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Study of the structure of crystalline fullerene C_{70} at pressures up to 33 GPa

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The results of the study of the effect of high pressure on the structure of fullerene C_{70} crystals are presented. X-ray structural analysis and Raman spectroscopy of fullerene C_{70} samples were carried at atmospheric pressure, as well as at pressures up to 33 GPa. High-pressure chambers with optically transparent diamond anvils were used for the study. Several phase transformations occurring under the action of high pressure, caused by the orientational structural transition and amorphization of fullerene crystals, were established.

Keywords: carbon materials, phase transitions, Raman spectroscopy, X-ray structural analysis.

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Introduction

Fullerenes are an allotropic form of carbon that represents closed molecules consisting of pentagons and hexagons with carbon atoms in apexes. The number of carbon atoms in fullerene molecules varies from 20 to 540. Atoms constituting fullerene are in sp^2-hybridization. The most comprehensively studied representative of the fullerene family is C_{60}, where carbon atoms form a truncated icosahedron consisting of 20 hexagons and 12 pentagons and resembling a football. The next widespread form is fullerene C_{70} that differs from fullerene C_{60} in a belt of 10 carbon atoms inserted into the equatorial region, as a result of which the molecule is elongated. C_{70} molecule is included in the D_{5h} point group [1–4].

Condensed systems — molecular crystals consisting of fullerene molecules — are also known as fullerites. In a crystal form, there is no chemical bond between individual fullerene molecules — molecules are held in the crystal by the Van der Waals forces. Thus, the interaction between carbon atoms within the molecule is much stronger than between the atoms of neighboring molecules. Considering that fullerenes are quite spherically symmetric structures themselves (depending on the number of carbon atoms), fullerene crystals have a close-packed structure. This is usually a face-centered cubic structure, but hexagonal and rhombohedral structures also occur [1,5,6]. In normal conditions, molecules rotate freely in lattice sites. When pressure is applied, free rotation stops and molecules are arranged with their poles in initial lattice direction with maintained uniaxial rotational motion [7].

In the crystal form, fullerene molecules easily form covalent bonds with their molecular neighbors when exposed to radiation, high temperatures or pressures — a so-called polymerization process of carbon nanostructures, fullerenes in this case. Polymerization of neutral C_{60} takes place at a pressure of several GPa. Depolymerization is possible at atmospheric pressure and temperatures of about 200°C. A rhombohedral phase is the most energetically unfavorable and is also the most widespread during high-pressure polymerization. Thus, transition to a more stable polymerized phase requires harder conditions, while transformation into an unstable monomeric phase is much easier [8].

At higher pressures, superhard phases may be formed, which is attributable to three-dimensional ordering of the sp^2-hybridized structure. High-temperature exposure leads to three-dimensional polymerization and formation of a disordered network with high density ofsp^3 states and then to formation of a diamond-like structure [8–10].

These transformations are studied in more detail in high pressure and/or temperature conditions in fullerene C_{60} crystals, which is attributable to their highest abundance and symmetry [4,10,11]. There are much less studies for a larger and more elongated C_{70}molecule [7,12,13]. Polymerization of fullerene C_{60} can be achieved much easier than of C_{70}molecules. While the structure of C_{60} molecule includes 30 double bonds, and each of them could be involved in the formation of chemical bonds with neighboring molecules, C_{70} has only ten double bonds capable of participating in polymerization, with five of them distributed radially around each pentagonal „polar cap“. Therefore, C_{70} is, in fact, much less reactive than C_{60} [7,14].

A single-dimensional polymerized C_{70}-based structure with a hexagonal lattice may be formed in monomeric crystals with hexagonal close packing at a relatively low pressure of 2.5 GPa and temperature of about 300°C [12]. Face-centered cubic structure is most widespread for fullereneC_{70}, and it had been assumed for a long time that C_{70} crystals with such lattice could not form any polymerized structures that had a long-range order due to the incompatible symmetry of the lattice and molecule structure. However, it was shown later that this was possible at pressures of about 10 GPa and temperatures of about 270°C [15].

Fullerenes are of interest for the synthesis of new functional materials on the basis of carbon nanostructures. Though graphene and carbon nanotubes are almost inert at low pressures, fullerenes are easily reactive and, thus, may act as „adhesive“ in the synthesis of such materials. Such polymer structures have unique physical and chemical properties. Fullerene molecules can be solvated in the matrix and, provided they are properly space-oriented, structures with desired properties may be created in high pressure conditions. The fact that molecular bond in C_{70} is strictly directional makes this molecule particularly suitable for such experiments and therefore detail study of its properties in high pressure conditions is of particular interest [7,14].

Previous studies observed orientational transitions at room temperature from face-centered cubic (FCC) to rhombohedral phase at pressures lower than 2 GPa [3,5,16–19]. In these studies, either X-ray patterns or Raman scattering spectra were recorded in high pressure conditions. Measurements were performed on different samples: initial phases and phase content depend on the synthesis technique and conditions [1]. As a consequence, precise critical pressures and the nature of phase transitions themselves are still controversial. *In situ* studies were performed to investigate high pressure impact on the fullerene C_{70} structure through measuring diffraction patterns and Raman scattering spectra on the same samples.

1. Samples and measurement procedure

Initial crystalline fullerene C_{70} sample was made at Emanuel Institute of Biochemical Physics, RAS. The crystalline fullerene C_{70} structure was qualified by X-ray diffraction in Cu-$K\alpha$ radiation using the Bruker ADVANCE D8 diffractometer. Measurements were performed by the laboratory of structural analysis methods and material and nanomaterial properties at the Institute of Natural Sciences and Mathematics, Ural Federal University.

The initial sample was also examined by Raman scattering spectroscopy using the Alpha 300 AR (WiTec GmbH) confocal Raman scattering microscopy system. A 488 nm solid-state laser was used as the source of the laser radiation. Measurements were performed at the Ural Shared Research Facility „Modern Nanotechnologies“ Ural Federal University.

In situ structural studies of the crystalline fullerene C_{70} samples were performed at high pressures in a diamond anvil cell by the X-ray diffraction and Raman scattering spectroscopy methods. Four-pin high-pressure chambers were used for the studies. A powdered C_{70} sample was placed into the diamond anvil cell into the 100 μm rhenium gasket hole. Argon was used as pressure transfer fluid. A method of pressure measurement by ruby luminescence lines was used to evaluate the cell pressure.

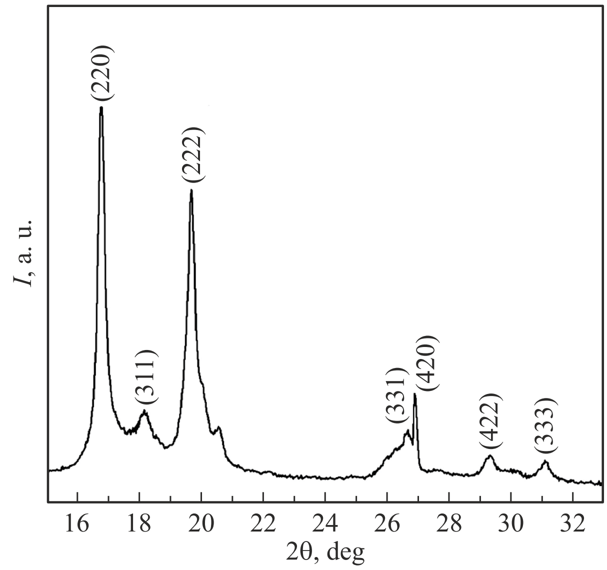

Figure 1. Diffraction pattern of the fullerene C_{70} sample at atmospheric pressure.

High-pressure diffraction patterns were measured on a rotating anode unit with Mo-$K\alpha$ radiation using the Rigaku diffraction pattern with the Osmic focusing X-ray optics and Bruker APEX CCD detector. Raman scattering spectroscopy was performed at high pressure and room temperature using the Dilor XY spectrometer and 514.5 nm argon laser.

2. X-ray diffraction

Figure 1 shows a diffraction pattern obtained for the initial fullerene C_{70} sample at atmospheric pressure and room temperature. Diffraction patterns were recorded using the Cu-$K\alpha$ radiation within 10−90°. The initial C_{70} sample is crystallized primarily in the FCC phase with the lattice parameter $a = 14.96$ Å, with a small addition of hexagonal close-packed phase (HCP). Most of the peaks correspond exactly to the FCC phase. The right shoulder of the peak of about 20° and some other peaks may be attributable to the presence of hexagonal packing clusters. The HCP phase is highly distorted or disordered.

Diffraction patterns at hydrostatic pressures up to 15 GPa (Figure 2) were recorded using the Mo-$K\alpha$ radiation. At atmospheric pressure, a set of peaks corresponding to the FCC phase may be identified. As the load increases, an orientational transition may be observed at pressures higher than 1 GPa. Molecular crystals are very complex crystallographically and identification of the obtained phases turns to be impossible. Previous studies performed at room temperature observed a transition from the FCC to rhombohedral phase at 0.35 GPa with co-existence of the FCC phase up to 1 GPa [5,16]. Lattice compression makes the elongated fullerene C_{70} molecules arranged in parallel,

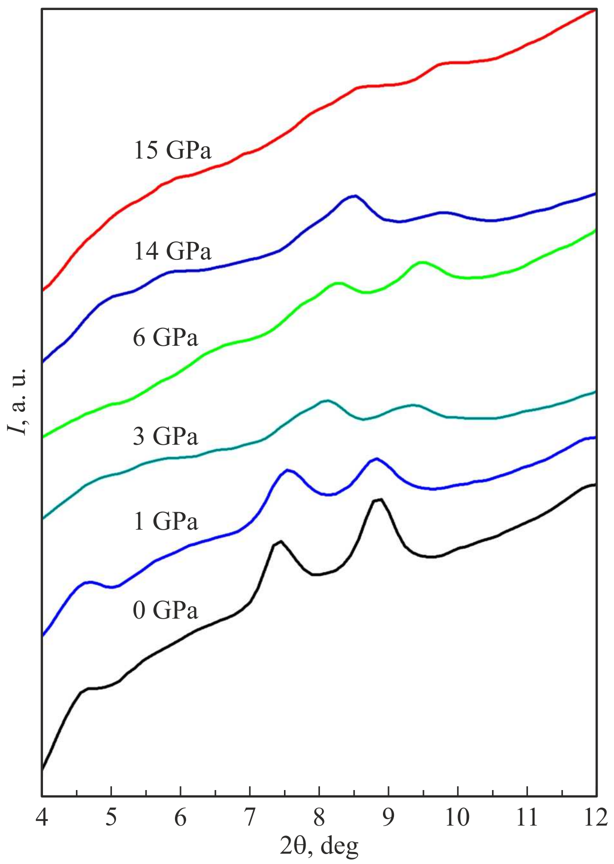

Figure 2. Diffraction pattern of the fullerene C_{70} sample at various pressures.

thus, improving the orientational order. In our case, similar variations in diffraction patterns are observed [16].

Previous studies suggest the presence of fullerene polymerization in the pressure range from 3 GPa to 14 GPa [12,15], however, this is not proved exactly. When the pressure reaches 14 GPa (Figure 2), most of the peaks become poorly perceptible, and as the load further increases, they disappear. At pressure higher than 14 GPa, transition to the amorphous carbon phase takes place [9,13].

3. Raman scattering spectroscopy

Figure 3 shows the results of *in situ* Raman scattering (RS) spectroscopy of fullerene C_{70} at pressures up to 32.8 GPa. A sample was placed into the gasket hole in the diamond anvil cell. Argon was used as pressure transfer fluid. A region at $\omega = 1332\,\mathrm{cm}^{-1}$ was removed from the spectra because strong vibrations prevail in this range that are induced by diamond anvils, and its contribution to the spectrum is dominating. Increase in the phonon signal from $1000\,\mathrm{cm}^{-1}$ is caused by low luminescence from electron-excited C_{70} molecules [20]. Raman scattering line at $1471\,\mathrm{cm}^{-1}$ is known to correspond to A_g breathing mode of the pentagonal cell of the C_{60} model [21]. The absence of a breathing mode of fullerene C_{60} at $496\,\mathrm{cm}^{-1}$ indicates that a peak with a frequency of about $1471\,\mathrm{cm}^{-1}$ is induced by C_{70} molecule and is not associated with the presence of C_{60} impurities. Considerable increase in the low-frequency spectrum intensity with the increase in pressure is typical for fullerenes [3].

Baric dependences of Raman scattering spectrum peak positions are shown in Figure 4, *a, b*. All peaks move towards higher frequencies as the pressure increases, with the exclusion of two phonon modes at 568 and $702\,\mathrm{cm}^{-1}$ whose frequencies decrease with pressure increase, which was observed earlier in [3]. At pressures higher than 14 GPa, most of the phonon modes of fullerene C_{70} are not traced, and only the most intense wide peak with a frequency of about $1567\,\mathrm{cm}^{-1}$ may be clearly observed (Figure 4, *b*). Baric dependence of FWHM of this peak is shown in Figure 4, *c*.

In the dependences of peak positions on pressure (Figure 4, *a, b*), considerable increase in the vibration frequency can be noted when reaching the pressure of 5 GPa. Stepwise change of the Raman scattering line width for a phonon with $1562\,\mathrm{cm}^{-1}$ indicates the presence of at least one orientational transition in the pressure range from 2 GPa to 5 GPa (Figure 4, *c*). In [3], the authors reported two phase transitions at pressures of about 2 GPa and 5.5 GPa, with the transition at 2 GPa being reversible. These observations were not confirmed, which is probably caused by various initial phases of fullerene C_{70} samples.

Figure 5 shows Raman scattering spectra of fullerene C_{70} from 1400 to $1800\,\mathrm{cm}^{-1}$ at various pressures. At 18.8 GPa,

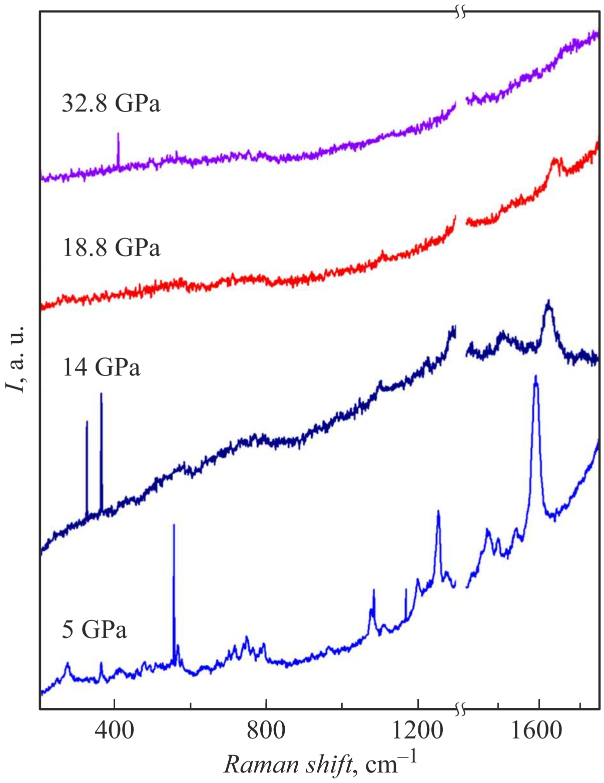

Figure 3. Raman scattering spectra of fullerene C_{70} at various pressures.

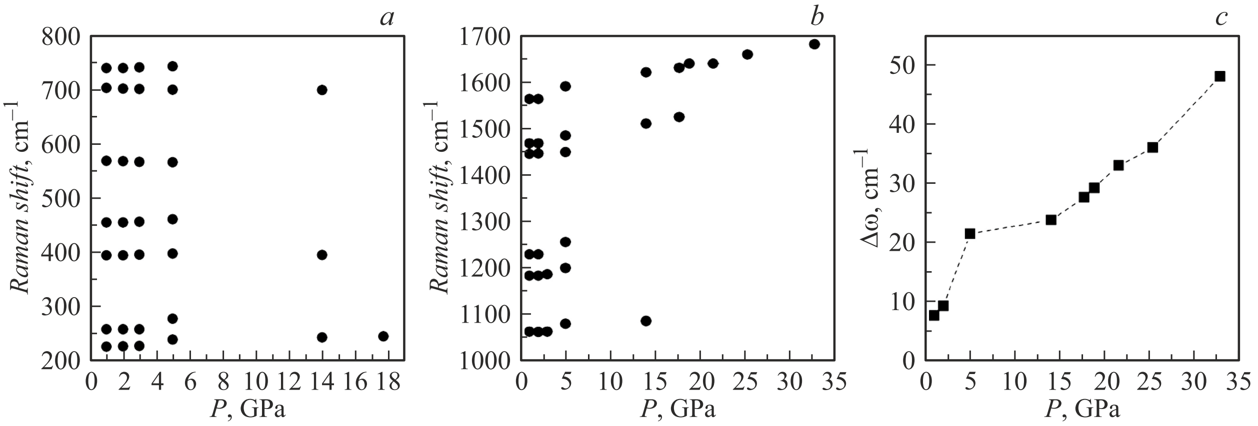

Figure 4. Baric dependences of RS spectra peak positions for fullerene C_{70} within 200–800 (*a*) and 1000–1700 cm^{-1} (*b*). Baric dependence of FWHM of the phonon maximum with a frequency of 1567 cm^{-1} (*c*).

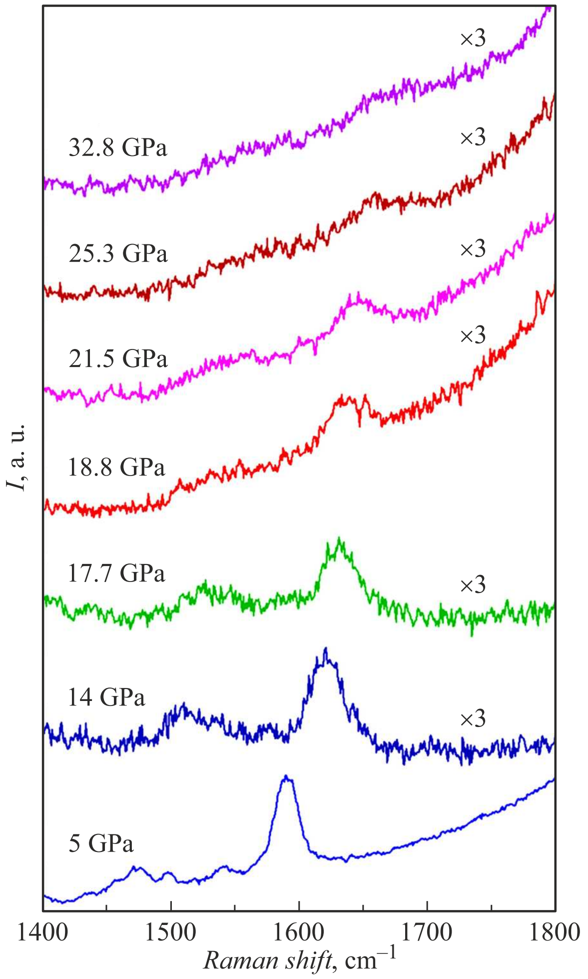

Figure 5. Raman scattering spectra of fullerene C_{70} within 1400–1800 cm^{-1} at various pressures.

splitting of the peak with 1567 cm^{-1} is clearly observed (with pressure growth, the peak shifts towards higher frequencies). At 18.8 GPa and higher, only a wide band with the center at 1680 cm^{-1} can be observed in the region, which may suggest particular transformations in the sample structure. Such changes in the spectra are attributable to high-pressure amorphization of fullerenes [3,17,19].

Raman scattering spectroscopy has previously shown that the crystalline fullerene amorphization is reversible at pressures up to at least 31 GPa [17], which was also supported by X-ray patterns of samples subjected to shockwave loading [6]. The amorphization process starts at pressures about 12 GPa, and at 18–20 GPa fullerene is completely transformed into the amorphous state [17–19]. Irreversible transition into the amorphous phase takes place at about 35 GPa [19].

The provided diffraction patterns, Raman scattering spectra and previous studies of high pressure impact on thermoelectric properties of fullerene C_{70} [22] suggest that the amorphization of fullerene C_{70} takes place in the pressure range of 14–18 GPa (Figure 2,5). Baric dependence of the phonon line width with 1567 cm^{-1} (Figure 4, *c*) also supports this assumption. Structural changes of a substance are usually substantially reflected on thermoelectric properties and are indicative of transformations throughout the volume of the studied substance, while the structural studies show only a local phase transformation.

At pressure higher than 18.8 GPa intense fullerene-specific peaks were observed in some spectra. For example, a spectrum measured at 32.8 GPa has a fullerene-specific peak with a frequency about 410 cm^{-1} (Figure 3). This peak indicates that some fullerenes change to the amorphous phase not fully. This also confirms that the amorphization is reversible at about 30 GPa [17].

Figure 6 shows the Raman scattering spectra of fullerene C_{70} before and after exposure to 46 GPa. The impact of high pressure on the thermoelectric properties of fullerene C_{70} was studied earlier [22]. The experiments used cells with anvils made from polycrystalline carbonado diamonds for pressurization. The structure of such synthetic diamond consists of interpenetrating diamond and metal-ceramic phase scaffolds, due to which the anvils have good electrical

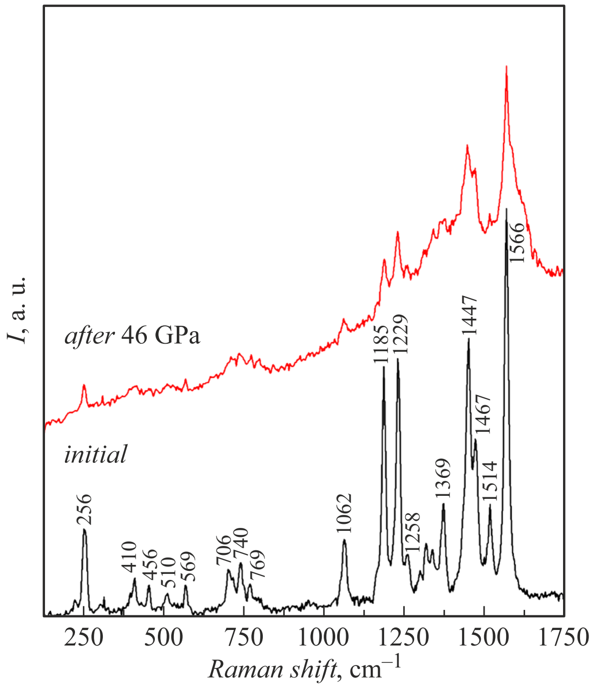

Figure 6. Raman scattering spectra of fullerene C_{70} before and after exposure to 46 GPa.

conductivity and may be used as contacts to the test sample. At the same time, the cell configuration prevents from examining the sample structure in high pressure conditions, therefore the samples were examined after removal from the diamond chamber.

Some Raman modes corresponding to fullerenes may be noted in the spectrum of the initial sample not exposed to high pressure (Figure 6). A peak with 496 cm^{-1} isn’t observed here either, which indicates that there are no or at least low content of C_{60} impurities [21]. The spectrum of a sample removed from the diamond anvil cell after exposure to 46 GPa clearly shows several Raman modes corresponding to fullerene. A Raman scattering spectrum was obtained earlier after exposure to 43 GPa and also showed fullerene’s structural features [13].

Thus, this finding suggests a higher structural stability of fullerene C_{70} compared with C_{60} [8,9]. At the same time, some experiments successfully achieved irreversible transformations in the sample structure in the same conditions. The structural study of a sample not exposed to pressure indicate high purity and predominance of the FCC phase. Considering this, experimental studies of thermoelectric properties suggest nonuniformity of cell pressure distribution in axial compression.

Conclusion

Thus, the obtained spectroscopic study data confirms that there is at least one orientational transition in the pressure range of 2−5 GPa, however, the structure of the obtained phases was not identified. Amorphization of fullerene C_{70} takes place in the pressure range of 14−18 GPa. Amorphization of fullerene C_{70} is partially reversible at hydrostatic pressures of about 33 GPa, which agrees with the previous findings [17]. In axial compression, maintenance of the fullerene C_{70} structure was observed at about 46 GPa. This result requires further studies in hydrostatic compression conditions.

Conflict of interest

The authors declare no conflict of interest.

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