Rigid crystalline phases of polymerized fullerenes

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Combining total energy and structure optimization calculations, we explored new possible crystalline phases of covalently bonded C_{60} fullerenes and determined their structural, elastic, and electronic properties. Motivated by reported observations that bulk structures of polymerized fullerenes may be stiffer than diamond, we have explored possible ways of fullerene polymerization and have identified 12 stable crystal structures as potential candidates. Even though all these phases are very stiff, none of them exceeds the bulk modulus of diamond. The electronic structure of three-dimensional crystals of polymerized C_{60} depends mainly on the packing structure of the system, with only minor modifications due to the specific inter-fullerene bonding.

Owing to the fact that the binding energy of carbon atoms in diamond and in graphite is roughly the same, whereas the atomic coordination number in graphite is lower than in diamond, the interatomic sp^2 bonds in graphite are intrinsically stronger than the sp^3 bonds in diamond. Still, diamond is known as the solid with the highest bulk modulus[1] of 443 GPa. Obviously, substantial effort has been invested to harness the toughness of the sp^2 bond in a three-dimensional (3D) atomic arrangement with a bulk modulus superior to that of diamond. In spite of serious theoretical attempts to utilize the stiffness of the sp^2 bond in a solid,[2] none of the postulated structures could rival diamond in its structural rigidity. Only on the nanometer scale do non-planar sp^2 bonded carbon structures including fullerenes[3] and nanotubes[4,5] show an extraordinary stability and stiffness.[6–11] The bulk modulus of a single C_{60} molecule is predicted to reach the value of[11] 717 GPa. Nevertheless, this superior stiffness of individual fullerenes is not reflected in the elastic properties of molecular crystals formed of fullerenes,[12] which are soft due to the weak inter-fullerene interaction.

Recent observations suggest that C_{60} fullerenes, which have polymerized into 3D crystals under high pressure and high temperature conditions, surpass diamond in hardness.[13] Some of the polymerized C_{60} crystals have been studied theoretically.[14] Optimized packing within selected finite-size C_{60} aggregates, but not infinite structures, has been suggested based on the comparison between simulated x-ray patterns and experimental data.[15] Theoretical calculations so far have failed to identify any structure with a bulk modulus comparable to the reported experimental data, which would exceed the value of bulk diamond. It has also been pointed out that the experimental methods used to identify the structure of polymerized fullerenes may not be conclusive.[16] The uncertainty regarding the atomic arrangement within super-hard polymerized C_{60} structures requires extensive additional studies.

Previous computational attempts to explore candidate systems for hard polymerized fullerenes were limited to few structures,[14] since the rehybridization occurring in fullerene polymers cannot be described reliably by analytical bond order potentials, and thus requires more sophisticated, computationally demanding total energy functionals. Due to the large number of degrees of freedom, unconstrained optimization of the atomic coordinates as a function of volume, and thus a reliable determination of the total energy and the bulk modulus is computationally prohibitive with *ab initio* total energy functionals.

Here we calculate the total energy of 12 stable polymerized fullerene phases using an electronic Hamiltonian that had been applied successfully to describe the formation of peapods,[17] multi-wall nanotubes,[18] the dynamics of the "bucky-shuttle",[19] and the melting of fullerenes.[20] The underlying parametrized total energy functional[21,22] is efficient enough to explore many structures, providing an adequate description of total energy changes associated with different bonding geometries. Our approach reproduces correctly the observed bulk modulus of cubic diamond. Also, as we discuss below, our results compare favorably with *ab initio* results,[14] which have been reported for a limited number of candidate systems. Besides the optimized geometry, we also determine the physical properties of candidate structures for super-hard crystalline materials.

Fullerenes such as C_{60} are known to form stable one-dimensional (1D) and two-dimensional (2D) polymers by the "cycloaddition" reaction, with "double bonds" facing each other in adjacent fullerenes.[23–25] Selected 1D and 2D polymer structures are shown in Fig. 1(a), with the nature of the bond depicted in Fig. 1(b). The interaction between such low-dimensional polymers in 3D assemblies is generally weak, similar to the inter-layer interaction in graphite. The prerequisite for making bulk structures incompressible is the formation of strong, covalent bonds between these low-dimensional polymers. Such a rehybridization is indeed expected to occur spontaneously under high temperatures and pressures, similar to the conversion of rhombohedral graphite to hexagonal diamond.[26]

Due to structural constraints, maximizing the inter-fullerene bonding is not as easy in 3D crystals as it is in one and two dimensions. Polymerization by cycloaddition, shown in Fig. 1(b), occurs at moderate temperatures and pressures. Under less favorable conditions, other covalent inter-fullerene bonds may be established, which would increase the number of favorable local bonding geometries and thus improve the degree of covalent bonding in bulk structures. Fullerene polymerization by reactions other than cycloaddition may require high temperature and pressure con-
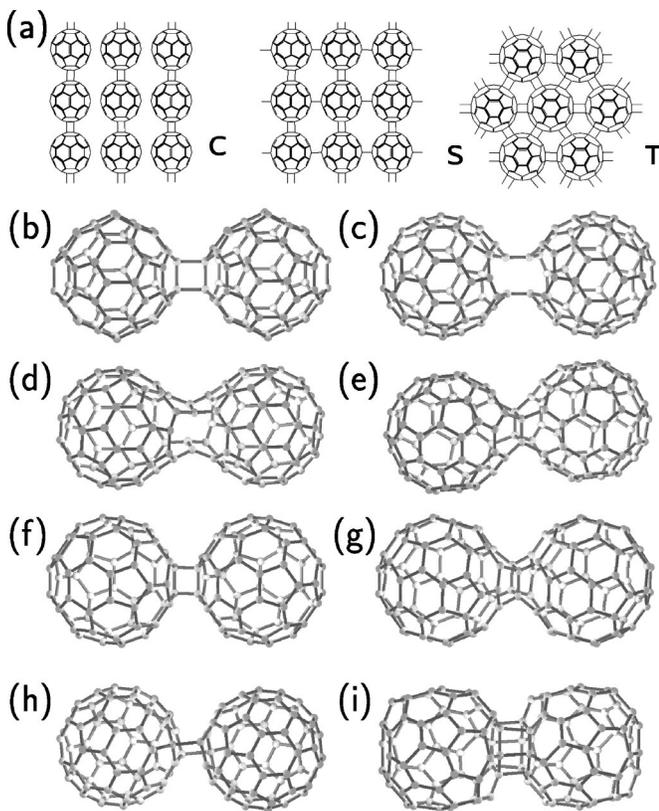
FIG. 1. Types of covalent bonding between C_{60} molecules. (a) Arrangement of polymerized C_{60} chains (C), a square (S) and a triangular (T) 2D lattice of polymerized C_{60} molecules. Polymerization in these low-dimensional structures occurs by the "cycloaddition" reaction, depicted in (b). The different inter-fullerene bonding schemes considered here are shown in (b)–(i). (b) C_{60} dimerization by the $66/66$ $(2+2)$ cycloaddition reaction, which converts pairs of "double bonds," facing each other in adjacent fullerenes, to single bonds, and leads to the formation of two new "single bonds" connecting the fullerenes. (c) Starting with structure (b), disruption of the two intra-fullerene bonds, affected by the cycloaddition, strengthens the inter-fullerene bonds and partly relieves structural strain. (d) Starting with the structure (c), rotation of the inter-fullerene bonds normal to the plane of the figure leads to the "open hinge" structure. (e) Compressing structure (d), the hinges may approach each other to form a four membered common ring. (f) $56/65$ $(2+2)$ cycloaddition, related to structure (b), but involving a pair of "single bonds" at the common pentagon-hexagon edge, rather than "double bonds" at the common hexagon-hexagon edge. (g) Starting with the structure (c), rotation of the inter-fullerene bonds normal to the plane of the figure leads to a new bonding scheme, which we call the $56/65$ four membered common ring. (h) Occurring mainly in body-centered orthorhombic fullerene lattices, the $(3+3)$ cycloaddition establishes a covalent bond along the cell diagonal between the closest atoms in adjacent fullerenes. (i) Occurring mainly in body-centered cubic fullerene lattices, $(6+6)$ cycloaddition connects two facing hexagons in adjacent fullerenes along the cell diagonal.

ditions, similar to those reported in Ref. 13. In our studies of bulk fullerene polymers we considered alternative inter-fullerene bonds, depicted by the different bonding schemes in Figs. 1(c)–(i), which have been suggested previously.[27,28]

Such strong inter-fullerene bonds have been recently observed to connect fullerenes during their fusion inside carbon nanotubes,[29–31] while subjected to effective high pressure conditions.[32]

The bonding schemes between C_{60} molecules, which we consider in the following, are depicted in Figs. 1(b)–(i). The most common polymerization involves the $66/66(2+2)$ cycloaddition, depicted in Fig. 1(b), involving "double bonds" at common hexagon-hexagon edges in adjacent fullerenes, which face each other. This bonding scheme connects fullerenes to form chain polymers, labeled by C in Fig. 1(a), by converting pairs of "double bonds," facing each other in adjacent fullerenes, to single bonds, and leads to the formation of two new "single bonds" connecting the fullerenes. Due to their partial sp^3 nature, the new bonds cause a corresponding structural relaxation within the fullerenes. Structures depicted in Figs. 1(c)–(e) may be derived from the structure in Fig. 1(b) by subsequent bond breaking and bond rotation. Disrupting the two intra-fullerene bonds, involved in the $(2+2)$ cycloaddition, stabilizes the inter-fullerene bonds and partly relieves structural strain, as depicted in Fig. 1(c). Due to the smaller number of structural constraints in this double chain (DC) configuration, this structure is less rigid than that in Fig. 1(b). In this system, all atoms have three neighbors, and all interatomic bonds are sp^2-like. Rotating the inter-fullerene bonds by 90° yields an open hinge (OH) structure with sp^2 bonded bridges, depicted in Fig. 1(d). We also note that these structures occur during the stepwise conversion of two C_{60} fullerenes to a C_{120} capsule by generalized Stone-Wales transformations.[32,33]

The open-hinge structure in Fig. 1(d) bears promise as a building block in materials with a high bulk modulus, since even its narrowest structural elements are graphene strips with an unusually high tensile strength. Among all the possible lattice geometries based on this bonding type, only one turned out to remain stable under compression. Compressing the open-hinge structure in Fig. 1(d) leads to a spontaneous formation of a bond connecting the bridges and the formation of a four membered common ring (FCR) between fullerene pairs. This compact covalent bonding arrangement results in a more stable and rigid bonding scheme, as depicted in Fig. 1(e), and appears to be another promising candidate for an ultra-hard fullerene based material. It is conceivable that the rigidity of the bulk material will scale with the number of four membered common rings it could accommodate.

With the particular symmetry of fullerene molecules and the geometrical constraints imposed by a lattice structure, it is impossible to simultaneously connect adjacent fullerenes by a particular type of bond. Design of an ultimately hard crystal may involve inter-fullerene bonding structures not considered before. One of the bonding schemes, which has not been considered before when constructing candidate super-hard C_{60} structures polymerized in 3D, is the $56/65(2+2)$ cycloaddition, very similar to $66/66(2+2)$ cycloaddition. The structure obtained by the $56/65(2+2)$ cycloaddition, shown in Fig. 1(f), is closely related to the structure shown in Fig. 1(b), but involves a pair of "single bonds" at the common pentagon-hexagon edge, rather than "double bonds" at the common hexagon-hexagon edge. The equilib-

rium structure and electronic properties of 2D polymerized C_{60} using this bonding type have been reported recently.[25] A similar bond rotation, which led to the FCR bonded structure in Fig. 1(e), could be carried out in the structure shown in Fig. 1(f), to yield a different bonding scheme, depicted in Fig. 1(g).

The bonding schemes described so far can form strongly connected 2D lattices, including those in Fig. 1(a), which can be stacked to form a 3D lattice. In close packed 3D structures, not all bonds between adjacent planes of polymerized fullerenes are normal to these planes. The bonding scheme is dictated by the size of the fullerene and the lattice type. There are two straightforward ways to connect C_{60} molecules along a diagonal in a unit cell, namely the $(3+3)$ cycloaddition and the $(6+6)$ cycloaddition, depicted in Figs. 1(h) and (i), respectively. In some lattices the inter-fullerene nearest neighbor distance along a particular direction may be too large for a covalent bond to form.

Using the different bonding schemes mentioned above, we have arranged C_{60} molecules in 16 different crystalline lattices, such as the simple cubic (SC), body-centered orthorhombic (BCO), face-centered cubic (FCC), and body-centered cubic (BCC) lattice. For the sake of convenience, we consider all these lattices as orthorhombic lattices with a basis, spanned by the orthogonal lattice vectors **a**, **b**, and **c**. We oriented the fullerenes in a way to form one of the bonds depicted in Figs. 1(b)–(g) along the lattice vector directions. Among these structures, the BCC phase formed by $(2+2)$ cycloaddition, and some of the BCO phases have been discussed in the literature previously. Our results agree very well with those of *ab initio* calculations for structural parameters and bulk modulus of the the published BCC and BCO phases,[14] and also with other structure optimization calculations for BCO phases.[15] Due to the constraints imposed by the unit cell geometry, the bond along the space diagonal in the BCO lattice is formed by the $(3+3)$ cycloaddition. The corresponding bond between the closest carbon atoms on neighboring fullerenes is shown in Fig. 1(h). In the SC lattice, all bonds occur along **a**, **b**, and **c**. In the BCC lattice, new bonds along the space diagonal are formed by the $(6+6)$ cycloaddition. In the FCC lattice, all inter-fullerene bonds, regardless of the direction, are formed by the $56/65(2+2)$ cycloaddition, as depicted in Fig. 1(f), or bonds involving a $56/65$ four membered common ring, depicted in Fig. 1(g).

To determine the physical properties of these systems, we first optimized the unit cell size for each structure using a conjugate gradient energy minimization, starting from the initial structures discussed above. We have used conventional orthorhombic unit cells in our total energy and electronic structure calculations. To determine the bulk modulus, we have calculated the total energy of the system as a function of unit cell size. All the atoms have been fully relaxed for each volume, and total energies have been determined for the relaxed structures. In Fig. 2 we show the energy per atom versus the relative volume change for the stiffest BCC and BCO structures. Unlike the BCC structure, the BCO phase maintains its stiffness under both tensile and compressive stress. We determine the bulk modulus, which is related to
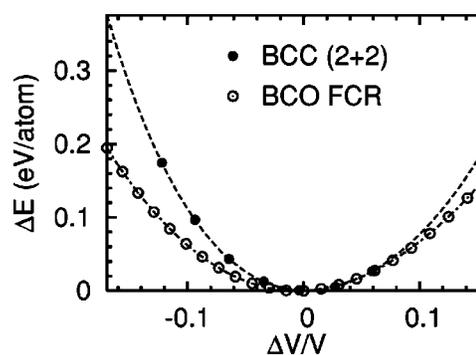
FIG. 2. Energy change per atom ΔE vs the relative volume change $\Delta V/V$ for the stiffest BCC and BCO structures. Closed circles are data points for BCC crystals, with bonds along the sides of the conventional unit cell formed by $(2+2)$ cycloaddition. A polynomial fit to the BCC data points, representing relaxed structures, is given by the dashed line. Open circles are the data points for the BCO lattice, containing four membered common ring (FCR) bonds between fullerenes. A polynomial fit to the BCO data points is given by the dash-dotted line.

the second derivative of the energy around the equilibrium, from the fitted polynomial functions.

We summarize the calculated structural, mechanical and electronic properties of the stable systems considered here in Table I. We denote the structures according to the lattice and bonding type. Since the type of diagonal inter-fullerene bonds is determined by the lattice type, we do not include this information in the structure notation. For each structure we list the cohesive energy E_{coh}, the bulk modulus B, the gravimetric density ρ, the fundamental band gap energy E_g, the density of states at the Fermi level $N(E_F)$, the number of atoms in the orthorhombic conventional unit cell N_c, and the dimensions a, b, c of the conventional unit cell. Four of the BCC structures, which we initially considered and which turned out to be unstable, are not listed in the table. Table I contains only one stable open hinge (OH) structure, since the OH bond in other structures is metastable and transforms into a FCR bond under compression.

Our results include physical properties of four different BCO phases. All BCO phases are rather close-packed and have a gravimetric density around 2.4 g/cm³, similar to the density reported in the experiment,[13] and show a metallic character. In the BCO $(2+2)$ structure, all inter-fullerene bonds along **a** and **b** are formed by $(2+2)$ cycloaddition, and no covalent bonds occur along the **c** direction. The bulk modulus $B \approx 166.7$ GPa of this structure is comparable to or higher than that of any elemental metal, yet its binding energy is still comparable to that of isolated C_{60} molecules. The rigidity of this BCO crystal increases, as inter-fullerene bonds along the **a**-axis are converted into four membered common rings, resulting in the BCO SFCR-I structure. Since the FCR bonding scheme is stiffer than that resulting from the $(2+2)$ cycloaddition, the bulk modulus in this system increases by 30%. We also find that the unit cell shrinks in the **a** and **b** directions, but expands along **c** direction. The energy gained by bringing the fullerenes closer to each other in the *a-b* plane outweighs the energy loss, associated with elongating the bonds along the cell diagonal.

TABLE I. Calculated physical properties of polymerized C_{60} crystal structures, as compared to cubic diamond. For each stable structure considered, we list the average cohesive energy E_{coh} per atom with respect to isolated atoms, the bulk modulus B, the gravimetric density ρ, the band gap energy E_g, and the density of states at the Fermi level $N(E_F)$ in electrons per eV. We also give the number of carbon atoms in the orthorhombic conventional unit cell, N_c, and the size of the conventional unit cell along the x, y, and z direction, given by a, b, c, respectively.

Structure	E_{coh}(eV)	B(GPa)	ρ(g/cm^3)	E_g(eV)	$N(E_F)$	N_c	a(Å)	b(Å)	c(Å)
BCO (2+2)	−7.253	166.7	2.43	0.00	5.5	120	8.80	8.80	12.7
BCO SFCR-I	−7.283	215.5	2.43	0.00	16.5	120	8.50	8.70	13.3
BCO SFCR-II	−7.298	160.2	2.38	0.00	4.4	120	8.50	8.75	13.3
BCO FCR	−7.284	254.1	2.45	0.00	11.2	120	8.60	8.60	13.2
BCC (2+2)	−6.825	369.7	2.61	2.03	0.0	120	9.71	9.71	9.71
BCC DC	−6.818	286.3	2.57	2.16	0.0	120	9.77	9.77	9.77
BCC FCR	−6.533	352.1	2.70	0.96	0.0	120	9.58	9.58	9.58
SC 2+2	−7.267	54.1	1.65	1.41	0.0	60	8.98	8.98	8.98
SC FCR	−7.327	184.7	1.84	1.99	0.0	60	8.65	8.65	8.65
SC OH	−7.356	166.1	1.81	0.96	0.0	60	8.71	8.71	8.71
FCC 2+2	−7.213	179.0	2.29	0.00	2.1	240	12.78	12.78	12.78
FCC FCR	−7.213	177.9	2.29	0.00	2.4	240	12.78	12.78	12.78
Diamond	−7.408	477[a]	3.51	5.4	0.0	8	3.57	3.57	3.57

[a]Calculated value. Experimental value is B=443 GPa (see Ref. 1).

The energetically more stable BCO SFCR-II structure with a single FCR is obtained by breaking the bonds along the **b** axis, formed by (2+2) cycloaddition, which relieves some of the strain along the diagonal (3+3) bonds, increasing the cell depth b, as listed in Table I. This phase is formed of arrays of 1D fullerene chains, polymerized with FCR bonds, inter-connected by (3+3) bonds to a 3D structure. Due to the lower number of covalent inter-fullerene bonds, the bulk modulus is lower in this system, close to the value of the BCO (2+2) phase. We find that for the same number of covalent inter-fullerene bonds, increasing the fraction of FCR bonds leads to higher bulk modulus values. Indeed, according to Table I, the stiffest BCO structure is the BCO FCR phase, with all inter-fullerene bonds along **a** and **b** formed by four membered common rings. The bulk modulus of this structure, B=254.1 GPa, compares favorably with the value found in cubic diamond,[1] B_{dia}=443 GPa, while the gravimetric density of the fullerene structure is lower than that of diamond. All the BCO phases we have investigated are very stable, with cohesive energies comparable to that of diamond. Also, based on comparing simulated x-ray patterns[15] with observed x-ray data,[13] BCO structures appear as the most likely components of the reported super-hard carbon phases. Since the highest bulk modulus of any BCO phase amounts to barely more than half the diamond value, these structures cannot account for the reported high bulk modulus values[13] of ≈500−900 GPa.

Since even a strong covalent connection between fullerenes along the **a** and **b** direction is not sufficient to yield a very high bulk modulus, we considered alternative bonding schemes with strong bonds also along the **c** direction. One realization of such a bonding scheme is the BCC lattice, with fullerenes in adjacent a-b planes close enough to

form covalent bonds along the **c** direction. According to Table I, all BCC phases have higher bulk modulus values than BCO or any other lattice types. As a matter of fact, the bulk modulus of the stiffest BCC phase is only 20% lower than that of cubic diamond, while the gravimetric density of this new phase is still 25% smaller than in diamond. In view of the optimized cell dimensions, which contain relatively large inter-fullerene distances that are incompatible with strong covalent bonds, we would expect the BCC phase to be barely stable. Under compressions, however, the high stiffness of this phase benefits from the rather incompressible (6+6) bonds along the cell diagonal, resulting in the highest bulk modulus value identified in this study.

The anticipated low stability of the elongated inter-fullerene bonds in the BCC phase is reflected in its lower stability with respect to the BCO phase according to Table I. As a matter of fact, in absence of steric constraints protecting the cubic symmetry, we should expect a spontaneous symmetry breaking, leading to a transformation of the BCC to the more stable BCO phase. This indeed occurs in the metastable BCC phase of C_{60} molecules, polymerized with four membered common rings in the a-b plane, with no covalent bonds along the **c** axis, and (6+6) connections along the unit cell diagonal.

As suggested above, the stiffness of the BCC structures under compression is in stark contrast to their much lower strength under tension. This is seen from the asymmetry of the elastic response of the BCC (2+2) lattice, shown in Fig. 2, which is very different from the almost symmetric elastic response of the BCO lattice subject to relative volume changes. Moreover, beyond a critical tensile strain, all BCC phases undergo structural changes, reflected in the lack of data points for the BCC (2+2) phase at large positive relative volume changes $\Delta V/V$ in Fig. 2.

All stable BCC phases listed in Table I exhibit identical bonding along the **a**, **b**, and **c** axes. We found all these structures to be insulators with a $1-2$ eV fundamental band gap, and a gravimetric density close to 2.6 g/cm^3. The stiffest BCC crystal is BCC $(2+2)$ with the bulk modulus $B \approx 370$ GPa. Since the double chain (DC) inter-fullerene connection is weaker, the BCC DC structure has a lower bulk modulus than BCC $(2+2)$, but is still stiffer than other lattice types due to the presence of the incompressible $(6+6)$ inter-fullerene connections along the cell diagonal. The dominant role of $(6+6)$ bonding in achieving a high stiffness is reflected in the similar bulk moduli of the BCC FCR and the BCC $(2+2)$ structures. Apparently, the intrinsic higher stiffness of FCR connections, which lead to high bulk modulus values in BCO lattices, is of secondary importance in this case.

As mentioned above, the marginal stability of the BCC lattice was caused by the large size of the C$_{60}$ molecule in the center of the cubic unit cell. We may expect that removal of the central fullerene will stabilize the cubic lattice by reducing the strain along the **a**, **b**, and **c** directions. Even though the resulting simple cubic phase should be energetically more favorable, the lower packing fraction of fullerenes may lower the bulk modulus. We have studied four different SC phases. Out of these, SC with a double chain bond transforms into the SC $(2+2)$ structure even under small pressure, thus eliminating it as a candidate for a super-hard structure. Since the compressibility of the SC lattice directly reflects the rigidity of the inter-fullerene connections along the cube edges, we can easily rationalize that the bulk modulus of SC FCR is the highest among the SC lattices, followed SC OH and finally SC $(2+2)$, the softest SC lattice. As seen in Table I, the gravimetric densities of all SC phases are approximately half the value of diamond. All SC fullerene crystals are insulators with a $\approx 1-2$ eV band gap. The SC OH phase with open hinge connections is unique in containing only three-fold coordinated carbon atoms, implying sp^2 interatomic bonding throughout the structure. This results in a high bulk modulus $B \approx 166$ GPa at a relatively low density of 1.81 g/cm^3. As a logical consequence, schwarzite or Mackay structures consisting of a simple cubic lattice formed by nanotubes with perfect sp^2 interconnects, should be extremely rigid. Due to the constraints associated with the cubic symmetry of such a structure, we find the number of atoms in C$_{60}$ to be insufficient to form such perfect sp^2 interconnects at the vertices.

The last lattice type we have investigated is FCC, where all inter-fullerene bonds are identical. We have considered 56/65 connections, displayed in Fig. 1(f), and 56/65 four membered common rings, shown in Fig. 1(g). In spite of the different bonding, the two structures share similar values of the bulk modulus, unit cell size and gravimetric density. The unexpected insensitivity of the bulk modulus $B \approx 180$ GPa to the bonding scheme is associated with extreme structural deformations of the fullerenes, which degrade substantially their initial structural rigidity. Consequently, the presence of strong covalent inter-fullerene bonds is only beneficial for an overall high structural stiffness, if fullerene deformations do not reduce the intrinsic rigidity of the molecule. We find both FCC phases to be metallic with a similar density of states at the Fermi level. As seen in Table I, the metallic behavior of FCC structures is unique among the cubic lattices.

A major advantage of fullerene based super-hard materials is their formation mechanism by self-assembly from sub-nanometer sized fullerenes. This is particularly beneficial when micrometer-sized voids are to be filled with a rigid structure to enhance the overall stiffness. The high structural rigidity of polymerized fullerenes is coupled with a low gravimetric density, which lies below the diamond value in all the compounds studied here, mainly due to the empty space inside the fullerenes. Nevertheless, we must notice that the stiffest phases tend to have the highest mass densities. As a matter of fact, among all crystalline materials, the system with the highest bulk modulus, diamond, distinguishes itself also by the largest number of atoms per unit volume.

In conclusion, we combined total energy and structure optimization calculations to explore the physical properties of new hard phases consisting of fullerenes polymerized in 3D. We have identified 12 different stable crystal structures that are very stiff. The bulk moduli we have found in 3D fullerenes crystals are as high as 80% of the diamond value, in contradiction to experiments reporting materials stiffer than diamond.[13] The BCC lattice structure, which shows the highest bulk modulus value among those addressed here, turned out to be the least stable among the structures investigated. The bulk modulus of other structures, which should form more readily under moderate conditions, lies below half the diamond value, but still exceeds that of most metals. The possibility of self-assembling these rigid structures from sub-nanometer C$_{60}$ fullerenes, which may be filled easily into nano-cavities in bulk structures, may lead to new materials with a superior stiffness and stability at high temperatures. The electronic properties of 3D structures formed of polymerized fullerenes depend on the lattice type, with BCO systems exhibiting metallic behavior, whereas the majority of cubic systems are insulators with a $\approx 1-2$ eV fundamental band gap.

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