

Transformations of C₆₀ fullerite under high-pressure high-temperature conditions

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Abstract. Depending on pressure–temperature conditions, fullerite crystals can transform as to the well-known carbon phases, graphite and diamond, and to new metastable crystalline and amorphous modifications. The mechanical properties, density and structural data of the latter are reviewed. It is concluded that the crystalline C₆₀ phases possess mechanical characteristics 2–3 times lower than that for the diamond; amorphous states of carbon with a large share of the sp³-configurations have mechanical properties close to those of the diamond. The analysis of current literature enables us to conclude that the diamond has the highest elastic moduli among the carbon materials studied up to date.

The discovery of fullerites, multiparticle convex-polyhedral carbon molecules such as C₆₀, C₇₀, etc., was one of the most exciting scientific events in the eighties [1]. Of these substances, the regular-truncated icosahedron C₆₀ molecule (see Fig. 1) has received the most attention. The development of effective fullerite synthesis and deep-cleaning technology in 1990 spurred studies in this area [1] and led, in particular, to the elaboration of the physics of fullerites, an entirely new direction in the molecular crystal physics. Fullerites constitute condensed phases of mutually linked fullerene molecules interacting through weak van der Waals forces.

Among many unusual fullerene properties, the remarkable mechanical and chemical stability of the C₆₀ molecule has long been recognized. Theoretically, the molecule must be stable to external deformations as well. For an individual C₆₀ molecule, the compressibility modulus B estimated formally as the product of volume times the second volume (geometrical volume of the molecule) derivative of energy (the sum of the energies of individual bonds) ranges from 720 to 900 GPa [2, 3], i.e. the C₆₀ molecule is 'less compressible' than a diamond crystal ($B \approx 450$ GPa). In principle, there is nothing unusual in carbon clusters having lower compressibility than diamond. For example, atoms in graphite planes are also bound stronger than in diamond, however, a weak interaction between the planes renders graphite soft and easily compressible ($B \approx 34$ GPa)[4].

A face-centred cubic (FCC) C₆₀ lattice under normal conditions also has high compressibility, which is about 50 times that of the free molecule value (the bulk modulus $B \approx 18$ GPa [5]). High compressibility of fullerite crystals is

due to a weak interaction between C₆₀ molecules. Notice that under normal conditions C₆₀ molecules are, on the average, $D \approx 0.7$ nm in diameter and that their closest neighbouring points are $l \approx 0.3$ nm apart [1], comparable to the graphite plane separation of 0.335 nm [6]. At the same time, the nearest-neighbour interatomic distance in the C₆₀ molecule is 0.144 nm within pentagons, the distance between the neighbouring vertices of adjacent pentagons being 0.139 nm [1] (Fig. 1).

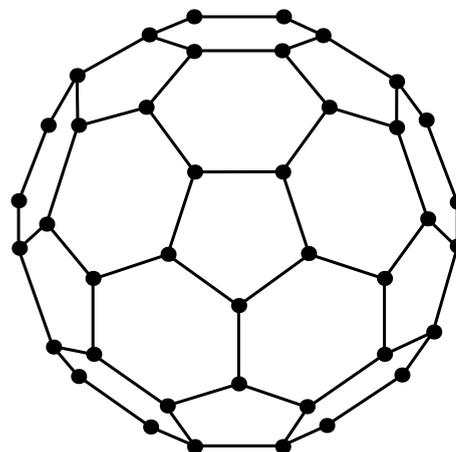


Figure 1. Truncated-icosahedron C₆₀ molecule formed by 20 hexagons and 12 pentagons.

It has been suggested [2, 3] that if under high pressures of order 50 GPa, molecular centres in a C₆₀ crystal come within about 0.7 nm of one another (which is the contact centre distance in the rigid spheres model), then the resulting crystal will have a bulk modulus of about 74% that for a free molecule (this figure being precisely the closest packing coefficient for spheres). The modulus estimate, $B \sim 620 - 720$ GPa, is 1.5 times as much as the corresponding diamond value. The same authors noted, however, that already at lower pressures the decomposition of C₆₀ molecules is a more likely event. Still it might be expected that, when under pressure, C₆₀ molecules may come sufficiently close to interact more strongly than through van der Waals forces. Presumably, this interaction may lead to high-density carbon phases other than the familiar stable diamond and graphite modifications.

Pressure-induced fullerite transformation have been an area of active investigation and a subject of more than 50 scientific publications since 1991. It turned out that at room temperature, as pressure is increased to 20–25 GPa from the atmospheric value (10^{-4} GPa), fullerite properties vary in a smooth way except for a weak anomaly occurring at the reorientation transition which takes place at 0.3–0.4 GPa [7]

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and was investigated in much detail at atmospheric pressure (transition temperature $T \approx 260$ K) [1]. For hydrostatic pressure $P > 25$ GPa, or at $P > 16–20$ GPa in the presence of strong shear strains, fullerite crystals exhibit structural transformations [5, 8–14]. At high temperatures, transformations in C_{60} crystals may even occur at lower pressures [15–20]. It should be noted that in most cases the newly formed carbon modifications are conserved as metastable on return to normal conditions.

A brief description of a characteristic sequence of high-pressure high-temperature transitions follows.

As C_{60} molecules are brought close enough together, covalent bond formation becomes a possibility [5, 15–21], and it is this circumstance which strongly hinders the molecules from coming still closer. The distance between neighbouring molecules cannot be less than 0.14–0.15 nm (the characteristic bond length in carbon materials) since at shorter distances repulsive shell-overlap forces increase dramatically. The centres of the neighbouring molecules then cannot get closer than within 0.85 nm, and hence the hypothetical low-compressibility phases [2, 3] are not realizable; instead, depending on specific P, T conditions, various C_{60} -based modifications form with covalent sp^3 or π bonds [15–20, 22, 23].

At relatively low (below 8 GPa) pressures, one- and two-dimensional polymerized C_{60} phases ranging from 1.8 to 2.5 g cm^{-3} in density ρ , may form [17, 18, 20, 22, 23]. Depending on the P, T -conditions, initially FCC crystals may transform into orthorhombic, tetragonal, rhombohedral, and other structures (Fig. 2). At pressures $P > 10$ GPa, even denser ($\rho \approx 2.5–2.8$ g cm^{-3}) crystal phases are possible [19]. The density and structure data suggest that the distances between C_{60} molecules for these phases are, in all three dimensions, comparable to the nearest-neighbour separation of carbon atoms in the molecule. Hence, these modifications may be regarded as either three-dimensional C_{60} polymerized phases or as ordered three-dimensional carbon lattices with individual properties of C_{60} molecules actually lost. Notice that these transformations occur at sufficiently high temperatures. With increasing pressure, the characteristic polymerization temperature lowers. The presence of nonhydrostatic conditions may affect considerably the type and position of the transition [5].

A further increase in pressure or temperature leads to the distortion and decomposition of the molecule, and to the formation of disordered phases with sp^3 and sp^2 carbon atoms in the amorphous network [9, 12, 13, 19]. Depending on the P, T -conditions, the fraction of sp^3 - and sp^2 -carbon configurations varies up to the ‘amorphous diamond’ state at high pressures, which entirely consists of atomic carbon in the sp^3 -state [12, 13]. The density of amorphous phases also depends on the synthesis conditions and covers the range 2.8–3.4 g cm^{-3} [12, 19]. Heating under pressure drives amorphous carbon forms to a mixture of the diamond and graphite phases having some stability regions on the phase P, T -diagram [14, 19].

We thus conclude that structures on the base of C_{60} molecules, and amorphous carbon forms obtained from fullerite at high pressures may be considered as intermediate states in nonequilibrium transformations of metastable C_{60} crystals into stable carbon forms, diamond and graphite. Such intermediate carbon phases are undoubtedly of interest both from the point of view of their mechanical characteristics and from that of electrical and optical properties.

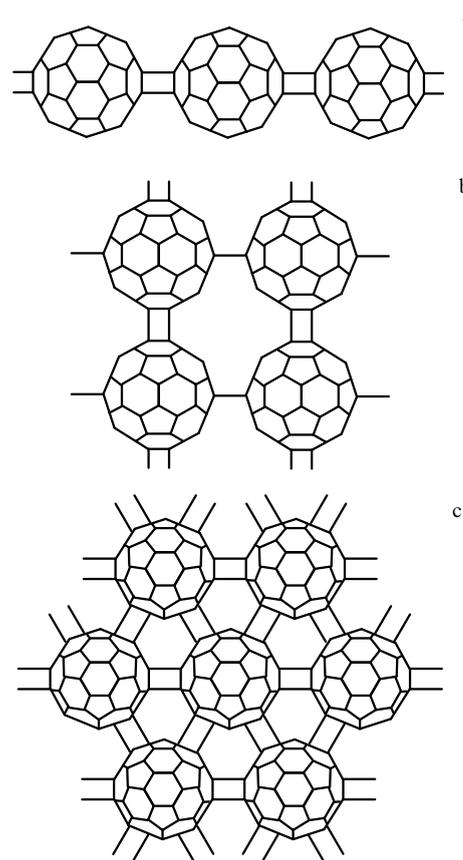


Figure 2. One- and two-dimensional polymerized fullerite structures modelling the orthorhombic (a), tetragonal (b), and rhombohedral (c) phases [22, 23].

Fullerite C_{60} , both in the FCC phase and in the orientationally ordered phase under pressure, constitutes a narrow-band semiconductor [1, 8, 24] whose forbidden band decreases with pressure. However, in the pressure range where fullerene molecules decompose and disordered phases form (20–25 GPa at room temperature; 12–15 GPa at $T = 400$ °C), the gap width increases [8], indicative of the formation of a high fraction of covalent sp^3 states. The conducting properties of one- and two-dimensional polymerized phases seem to be strongly dependent on the type and geometry of the bonds which occur between the C_{60} molecules (see, for example, [22, 25]). Active studies in this area have only recently begun.

Raman spectra of some of metastable C_{60} phases are shown in Fig. 3 together with the corresponding X-ray diffraction structural data. Surprisingly, the ordered modification (curve 2) has a Raman spectrum which, in the absence of structural data, could be ascribed to a disordered phase. This indicates the need for a more accurate interpretation of high-pressure Raman spectra. For example, in [9, 10] broad asymmetric Raman peaks in the interval 1300–1650 cm^{-1} were attributed (structural data lacking) to the transition to an amorphous phase.

From the standpoint of the search for superhard materials, the elastic and mechanical properties of new carbon phases are attracting particular interest. Even in the early works on fullerite under pressure it was realized that the new forms have high bulk moduli and possibly high hardness [5]. The observation of plastic deformation traces left by a high-pressure fullerite phase on a diamond anvil [26] suggested that

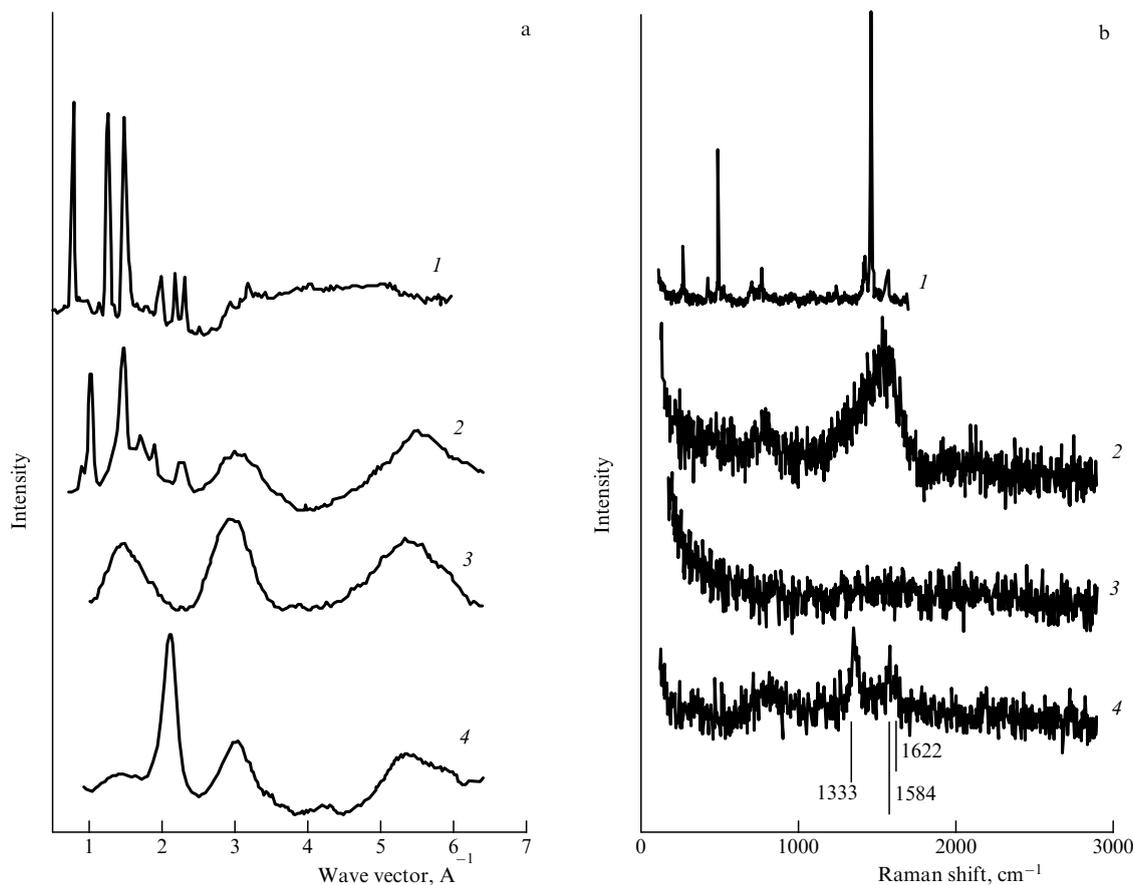


Figure 3. X-ray structural factors (a) and Raman spectra (b) for the original fullerite (1) and for samples obtained from C₆₀ by heating under high pressures (12.5 GPa), from [19]; 2 corresponds to the FCC phase of covalently bounded C₆₀ molecules; 3 is the amorphous carbon with predominantly sp³ bonds; 4 is a disordered phase with partial diamond and graphite ordering due to a high-temperature (700 °C) heating under pressure. Raman peaks for diamond (1333 cm⁻¹) and polycrystalline graphite (1584 and 1622 cm⁻¹) are indicated [6].

high-pressure C₆₀ phase modifications harder than diamond are possible. Unfortunately, high-pressure fullerite phases remained unidentified in that and indeed in most of the later studies in this area. There have been reports, both in scientific and popular scientific publications [27, 28], of both the polymer and amorphous carbon forms with hardness exceeding that of diamond. Conclusions about hardness have been drawn from scratch tests based on the relative mineralogical scale of Mohs. The observation of fullerite-produced 'amorphous diamond' harder than sapphire [12, 13] was also based on the scratching technique.

It is to be noted that the Mohs's scratching scale is very rough, nor is it adequate enough for superhard materials. While corundum and diamond have respective hardnesses of 9 and 10 units in this scale, direct measurements indicate that the Vickers hardness of the former ($H_V \approx 25$ GPa) is 3 to 5 times lower than that of the latter ($H_V \approx 70-140$ GPa [6]). Thus, materials in the 20–140 GPa hardness range from will all have close Mohs's hardnesses in the range 9 to 10. Besides that the materials scratch one another often does not imply that their hardnesses are the same. The ability to scratch depends on experimental conditions such as the applied load, the shape and chamfer radius of the scratching tip, etc.

Processing fullerite at various temperatures at 12.5-GPa pressure has produced a wide spectrum of intermediate carbon phase modifications occurring during the transformation of fullerite into a diamond-graphite mixture [19]. Synthesizing both the C₆₀-based phases and amorphous

carbon modifications in the form of bulk samples (cylinders 2 mm in diameter and 2 mm in height) allowed, for the first time, their mechanical properties to be studied quantitatively. The C₆₀ phases with density $\rho \approx 2.5-2.8$ g cm⁻³ were found to have Young's moduli $E \approx 300-400$ GPa, Vickers hardnesses $H_V \approx 20-30$ GPa, and yield strengths $\sigma_y \approx 10-15$ GPa. These values are 2 to 4 times inferior to the diamond properties ($E \approx 1100$ GPa, $H_V \approx 70-140$ GPa, $\sigma_y \approx 30-60$ GPa [6]). Interestingly, these 'polymer' modifications possess high plasticity even at room temperature, a unique feature among materials of this hardness. Notice that for superhard materials the bulk modulus B is generally 40–50% of the Young's modulus [6], i.e. for the 'polymer' phases $B \approx 120-200$ GPa. This estimate is consistent with the compressibility result [5] that the bulk modulus of fullerite at $P \approx 20-25$ GPa (the room-temperature polymerization pressure) equals 120–150 GPa. Theoretical estimates for the modulus B of two-dimensional polymerized phases [23] yield $B \approx 170$ GPa, also in good agreement with experimental data [19].

Amorphous carbon modifications with a high (up to 80%) fraction of sp³ configurations and with density $\rho \approx 3-3.2$ g cm⁻³ have a Young's modulus $E \approx 70$ GPa, hardness $H_V \approx 60-80$ GPa, yield strength $\sigma_y \approx 35-45$ GPa, and crack resistance coefficient $K_{IC} \approx 12-15$ MN m^{-3/2} (see Ref. [29] for details of the measurement technique). Hence, amorphous phases have only slightly inferior mechanical properties compared to diamond, and their resistance to

crack is even 1.5 to 2 times higher (for diamond, $K_{IC} \cong 5\text{--}12 \text{ MN m}^{-3/2}$ [6]).

Notice that except for Young's modulus, which depends primarily on microscopic interatomic forces, all the other mechanical parameters (hardness, strength, yield strength, and crack resistance) are also highly dependent on the amount of impurities and defects and on the size and morphology of grains in a particular sample — hence, a wide spread of diamond characteristics listed above. In terms of hardness, diamond samples vary by a factor of 2, from 70 to 140 GPa. Indeed, ultrafine-grain diamond polycrystals with hardness $H_V > 200 \text{ GPa}$ exist. In two extreme cases, a single crystal with no vacancies and dislocations on the one hand, and an amorphous or crystalline ultrafine-grain sample on the other, a solid with a hardness of the order of shear modulus G is possible (for diamond, $G \cong 450 \text{ GPa}$ [6]).

Thus, by applying high pressures, high-density C_{60} solid modifications or amorphous sp^3 -rich forms can be obtained from fullerite samples. However, the idea of producing a C_{60} -based substance with elastic moduli and hardness higher than in diamond seems to have proven erroneous. Of all the materials currently known, diamond has the highest elastic moduli. In regard to hardness, as noted above it depends strongly on the impurity and defect concentrations in a particular sample studied. In addition, the experimentally monitored hardness depends on the magnitude of the load applied. The values listed above correspond to loads in the range 5–20 N. As the load is decreased, the measured hardness may increase severalfold, ultimately approaching the perfect crystal value and thus assuming a value on the order of the shear modulus. A hardness comparison for materials with relatively close characteristics is only correct for equal applied loads.

Notice that there is a correlation between elastic moduli and the specific volume per atom, or more precisely per valent electron. This correlation can be understood either by analyzing various electronic contributions to the binding energy of the solid, or by treating the interatomic interaction in a simplified manner in terms of individual chemical bonds with specified energy and stiffness [30, 31]. For substances with the same set of atoms, in the first approximation a comparison of ordinary densities is enough. Thus, the density of diamond (3.52 g cm^{-3}) exceeds that of fullerite ($\cong 1.7 \text{ g cm}^{-3}$), graphite ($\cong 2.3 \text{ g cm}^{-3}$), and polymer C_{60} -based phases ($2.5\text{--}2.8 \text{ g cm}^{-3}$), but is about half the value ($\cong 6.3 \text{ g cm}^{-3}$) pertaining to what is arbitrarily called the 'free C_{60} density'. Recall that our previous estimate of the C_{60} bulk modulus is also nearly two times that of the diamond value. It is to be emphasized again that there is nothing unusual in the fact that the moduli of C_{60} clusters exceed those of diamond. The spectacular estimates mentioned above are in fact due to some kind of misunderstanding. If a small ($N < 60$) carbon clusters are considered, one finds that their conditional 'bulk moduli' and 'density' are even higher. Thus, based on the geometrical volume of the cluster under study, an isolated hypothetical tetrahedron, octahedron, or cube of carbon atoms with diamond-lattice bonds will each have a conditional 'bulk modulus', respectively, 40, 20, and 9 times higher than in diamond.

Curiously, the relation between the density and elastic characteristics in ordered three-dimensional polymerized fullerite phases is in good agreement with the relevant theoretical predictions for disordered sp^2 – sp^3 carbon patterns with varying fraction of tri- and tetravalent states [32]. Trivalent

(sp^2 -state) atoms have shorter and more rigid bonds than sp^3 -state ones, as already discussed for the case of graphite. However, increasing the fraction of sp^2 states in amorphous carbon patterns reduces the average coordination number and, as a consequence, leads to a significantly less topological stiffness of the pattern [33], and to lower density. For a general disordered-covalent structure, reducing the average number of nearest neighbours Z further first leads to a loss of the three-dimensional stiffness ($Z = 2.67$) and then to the complete loss of topological stability ($Z = 2.4$) [33].

The C_{60} -molecule bonds are also shorter and stiffer than in the diamond lattice. However, the covalent bonds appearing at high pressures not only prevent C_{60} molecules from further approaching one another, but also noticeably violates the uniformity in the compression of fullerite molecules and subsequently leads to their deformation and decomposition.

To summarize, the elastic and mechanical properties of carbon in both the ordered and disordered sp^2 -rich states are inferior to those of diamond. Thus, the highest density and best mechanical properties among the currently known bulk carbon materials occur in diamond.

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