Quantum Confinement and Fullerenelike Surface Reconstructions in Nanodiamonds

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We present x-ray absorption and emission experiments and *ab initio* calculations showing that the size of carbon diamond must be reduced to at least 2 nm, in order to observe an increase of its optical gap, at variance with Si and Ge where quantum confinement effects persist up to 6–7 nm. In addition, our calculations show that the surface of nanodiamond particles larger than $\simeq$ 1 nm reconstructs in a fullerenelike manner, giving rise to a new family of carbon clusters: bucky diamonds. Signatures of these surface reconstructions are compatible with pre-edge features observed in measured absorption spectra.

Nanometer sized diamond is a constituent of diverse systems [1] including interstellar dusts and meteorites [2–5], carbonaceous residues of detonations [6], and diamondlike films [7–9]. More than a decade ago Lewis *et al.* [2] reported the presence of diamond nanoparticles in carbonaceous chondrites, the grain sizes varying from 1.4 to $\simeq$ 4 nm, with a distribution peaked around 2.6 nm. In order to test the different hypotheses suggested in the literature to explain the origin of these diamond nanoparticles [4], structural models are essential, but yet unavailable. In particular, models for the surface structure of nanodiamonds are required to explain the data collected for nanodiamond in meteorites. While the structural properties of nanodiamond are basically unexplored, a report [8] on its electronic properties has recently appeared in the literature. It suggests that reducing the size of diamond to the nanoscale may have stronger effects on its optical gap than, e.g., in the case of Si and Ge, and that the gap of particles with a diameter as big as 27 nm could still be larger than that of the bulk [8].

In this Letter we present *ab initio* calculations and x-ray absorption and emission experiments on the effect of quantum confinement and surface reconstructions in nanosized diamond. Our results show that the diameter of carbon diamond must be smaller than at least 2 nm in order to observe an optical gap larger than that of the bulk, contrary to what was reported in previous experiments, and at variance with Si and Ge[10–12]. In addition, based on *ab initio* simulations, we propose evidence for a new family of carbon clusters: bucky diamonds. These are bare carbon nanoparticles consisting of a diamond core and a fullerenelike reconstructed surface. Our theoretical findings on bucky diamond are consistent with pre-edge features observed in measured absorption spectra.

We performed *ab initio* calculations using density functional theory (DFT) [13], and carried out x-ray absorption and emission measurements on nanodiamonds synthesized in detonation waves from high explosives. In our DFT calculations, performed within both the generalized gradient approximation (GGA) [14] and the time-dependent local density approximation (TDLDA)[15], we used a pseudopotential, plane wave approach. The x-ray absorption and soft x-ray fluorescence experiments were carried out at the Stanford Synchrotron Radiation Laboratory and at the Advanced Light Source in Berkeley. The sample size and crystallinity were verified by electron diffraction and high resolution transmission electron microscopy (HRTEM). The intense peaks of the electron diffraction pattern, shown in Fig. 1, indicate a high diamond content of the sample. The HRTEM further revealed the crystallinity of the samples with enhanced atomic layers. It is worth noticing that contrary to nanodiamonds found in meteorites [4], we did not observe a significant proportion of twinned diamond crystals. A detailed analysis of the HRTEM images showed a nanodiamond size distribution of 4 ± 1 nm.

We first discuss the properties of small nanoparticles, i.e., particles with diameter less than $\simeq$ 1 nm, and then
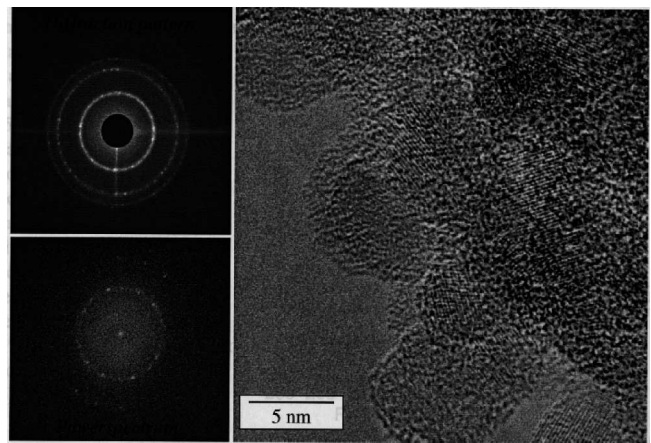

FIG. 1. Electron diffraction pattern (top left), power spectrum (bottom left), and HRTEM picture of the edge zone of a collection of nanodiamonds.

we will analyze in detail larger nanodiamonds. The theoretical results obtained for the energy gaps of hydrogenated nanodiamond clusters as a function of size are reported in Fig. 2. The picture shows both the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied (LUMO) as calculated within GGA and energy gaps obtained using the time-dependent formulation. The two methods show a rapid decrease of the energy gap from a value of 8.9 eV in methane to 4.3 eV in $C_{87}H_{76}$. This value is remarkably close to that of the optical gap in bulk diamond (4.23 eV) obtained using the same theory and the same numerical approximations (e.g., energy cutoff) as those used for the nanodiamond calculations. The computed bulk gap is smaller than the experimental one (5.47 eV), due to well-known errors of local density approximations which usually underestimate band gaps in semiconductors and insulators. However we expect trends of the optical gaps as a function of size to be well reproduced within GGA, as we found in the case of Si [11].

We note that similar to silicon clusters [20], the onset of TDLDA spectra of hydrogenated diamond nanoparticles
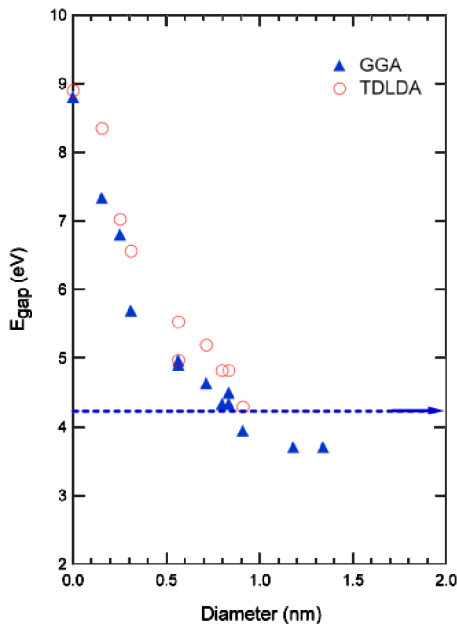

FIG. 2 (color online). Energy gap versus diameter (nm) for hydrogen passivated carbon nanoclusters, as obtained using density functional theory (DFT). All the initial structures were relaxed using the JEEP first principles molecular dynamics code [16]. After performing DFT geometry optimizations, we carried out calculations of single particle energy gaps (HOMO-LUMO, triangles), and we then performed TDLDA calculations [15] using the ABINIT code[19] (circles). The dashed line shows the bulk (indirect) GGA gap value. We note that for the largest clusters ($C_{87}H_{76}$, $C_{148}H_{120}$, and $C_{211}H_{140}$) the GGA gap value is indeed lower than the bulk value. This effect is caused by the stress induced by the hydrogen atoms on the surface and the subsequent carbon lattice relaxation.

exhibits excitations of very low oscillator strength. The energy of these excitations is close to the GGA gap, while the first intense peak in the TDLDA spectrum is typically 0.5 eV higher in energy than the GGA gap. At 1 nm, the difference between the TDLDA and GGA energy gaps is about 0.1–0.2 eV and the energy gap of the nanoparticle is very close to that of the bulk. This indicates that there is no appreciable quantum confinement effect on the optical gap of nanodiamond for sizes larger than 1–1.2 nm, contrary to what is found in Si and Ge with the same theoretical tools [11,12]. These findings were substantiated by performing quantum Monte Carlo (QMC) calculations [21]. Our estimate for the QMC optical gap of $C_{66}H_{64}$ together with the value reported in the literature for CH_4 [22] shows a much more rapid decrease in the optical gap of diamond than in that of Si and Ge, as a function of increasing nanoparticle size. At 0.8 nm the nanodiamond gap is only ~25% higher than the bulk value and we estimate that the QMC nanodiamond gap becomes very close to that of the bulk at $\simeq 2$ nm.

Depending on preparation conditions, nanodiamonds produced experimentally may not have an ideal diamond surface saturated by hydrogen atoms, but rather exhibit reconstructed surfaces. To investigate the effect of surface reconstruction on hydrogenated nanoparticles, we studied some representative cases, i.e., the 29, 66, 147, 211, and 275 carbon atom clusters. Starting from the unrelaxed, fully hydrogenated geometries, we removed pairs of hydrogens whose interatomic distances were within 5% of the H_2 bond length. All surfaces spontaneously reconstructed at low temperature but the reconstruction induced small changes in the GGA gap values.

The results of our calculations, showing that quantum confinement has no appreciable effect on the optical gap of diamond clusters for diameter larger than 1 nm, are consistent with the measured emission and absorption spectra. The experiments were performed on samples of 4 ± 1 nm in size, which were heated and then cooled several times to insure that no impurities be present. Figure 3 shows the valence and conduction spectra of diamond clusters, compared to those of bulk diamond and graphite, as obtained using x-ray emission and absorption techniques, respectively. The nanodiamond K-edge absorption and emission show the same basic spectral features in bulk diamond and in the nanoparticles. In particular, we did not observe any blueshift in the position of nanodiamond conduction and valence band edges, when compared to the bulk, contrary to a recent experimental investigation [8]. The authors of Ref. [8] reported a rather large conduction band shift in diamond clusters grown by chemical vapor deposition. We believe that in Ref. [8] the poor crystallinity (presence of amorphous carbon) of the nanoparticles and a high graphite content may be responsible for the deviation of the nanoparticle spectra from that of bulk diamond. The spectra reported in Fig. 3 also provide additional,
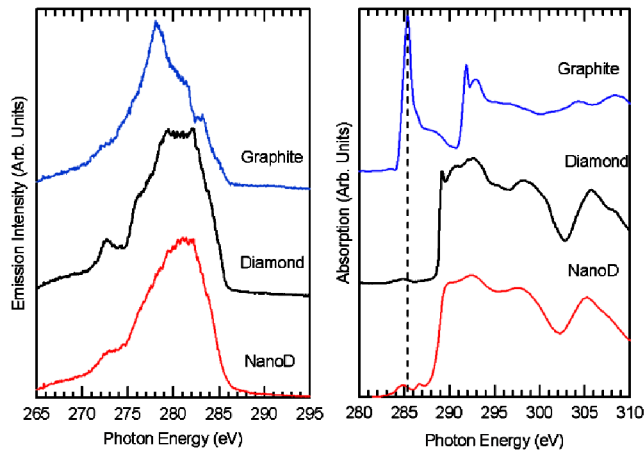
FIG. 3 (color online). Emission (left panel) and absorption (right panel) spectra of nanodiamond compared to bulk diamond and highly oriented pyrolytic graphite (HOPG). The energy scale of carbon x-ray-absorption spectroscopy (XAS) spectra was calibrated to the π resonance of HOPG set to 285.38 eV. It is clear from these spectra that there is no blueshift in the nanodiamond conduction band edge with respect to that of bulk diamond. The electronic structure of the valence band was monitored by soft x-ray fluorescence spectroscopy.

interesting information. The core exciton feature clearly observed in the K-edge absorption of bulk diamond is broadened in the nanodiamond spectra. This may be due to a decrease in lifetime of the core-hole excitation due to confinement of the electron and core hole in the small diamond nanoparticles. We also note that the depth of the secondary gap at 303 eV is shallower in the nanodiamond spectra than in the bulk. This effect has been previously observed and attributed to decreasing diamond crystallite size [23].

Finally we note the presence of pre-edge features in the x-ray absorption spectrum of nanodiamond, which are absent in bulk diamond and graphite (see Fig. 4). Even though π transitions are not present in bulk diamond (contrary to graphite), one observes a small amount of π excitations in the bulk spectra due to unoccupied π bands at the diamond (111) surface. A similar feature is also observed in the nanodiamond spectra. However the pre-edge feature at 286.7 eV is not observed in the bulk. This cannot be associated to a hydrogen terminated diamond surface since it persisted after the sample was annealed above the hydrogen desorption temperature. Indeed, we found that this peak can be attributed to a fullerenelike surface reconstruction occurring in nonhydrogenated nanoparticles, as we discuss below.

We studied in detail the surface reconstruction of nonhydrogenated clusters of 1.4, 2, and 3.0 nm, using quantum simulations. We could use ab $initio$ GGA calculations for the smaller cluster size but we had to resort to semiempirical tight-binding (TB) Hamiltonians [24] in the latter cases, since the number of atoms is too large to be efficiently handled from first principles. Figure 5
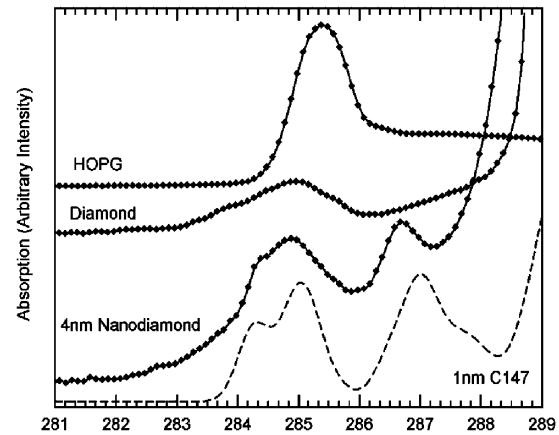

FIG. 4. Details of the XAS spectra presented in Fig. 3, right panel: the pre-edge signal of the 4 nm nanodiamond powder spectra differs significantly from those of both diamond and graphite (HOPG). The computed density of unoccupied states (dashed line) of the 1 nm, fully reconstructed, C147 cluster is shown for comparison. The energies were shifted to make the C147-HOMO coincide with the bulk diamond valence band maximum, and a Gaussian broadening of 0.25 eV was applied to the computed spectrum. The pre-edge peaks are the signature of a mixture of pentagons and hexagons on the reconstructed surface of the diamond core (see Fig. 5). The energy differences between the 4 nm cluster experimental prepeaks and the 1 nm cluster computed prepeaks are due to different hexagon/pentagon ratios and to the GGA approximation.

shows our results for the surface reconstruction of 147 ($\simeq 1.2$ nm) and 275 ($\simeq 1.4$ nm) carbon clusters. Starting from ideally terminated diamond particles, the reconstruction occurs spontaneously at low temperature in our ab $initio$ simulations [18]. First we observed a
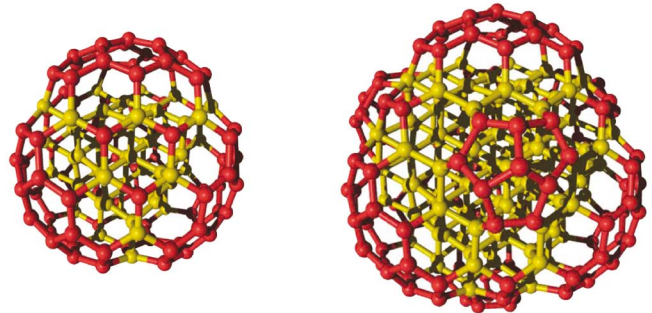

FIG. 5 (color). Ball and stick representation of two $bucky$ $diamond$ clusters: C_{147} and C_{275} ($\simeq 1.2$ and 1.4 nm in diameter, respectively). These carbon clusters have a diamond core (yellow) and a fullerenelike reconstructed surface (red). Similar reconstructions were found for 2 and 3 nm clusters and for clusters as small as C_{66}. The surface reconstructions obtained by ab $initio$ computer simulations give rise to pre-edge signatures in the absorption spectra (see Fig. 4). Both the highest occupied and lowest unoccupied states of bucky diamonds are localized at the surface and interface between the diamond core and the fullerenic surface.

graphitization of the first atomic layer of the (111) facets, followed by the formation of pentagons linking the graphene fragments with the underneath atoms. This provided further curvature to the surface which eventually adopted a geometrical arrangement very similar to that of half a C_{60} molecule. Our TB simulations show similar surface reconstructions for 2 and 3 nm clusters (705 and 2425 atoms, respectively) [25].

These reconstructions induce an effective tensile stress acting on the core of the nanocluster: this effect is at variance with the one found in Si and Ge dots where surface reconstruction is very different from the one found here and it induces an effective compression on the nanoparticle core [26]. We note that the barrier between the ideal surface structure and the reconstructed surface is size dependent and increases as the size of the nanoparticle is increased, to become of the order of several tens of eV, as found in bulk diamond [27]. The comparison between our *ab initio* calculations and the measured spectra indicates that the surface reconstruction of nanodiamond which we have identified by computer simulations is responsible for the features observed in absorption spectra (Fig. 4).

These findings point at the existence of a new family of carbon clusters, bucky diamonds, i.e., carbon nanoparticles with a diamond core of a few nm and a fullerenelike surface structure. We expect these novel carbon nanoparticles to be present not only in carbonaceus residues of detonation but also as inclusions of diamondlike films and in meteorites. Work is underway to investigate the high stability of ~1.5 nm nanodiamond particles found in meteorites, which are most likely bucky diamonds with first-row impurities at the surface, e.g., nitrogen.

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

[2] R. S. Lewis, M. Tang, J. F. Wecker, E. Anders, and E. Steel, Nature (London) **326**, 160 (1987).

[3] R. S. Lewis, E. Anders, and B. T. Draine, Nature (London) **339**, 117 (1989).

[4] T. L. Daulton et al., Geochim. Cosmochim. Acta **60**, 4853 (1996).

[5] H. G. M. Hill, A. P. Jones, and L. B. d'Hendecourt, Astron. Astrophys. **336**, L41 (1998).

[6] N. R. Greiner, D. S. Phillips, J. D. Johnson, and A. F. Volk, Nature (London) **333**, 440 (1989).

[7] K. E. Spear, J. Am. Ceram. Soc. **72**, 171 (1989).

[8] Y. K. Chang et al., Phys. Rev. Lett. **82**, 5377 (1999).

[9] D. M. Gruen, MRS Bull. **26**, 771 (2001).

[10] W. L. Wilson, P. F. Szajowski, and L. E. Brus, Science **262**, 1242 (1993); J. R. Heath, J. J. Shiang, and A. P. Alivisatos, J. Chem. Phys. **101**, 1607 (1994); T. van Buuren, L. N. Dinh, L. L. Chase, W. J. Siekhaus, and L. J. Terminello, Phys. Rev. Lett., **80**, 3803 (1998).

[11] A. Puzder, A. J. Williamson, J. C. Grossman, and G. Galli, Phys. Rev. Lett. **88**, 263 (2002).

[12] S. Ogut, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. Lett. **79**, 1770 (1997); F. Reboredo and A. Zunger, Phys. Rev. B **62**, R2275 (2000).

[13] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] M. E. Casida, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996). In our TDLDA calculations, the number of empty states was taken 3 times as large as the number of occupied states for clusters smaller than 0.5 nm. For the largest clusters, the 600 lowest energy excitations were included. By varying the width of this energy window, we verified that the computed excitation spectra were converged up to at least 2.5 eV above the LUMO level.

[16] Our DFT calculations were carried out using a first-principles molecular dynamics code, JEEP 1.8.0 (F. Gygi, JEEP 1.8.0, LLNL, 1999–2001). We used norm conserving nonlocal pseudopotentials of the Hamann type [17] and we used Car-Parrinello–type simulations [18] for structural relaxations.

[17] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[18] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[19] The ABINIT code is a common project of the Universite Catholique de Louvain, Corning Incorporated, and other contributors (http://www.abinit.org).

[20] I. Vasiliev, S. Ogut, and J. R. Chelikowsky, Phys. Rev. Lett. **86**, 1813 (2001).

[21] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001); A. Williamson, R. Q. Hood, and J. C. Grossman, Phys. Rev. Lett. **87**, 246406 (2001).

[22] J. C. Grossman, M. Rohlfing, L. Mitas, S. G. Louie, and M. Cohen, Phys. Rev. Lett. **86**, 472 (2001).

[23] F. L. Coffman et al., Appl. Phys. Lett. **69**, 568 (1996).

[24] We performed constant number of particles, volume, and temperature Monte Carlo simulations using the potential from M. S. Tang, C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **53**, 979 (2001).

[25] We tested the transferability of the TB parameters by performing two relaxations of the 1.4 nm particle, one using *ab initio* molecular dynamics and one using TB Monte Carlo. The final structures were the same, with only minor angular variations and a slightly larger curvature for the *ab initio* reconstructed surface.

[26] L. Pizzagalli, G. Galli, J. E. Klepeis, and F. Gygi, Phys. Rev. B **63**, 5324 (2001); F. Reboredo et al. (to be published).

[27] A. de Vita, G. Galli, A. Canning, and R. Car, Nature (London) **379**, 523 (1996).