The superhard crystalline three-dimensional polymerized $C_{60}$ phase

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Abstract

The profile analysis of the diffraction patterns, obtained for $C_{60}$ samples quenched from high pressure 13 GPa and temperature 670–820 K, yields proof of the formation of three-dimensional (3D) polymerized $C_{60}$ phase. The superhard phase manufactured after 13 GPa, 820 K treatment is characterized by common four-sided ring and $(2+2)$ fullerene cycloadditions in the layer, and $(3+3)$ bondings between layers. The unit cell parameters of its body-centred orthorhombic $Immm$ crystal structure refined by Rietveld program are equal to: $a = 0.867(4)$, $b = 0.881(1)$, and $c = 1.26(0)$ nm. Lattice dynamics simulation of 3D polymerized $C_{60}$ has shown that sound velocities, bulk modulus and broad bands in Raman spectra agree well with the measurements. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Very recently, a completely new area in the exploration of carbon structures started with the discovery by Kroto et al. of molecular carbon in the form of $C_{60}$ [1]. The enormous research activity began since the polymerization of $C_{60}$ molecules was found after UV-radiation and high-pressure-high-temperature treatment. Processes of 1D- and 2D-polymerization of $C_{60}$ molecules and crystal structures of the pressure- and temperature-induced phases have been investigated [2–4]. It was concluded that individual molecules had been linked together by covalent intermolecular bonds, and also suggested that the probable bonding was a $(2+2)$ cycloaddition [2]. In our earlier papers [5–8] the superhard $C_{60}$ phases with hardness [9] and bulk modulus [10] exceeding those of diamond have been found after high pressure up to 13 GPa and high temperature up to 2100 K treatment. The unusual elastic properties of superhard phases [10] have been qualitatively explained by the three-dimensional (3D) polymerization of $C_{60}$ molecules [5]. The structures of crystalline superhard phases have been determined as quasi-face-centred cubic (FCC) with smaller cubic parameter $a = 1.22–1.24$ nm, than that of the pristine FCC $C_{60}$-phase. In our work [7], carried out together with the ESRF collaborators, unusual ellipsoidal Debye–Sherrer diffraction patterns are observed which shows that the giant anisotropic deformation is retained in the quenched samples and

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unambiguous proof (such as the strongly reduced intermolecular distances in all three dimensions) for the existence of 3D polymerized C$_{60}$ phases provided. In addition, our Raman investigation [5,6] of superhard phases shows that the single broad band is observed at $\omega > 1000$ cm$^{-1}$ that may be interpreted as a structure transition from a molecular structure to a continuous network due to the formation of covalent intermolecular bonds. However, earlier there was no model of 3D polymerized solid C$_{60}$ which should show the process of the structure distortion including the change of both the chemical bonds and the atom positions from the beginning of the formation of superhard phases. In the present paper we have determined the crystal structure of superhard C$_{60}$ phase and have proposed the way of conversion from the hard (H) phase into the superhard (SH) one.

2. Results and discussions

Earlier [5,6] we have indexed diffraction patterns of superhard crystalline phases on the base of the orthorhombic body-centred (BCO) unit cell with parameters which are approximately equal to half of a face-diagonal of the FCC structure. The high value of density (3.4–3.2 g/cm$^3$) calculated from X-ray data for BCO-phases corresponded to experimental ones. This value has been measured from the whole sample, contained both amorphous and crystalline phases. The inhomogeneity of samples is formed under large gradients in the pressure chamber [5,10]. We have redetermined the densities of the separate parts of a sample. The density of the crystalline phase is in the 2.2–2.5 g/cm$^3$ range (Table 1). Taking into account these value of densities, we will consider the structures of superhard phase and its hard precursor.

As in the case of 2D polymerization of C$_{60}$ [11], we have suggested that at the first stages the polymerization begins from (2 + 2) cycloaddition of C$_{60}$ molecules, and chains of molecules are formed in the [110] direction of molecular FCC structure. First we have chosen the pseudo-tetragonal BCO unit cells with parameters: $c = 1.26$ and 1.29 nm, $a \equiv b = c/\sqrt{2}$ instead of the FCC-cells with $a = 1.26$–1.29 nm. Then the unit-cell parameters have been refined using DICVOLV [12] and Rietveld programs [13]. Table 1 shows unit cell parameters of two samples obtained after 13 GPa (670 and 820 K). The hardness of the first sample (H) is such as the cubic boron nitride one. The hardness of the second sample (SH) is compared with the diamond one. The calculated volume per molecule (0.517 and 0.481 nm$^3$) is substantially lower than that in 1D and 2D polymers of C$_{60}$ (0.650 and 0.597 nm$^3$, respectively [4]). We have determined the BCO structures with space group I$\text{mmm}$ and 9 independent carbon atoms as in the case of the 1D polymerized orthorhombic phase [4,11]. The chained layers are closed in the both $(x, y)$ plane and vertical direction under high pressure. At the high temperatures anisotropic oscillations of atoms should induce an appearance of bonds between $(x, y)$ layers along [001]-direction because parameter $c = 1.26$–1.29 nm is smaller than 1.42 nm cubic parameter of pristine FCC. Thus, the central molecule of the bco unit cell is connected with 4 neighbour molecules of $(x, y)$ plane as well as with 4 upper and 4 lower neighbour molecules. It is well-known that the central molecule has the closest distance up to the neighbouring molecules along any space diagonal of bco unit-cell. We have found

<table>
<thead>
<tr>
<th>Phase</th>
<th>$P$ (GPa)</th>
<th>$T$ (K)</th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$c$ (nm)</th>
<th>$V$ (nm$^3$)</th>
<th>Distances$^a$ between centers of molecules, (nm)</th>
<th>$\rho_{\text{m}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{v}}$ (g/cm$^3$)</th>
<th>Hardness (GPa)</th>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>–</td>
<td>–</td>
<td>1.002</td>
<td>1.002</td>
<td>1.417</td>
<td>0.711</td>
<td>1.002</td>
<td>1.68</td>
<td>–</td>
<td>soft</td>
</tr>
<tr>
<td>H</td>
<td>13</td>
<td>670</td>
<td>0.873</td>
<td>0.916</td>
<td>1.294</td>
<td>0.517</td>
<td>0.87/0.92/0.91</td>
<td>2.3</td>
<td>2.3</td>
<td>60</td>
</tr>
<tr>
<td>SH</td>
<td>13</td>
<td>820</td>
<td>0.867</td>
<td>0.881</td>
<td>1.260</td>
<td>0.481</td>
<td>0.87/0.88/0.88</td>
<td>2.48</td>
<td>2.5</td>
<td>150</td>
</tr>
</tbody>
</table>

$^a$Three distances between molecules are calculated from the parameters of the unit-cell and its space diagonal.
atoms of the central molecule which are located most closely to atoms of neighbouring-layer-molecules: if the undistorted $C_{60}$ molecules locate in the experimental orthorhombic bco-unit-cell, the atoms numbers 3 and 6 in the Fig. 1 are the closest ones.

Considering the form of molecule $C_{60}$ as sphere-like one with $(2 + 2)$ bonding along $a$-axis we have simulated diffraction pattern of H-phase and have obtained good fitness to experimental profile. Note, this pattern is not similar to 1D polymer one [4] because of the smaller distance between molecules of the neighbouring layers in H-phase. The diffraction patterns of H- and SH-crystalline phases are similar, but they differ in the intensity ratio of peaks (Fig. 2). Since the $I(111)/I(200)$ ratio of H-phase diffraction pattern is the same as the molecular FCC one [14] with parameter $a = 1.294 \text{ nm}$, structure of H-phase is closer to the cubic one with sphere-like shape of molecules. Whereas this ratio of SH-pattern does not correspond to the ratio of FCC structure with parameter $a = 1.260 \text{ nm}$: the first-peak-intensity of SH-phase should be smaller in the case of FCC structure. We have proposed that the discrepancy is caused by shape distortion of $C_{60}$ cage.

We have determined a change of the $C_{60}$ molecule shape or the cage deformation, for the first turn a change of bonds in $(x, y)$ layer. There are the shorter distances between centres of molecules ($0.86-0.88 \text{ nm}$) in structure of SH-phase (Table 1) than ones in H-phase. The intermolecular distances in SH-phase point to the other character of molecular bonding than $(2 + 2)$ cycloadditions in the both $a$ and $b$ axes. We looked over the known types of the cycloaddition: $(2 + 2)$ [2], $(2 + 4)$ [15], $(6 + 6)$ [16] which have been applied to polymerized $C_{60}$ phases, but nothing to be fitted to our experimental diffraction profile. Among several types of the $C_{60}$ dimer combinations the common four-sided ring fragment proposed by E. Osawa et al. [17] is proved to be more suitable to our SH-structure: molecules have been coalesced by four atoms of the common cycle, that is, $(2 + 2)$ cycle turns to $90^\circ$ along the axis $z$ and becomes perpendicular to a chain axis. Distances between neighbour ‘coalescent’ molecules are equal to $0.87 \text{ nm}$ [18], that approximately corresponds to $a$ or $b$ unit cell parameters in the Table 1. We suppose that this bonding may be formed under high-pressure conditions and the interlayer bond between neighbouring $(x, y)$-layers is produced by the bonding that is characteristic for $(3 + 3)$ bonding in the $\text{d(1.5),(6.10)methano-cyclodecane}$ molecule. We think that $(3 + 3)$ cycles are formed by equivalent atoms 3 and 6 which are bound in pairs with the corresponding atoms of neighbouring molecules.
The best fitting model of polymerized SH-phase structure have been derived only using the proposed (3 + 3) bonding of \((x, y)\) layers, the \((2 + 2)\) bonding along \(a\) axis and common four-sided ring bonding along \(b\) axis. The calculation of atom positions has been carried out in the framework of HYPERCHEM-programme by molecular mechanics (MM) method [19] at the energy optimization of the cluster-geometry of polymerized \(C_{60}\) molecules located in the centre and vertexes of parallelepiped. The activation energy for the thermal dissociation of different \(C_{60}\) dimers and trimers calculated by QMD [20], MNDO/PM3 [18], and AM1 [17] differ from one to another. However, in spite of the differences of values obtained in the results of the calculations, these methods lead to analogous tendencies for a change in the energy characteristics of these clusters. For example, the energy of \(C_{60}\) dimerization increases from \((2 + 2)\) dimer 0.007 eV/atom [20], 0.012 eV/atom [18], 0.013 eV/atom [17]) to common four-sided ring dimer 0.029 eV/atom [18], 0.026 eV/atom [17]). Our estimations by the MM method give 0.002 eV/atom for \((2 + 2)\) dimer and 0.007 eV/atom for common four-sided ring dimer. The appearance of eight \((3 + 3)\) bonds of linked layers into the 3D carcass structure provides a high energy gain 0.092 eV/atom for the SH-phase. The bonding of central molecule with four molecules of \((x, y)\) plane has been taken into account. The coordinates of the central molecule are chosen as basic for the determination of SH-structure.

We have refined the atomic positions with use of Rietveld refinement [13] in order to obtain good coincidence with the experiments. Table 2 shows the atom positions of the SH-structure. The intermolecular bond lengths are equal to 0.151 nm for \((3 + 3)\) cycles and 0.161 nm for \((2 + 2)\) cycles. Fig. 2 shows the calculated profiles by thin lines and the deformed \(C_{60}\) cages for each structure type. The small (10%) preferred orientation in the \([111]\) direction was calculated by the March–Dollase model in accordance with observed preferred orientation in the pressure-induced phases; the thermal Debye–Waller factor was selected as 0.7. The weighted pattern \(R_{wp}\) factor is equal to 10%. It is a good fitness for poor diffraction patterns with 7 broad peaks and 27 independent parameters. One can remark that the \(R_{wp} = 8\%\) for the pristine molecular fullerite [14]. The fit to diffraction profile of SH-phase depends on the ninth atom position of a \(C_{60}\) cage strongly, the best fit is obtained by pressing of the ninth atom in the depth of a \(C_{60}\) sphere. Probably, such pits may form the additional charge centres since the SH-diffraction pattern is similar to FCC structure for two kinds of atoms as sodium chloride.

It should be noted that the diameter of \(C_{60}\) cage of SH-phase diminishes in \((x, y)\)-plane in comparison with \(C_{60}\) molecule structure because the 3 and 6 atoms are pulled strongly from the ball surface. That is why the lattice parameter \(a\) is equal to 0.867 nm. The presence of common four-sided rings decreases the quantity of pentagons in a \(C_{60}\) cage of SH-phase from 12 to 8. Thus SH-structure may be presented as the corrugated graphene sheets penetrated each other in three \((a, b, c)\) directions, and they are linked by \(sp^3\) bonds in the points of intersections. In this way, each \(C_{60}\) molecule of the SH-phase binds not only with 4 molecules of \((x, y)\) layer, but also with 8 molecules of neighbouring layers. As a result, each molecule has 12 neighbours and contains 24 \(sp^3\) atoms of 60.

The formation of SH-structure may be confirmed by the Raman spectra. Fig. 3 compares the experimental Raman spectrum of SH-phase polycrystal [5] with the computed projected density of vibrational states. We could separate contributions of \(sp^3\) - and \(sp^2\)-bonded carbon atoms. We believe that the very large bandwidth \((> 100 \text{ cm}^{-1})\) of Raman bands gives evidence of the strong disorder of the crystal, in consequence of which the Raman spectrum is proportional to the density of vibrational states. It was shown earlier [21] that the Raman scattering from \(sp^2\)-bonded carbon material is \(\sim 100\) times

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.088</td>
<td>0.500</td>
<td>0.060</td>
</tr>
<tr>
<td>C2</td>
<td>0.158</td>
<td>0.354</td>
<td>0.110</td>
</tr>
<tr>
<td>C3</td>
<td>0.091</td>
<td>0.337</td>
<td>0.218</td>
</tr>
<tr>
<td>C4</td>
<td>0.137</td>
<td>0.173</td>
<td>0.238</td>
</tr>
<tr>
<td>C5</td>
<td>0.000</td>
<td>0.081</td>
<td>0.260</td>
</tr>
<tr>
<td>C6</td>
<td>0.280</td>
<td>0.090</td>
<td>0.220</td>
</tr>
<tr>
<td>C7</td>
<td>0.310</td>
<td>0.130</td>
<td>0.110</td>
</tr>
<tr>
<td>C8</td>
<td>0.407</td>
<td>0.000</td>
<td>0.062</td>
</tr>
<tr>
<td>C9</td>
<td>0.164</td>
<td>0.210</td>
<td>0.057</td>
</tr>
</tbody>
</table>
Fig. 3. Calculated projected densities of vibrational states for $sp^2$-bonded carbon atoms (1) in the SH-type $C_{60}$ crystal; the experimental Raman spectrum (2) of this crystal was taken from [5]. Lattice dynamics of fullerenes with covalent bonds have been analyzed by means of the Keating’s three-particle potential $\Phi_{24}$, taking into account both two-particle and three-particle interactions of each atom with nearest atoms. In the general case of three identical nearest atoms, as it takes place in fullerite, the quadratic term will depend on six parameters out of which two are connected by the equilibrium condition $(\delta \Phi / \delta r)$. Hence one can expect that, in the main, the contribution from $sp^2$-bonded carbon atoms will be exhibited in the Raman spectra. As it is seen from Fig. 3, the calculated projected densities of vibrational states for $sp^2$-bonded carbons correlates with the Raman spectrum, in which instead of the line spectrum characteristic of the $C_{60}$ crystal at lower temperature treatment is mainly observed the broad intense band near 1550 cm$^{-1}$.

In the calculations of lattice dynamics of the $C_{60}$ crystal of SH-phase we took into consideration that the cell consists of one formula unit (60 atoms) including 24 $sp^3$- and 36 $sp^2$-bonded carbon atoms. The potential parameters for $sp^3$- and $sp^2$-bonded carbon atoms were found by fitting the calculated dispersion curves of diamond and graphene sheet, respectively, to the experimental ones [22,23]. In this crystal there are three types of bonds joining the nearest carbon atoms with the different bonding: $sp^1$–$sp^3$, $sp^3$–$sp^2$ and $sp^2$–$sp^2$. We have used the graphene parameters for the $sp^2$–$sp^2$ bonds, while the diamond parameters have been used for the other bonds.

The calculation of the dispersion curves along the crystallographic axes $a$, $b$ and $c$ has shown that the curves are stable along these directions. The acoustical branches split into 3 components: (two transverse (TA) branches and one longitudinal (LA) branch) along all directions. The slope of acoustical curves in the centre of the Brillouin zone enabled us to estimate the velocity of acoustical waves (Table 3). The experimental values of velocities were obtained for polycrystalline samples ($V_{exp}^{TA} = 7.2–9.6$ km/s, $V_{exp}^{LA} = 17–26$ km/s depending on the synthesis [10]) and they are in the qualitative agreement with the calculated mean velocities ($V^{TA} = 10.3$ km/s, $V^{LA} = 21.6$ km/s). Using the calculated mean velocities, we have estimated the bulk modulus to be equal to $K \approx 800$ GPa, that was in accord with the experimental ones ($690–1700$ GPa depending on the synthesis [10]) and exceeded that of diamond ($K \approx 580$ GPa [10]).

Thus, the H- and SH-structures alter in the sequence H $\rightarrow$ SH as the synthesis parameters (pressure and temperature) increases. The SH-type of structure is the most energy advantageous ($0.092$ eV/atom) and it is formed only at the highest parameters (13 GPa, 820 K). The crystal structure of SH-phase is very stable, it remains at 13 GPa up to 1200 K with both some distortions and the gradual increase of amorphous halo [5]. Above 1200 K the crystalline state is completely disappeared. The SH-phase is the hardest one and its bulk modulus is the highest one. The intermolecular bond lengths are shortened in comparison with H-phase ones. The pentagon quantity diminishes in the sequence H $\rightarrow$ SH and the hexagon quantity increases. When (3 + 3) cycles appear, the short bonds between the atoms $sp^1$–$sp^3$, $sp^3$–$sp^2$ and $sp^2$–$sp^2$.

In the following table, the velocities of transverse ($V_{1}^{TA}$ and $V_{2}^{TA}$) and longitudinal ($V_{1}^{LA}$) acoustical waves (in km/s) along crystallographic axes.

<table>
<thead>
<tr>
<th>Direction</th>
<th>$V_{1}^{TA}$</th>
<th>$V_{2}^{TA}$</th>
<th>$V_{1}^{LA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\parallel$</td>
<td>7.5</td>
<td>11.1</td>
<td>18.2</td>
</tr>
<tr>
<td>$\parallel$</td>
<td>7.9</td>
<td>10.3</td>
<td>19.8</td>
</tr>
<tr>
<td>$\parallel$</td>
<td>12.1</td>
<td>13.2</td>
<td>26.8</td>
</tr>
</tbody>
</table>
and 6 destroy the pentagon vibrations. The decrease of the pentagon quantity in the SH-phase structure causes a disappearance of the pentagonal mode at 1460 cm\(^{-1}\) in Raman spectra which is characteristic for pristine \(C_{60}\). The H-structure can be suggested as a precursor of SH-phase because it can be described as structure of \((3 + 3)\)-bonded cross-linked chains. The \((3 + 3)\) bondings transform the molecular structure of pristine \(C_{60}\) into the 3D network and therefore Raman spectra of 3D structure distinct from ones of pristine crystal and 2D phases. The resemblance of spectra SH- and H-phases may evidence a presence \((3 + 3)\) bonding in both structures. The presence of corrugated graphene sheets probably provides the high bulk modulus and high value of sound velocity. The shape distortion of \(C_{60}\) cages is getting more strong from H- to SH-phases. The crystal structure of the SH-fullerite phase and the detailed explanation of the nature of the bonding of \(C_{60}\) cages, determined here, give a clear understanding of the nature of its unusual physical properties. The good fitting of our simulations of X-ray, Raman and elastic data clearly show that the SH-phase is three-dimensional polymerized state where new both \((3 + 3)\) bondings and common four-sided rings between \(C_{60}\) cages provide high bulk modulus and the stability of the crystal structure.

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