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Concentric-shell fullerenes and diamond particles: A molecular-dynamics study

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Concentric-shell fullerenes are generated from diamond nanoparticles of 1.2 nm to 1.4 nm diameter by means of molecular dynamics simulations based on approximate Kohn-Sham equations. The diamond-to-concentric-shell fullerene transformation observed at temperatures from 1400 K to 2800 K starts at the surface of the diamond particle. Subsequently, the core of the particle gets disordered and the information about the initial atomic structure becomes lost. The final structure consists of two concentric graphitic shells. The intershell spacing of the generated concentric-shell fullerenes is distinctly below the interlayer distance of graphite. It is demonstrated that sp^3-like cross links appear between the shells. Simulated irradiation accelerates the transformation but reduces the number of cross links. [S0163-1829(99)14039-6]

Concentric-shell fullerenes consist of concentric graphitic shells and can be prepared by electron irradiation of graphitic material[1,2] or by thermal annealing of ultrafine diamond particles.[3] The extremely high pressure in the core of the concentric-shell fullerenes gives rise to their use as pressure cells for diamond formation.[4,5] A recent model explains aspects of the structural transformation of graphitic concentric-shell fullerenes to diamond and vice versa[6] but requires the existence of a phase boundary between the transforming components. In order to find out the very reason for the nucleation of diamond in concentric-shell fullerenes, atomistic models for the latter ones are required. We generate such models simulating the transformation of diamond particles into two-shell concentric-shell fullerenes by means of molecular dynamics. The interatomic forces are calculated using approximate Kohn-Sham (KS) equations.[7–10] Diamond particles consisting of 150 or more atoms can transform into two-shell nested fullerenes. Simulated irradiation accelerates the transformation and modifies the main characteristics of the concentric-shell fullerenes generated: the high pressure in the core and the number of sp^3-like cross links between the concentric graphitic shells.

The experiments have shown that ultrafine diamond particles may transform into nested fullerenelike carbon structures at temperatures between 700 K and 1200 K.[3] The reverse process—the conversion of the cores of concentric-shell fullerenes to diamond—has been demonstrated via electron irradiation at specimen temperatures above 900 K by Banhart and Ajayan.[4,5] The diamond-to-concentric-shell fullerene transformation starts at the surface of the particle[3] whereas the formation of diamond in a carbon nested fullerene begins in the center of the latter.[4,5] Graphitization of diamond surfaces has theoretically been proved by molecular dynamics simulations based on a quantum-mechanical first-principles method[11,12] and a density-functional tight-binding (DF-TB) scheme.[13] A model for the radiation-induced transformation of graphite to diamond and vice-versa developed by Zaiser and Banhart[6] gives an explanation for the growth of a diamond nucleus in a graphitic concentric-shell fullerene provided that the diamond nucleus is already present. Banhart[5] considered the high pressure in the concentric-shell fullerene to be the most essential precondition for the nucleation of diamond in the core of concentric-shell fullerenes. Additionally, he supposed sp^3-like cross links to appear between adjacent graphitic shells.

We have developed a microscopic model for the formation of concentric-shell fullerenes. Our model explains the properties of the core of concentric-shell fullerenes on an atomistic scale including the origin of diamond nucleation. In this sense, our model is complementary to the theory by Zaiser and Banhart.[6] We have applied a reaction path which has been experimentally shown to exist,[3] namely that starting from the well-defined atomic structure of diamond. The coordinates for the starting model were generated by a spherical cut out of an extended diamond structure. The number of atoms per particle ranged from 122 to 275. The particles were subjected to temperatures between 1400 K and 2800 K and the evolution of the system was simulated using molecular dynamics. The Newtonian equations of motion were solved simultaneously with approximate Kohn-Sham (KS) equations, describing the electronic states with a LCAO (linear combination of atomic orbitals) ansatz for the KS orbitals. The density-functional-based tight-binding method (DF-TB) used is described in detail elsewhere.[8–10] This method has already been applied successfully to studies of, for example, the structure and stability of fullerenes (cf. Refs. 14 and 15), the graphitization of diamond surfaces,[13] and multifragmentation processes in $C_{60}^{+}+C_{60}$ collisions.[16,17] The equations of motion were integrated numerically (Verlet algorithm) in time steps of 1.2 fs for a total simulation time of up to 50 ps, and at each time step the forces were calculated on the base of the method mentioned above. The temperature was rescaled after each 30 or 50 time steps. To simulate radiation effects, a random kick was given to an atom selected by chance in intervals of 30 to 50 time steps. The maximum kinetic energy transmitted to an atom per kick was 40 eV. For comparison, the threshold energy necessary for

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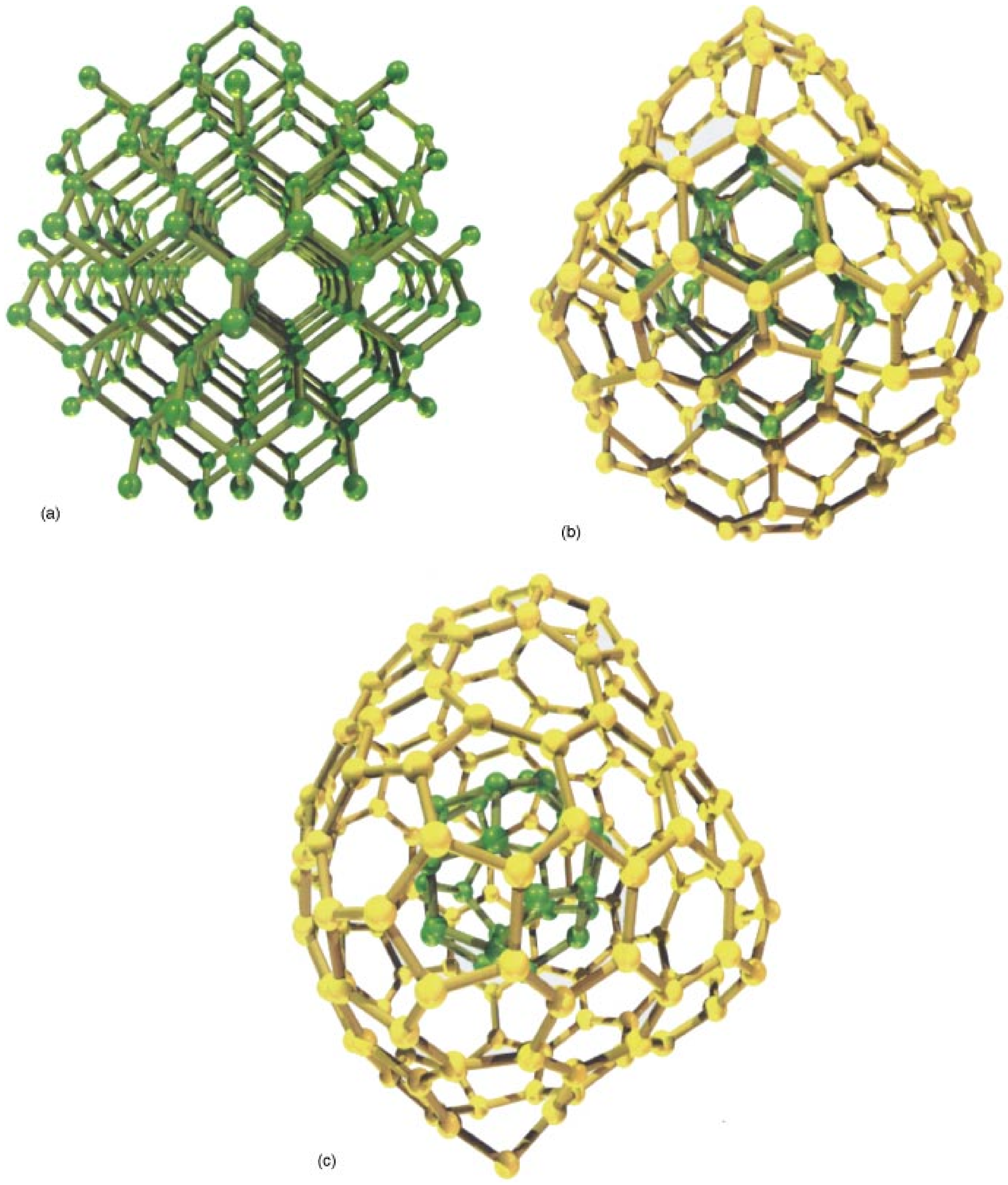

FIG. 1. (Color) Transformation of a diamond particle into a concentric-shell fullerene at 1600 K under simulated irradiation. (a) Initial state: a 191-atom diamond. (b) Intermediate state after 1 ps: a spherical graphitic cage (yellow) with a diamondlike core (green). (c) Final state after 40 ps: a two-shell nucleus of a concentric-shell fullerene (green: inner shell, yellow: outer shell).

the displacement of one atom is of the order of 10 to 25 eV in graphite and 35 eV in diamond (cf. Ref. 5).

Using this procedure we analyzed the structural evolution of about 50 diamond particles. The diamond particles of 1.1 nm size (about 120 atoms) and some of the larger ones underwent fragmentation processes and formed fullerenelike cages. Most of the diamond particles with 150 atoms or more, i.e., a diameter of at least 1.2 nm, transformed to form concentric-shell fullerenes consisting of two concentric graphitic shells. Figure 1 illustrates the transformation process.

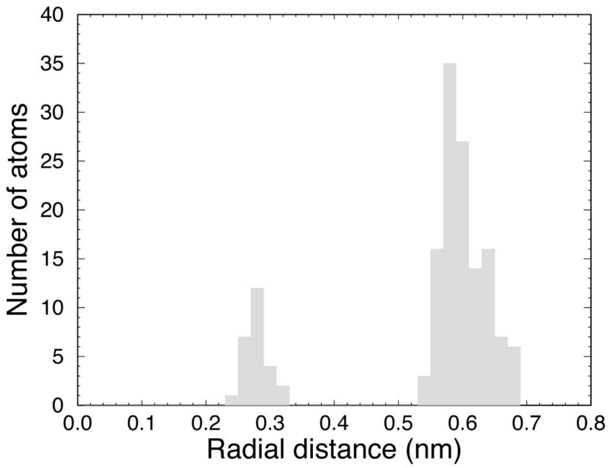

FIG. 2. Number of atoms vs distance from the center of mass of the particle shown in Fig. 1(c).

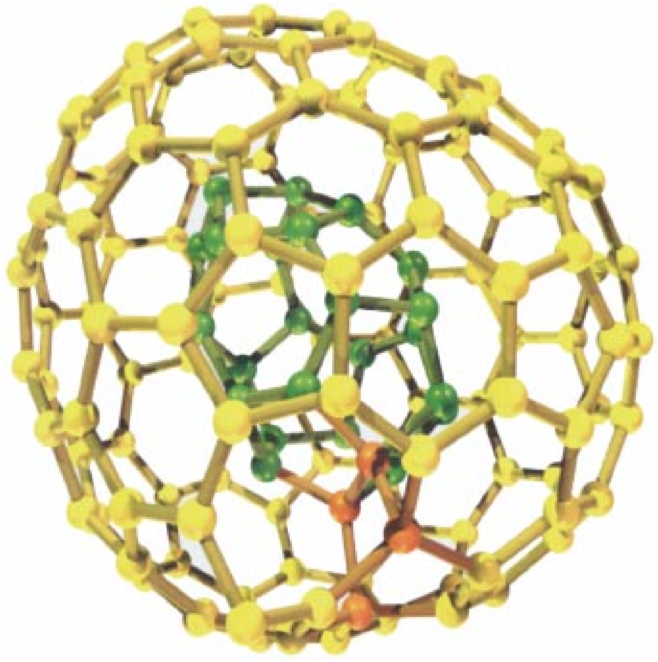

FIG. 3. (Color) Concentric-shell fullerene with cross links between the two concentric shells (green: inner shell, yellow: outer shell, red: cross links with diamondlike coordinated atoms).

The initial diamond particle consisted of 191 atoms [Fig. 1(a)]. The mean accumulated energy transferred to each atom by simulated irradiation was 80 eV, whereby the temperature (1600 K) was kept constant by repeated rescaling as explained above. The total simulation time was 40 ps. During the initial period of about 1 ps, the diamond particle graphitizes at the surface forming a graphitic cage with a diamondlike structure inside [Fig. 1(b)]. In a real experiment, this state would represent the true initial state of the transformation. Then, the diamond short-range order in the core of the particle gets more and more disordered whilst some carbon atoms leave the cluster. At this stage the information about the initial atomic structure of the original particle becomes lost and the subsequent evolution can be considered as typical for the formation of concentric-shell fullerenes from many different types of precursors, i.e., amorphous, graphitic or diamond-like carbon nanoparticles. The final structure consists of two concentric graphitic shells and represents a nucleus of a so-called carbon onion. It should be noted that the cross links observed in the final stable state are not residues of the starting structure but have been formed during the evolution and stabilization of the inner shell. In Fig. 2, the number of atoms vs distance from the center of mass of the particle is plotted for the cluster shown in Fig. 1(c). The two shells are distinctly separated and the difference of the mean radius of the outer and the inner shell is 0.31 nm.

The smaller diamond particles consisting of 159 atoms could transform spontaneously, i.e., without simulated irradiation, within a total simulation time of about 10 ps. The additional stimulation of the system by simulated irradiation accelerates the transformation processes. The diamond particles consisting of 191 or more atoms, however, did not transform completely within the limited simulation time if no irradiation was applied.

Table I presents typical parameters of the transformation process and the concentric-shell fullerenes that were generated. The data are representative for more than 50 different simulations. The distance between the shells is considerably smaller than the value 0.335 nm for the interlayer distance in graphite. This is in accordance with the experimental

TABLE I. Here N_0 is the number of atoms of the original diamond cluster; D is the corresponding diameter of the particle; T is the temperature of the cluster during the simulation; t_{total} is the total simulation time; E is the mean accumulated energy transfer per atom by simulated irradiation; N_1 and N_2 are the number of atoms on the inner and outer sphere of the concentric-shell fullerene, respectively; d is the interlayer distance between the shells and the number of cross links denotes the number of sp^3-like bonds between them.

N_0	D (nm)	T (K)	t_{total} (ps)	E (eV)	N_1	N_2	d (nm)	Cross links
159	1.2	1600	12	0	31	118	0.27	3
159	1.2	2100	47	62	26	119	0.28	1
191	1.3	1600	40	80	26	126	0.31	0
191	1.3	1700	32	24	33	129	0.29	1
275	1.4	2800	19	24	2+52	184	0.26	4
275	1.4	2500	44	280	40	155	0.27	1

observations.[4,5] The number of atoms per spherical shell fluctuates and in one of the examples the inner shell is not empty but contains a carbon dimer. In general, the topology of the individual carbon shells has some resemblance to the corresponding fullerenes.[18] There are pentagons and hexagons but also polygons with four and seven vertices. The distribution of the nearest neighbor distances within the individual shells of the concentric-shell fullerene nuclei is in the range between 0.138 nm and 0.150 nm, i.e., similar to the C-C bond lengths in fullerenes.[19,20]

In most of the nested fullerenelike clusters the two concentric shells are connected by cross links, i.e., one atom belonging to the inner shell and another situated on the outer shell are connected by a bond with sp^3 character. Figure 3 shows such an example. The two atoms connecting the adjacent shells are tetrahedrally coordinated. The bond length (0.154 ± 0.06) nm is comparable to that of diamond, and the bond angles, $109°\pm10°$, correspond also to values characteristic for sp^3 bonding. The appearance of sp^3-type cross links is supposed to be essential for the nucleation of diamond in concentric-shell fullerenes.[4] Here we give evidence for their existence.

As has been already mentioned, simulated irradiation accelerates the formation of the two-shell concentric-shell fullerenes. However, the data given in Table I show that simulated high irradiation intensity reduces the number of sp^3 cross links and enhances the distance between the concentric graphitic shells. Low intershell distances are tantamount to high pressure which is, on the other hand, a precondition for the formation of diamond. For a contraction of graphite in c direction down to the intershell distances obtained in the simulation presented here (see Table I) a very high pressure (e.g., 36 GPa for 0.28 nm[4]) would be necessary. Furthermore, the sp^3-like cross links within the concentric-shell fullerenes are supposed to act as seeds for the creation of diamond.[4,5] Therefore, we suggest that irradiation during the formation of concentric-shell fullerenes could be used as a process parameter in order to balance the rate of nested fullerene production versus the tendency to form diamond within the concentric-shell fullerene core.

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