

same density. We have argued that the only local configurations that can increase the density above the Penrose value are DC-clusters, and that the increase in density is due to the B-overlap of core-areas, which is the same for each DC-cluster. The corollary is that the hypothetical tiling has the same density of DC-clusters and, hence, the same density of B-overlaps surrounded by DC-clusters as Penrose tiling. But by definition, the non-Penrose tiling must also have patches with non-zero area measure which violate the Penrose matching rules, and so cannot belong to the core-area of any C-cluster. As the DC-cluster density is the same but there are these patches, it would appear that the average area per C-cluster must be less than the Penrose density. The only conceivable exception would be if there happen to be additional B-overlaps which do not belong to DC-clusters whose overlap area exactly compensates the area of the patches. Even this possibility can be eliminated because the corollary states that  $R_{DC} = \tau^{-2}$ , which means that the density of C-clusters remains unchanged under deflation and rescaling. Yet, the patches grow: a patch excluded from a C-cluster must also be excluded from a DC-cluster, but, also, some C-clusters that border the patches cannot be part of a DC-cluster and add to the patch area (H.-C.J. and P.J.S., manuscript in preparation). As the number of C-clusters remains fixed but the patches grow, the C-cluster density in the deflated tiling must be less than the Penrose value. This contradicts the corollary; hence, uniqueness is established.

The two new approaches to Penrose tiling—a single tile type and maximizing cluster density—can be continued. Together, they suggest that relatively simple criteria can lead to quasicrystal

formation, shedding new light on an old mystery. They suggest that quasicrystals can be understood by considering the energetics of microscopic clusters and that cluster overlap is an important structural element<sup>6</sup>. The concept can be studied using the atom clusters of known quasicrystals. Our two-dimensional tiling results can most readily be applied to decagonal quasicrystals which have periodically spaced layers with Penrose tiling structure. The extension to three-dimensional, icosahedral symmetry is a future challenge. If these principles can be established, they may enable the reliable prediction of new quasicrystals. □

Received 18 March; accepted 11 June 1996.

1. Levine, D. & Steinhardt, P. J. *Phys. Rev. Lett.* **53**, 2477–2480 (1984); *Phys. Rev.* **B34**, 596–616 (1986).
2. Steinhardt, P. J. *Am. Scientist.* **74**, 586–597 (1986).
3. Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. *Phys. Rev. Lett.* **53**, 1951–1954 (1984).
4. Penrose, R. *Bull. Inst. Math. and its Appl.* **10**, 266–269 (1974).
5. Gummelt, P. *Geometriae Dedicata* (in the press).
6. Jeong, H.-C. & Steinhardt, P. J. *Phys. Rev. Lett.* **73**, 1943–1946 (1994).
7. Henley, C. L. in *Quasicrystals, The State of Art* (eds DiVincenzo, D. P. & Steinhardt, P. J.) 429–524 (World Scientific, Singapore, 1991).
8. Goldman, A. et al. *Am. Scientist.* **84**, 230–241 (1996).
9. Burkow, S. J. *Phys.* **2**, 695–706 (1992); *Phys. Rev. Lett.* **67**, 614–617 (1991).
10. Steurer, W., Haibach, T., Zhang, B., Kek, S. & Luck, R. *Acta Crystallogr.* **B49**, 661–675 (1993).
11. Aragon, J. L., Romeu, D. & Gomez, A. *Phys. Rev.* **B44**, 584–592 (1991).
12. de Bruijn, N. G. K. *Nederl. Akad. Wetensch. Proc.* **A84**, 1–38 (1981).

ACKNOWLEDGEMENTS. We thank F. Gähler for bringing P. Gummelt's work to our attention and for many helpful comments and criticism. We also thank P. Gummelt for sharing her results before publication. This work was supported by the Department of Energy at Univ. Pennsylvania (P.J.S.) and by the USNSF at Univ. Maryland (H.-C.J.).

CORRESPONDENCE should be addressed to P.J.S. (e-mail: steinh@steinhardt.hep.upenn.edu).

## Carbon onions as nanoscopic pressure cells for diamond formation

F. Banhart\* & P. M. Ajayan†

\* Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstrasse 1, 70569 Stuttgart, Germany

† Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, 70174 Stuttgart, Germany

**SPHERICAL particles of carbon consisting of concentric graphite-like shells ('carbon onions') can be formed by electron irradiation of graphitic carbon materials<sup>1,2</sup>. Here we report that, when such particles are heated to  $\sim 700^\circ\text{C}$  and irradiated with electrons, their cores can be transformed to diamond. Under these conditions the spacing between layers in the carbon onions decreases from 0.31 nm in the outer shells (slightly less than the 0.34-nm layer spacing of graphite) to about 0.22 nm in the core, indicating considerable compression towards the particle centres. We find that this compression allows diamond to nucleate—in effect the carbon onions act as nanoscopic pressure cells for diamond formation.**

We found recently that electron-irradiation-induced damage to carbon onions is annealed *in situ* at high specimen temperatures<sup>3</sup>. This enables us to generate and observe onion-like particles with essentially undistorted shells. We used a high-voltage transmission electron microscope (Jeol ARM 1250) operating at 1,250 kV, capable of heating the specimen up to  $800^\circ\text{C}$ . By using a drift compensating system<sup>4</sup>, a point resolution of 0.12 nm was achieved over the whole temperature range. A total pressure of  $2 \times 10^{-6}$  Pa and a hydrogen partial pressure of  $6 \times 10^{-7}$  Pa prevail in the microscope column. Hence, the influence of any gaseous and other impurities can be neglected. Samples containing the well known carbon nanotubes and nanoparticles<sup>5</sup> were irradiated and imaged at specimen temperatures between 650 and  $750^\circ\text{C}$ . Onions with perfectly undistorted shells formed at these

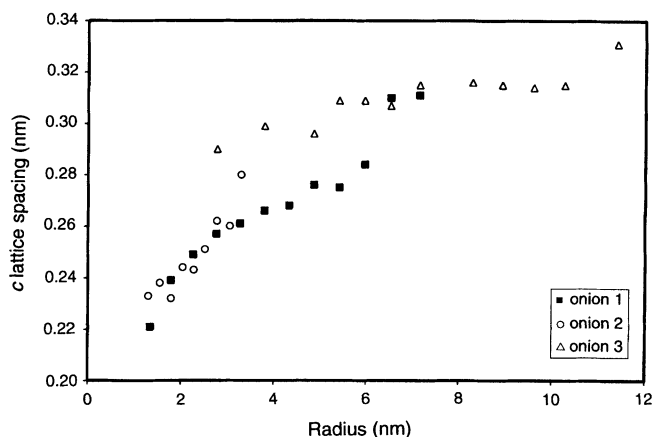


FIG. 1 Distance between the c layers of carbon onions generated at high temperatures as a function of the radius of the shells. Onion 1 (■) has graphitic shells down to the centre (generated at  $700^\circ\text{C}$ ). Onion 2 (○) has a hollow core of 2.5 nm diameter (generated at  $400^\circ\text{C}$ ). Onion 3 (△) has a diamond core of 4.5 nm diameter (generated at  $730^\circ\text{C}$ ).

specimen temperatures under irradiation at high beam intensity ( $200 \text{ A cm}^{-2}$ ).

In all particles showing straight lattice fringes, such as the nanotubes, the distance between the basal lattice planes is, as expected, close to that of graphite, 0.34 nm. But in the onions, the distance between the lattice planes decreases from outside to inside (Fig. 1). The outermost shells already show a reduced spacing. The lowest value we measured close to the centre was 0.22 nm. After these compressed onion structures are formed, less than one hour of further irradiation at high or reduced beam intensity ( $20 \text{ A cm}^{-2}$ ) results in the formation of crystallites in the cores of many irradiated onions with more than 15 shells (Fig. 2). The analysis of the lattice images and diffractograms showed that the crystal structure fits precisely to that of cubic diamond. Convergent beam electron diffraction (CBED) with a small electron probe focused onto the diamond cores showed up to

eight reflections of different order that perfectly match to the distance between lattice planes in cubic diamond, and selected-area electron diffraction reveals the most intense rings of cubic diamond (Fig. 3). Energy dispersive X-ray analysis (EDX) with the same small probe showed the carbon  $K\alpha$  line as the only relevant peak in the spectrum. We were able to reproduce the transformation of the cores of onions into diamond in a 400-kV microscope, though with less image resolution.

The crystalline regions grow under irradiation; some onions develop a monocrystalline (Fig. 2a), others a polycrystalline core (Fig. 2b) with sizes ranging from 2 to 50 nm. Typical  $\langle 111 \rangle$  twins are observed in many of these diamond crystallites. After diamond

crystals are formed in the core, the  $c$  lattice spacing of adjacent graphite planes relaxes to slightly higher values (0.25–0.3 nm), compared to onions where no diamond was formed (Fig. 1). On cooling the specimen to room temperature the diamond crystals are found to be stable, whereas the surrounding graphite structure becomes highly defective (Fig. 4), as observed in earlier room-temperature irradiation studies<sup>3</sup>.

It is apparent that the reduced graphite layer spacing and the nucleation of diamond result from a contraction of the whole irradiated particle. Graphite is very strong in the  $a$ – $b$  plane, so we may consider these onions as extremely rigid 'pressure vessels'. We believe that sputtering-induced mass loss from the outer shells

and the dynamics of migration of interstitials are responsible for the contraction of the whole particle<sup>3</sup>. The outermost two shells of smaller onions already exhibit a reduced spacing (typically 0.28 nm) and as no external pressure can exist, we conclude that already the outermost shell compresses by itself. The nonlinear extrapolation of the measured compression modulus of graphite<sup>6</sup> shows that, for a contraction of the graphite lattice in the  $c$  direction down to a lattice spacing of 0.28 nm, a pressure of 36 GPa is necessary. If we relate this pressure  $p$  to the tensile stress  $\sigma$  within the shell by the Poisson formula  $p = 2\sigma t/R$  (where  $t$  denotes the thickness of the layer, which we assume to be the  $c$  lattice spacing in graphite<sup>7</sup> (0.34 nm), and  $R$  is the radius of the shell) we obtain extremely high values for  $\sigma$ ; several hundred gigapascals for outer shells of a few nanometres radius. Also, if we consider the wall of a hollow onion as a continuum, the ratio  $2t/R$  being close to unity, we obtain stresses  $\sigma$  of the order of 50–100 GPa within the wall. These estimated values are much higher than the measured tensile strength of graphite whiskers (20 GPa; ref. 8). It may then be reasonably assumed that the graphite planes in such onions are highly corrugated<sup>9</sup> with some  $sp^3$  bond character between the layers. The pressure prevailing inside the onions may be so high that conditions much above the graphite/diamond equilibrium phase line could exist, and the nucleation of diamond could readily occur. At room temperature, however, the lattice of the irradiated onions is disrupted by many boundary-like defects which drastically

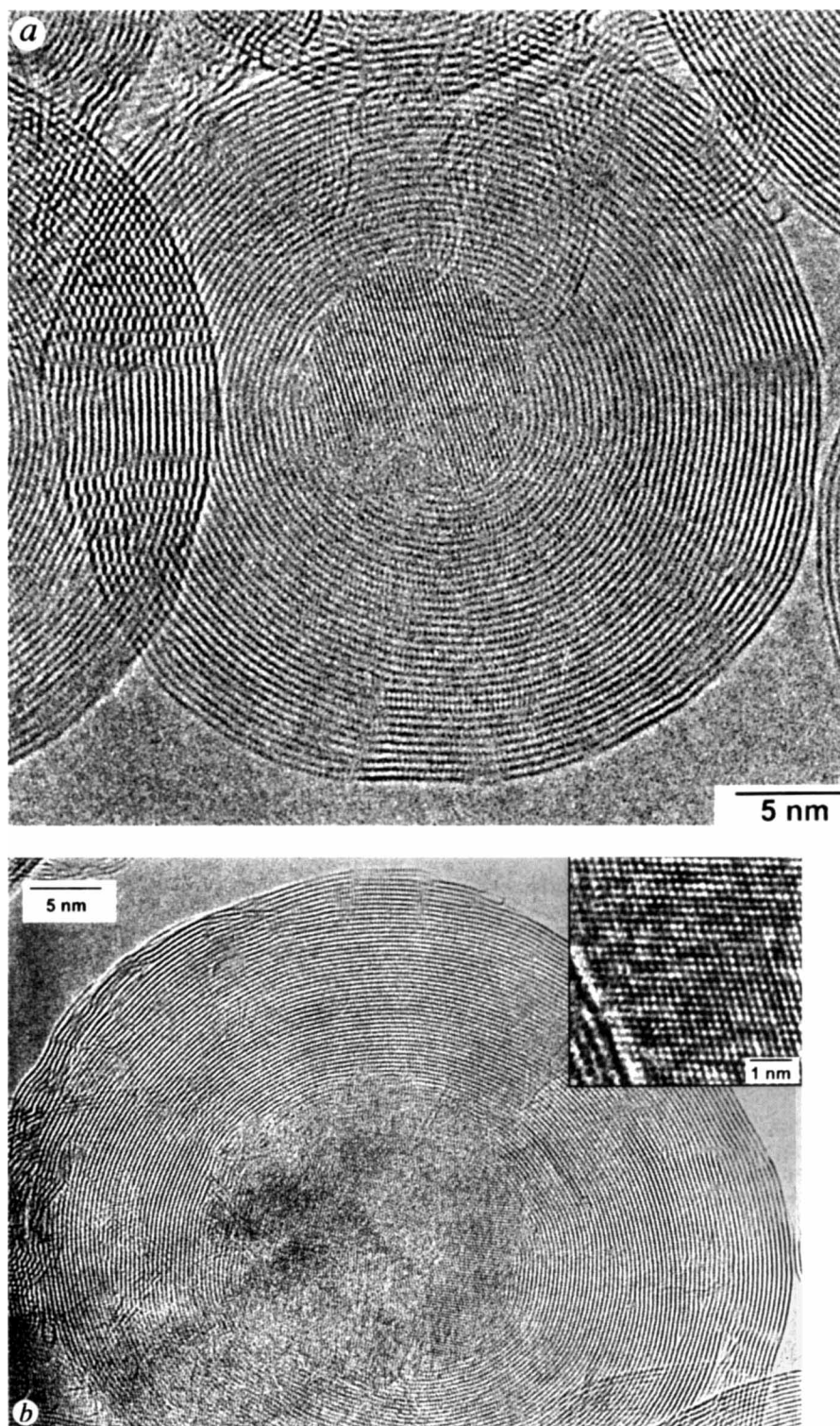


FIG. 2 a, Spherical particle consisting of onion-like shells with a monocrystalline diamond core 10 nm in size. The core shows the  $\langle 111 \rangle$  lattice fringes of diamond with a separation of 0.206 nm. The particle was generated under electron irradiation at 730 °C. b, Carbon onion with a polycrystalline diamond core about 20 nm in size, generated during irradiation at 730 °C. Only diamond crystallites with  $\langle 111 \rangle$  lattice planes close to the Bragg position (that is, in the right part of the diamond core) can be identified as such. The lattice image of the core corresponds to cubic diamond. Some distortions result from overlapping disordered graphite layers. Inset, CCD image of a section of a monocrystalline diamond core, almost in  $\langle 110 \rangle$  projection, which has grown inside a large onion. Part of an overlapping onion is visible in the lower left corner of the inset.

FIG. 3 Selected-area electron diffraction patterns from several carbon onions (a), some of them containing a diamond core, and for comparison from unirradiated source material consisting of polyhedral graphitic particles (b, same scale). The most intense reflection rings of cubic diamond are indexed. The compressed irradiation-induced onions show a broad distribution of graphite lattice spacings, so the graphite rings are considerably smeared. In contrast, the diamond crystals in the cores of the onions exhibit sharp reflections.

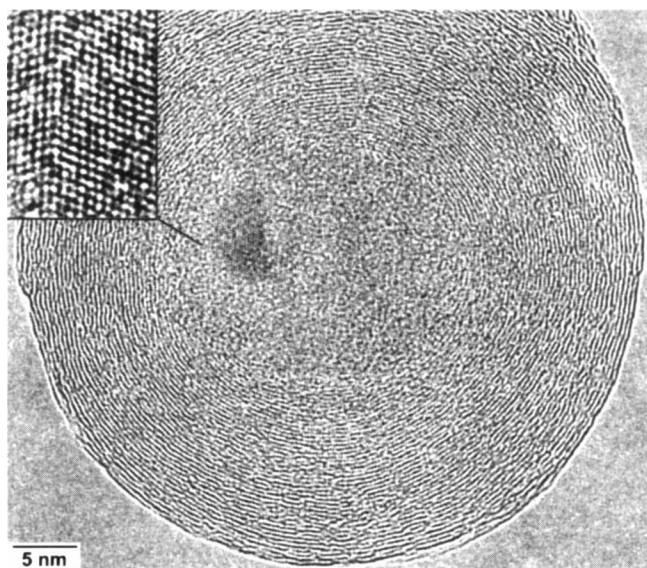
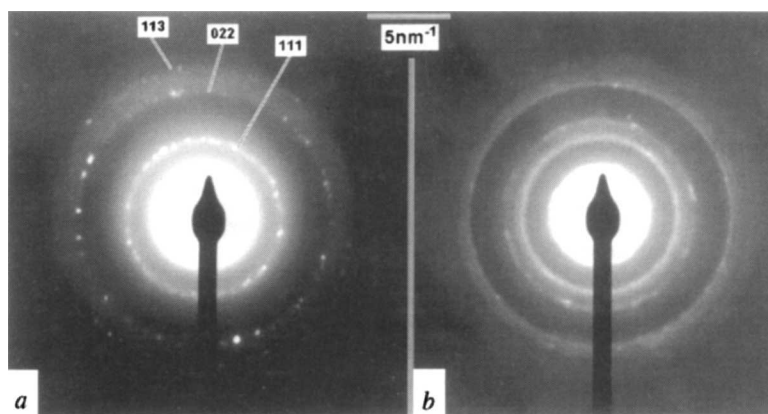


FIG. 4 Onion with a diamond core, formed under irradiation at 700 °C and cooled to room temperature. Irradiation at room temperature has generated a high density of defects in the graphitic shells of the onion. The diamond core, however, remains almost unaffected. A twinned diamond crystallite is seen almost in  $\langle 110 \rangle$  projection (shown enlarged in the inset).

reduce the stability of onions and prevent their contraction, thus explaining why formation of diamond does not occur.

In this experiment it is possible to observe the moving boundary between graphite and diamond during growth of the diamond crystals on an atomic scale. In some regions of the cores we observed that a transformation of  $\langle 0001 \rangle$  graphite planes to  $\langle 111 \rangle$  diamond planes occurs, as has been proposed for the reverse transformation<sup>10</sup>. As the densities of (unstrained) graphite and diamond are different ( $2,250 \text{ kg m}^{-3}$  compared to  $3,510 \text{ kg m}^{-3}$ , respectively) the collapse of the centre of the onions during the transformation could lead to a decrease in pressure, resulting in the observed expansion of the graphite lattice around the diamond cores (Fig. 1). In this experiment the irradiation-induced introduction of defects leads to dangling bonds between the layers and may thus promote the corrugation of the graphite planes. The presence of vacancies and interstitials, which are continuously generated during the irradiation, could lower the energy barrier for the transformation of graphite to diamond as proposed by Bar-Yam and Moustakas<sup>11</sup>

The transformation of graphite into diamond is of considerable technical interest<sup>12,13</sup>. Although graphite can be converted to diamond by the application of high temperature and high pressure, the high stability of the basal graphite planes requires that conditions much above the graphite–diamond phase boundary<sup>14</sup>, or the presence of catalysts, are necessary for diamond formation. The growth of CVD diamond at low temperature and pressure needs the presence of atomic hydrogen<sup>13,15</sup>. The conversion of  $\text{C}_{60}$  to diamond has been achieved at room temperature and pressure of 20 GPa (ref. 16). We believe that our finding of a new way to convert graphite-like carbon to diamond could lead to new understanding of the nature of the direct graphite–diamond transition. Moreover, carbon onions with compressed shells might show interesting properties such as modified electrical conductivity or a localization of electrical charge. Also, foreign materials inside hollow graphitic particles<sup>17</sup> could be subjected to extreme pressures by applying irradiation at high temperature. □

Received 24 April; accepted 11 June 1996.

1. Kroto, H. W. *Nature* **359**, 670–671 (1992).
2. Ugarte, D. *Nature* **359**, 707–709 (1992).
3. Banhart, F., Ajayan, P. M., Redlich, Ph. & Füller, T. *Phys. Rev. Lett.* (submitted).
4. Höschen, R., Sigle, W. & Philipp, F. in *Proc. 11th European Congress on Microscopy* (in the press).
5. Ebbesen, T. W. & Ajayan, P. M. *Nature* **358**, 220–222 (1992).
6. Lynch, R. W. & Drickamer, H. G. *J. chem. Phys.* **44**, 181–184 (1966).
7. Ruoff, R. S. & Ruoff, A. L. *Nature* **350**, 663–664 (1991).
8. Bacon, R. J. *appl. Phys.* **31**, 283–290 (1960).
9. Sandré, E., Julien, J.-P. & Cyrot-Lackmann, F. *J. Phys. Chem. Solids* **55**, 1261–1268 (1994).
10. De Vita, A., Galli, G., Canning, A. & Car, R. *Nature* **379**, 523–526 (1996).

11. Bar-Yam, Y. & Moustakas, T. D. *Nature* **342**, 786–787 (1989).
12. Clarke, R. & Uher, C. *Adv. Phys.* **33**, 469–566 (1984).
13. Angus, J. C. & Hayman, C. C. *Science* **241**, 913–921 (1988).
14. Bundy, F. P. *Physica A156*, 169–178 (1989).
15. Lambrecht, W. R. L. et al. *Nature* **364**, 607–610 (1993).
16. Núñez Regueiro, M., Monceau, P. & Hodeau, J.-L. *Nature* **355**, 237–239 (1992).
17. Ruoff, R. S., Lorents, D. C., Chan, B., Malhotra, R. & Subramoney, S. *Science* **259**, 346–347 (1993).

ACKNOWLEDGEMENTS. We thank R. Höschen for indispensable technical assistance. P.M.A. acknowledges the Alexander-von-Humboldt-Stiftung for support.

CORRESPONDENCE should be addressed to F.B. (e-mail: banhart@wseix.mpi-stuttgart.mpg.de).