it fourfold coordinated. The bonding energies [10] of these molecules are displayed in Fig. 2. The different curves correspond to different pathways of partially filling the second through seventh shells. The triplet of numbers labeling each curve indicates the numbers of carbon atoms, hydrogen atoms, and C-C bonds added at each step as the cluster is expanded. For example, the upper curve in the 20 to 40 atom region corresponds to the addition of one carbon atom to the second shell, and a net increase of two C-H bonds (due to the addition of two H atoms) and one C-C bond at each step. The lower curve in the 20 to 40 atom region corresponds to partial but simultaneous filling of the second and third shells. This accretion path allows more efficacious bonding and thus lies lower in energy than the pathway that fills one shell at a time (upper curve). This example illustrates the importance of kinetics in the creation of stable hydrogenated molecules. As the size increases, more pathways become accessible, some of which are illustrated in Fig. 2. Interestingly, a number of larger hydrogenated molecules are more stable than $C_{20}H_{20}$ (which is known to exist experimentally), at least in terms of bonding energy. Our study does not take into account strain, which will also affect the stability of molecules (see discussion below).

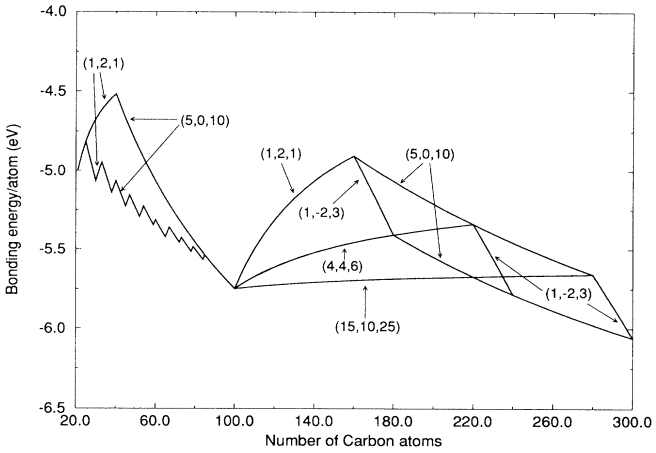

FIG. 2. Bonding energy of molecules built from icosahedral carbon structures with the dangling bonds of surface atoms saturated by hydrogen. The triplet of numbers labeling each curve represents the number of carbon atoms, hydrogen atoms, and C-C bonds added in each increment as the molecule is expanded along a given pathway.

In order to elucidate the physical properties of our model, we studied the electronic states of isolated icosahedral carbon clusters and crystals composed of such units, using the tight binding approximation [11]. The electronic density of states for a C_{100} cluster is shown in Fig. 3. The gap states (in the -2 to 5 eV range) of C_{100} are comprised primarily of nonbonding and π-bonding orbitals of the 60 surface atoms. In contrast, the electronic spectrum of $C_{100}H_{60}$ (not shown) contains no states in the gap range, illustrating that hydrogenation saturates the outer orbitals to produce molecules with large gaps between the highest occupied molecular orbital and the lowest unoccupied molecular orbital that are likely to be stable. The density of states of the C_{100} and C_{300} clusters are seen from Fig. 3 to be quite similar. One important difference is that the gap states of C_{100} split into two peaks. This distinction results from the atomic arrangement at the surface which suppresses π bonding in C_{300} relative to that in C_{100}.

In order to explore the possible relation between these icosahedral clusters and the structure of collapsed fullerite, we constructed solid forms from the clusters. One can imagine filling space by continuing to build the icosahedral structures radially outward. An infinitely

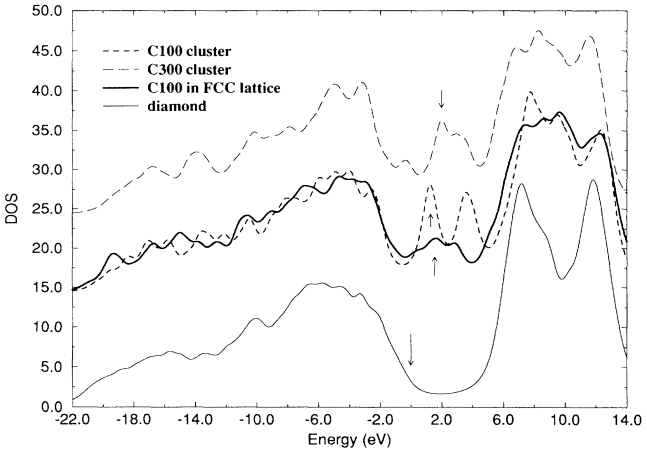

FIG. 3. Density of states for the isolated C_{100} and C_{300} clusters, for the C_{100}-based fcc lattice, and for the primitive diamond lattice. Curves are shifted for clarity. Arrows mark the Fermi level of each structure. The zero of energy corresponds to the highest occupied level (valence band maximum) of diamond. A uniform Lorenzian smoothing of width 0.6 eV is used.

large structure would be analogous to a single quasicrystal.

However, since the bond angles are not exactly tetrahedral, bond distortions arise with the addition of successive shells, producing significant strain as is seen from the increase in maximum bond lengths with cluster size (Table I). This observation suggests that very large clusters are probably unstable. An alternative solid form could involve a close packing of finite sized icosahedral clusters. We searched for close packing crystalline arrangements of clusters which maximize the density as well as minimize the energy. We used combinations of the 20, 100, 300, and 650 atom clusters as bases for several Bravais lattices, and varied the lattice constants and orientations of the clusters with respect to the lattice vectors to find the optimal configuration. The lowest energy structure we obtained was an fcc lattice of C_{100} units with a lattice constant of 13.84 Å, an energy of -6.77 eV/atom, and a density of 0.151 atom/Å^3. This density is 1.8 times that of the C_{60} fcc lattice at normal conditions, and is larger than the density of all other forms of carbon except those of diamond and the simulated diamondlike amorphous carbon [12].

The fcc lattice of C_{100} units significantly reduces the density of states in the gap region (Fig. 3) by increasing to four the coordination of most surface atoms through intercluster bonding [13]. The close resemblance of the density of states of the C_{100} fcc lattice (and also of the isolated C_{100} and C_{300} clusters) to that of diamond is a reflection of the tetrahedral bonding in our model structures. The possibility that this model is related to the structure of the CF phase will be investigated by first considering results from optical experiments. These experiments [6,14] indicate that CF has a sizable band gap in the electronic spectrum containing a low density of states, a characteristic which is exhibited by our close packed lattice of C_{100} units (Fig. 3). Furthermore, Moshary *et al.* [6] report that although the CF phase is almost optically transparent up to frequencies 22×10^3 cm^{-1}, it does have greater optical absorption than diamond. Consistent with this observation, our calculations show that an fcc crystal of C_{100} units would be more optically absorptive than diamond in the 0 to 5 eV range, due to the greater density of states in the gap region (Fig. 3).

Our model may also provide insight to the vibrational properties of CF. Raman scattering spectra [6,14] of CF do not contain sharp peaks corresponding to diamond or graphite. A broad line resembling that of a mostly threefold coordinated amorphous carbon is seen at 1550 cm^{-1}, indicating the presence of strongly bonded atoms. Our calculation of the phonon spectrum of a single C_{100} unit yields frequencies only below 1400 cm^{-1}, due to the absence of bonds stronger than single bonds. Thus, in order to explain both the optical absorption and Raman experiments, CF must contain fourfold coordinated atoms as well as more strongly bonded atoms. The latter type of atoms could form an amorphouslike [15] connective material between C_{100} units. Finally, a disordered packing of C_{100} units has a radial distribution function which exhibits significant correlations at intermediate distances, a feature that is absent in amorphous carbons [12]. The structure factor, $S(q)$, of this solid has a double peak structure in the $q=2.5$ to 3.5 Å^{-1} range as well as a peak at approximately $q=1.2$ Å^{-1}. Such features could be detected by x-ray scattering experiments.

The phase transformation from an fcc lattice of C_{60} units to CF under pressure is a complex process, which begins with an increase in interaction between neighboring C_{60} molecules, and hence a decrease in their rotational freedom. We have investigated possible transformation paths connecting the fcc C_{60} lattice to a material containing C_{100} clusters. In one simulation we start with a lattice of stationary C_{60} molecules and move the molecules together uniformly until they begin to interact, at which point uniaxial compression is applied in order to mimic experimental conditions for production of CF [6]. At each step of the uniaxial compression all distances in the direction of compression are reduced uniformly, while each atom is allowed to move in the direction perpendicular to the compression. The optimal lateral positions of the atoms are found at each step through a Monte Carlo energy minimization (using Tersoff's empirical potential) subject to the unbroken symmetries. For comparison we have also calculated the energy as a function of volume for uniform compression of the fcc C_{100} and the primitive diamond lattices. The results are shown in Fig. 4. It is interesting that the curves for uniaxial compression of the C_{60} lattice, uniform compression of the C_{100} lattice, and uniform compression of bulk diamond all intersect at the same point, very close to the density region where the transition to CF is observed experimentally [16]. We

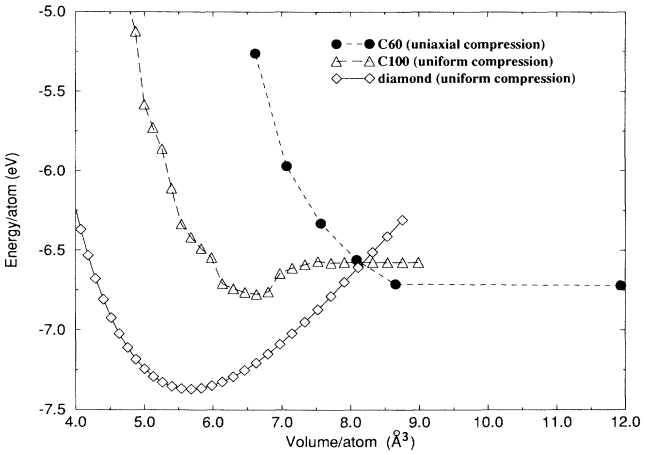

FIG. 4. Energy vs volume for the diamond, C_{100}, and C_{60} lattices under compression (see text).

have also considered uniform compression of C_{60} lattices for several choices of the orientation of the C_{60} unit, which give energy versus volume curves very close to the uniaxial compression curve. We infer from these comparisons that, depending on the kinetics of compression, formation of a C_{100}-related structure could be possible under conditions that make transformation to the diamond lattice kinetically unfavorable. We suggest that the presence of a large number of pentagons in the original C_{60} lattice may enhance this possibility.

In summary, we have proposed a new class of compact carbon clusters. These clusters, which are the diamond analogs of the fullerenes, incorporate tetrahedral rather than graphiticlike bonding into spherical units with icosahedral symmetry. The clusters of size 20, 100, 300, and 650 which satisfy the requirement of fourfold coordination of bulk atoms and threefold coordination of surface atoms were examined in detail. The icosahedral carbon clusters could form the cores of hydrogenated molecules which may be produced experimentally under the proper conditions of hydrogen saturation and pressure. The C_{100} clusters may also serve as a model for the newly discovered CF phase of carbon [6], giving plausible explanations for several experimental observations.

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