New Superhard Phases for 3D C$_{60}$-based Fullerites

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We have explored new possible phases of 3D C$_{60}$-based fullerenes using semiempirical potentials and ab-initio density functional methods. We have found three closely related structures - two body centered orthorhombic and one body centered cubic - having 52, 56 and 60 tetracoordinated atoms per molecule. These 3D polymers result in semiconductors with bulk moduli near 300 GPa, and shear moduli around 240 GPa, which make them good candidates for new low density superhard materials.

Superhard materials are of obvious practical and theoretical interest. Among them, diamond is still the undisputed hardest substance, and will take some beatings. Its hardness comes from the stiffness of its tetravalent carbon bonds, which are also the basis of the widely used diamond-like coatings. However, natural diamond is rare and its industrial production expensive. For this reason, much experimental and theoretical work has been devoted to studying novel potential candidates for hard materials. For instance, another carbon-based crystal, 3D $sp^2$ carbon [1], was theoretically predicted to be even harder than diamond but never synthesized. Very recently, a high pressure phase of silicon clathrates was studied [2]. Its bulk modulus resulted to be 90 GPa, very close to that of the normal silicon cubic crystal, leading to the speculation that, if constructed with carbon instead of silicon, it could be as hard as diamond. A similar idea was proposed for $\beta$-C$_3$N$_4$ in relation to $\beta$-Si$_3$N$_4$ [3] but because only small quantities of the former material are available, it remains to be proven that the substance is indeed harder than diamond. A general theoretical approach to study hardness in any of its definitions is difficult, if not impossible, to perform. Traditionally, it has been linked to a large bulk modulus but it has been shown recently to correlate better with the shear modulus of the material [4]; diamond is the leading system in both cases, with 443 and 535 GPa, respectively.

The discovery of C$_{60}$ in 1985 as a third form of crystalline carbon [5] was the kick-off for one of the most stimulating fields for research in materials science in the last decades. For the first years after its discovery and massive production, the known solid state phases of pure C$_{60}$ were nearly ideal molecular crystals [6]. However, from the very beginning, there were speculations on the possibility of obtaining crystals in which the C$_{60}$ molecules were covalently bonded to each other, by means of high pressures and temperatures [7,8]. Since then, several papers [9,10] have appeared reporting a variety of experimental results in this line (see Ref. [11] for an updated review of the field).

Nuñez-Regueiro et al. [14] reported the crystal structures of partially covalent forms of C$_{60}$. They observed a crystal containing linear chains of polymerized fullerene molecules and also two structures, one rhombohedral and one orthorhombic, of covalently bonded molecular planes (2D C$_{60}$). The structures are formed by bonding through 2+2 cycloadition reactions between neighboring molecules with a carbon hybridization change from $sp^2$ to $sp^3$; chains and planes are bound together by Van der Waals interactions. More recently, the realization of 3D C$_{60}$-based fullerite has been reported [17]. At least four crystal structures were found to be compatible with the X-ray data: rhombohedral, orthorhombic (pseudo tetragonal), tetragonal and simple cubic. Of these, the first two are formed by stacking covalent rhombohedral and tetragonal planes. Blank and coworkers [18] have reported the obtention of 3D fullerene solids of extremely low compressibility, and very recently a superhard structure has been also reported in detail by Chernozatonskii et al. [16]; the crystal is body centered orthorhombic, quasi fcc, and each molecule develops two intermolecular bonds with each of its 12 neighbors, presenting corrugated surfaces. From the theoretical side, Okada et al. [21] have reported calculations on a possible structure for pseudo-tetragonal (body centered orthorhombic) covalently bonded 3D C$_{60}$, which might be obtained by applying a uniaxial pressure of about 20 GPa to pseudo-tetragonal polymerized layers of C$_{60}$. This phase would be metallic with a high density of states at the Fermi level, and the C$_{60}$ molecules would be highly corrugated.

In this work we report new 3D C$_{60}$-based fullerite phases which have a direct relation with the most probable precursors: polymerized linear chains and orthorhombic planes, while the molecules preserve their convexity. We will show that our proposed structures have low compressibilities and large shear moduli and therefore are excellent candidates for hard materials.
FIG. 1. Views of the crystal structure of the proposed hard (56-4) fullerene solid. The hexagonal turrets connecting nearest neighbors molecules are clearly seen in d). Tricoordinate atoms are shown in black.

We have proceeded as follows: an initial search of the stable or metastable structures was done using Tersoff potentials [21], which are known to provide a good description of carbon fullerenes [22,23], including several polymeric phases [24]. Once the potentially interesting structures were found, these were used as starting points for more detailed and accurate ab-initio calculations. The structure, stability and electronic properties of each phase were obtained, allowing the complete relaxation of cell parameters and atomic coordinates, and analyzed; all data we will give here (except for the calculated vibrational frequencies) are those of the final ab-initio results.

The ab-initio calculations were performed using a numerical-atomic-orbital density functional (DFT) method described in detail elsewhere [25]. It has been already applied to large fullerene molecules and nanotubes [26], and many other systems [27]. The calculations are done using the Generalized Gradient Approximation for the exchange-correlation, as parametrized by Perdew, Burke and Ernzerhof [28]. Core electrons are replaced by nonlocal, normconserving pseudopotentials [29] factorized in the Kleinman-Bylander form [30], whereas valence electrons are described using linear combinations of pseudo-atomic orbitals. In this work we have used a split-valence double-ζ basis set, supplemented with polarization d orbitals (DZP) [31]. The radial cutoffs were 4.2 and 5.0 a.u. for the s and p orbitals respectively. We have carried out tests using a triple-ζ basis set, finding only minor changes in the lattice constants (less than 0.3 %) and elastic moduli. The charge density was expanded in plane waves with a large cutoff of more than 150 Ry (the exact values vary slightly, depending on the volume). With these parameters we have obtained a
bulk modulus for diamond of 430 GPa, in good agreement with known values [3]. The relaxation of the cell parameters and atomic coordinates was performed using conjugated gradient minimizations at fixed pressure.

Starting from two experimentally observed 1D and 2D polymerized body centered orthorhombic C_{60} structures, we obtain two new metastable 3D phases. These have 52 and 56 tetracoordinated atoms per molecule, respectively, and we will refer to them as (52-8) and (56-4). The (56-4) structure is obtained by applying uniaxial pressure along the stacking direction of a 2D polymer, while for the (52-8) one the pressure is applied in the plane perpendicular to the direction of linear chains. In those phases, the individual molecules preserve their convexity as well as the bonds between C_{60} molecules originally present in the chains or planes (4 and 8, respectively). In both cases, six new bonds are formed with each of the new nearest neighbor molecules in the body centered position. Both structures are intimately related to one proposed by O’Keeffe, based on purely geometric arguments [3]: it is possible to construct a body centered cubic crystal with T_{h} symmetry, having all carbon atoms with coordination four, connected by bonds of equal length. We have also studied this phase, from which, once all independent degrees of freedom are relaxed, a (60-0) structure is obtained. From the electronic point of view, all the new structures are semiconductors, with band gaps larger than 2 eV. A general view of the (56-4) structure is schematically shown in Fig. 1, where also the few remaining sp^{2} atoms can be seen. The (52-8) phase differs from the (56-4) in that both the (001) and the (010) planes look like the (001) plane in Fig. 1. For the (60-0) structure, the (001), (010) and (001) planes, which are equivalent by symmetry, are bonded as in Fig. 1a.

Table I shows the relevant structural data and physical parameters of the new fullerenes [22]. The specific volumes lie between those corresponding to graphite (9 Å^{3}/atom) and diamond (5.6 Å^{3}/atom) but due to the covalent intermolecular bonds are much smaller than those of Van der Waals C_{60} and C_{70} crystals (≈ 11.5 Å^{3}/atom). The length of the bonds between tricoordinated atoms is about 1.35 Å; between tri- and tetracoordinated atoms about 1.48 Å; the remaining intramolecular bond lengths range from 1.48 to 1.70 Å. The bonds forming the hexagonal turrets which connect molecules in the body centered position are about 1.57 Å long, and those connecting second neighbor molecules 1.62 and 1.66 Å. As expected, the bond angles are grouped around the values of graphite, diamond, and 90 degrees; the latter are associated with the turrets and intermolecular second neighbor bonds. For (60-0), where only sp^{3} bonds are present, we obtain bonding distances of 1.475, 1.548 and 1.56 Å. Regarding the intermolecular distances between first neighbor molecules in the (110) plane (i.e., those corresponding to the maximum number of covalent bonds between C_{60} molecules), the typical values are around 8.4 - 8.5 Å, which agree very well with those experimentally found by Marquez et al. [17] (8.40 and 8.80 Å).

The number of sp^{3} bonds suggested the interesting possibility of low compressibility materials, and in fact our structures have bulk and shear moduli around 300 GPa and 240 GPa, respectively. They should be compared to the values calculated with the same method for diamond, 430 and 560 GPa. According to the empirical relation found by Teter between hardness and shear modulus [4], these values would correspond to a hardness of about 40 Vickers, which would place them among the ten or so hardest known systems, at the lower limit of superhard materials. It is also interesting that the hardness expected for these phases comes together with a considerable lightness of the materials, since the densities are about 30 % smaller than that of diamond.

Energy vs. volume curves for the new phases are shown in Fig. 2. It can be seen that the (56-4) and (52-8) structures have almost the same equilibrium energy and are more stable than the (60-0) by about 1 eV. A suggested (56-4) → (60-0) transition is found at about 14 GPa, in which the (56-4) structure is compressed along one of its axes. We have also recalculated the structure of Okada et al. [19] finding that the (56-4) crystal is lower in energy by almost 2 eV, and has a smaller volume. The structures obtained in this work (and that of Ref. 20) are metastable with respect to the corresponding precursor planes and chains, and correspond to local minima in configuration space. However, as seen in Fig. 2, they have a large stability range, and require quite considerable amounts of energy to be dissociated.

Table I. Unit cell parameters (Å); specific volumes v (Å^{3}/atom) and Bulk Moduli B_{o} (GPa) for the new proposed structures.

| Structure | a     | b     | c     | v     | B_{o} |
|-----------|-------|-------|-------|-------|-------|
| 52-8      | 9.90  | 9.76  | 9.92  | 7.99  | 298   |
| 56-4      | 9.76  | 9.78  | 9.88  | 7.86  | 300   |
| 60-0      | 9.73  | 7.67  |       |       | 295   |

FIG. 2. Energy vs. volume curves for the (56-4) (solid lines), (52-8) (dotted lines) and (60-0) (dashed lines) structures.
FIG. 3. Vibrational densities of states for the C$_{60}$ molecule and the (52-8), (56-4) and (60-0) structures.

It is interesting to note that these phases could be recognized by vibrational spectroscopy methods. Fig. 3 shows the vibrational DOS for the isolated C$_{60}$ molecule, and the (52-8), (56-4) and (60-0) structures, calculated using the potentials described in Ref. [23]; the bands above 1500 cm$^{-1}$, which are related to graphite-like vibrations in C$_{60}$ (the in-plane optical frequencies of graphite lie around 1590 cm$^{-1}$), completely disappear in the (60-0) crystal; only four isolated optical bands remain in the (56-4) compound, and eight in the 52-8 one.

In conclusion, we have studied new phases of 3D C$_{60}$-based fullerenes which seem to have quite interesting features: their bulk moduli are about 70% of diamond and their shear moduli compare with those of the hardest systems known; the phases are extremely compact, although the crystals would be light compared to most other hard materials; the original convexity of the molecules is preserved - corrugation is a costly energy consuming process; and the (52-8) and (54-6) structures are directly related to polymerized chains and layers, which seem to be most likely precursors for 3D polymerized phases, and could probably be obtained at extreme, possibly uniaxial, pressures. The present result, joined to that of the metallic phase reported by Okada et al. [20] and the latest experimental data, suggest an exciting scenario for research on new fullerene based materials.

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