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Features of dependence of Raman spectra of cluster structures of three-dimensionally polymerized fullerite on pressure

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We study the effect of high hydrostatic pressure on 3D polymerized fullerite C_{60}. We do not observe further structural changes until 150 GPa after a formation of 3D C_{60} under hydrostatic pressure 28 GPa. It is experimentally shown that the obtained samples consist of different clusters formed by sp^3 bonds with a different set of force constants, the values of which vary within 20% and exceed the diamond force constants by the factor of 1.3−1.5. The influence of the exposure of laser radiation on the process of 3D polymerization of C_{60} under pressure was found. Increasing of the exposure by the factor of 15 leads to a decrease in the bulk modulus of 3D C_{60} from 610 GPa to 504 GPa.

Keywords: bulk modulus, ultrahard fullerite, high pressures, Raman spectroscopy.

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1. Introduction

A phase diagram of carbon containing a new diamond instability region has been proposed recently in [1,2]. it was conformed experimentally that the formation of diamonds ceases within the pressure interval from 55 to 115 GPa, and the already formed diamonds turn into fullerene-like structures cross-linked under pressure by sp^3 bonds. These structures may contain phases of ultrahard fullerite that has been discovered more than 25 years ago [3]. It was demonstrated in numerous experimental studies that the hardness and the bulk modulus of ultrahard states derived from fullerene C_{60} vary within fairly wide intervals (150−300 and 600−1000 GPa, respectively) depending on the conditions to which the initial C_{60} was exposed: the stress tensor, the plastic deformation magnitude, and the temperature [3]. If the temperature is increased to the Debye temperature of diamond in the region of diamond stability (5−55 GPa), ultrahard fullerite transforms partially or completely (depending on the time of high-temperature exposure) into diamond [4,5].

The structural analysis of ultrahard fullerite is made difficult by the fact that the obtained samples do not feature translation symmetry on scales above ~ 2 nm (the likely reason for this is the lack of a fourth-order rotation axis: C_{60} only has fifth-, third, and second-order rotation axes). It was demonstrated experimentally that ultrahard states form in the process of 3D polymerization of C_{60}. At room temperature, this process illustrates directly the recently discovered effect of catalytic polymerization and depolymerization of fullerene. Distorted BCC and FCC structures containing 70% of sp^3 bonds are normally observed for 3D C_{60} phases [3].

The results of computer simulations demonstrate that the bulk modulus of materials formed by carbon nanoclusters produced as a result of 3D polymerization of C_{60} may exceed 1000 GPa [6]. Further experimental and theoretical studies revealed that high values of elastic moduli are attributable to the fact that the force constants increase as carbon nanoclusters become smaller in size [7–9].

A pertinent question arises in the context of mechanical and structural peculiarities of ultrahard fullerite: what structural changes may occur in ultrahard fullerite both under a pressure of 55−115 GPa (i.e., in the region where fullerene-like phases are stable) and under pressures exceeding 115 GPa (in the region where diamond becomes stable again)? In the present study, the elastic properties of nanoclusters forming ultrahard 3D C_{60} at room temperature are examined experimentally under pressures up to 150 GPa.

2. Experiment

Fullerene C_{60} of a 99.99% purity was used. High-pressure studies were performed in a chamber with diamond anvils (CDA) with the use of tungsten gaskets. C_{60} was loaded in a NaCl environment that served as the pressure transmitter. Beveled anvils were used in experiments with pressures up to 150 GPa. The working area was 50 μm in size, and the gasket aperture diameter was 25 μm. Non-beveled anvils were used in experiments with pressures up to 80 GPa. The working area was 200 μm in size, and the gasket aperture diameter was 70 μm. Raman spectra were recorded with a Renishaw inVia microscope. The excitation radiation wavelengths were 405 and 532 nm. The laser was focused to a 1–2 μm spot on the sample. The pressure was determined by piezospectroscopy based on Raman spectra of the stressed diamond anvil tip [10].

3. Results and discussion

3.1. Transformations of C_{60} under pressures up to 150 GPa

It is common knowledge that C_{60} subjected to hydrostatic loading transforms into ultrahard 3D C_{60} under pressures exceeding 25 GPa (the transition pressure decreases to 18 GPa under the influence of shear deformation) [5]. This effect is seen clearly in the Raman spectra presented in Fig. 1. The spectrum of 3D C_{60} [11] is observed in our study under a pressure of 25 GPa. The distinctive spectrum of 3D C_{60} [11,12] consists of two broad bands around 1560 cm^{-1} and 600 cm^{-1} [11] (Fig. 2). Spectra were measured at the lowest laser power (1 mW) sufficient for such measurements. The measurement time was 10 min, and the excitation radiation wavelength was 532 nm.

The intensity of the 1560 cm^{-1} high-frequency mode starts decreasing under pressures above 80 GPa, and this line vanishes completely (along with the low-frequency mode around 600 cm^{-1}) under pressures above 101 GPa (Fig. 1). At this point, there is no reason to associate the vanishing of modes with a phase transition: the pressure of $\sim$ 100 GPa falls within the range of stability of fullerene-like structures, and the formation of diamond is expected to occur under pressures above 115 GPa [1,2]. However, diamond did not form in this experiment under pressures of 115–150 GPa: the Raman spectrum of 3D C_{60} was restored after unloading. The spectra in Fig. 2 suggest that the samples of 3D C_{60} obtained by applying shear deformation under a pressure of 20 GPa [11] do not differ from those obtained under hydrostatic loading to 150 GPa.

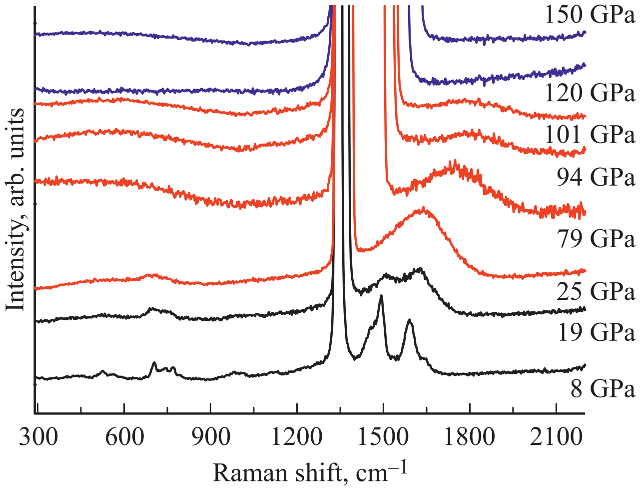

Figure 1. Pressure-induced transformation of Raman spectra of fullerene C_{60}.

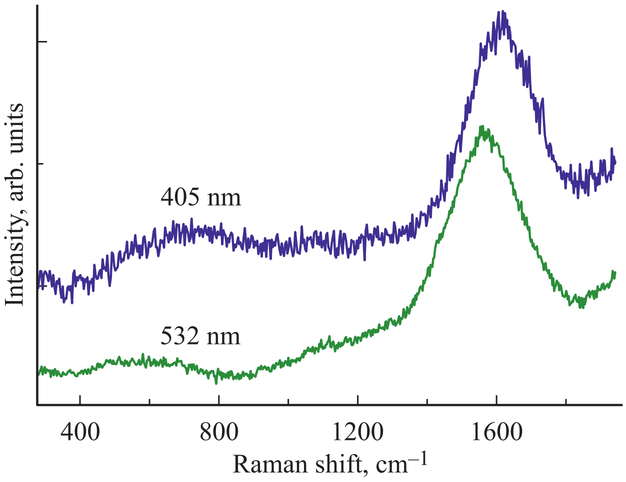

Figure 2. Raman spectra of the 3D C_{60} sample. Spectra obtained prior to unloading were measured at a laser power of 1 mW. The measurement time was 10 min, and the excitation radiation wavelengths were 405 and 532 nm.

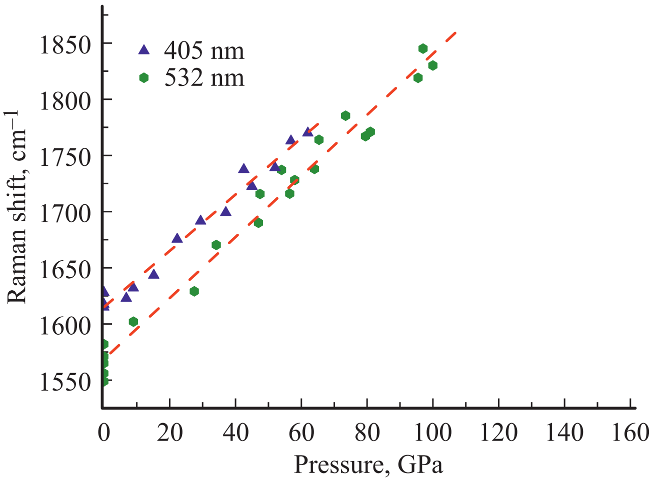

Figure 3. Dependence of the Raman frequency of 3D C_{60} on pressure. Spectra were measured at a laser power of 1 mW, the measurement time was 10 min, and the excitation radiation wavelengths were 405 nm (triangles) and 532 nm (circles). The presented data cover the interval from the phase formation under 25 GPa to a pressure of 101 GPa under which the spectrum of 3D C_{60} was still observed.

The dependence of the Raman frequency on pressure (Fig. 3) allows one to determine bulk modulus B_0 of the material using the known relation between Grüneisen parameter γ_i and phonon frequency ω_i [13]:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} = B_0 \frac{\partial \ln \omega_i}{\partial P}. \qquad (1)$$

Materials formed by covalently bound atoms have $\gamma \approx 1$ [13] (specifically, diamond has 0.96 and graphite (along the graphite layer) has 1.1 [11]).

Points corresponding to 3D C_{60} are shown in Fig. 3. Spectra were measured at a laser power of 1 mW, the measurement time was 10 min, and the excitation radiation wavelengths were 405 nm (triangles) and 532 nm (circles). The data in Fig. 3 cover the interval from the phase formation under 25 GPa to a pressure of 101 GPa under which the spectrum of 3D C_{60} was still observed (with excitation at 532 nm). Data obtained in the process of unloading are also presented. The dashed line is the result of linear least-squares interpolation. Bulk modulus $B_0 = 577 \pm 19$ GPa for an excitation radiation wavelength of 532 nm is determined based on the slope of the line in Fig. 3 and relation (1). This value of B_0 is close to the one calculated in [11] (585 GPa). Since the loading conditions in [11] were not hydrostatic, a more complex procedure for estimating the bulk modulus, which involved analyzing the stress tensors of the sample and the stressed diamond anvil tip, had to be used there.

Thus, ultrahard ferrite is preserved under hydrostatic loading (at room temperature) up to at least 150 GPa. Three-dimensional C_{60} forms in the first region of diamond stability (5−55 GPa) in the phase diagram of carbon [1,2]. The structure of ultrahard ferrite does not undergo any significant changes in the region of diamond instability (stability of fullerene-like structures, 55−115 GPa), is preserved in the second region of diamond stability (upward of 115 GPa), and also persists in the region of graphite stability (below 5 GPa). Notably, the sample obtained under hydrostatic loading to 25 GPa is equivalent to the sample with 3D polymerization initialized in it by applying shear deformation under a pressure of 20 GPa.

3.2. Dependence of Raman modes of 3D C_{60} on the excitation radiation wavelength. Bulk modulus

As was demonstrated experimentally and discussed in detail in [7], the mode around 1560 cm^{-1} observed in the spectra of 3D C_{60} corresponds to sp^3 bonds. When the excitation radiation wavelength switches from green (where the scattering cross-section of sp^2 bonds is two orders of magnitude higher than the one of sp^3 bonds) to an ultraviolet wavelength of 257 nm (where the scattering cross-section of sp^2 and sp^3 bonds are equal), the intensity of this mode remains almost unchanged, but an intriguing „resonance“ shift from 1550−1560 cm^{-1} to 1610−1640 cm^{-1} at an excitation radiation wavelength of 257 nm [7,12] and to 1490 cm^{-1} at 632 nm [4] is observed. The results of computer simulations suggest that the length of sp^3 bonds in carbon nanoclusters differs depending on the position of atoms (specifically, the bond lengths at the center are not the same as those near the surface); therefore, sets of force constants k also differ [6–9]. Note that [14]. For comparison, the Raman frequency of diamond is 1333 cm^{-1}, and covalent bonds in ultrahard ferrite are 1.3−1.5 times stiffer than the ones in diamond. Thus, the observed „resonance“ shift of the 1560 cm^{-1} mode may be attributed to the dependence of the Raman scattering cross-section on the specific features of local bonding in nanoclusters. In other words, the Raman spectrum of sp^3 nanoclusters is characterized by a broad line from ~ 1490 cm^{-1} to ~ 1640 cm^{-1} shaped in accordance with a set (tensor) of force constants that differ within 20% ($\omega^2 \propto k$). When the excitation radiation wavelength changes, the relative intensity of the corresponding regions of one broad spectral line increases. In the present study, a shift from 1568 cm^{-1} ($\lambda_{\text{ex}} = 532$ nm) to 1620 cm^{-1} ($\lambda_{\text{ex}} = 405$ nm) was observed (Fig. 2).

In general, when determining the elastic moduli of a material with bonds having different force constants present in it, one should consider their overall contribution [14] or apply the procedure of averaging of force constants in nanoclusters proposed in [9]. This requires analyzing the variation of both frequencies and intensities of Raman spectra induced by a change in the excitation radiation wavelength. Additional data on the dependence of cross-sections on the values of force constants (or bond lengths [9]) are also needed.

When the bulk modulus is estimated using formula (1), averaging over the contributions of different bonds (with their own force constants) to this modulus is implied. If the modulus derived from (1) is independent of the excitation radiation wavelength, one can say that the obtained bulk modulus value is exact. The present case is more complicated. The bulk modulus calculated in accordance with (1) (Fig. 3) is $B_{0(405)} = 644 \pm 27$ GPa at an excitation radiation wavelength of $\lambda_{\text{ex}} = 405$ nm and $B_{0(532)} = 577 \pm 19$ GPa at $\lambda_{\text{ex}} = 532$ nm. Thus, the bulk modulus calculated using the relation between the Raman frequency and pressure depends on the excitation radiation wavelength. The difference between the obtained modulus values exceeds the experimental error. This effect is attributable to the presence of two types of clusters, which are formed by bonds with different sets of force constants, in the sample structure. The estimate of the bulk modulus of the sample obtained in accordance with the procedure of averaging of force constants proposed in [9] is $B_0 = 0.5(B_{0(405)} + B_{0(532)}) = 610$ GPa.

The emergence of different types of clusters is induced by the process of 3D polymerization of C_{60}. A version of the BCC structure formed by C_{60} molecules with $(6+6)$ bonding was proposed in [15]. This type of 3D polymerization results in the formation of smaller polyhedra between C_{60}. These polyhedra form from fragments of C_{60} and 4-member rings linking the neighboring C_{60}. Each BCC cell of this structure contains six distorted truncated octahedra (consisting of eight hexagons and six squares (24 atoms) with an approximate diameter of 4.5 Å) and six dodecahedra (consisting of four hexagons, four pentagons, and four squares with an approximate diameter of 4 Å) [15]. The covalent bond angle in such fullerene-like structures is close to the tetrahedral position of sp^3 [16–18]. Therefore, the model of chaotic close packing of rigid spheres [19,20] may be used to characterize the amorphous structure of 3D C_{60}. The space in this model may be filled with Bernal

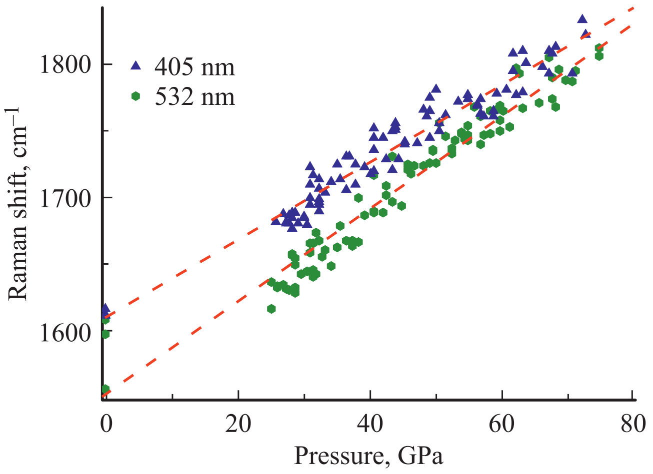

Figure 4. Dependence of the Raman frequency of 3D C_{60} on pressure. Spectra were measured at a laser power of 15 mW, the measurement time was 10 min, and the excitation radiation wavelengths were 405 nm (triangles) and 532 nm (circles).

polyhedra containing atomic spheres at each vertex. One half of the void space of an amorphous material is accounted for by octahedral and tetrahedral voids at a ratio of 1 : 2.5, and the other half corresponds to complex polyhedra.

3.3. Effect of photoinduced 3D polymerization of C_{60}

The method of initialization of a phase transition by the application of shear deformations becomes inapplicable after the formation of ultrahard ferrite, since the sample slips on diamond anvils when they are rotated in a shearing chamber, thus inducing plastic deformation of diamond instead of the 3D polymerization of C_{60} [3,11,12]. The effect of photoinitialization of the transition of diamond into fullerene-like structures under pressures of 55–115 GPa was discovered in [7]. The same method was used in the present study. Just as in the previous experiment, the C_{60} sample was loaded in hydrostatic conditions (in a NaCl environment). Following [7], a laser power of 15 mW and a measurement time of 10 min were set for spectral measurements under pressures exceeding 25 GPa.

Figure 4 presents the pressure dependences of the Raman frequency of 3D C_{60} at excitation radiation wavelengths of 405 and 532 nm. Dashed lines represent the results of linear least-squares interpolation of data for 405 and 532 nm. The radiant exposure and the radiation intensity in spectrum measurements in this experiment are 15 times higher than in the previous one. With an increased exposure, the peak around 1560 cm^{-1} vanishes completely from the Raman spectrum under a pressure of 75 GPa. For comparison, this peak vanished under a pressure exceeding 101 GPa in the previous experiment with a lower exposure. The observed vanishing of this peaks is reversible. When the pressure is reduced, the line around 1560 cm^{-1} reappears in the spectra.

The bulk modulus calculated in accordance with (1) (Fig. 4) is $B_{0(405)} = 558 \pm 14$ GPa at an excitation radiation wavelength of $\lambda_{\text{ex}} = 405$ nm and $B_{0(532)} = 449 \pm 12$ GPa at $\lambda_{\text{ex}} = 532$ nm. Just as in the previous case, two types of clusters, which are formed by bonds with different sets of force constants, are present in the sample structure. The bulk modulus of the sample obtained with an increased radiant exposure under pressure is $B_0 = 0.5(B_{0(405)} + B_{0(532)}) = 504$ GPa. Thus, the bulk modulus decreases from 610 to 504 GPa when the radiant exposure increases by a factor of 15.

4. Conclusion

It was demonstrated experimentally that 3D C_{60} is formed by sp^3 bonds with their force constants varying within 20% and being 1.3–1.5 times higher than the force constants of diamond.

The bulk modulus of 3D C_{60} calculated using the relation between the Raman frequency and pressure depends on the excitation radiation wavelength. This effect is attributable to the presence of at least two types of clusters, which are formed by bonds with different sets of force constants, in the sample structure.

Following the formation of 3D C_{60} under hydrostatic loading to 25 GPa, no further structural changes are observed under increasing pressure up to at least 150 GPa.

It was found that the laser radiant exposure has an effect on C_{60} under pressure. The bulk modulus of 3D C_{60} decreases from 610 to 504 GPa when the exposure increases by a factor of 15.

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Conflict of interest

The authors declare that they have no conflict of interest.

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