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Coexistence of bucky diamond with nanodiamond and fullerene carbon phases

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The transformation of nanodiamonds into carbon onions, and vice versa, has lead to the introduction of a new intermediate phase of carbon, coined ''bucky diamond,'' with a diamond core encased in an onion-like shell. Using a model based on the atomic heat of formation to describe the phase stability of carbon nanoparticles, we have calculated the relative stability of bucky diamonds and carbon onions for comparison with previous results for nanodiamond and fullerenes. Our results show that bucky diamond occupies a coexistence region, spanning the calculated upper limit of fullerene stability and the lower limit of nanodiamond stability.

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The phase transition of diamond nanocrystals to carbon onions has been observed experimentally[1–3] with a transformation temperature that is dependent on the size of the particle and has been modeled theoretically[4–8] at various levels of sophistication. Similarly, the reverse transformation of carbon onions to nanocrystalline diamond has also been observed experimentally[9–13] and modeled[14] by means of atomic-scale computer simulations. However, in most cases a pure carbon onion or nanodiamond is not the final product. More often than not, an intermediary is formed, with a diamond-like core and an onion-like outer shell.

Recent studies concerning these intermediaries, both experimental and theoretical, have suggested that a new class of carbon be established to describe them.[15] Termed ''bucky diamond,'' this class is characterized by a nanodiamond core partially or completely shrouded in a fullerene-like outer shell.[8,15–17] The fullerene-like surfaces are formed by graphitization of the (111) surface facets. The introduction of the bucky diamond class does, however, raise questions as to where these structures fit into current theories regarding the relative stability of carbon phases at the nanoscale.

A number of theoretical models have been proposed regarding the stability[4,18–24] of carbon nanoparticles. These models predict that for particles under 5–6 nm in diameter nanocrystalline diamond is more stable than graphite. As an extension of this, we have recently outlined a model for examining the relative stability of graphite, nanodiamond, and fullerenes.[25] It was confirmed that relaxed nanodiamonds are more stable than graphite for crystals consisting of fewer than 24 398 atoms. This equates to a cubic crystal diameter of approximately 5.2 nm, beyond which graphite is the stable form of carbon and diamond is metastable. Our model also predicted that at the ultrananoscale fullerenes, and not nanodiamond, are the most stable allotrope. This intersection occurred at 1127 atoms, which is approximately equivalent to cubic nanodiamond crystals of 1.9 nm in diameter. These results indicated a ''window'' of stability for nanodiamond, in the range of approximately 1.9–5.2 nm in diameter, and in all but this range (∼1127 to ∼24 398 atoms), nanodiamond is metastable.

The model presented in Ref. 24 describes the atomic heat of formation of fullerenes and carbon onions $[\Delta H_f^0(F)]$ and diamond $[\Delta H_f^0(D)]$ clusters in terms of the C-C bond energy E_{CC} and dangling bond energy E_{DB}, and is linearly dependent upon the number of surface bonds per carbon atom, $N_{\mathrm{DB}}/N_{\mathrm{C}}$:

$$\frac{\Delta H_f^0(D)}{N_{\mathrm{C}}}=2E_{\mathrm{CC}}^D+\frac{N_{\mathrm{DB}}}{N_{\mathrm{C}}}\left(E_{\mathrm{DB}}^D-\frac{1}{2}E_{\mathrm{CC}}^D+\Delta H_f^0(DB)\right)+\Delta H_f^0(C), \tag{1}$$

$$\frac{\Delta H_f^0(F)}{N_{\mathrm{C}}}=\frac{3}{2}E_{\mathrm{CC}}^F+\Delta H_f^0(C)+\frac{E_{\mathrm{strain}}^F}{R^2}+\frac{1}{2}E_{\mathrm{CC}}^{\mathrm{vdw}}, \tag{2}$$

where N_{C} is the number of carbon atoms, N_{DB} is the number of dangling bonds on the surface of the particle, R is the radius of curvature of the fullerenes (equal to the mean radius of curvature), $\Delta H_f^0(C)$ is the standard heat of formation of carbon at 298.15 K, E_{strain}^F is the strain energy associated with the fullerene curvature, and $E_{\mathrm{CC}}^{\mathrm{vdw}}$ is the van der Waals attraction between onion layers. Fullerenes do not have interlayer attraction, so for fullerenes $E_{\mathrm{CC}}^{\mathrm{vdw}}=0$. As has been found, hydrogenation of nanodiamond surfaces eliminates bucky diamond formation;[26] hydrogen-terminated particles have not been considered here.

In the present study the number of C-C bonds and (most importantly) the number of dangling bonds have been determined using free nanodiamonds and carbon onions, ranging in size from 29 to 323 atoms. These nanoparticles have been structurally relaxed using the Vienna *ab initio* simulation package (VASP) (Refs. 27 and 28) to form bucky diamonds showing varying degrees of delamination. We used ultrasoft, gradient-corrected Vanderbilt-type pseudopotentials[29] as supplied by Kresse and Hafner,[30] and the valence orbitals are expanded on a plane-wave basis up to a kinetic-energy cutoff of 290.00 eV. The crystal relaxations were performed in the framework of density functional theory (DFT) within the generalized-gradient approximation (GGA), with the exchange-correlation functional of Perdew and Wang (PW91).[31] A detailed description of this technique may be found in Ref. 32. This relaxation method has been successfully applied to bulk diamond, with results in excellent agreement with experiment and all electron methods.[33] Examples of the resulting structures are shown in Fig. 1.

While the model is purely theoretical, the terms in Eqs. (1) and (2) have been calculated using results from the VASP calculations. Previously, the cohesive energy of nanocrystal-

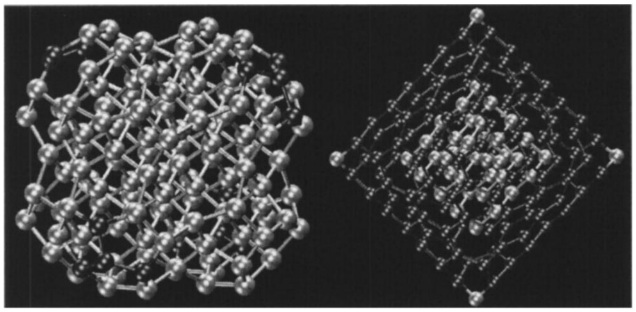

FIG. 1. Examples of bucky diamond structures comprising 142 atoms (left) and 165 atoms (right), graphitized atoms with sp^2 hybridization shown in dark gray.

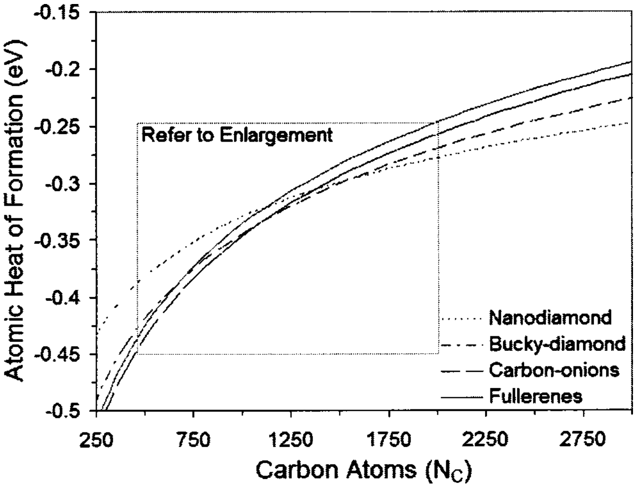

FIG. 2. Extrapolation of the atomic heat of formation of carbon nanoparticles as a function of particle size.

line diamond has been calculated[8] and found to be 7.71 eV. This equates to $E_{\rm CC}^D = 3.855$ eV for relaxed dehydrogenated nanodiamond. From the same linear fit to the spin-polarization-corrected energy per ion versus number of dangling bonds per ion (outlined in Ref. 8) the slopes give $E_{\rm DB}^D = 1.619$ eV for nanodiamond. Similarly, the strain energy and cohesive energy obtained for fullerenes are 5.19 and 7.81 eV, respectively,[25] with the fullerene C-C bond energy extracted directly from the cohesive energy [as $E_{\rm cohesive} = (3/2) E_{\rm CC}^F$].

Using the value of $\Delta H_f^0(C) = 7.432$ eV, the atomic heats of formation for relaxed nanodiamond crystals were then plotted as a function of the number of carbon atoms. The resulting plots are curves, as R^2 is proportional to N and $N_D B/N_{\rm C}$ versus $N_{\rm C}$ is nonlinear. An empirical best fit (to which no physical meaning is assigned) was applied to the data sets and the point of intersection determined, giving an estimate of the number of atoms at which a transition in phase stability occurs. The intersection for nanodiamond and fullerenes occurred at 1127 atoms and is included as part of Figs. 2 and 3.

In the previous study, the nanodiamond structures considered were those that consisted of mostly sp^3-bonded atoms (therefore characterized as being predominantly nanodiamond), but did not consider bucky diamond or carbon onions. In the present study, the bucky diamonds have been treated in the same manner as nanodiamonds by applying Eq. (1), although obviously $N_{\rm DB}/N_{\rm C}$ is different for nanodiamonds and bucky diamonds of similar diameter. Octahedral, cuboctahedral, and cubic morphologies have been considered, characterized by combinations of C(111), C(110), and C(100) surfaces. The carbon onions are treated as nested fullerenes by applying Eq. (2), with the van der Waals attraction $E_{\rm CC}^{\rm vdw} = 0.056$ eV, as calculated by Guo[34] using a graphite force field. Error bars have been included, indicating the quality of fit of the model to the calculated values.

The atomic heat of formation as a function of particle size for bucky diamond and carbon onions has then been extrapolated along with the nanodiamond and fullerene results, as shown in Fig. 2. Here three main points are evident. First, the sp^2-bonded fullerenic structures are most stable below about 900 atoms, and although the carbon onion and fullerene results converge below 250 atoms, they diverge very slowly beyond this value, confirming that the cohesive energy and strain energy of these structures dominate the formation energy and the contribution from interlayer attraction is small. In fact, the carbon-onion and fullerene results are indistinguishable (within uncertainties) below approximately 2000 atoms. Second, the atomic heat of formation of bucky diamond is more akin to the carbon onions than the nanodiamonds, the latter being the least stable below 1100 atoms, but most stable beyond 1600 atoms. Finally, in the region from ~500 to ~1850 atoms the simulations predict that a coexistence region has been formed, as shown in Fig. 3.

In this range, the coexistence of bucky diamond with the other carbon nanoparticles may be further broken into three subregions, marked as *A*, *B*, and *C* in Fig. 3. Within subregion *A* (from ~500 to ~900 atoms), the atomic heat of formation of bucky diamond is indistinguishable from that of fullerenes (within uncertainties), with carbon onions being the most stable form of carbon and nanodiamond the least stable. There is, however, an intersection at ~700 atoms,

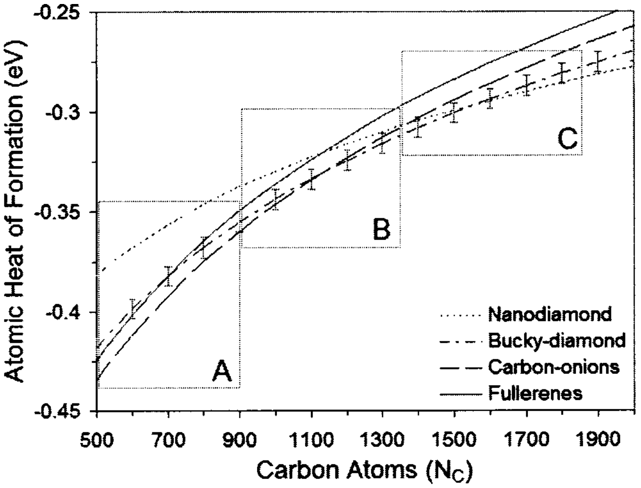

FIG. 3. Atomic heat of formation of carbon nanoparticles, indicating the relative subregions of coexistence of bucky diamond with other phases. Uncertainties indicated for bucky diamond only.

TABLE I. Summary of allotropes coexisting with bucky diamond, with size ranges and corresponding cubic nanodiamond diameter. Regions indicated in Fig. 2.

Region	Coexisting allotropes	Atoms (N_{C})	Nanodiamond diameter (D)
A	Bucky diamond and fullerenes	$\sim 500 < N_{\mathrm{C}} < \sim 900$	$\sim 1.4\ \mathrm{nm} < D < \sim 1.7\ \mathrm{nm}$
B	Bucky diamond and carbon-onions	$\sim 900 < N_{\mathrm{C}} < \sim 1350$	$\sim 1.7\ \mathrm{nm} < D < \sim 2.0\ \mathrm{nm}$
C	Bucky diamond and nanodiamond	$\sim 1350 < N_{\mathrm{C}} < \sim 1850$	$\sim 2.0\ \mathrm{nm} < D < \sim 2.2\ \mathrm{nm}$

where bucky diamond becomes more energetically favored than fullerenes. Subregion B between ~900 and ~1350 atoms, where bucky diamond and carbon onions coexist (within uncertainties), contains an intersection at ~1100 atoms. This intersection, where the bucky diamond structure becomes more favorable than carbon onions, is very close to the intersection of nanodiamonds and fullerenes at 1127 atoms, suggesting that at approximately 1120 atoms a sp^3-bonded core becomes more favorable than a sp^2-bonded core, irrespective of the surface structure. In subregion C, bucky diamond is found to coexist with nanodiamond (within uncertainties) between ~1350 and ~1850 atoms, intersecting with nanodiamond at ~1550 atoms.

Although bucky diamond has the lowest atomic heat of formation between ~1100 and ~1550 atoms, due to uncertainties it cannot be said that bucky diamond is the most stable state in this range. Almost in the center of this range is the intersection of carbon onions and nanodiamond at ~1350 atoms, at a slightly higher energy (also just within uncertainties). In general, Figs. 1 and 2 show that the existence of bucky diamonds provides a smooth transition from fullerenes to nanodiamond, rather than an abrupt change in phase stability predicted by other models. These results are summarized in Table I, along with the approximate diameter of a nanodiamond crystal within each region, regardless of whether nanodiamond is stable or metastable.

In conclusion, the results of our model, based on the extrapolated atomic heat of formation, show that the bucky diamonds (consisting of nanodiamond cores encased in carbon-onion-like outer shells) occupy a coexistence region of stability with both fullerenic and nanodiamond phases. This coexistence region extends from ~500 to ~1850 atoms and represents cubic nanodiamonds from ~1.4 to ~2.2 nm in diameter. Although a skilled experimentalist may produce nanodiamonds, bucky diamonds, or carbon onions as desired, this model provides a useful tool in describing the structure of synthesized[15] and interstellar nanosized diamond.[35,36]

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[1] V. L. Kuznetsov, A. L. Chuvilin, Y. V. Butenko, I. Y. Mal'Kov, and V. M. Titov, Chem. Phys. Lett. **209**, 72 (1994).

[2] V. L. Kuznetsov, I. L. Zilberberg, Y. V. Butenko, A. L. Chuvilin, and B. Seagall, J. Appl. Phys. **86**, 863 (1999).

[3] S. Tomita, T. Sakurai, H. Ohta, M. Fujii, and S. Hayashi, J. Chem. Phys. **114**, 7477 (2001).

[4] N. W. Winter and F. H. Ree, J. Comput.-Aided Mater. Des. **5**, 279 (1998).

[5] F. H. Ree, N. W. Winter, J. N. Glosli, and J. A. Viecelli, Physica B **265**, 223 (1999).

[6] F. Fugaciu, H. Hermann, and G. Seifert, Phys. Rev. B **60**, 10 711 (1999).

[7] H. Hermann, F. Fugaciu, and G. Seifert, Appl. Phys. Lett. **79**, 63 (2001).

[8] A. S. Barnard, S. P. Russo, and I. K. Snook, Philos. Mag. Lett. **83**, 39 (2003).

[9] F. Banhart and P. M. Ajayan, Nature (London) **382**, 433 (1996).

[10] F. Banhart, J. Appl. Phys. **81**, 3440 (1997).

[11] M. Zaiser and F. Banhart, Phys. Rev. Lett. **79**, 3680 (1997).

[12] Ph. Redlich, F. Banhart, Y. Lyutovich, and P. M. Ajayan, Carbon **36**, 561 (1998).

[13] M. Zaiser, Y. Lyutovich, and F. Banhart, Phys. Rev. B **62**, 3058 (2000).

[14] R. Astala, M. Kaukonen, G. Jungnickel, Th. Frauenheim, and R. M. Nieminen, Phys. Rev. B **63**, 081402 (2001).

[15] J. Y. Raty, G. Galli, C. Bostedt, T. W. Buuren, and L. J. Terminello, Phys. Rev. Lett. **90**, 037401 (2003).

[16] A. S. Barnard, S. P. Russo, and I. K. Snook, Diamond Relat. Mater. (to be published).

[17] O. A. Shenderova, V. V. Zhirnov, and D. W. Brenner, Crit. Rev. Solid State Mater. Sci. **27**, 227 (2002).

[18] J. A. Nuth, Nature (London) **329**, 589 (1987).

[19] P. Badziag, W. S. Veowoerd, W. P. Ellis, and N. R. Greiner, Nature (London) **343**, 244 (1990).

[20] M. Y. Gamamik, Nanostruct. Mater. **7**, 651 (1996).

[21] N. M. Hwang, J. H. Hahn, and D. Y. Yoon, J. Cryst. Growth **160**, 87 (1996).

[22] N. M. Hwang, J. H. Hahn, and D. Y. Yoon, J. Cryst. Growth **162**, 55 (1996).

[23] P. Keblinski, S. R. Phillpot, D. Wolf, and H. Gleiter, Nanostruct. Mater. **12**, 339 (1999).

[24] Q. Jiang, J. C. Li, and G. Wilde, J. Phys.: Condens. Matter **12**, 5623 (2000).

[25] A. S. Barnard, S. P. Russo, and I. K. Snook, J. Chem. Phys. **118**, 5094 (2003).

[26] A. S. Barnard, S. P. Russo, and I. K. Snook, Int. J. Mod. Phys. B (to be published).

[27] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993).

[28] G. Kresse and J. Hafner, Phys. Rev. B **54**, 11 169 (1996).
[29] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[30] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[31] J. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[32] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **53**, 7334 (1996).
[33] A. S. Barnard, S. P. Russo, and I. K. Snook, Philos. Mag. B **82**, 1767 (2002).
[34] Y. Guo, Ph.D thesis, California Institute of Technology, 1992.
[35] R. S. Lewis, M. Tang, W. F. Wecker, E. Anders, and E. Steel, Nature (London) **326**, 160 (1987).
[36] R. S. Lewis, E. Anders, and B. T. Draine, Nature (London) **339**, 117 (1989).