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Phase Transitions and Photoinduced Transformations at High Pressure in the Molecular Donor–Acceptor Fullerene Complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$

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Abstract—The Raman spectra of crystals of C_{60} fullerene–cadmium diethyldithiocarbamate molecular donor–acceptor complexes $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ were measured at pressures of up to 17 GPa, and the crystal lattice parameters of these complexes were determined at pressures of up to 6 GPa. An increase in pressure up to ~2 GPa leads to changes in the Raman spectra, which are manifested by splitting of the intramolecular $H_g(1)$ – $H_g(8)$ phonon modes and by softening of the $A_g(2)$ mode of the C_{60} molecule. A further increase in pressure up to 17 GPa does not induce significant new changes to the Raman spectra, while a decrease is accompanied by the reverse transformation at a pressure of about 2 GPa. The pressure dependence of the lattice parameters also exhibits a reversible feature at 2 GPa related to a jumplike decrease in compressibility. All these data are indicative of a phase transition in the vicinity of 2 GPa related to the formation of covalent bonds between C_{60} molecules and, probably, the appearance of C_{120} dimers in fullerene layers. It was also found that, in the pressure interval from 2 to 6.3 GPa, the Raman spectra of complexes exhibit photoinduced transformations under prolonged exposure to laser radiation with a wavelength of $\lambda = 532$ nm and power density up to 5000 W/cm^2 . These changes are manifested by splitting and softening of the $A_g(2)$ mode and resemble analogous changes accompanying the photopolymerization of C_{60} fullerene. The intensity of new bands exhibits exponential growth with increasing exposure time. The photopolymer yield depends on both the laser radiation power and external pressure. The $A_g(2)$ mode splitting under irradiation can be related to the formation of photo-oligomers with various numbers of intermolecular covalent bonds per C_{60} molecule.

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1. INTRODUCTION

In recent years, the synthesis of donor–acceptor complexes of fullerenes and investigations of their crystalline structure, electrical, magnetic, and optical properties, and behavior at high pressures have received much research interest [1–6]. These complexes belong to molecular crystals and possess an ordered layered structure of fullerene layers alternating with molecular donor layers. The interaction of molecules both inside and between layers is of the van der Waals type. The interest in high-pressure investigations is related to the possible pressure-induced charge transfer from donor to acceptor in neutral and weakly ionic complexes, which should lead to modification of their electrical and optical properties. As the pressure increases, the highest occupied molecular orbital (HOMO) level of the donor and lowest unoccupied molecular orbital (LUMO) level of the acceptor approach each other and the overlap of their electron clouds increases, which stimulates charge transfer from a molecular donor to fullerene (acceptor), especially if complexes in the initial state are partly ionic. In contrast, shorter distances between fullerene mole-

cules in layers of complexes under pressure can lead to the formation of covalent bonds between these molecules and thus provide some possibilities for their controlled polymerization in layers and the formation of new planar fullerene polymers.

The possible formation of covalent bonds between C_{60} molecules in crystals and films is related to the presence of 30 unsaturated double C=C bonds in an isolated C_{60} molecule, in which all carbon atoms exhibit sp^2 hybridization. As is known, the exposure of fullerene to visible light with an intensity above 5 W/cm^2 leads to the appearance of photopolymers in the surface layer of C_{60} crystals and films [7]. Ordered polymer chains are also formed in fullerite crystals intercalated by alkali metals [8, 9], while the treatment of fullerene at a high pressure and temperature leads to the formation of crystalline C_{60} polymers [10, 11]. The rupture of double C=C bonds is accompanied by the formation of single covalent C–C bonds between pairs of carbon atoms in neighboring molecules (the so-called [2 + 2] cycloaddition reaction). As a result of this interaction, each fullerene molecule acquires two carbon atoms with sp^3 hybridization of electron orbit-

als, the molecular symmetry decreases, and degenerate molecular phonon modes exhibit splitting. In addition, the rupture of double bonds decreases the rigidity of the molecular framework and leads to softening of the fully symmetric $A_g(2)$ mode corresponding to in-phase tangential vibrations of carbon atoms with simultaneous contraction of the carbon pentagon and extension of the carbon hexagon. The $A_g(2)$ mode frequency sequentially decreases in various crystalline forms of fullerene with increasing number of sp^3 hybridized electron orbitals per C_{60} molecule [10–14].

Experimental investigations of the donor–acceptor complexes of fullerenes under hydrostatic compression revealed sharp changes in their Raman spectra at certain pressures. The Raman spectra of a fullerene–ferrocene molecular complex $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ measured at high pressures evidenced a phase transition in the vicinity of 5 GPa related to charge transfer with the formation of polymer bonds between molecules in fullerene layers [3]. Analogous changes were observed in the Raman spectra of fullerene–ferrocene molecular complexes $C_{70} \cdot \{Fe(C_5H_5)_2\}_2$ at 3 and 8 GPa, which were interpreted as the formation of dimers and linear chains of negatively charged C_{70} molecules upon the pressure-induced charge transfer [6]. In addition, structural investigations of these complexes at high pressures revealed peculiarities in the pressure dependence of their lattice parameters at 2.5 and 8 GPa [6].

In recent investigations of neutral fullerene molecular donor–acceptor complexes $\{Pt(dbdtc)_2\}_2 \cdot C_{60}$ ($C_{30}H_{28}PtN_2S_4$ = platinum dibenzylthiocarbamate) and $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ ($C_{20}H_{40}Cd_2N_4S_8$ = cadmium diethyldithiocarbamate), we have observed sharp changes in the Raman spectra of these complexes in the vicinity of 1 and 2.5 GPa [4, 5]. These pressure-induced reversible variations were related to the formation of covalent bonds between C_{60} molecules in fullerene layers. Previous investigations of fullerene–tetramethyltetraselenafulvalene complexes $\{C_{10}H_{12}Se_4(CS_2)_2\} \cdot C_{60}$ by Raman spectroscopy at high pressure revealed splitting and softening of the intramolecular modes of fullerene, which was related to an irreversible phase transition at 5 GPa [15]. We also observed reversible changes in the Raman spectra of fullerene molecular donor–acceptor complexes $\{Ni(nPr_2dtc)_2\} \cdot (C_{60})_2$ and $\{Cu(nPr_2dtc)_2\} \cdot (C_{60})_2$ at pressures within 0.5–2.5 GPa, which could be related to both charge transfer and covalent bond formation between fullerene molecules [16].

The results of X-ray diffraction (XRD) studies of the structure C_{60} ionic complexes at low temperature also evidenced changes in the ordering of molecules in fullerene layers near liquid nitrogen temperature. A decrease in temperature (which is equivalent to some compression) led to the formation of $(C_{120})^{2-}$ fullerene dimers in which negatively charged fullerene molecules were linked by single C–C or double C=C bonds [17, 18].

In this work, we measured the Raman spectra of fullerene–cadmium diethyldithiocarbamate molecular donor–acceptor complexes $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ at pressures up to 17 GPa and studied the pressure dependence of the crystal lattice parameters of these complexes at pressures up to 6 GPa. The results reveal characteristic changes in the spectra measured at 2 GPa, which are manifested by splitting of the intramolecular $H_g(1)$ – $H_g(8)$ phonon modes and by softening of the $A_g(2)$ mode of the C_{60} molecule. The pressure dependence of the unit cell volume and lattice parameters also exhibits a reversible feature at 2 GPa that related to a jumplike decrease in compressibility. All these data are indicative of a phase transition, which is most probably related to the formation of covalent bonds between C_{60} molecules in fullerene layers. It was also found that, in the pressure interval from 2 to 6.3 GPa, the Raman spectra of complexes exhibited photoinduced transformations resembling those accompanying the photopolymerization of C_{60} fullerene. The photopolymer yield exhibited exponential growth with increasing exposure time and accelerated with increasing laser power. Outside the indicated pressure interval, photopolymerization of C_{60} was not observed even at a maximum power density of the laser radiation.

The Raman spectra exhibited no sharp changes at pressures in the region of 17 GPa, where the average distances between fullerene molecules are close to the intermolecular contacts in planar crystalline C_{60} polymers. With decreasing pressure, the Raman spectra exhibited reversible variation and were similar to those measured for an increase in pressure, with the reverse transition in the vicinity of 2 GPa. We believe that the changes observed in the Raman spectra and a jumplike decrease in compressibility at 2 GPa are related to the appearance of covalent bonds between C_{60} molecules in fullerene layers and, probably, the formation of fullerene dimers. The photoinduced transformations in the pressure interval from 2 to 6.3 GPa lead to the formation of C_{60} oligomers with various numbers of intermolecular bonds per fullerene molecule.

2. EXPERIMENTAL

The $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ ($C_{20}H_{40}Cd_2N_4S_8 \cdot C_{60}$) molecular complex was synthesized by slow evaporation of a solution containing C_{60} fullerene and cadmium diethyldithiocarbamate according to the method described previously [1]. The structural analysis of $\{Hg(dedtc)_2\}_2 \cdot C_{60}$ samples showed that the crystals of this complex possess a monoclinic structure (space group $P2_1/c$) with the unit cell parameters $a = 16.368(3)$ Å, $b = 17.056(2)$ Å, $c = 10.6650(15)$ Å, $\beta = 100.058(14)^\circ$, and $V = 2931.63$ Å³ [5]. The compound has a layered structure in which layers of close-packed C_{60} molecules alternate with layers of cadmium diethyldithiocarbamate. Each fullerene molecule has six neighbors within the layer, and the shortest distances

between the centers of nearest-neighbor molecules are 10.058 Å (four neighbors) and 10.665 Å (two neighbors). Under normal conditions, fullerene molecules in the complex are isolated from each other so that covalent C—C bonds between them never form. At the same time, the shortest distances between these molecules are such that numerous van der Waals C—C contacts with a characteristic length of 3.30–3.68 Å are formed.

The Raman spectra were measured in the backscattering geometry on an Acton SpectraPro-2500i spectrograph equipped with a CCD Pixis2K detector cooled to -70°C and an Olympus microscope. The XRD measurements were performed using an Oxford Diffraction Gemini-R four-circle diffractometer on well-faceted crystals with a mirror finished surface in the form of plates with lateral dimensions of about 100 μm and a thickness of about 20 μm .

The Raman spectra were excited by a diode-pumped single-mode laser operating at a wavelength of 532 nm. The laser beam was focused onto the sample via an Olympus microscope with $\times 50$ objective into a spot with a diameter of about 3 μm (with allowance for image defocusing by diamond anvils). The laser radiation line in the scattered beam was suppressed by an optical supernotch filter with an optical density of $OD = 6$ and a bandwidth of 160 cm^{-1} . The exciting radiation intensity in front of the high-pressure cell was about 0.35 mW.

The Raman spectroscopy measurements at high pressure were performed in a diamond anvil cell of Mao–Bell type using a 4 : 1 methyl/ethyl alcohol mixture as a pressure-transmitting medium. The XRD measurements were performed in a cell with Beller-type diamond anvils. The use of these anvils with conical base pads increased the angular aperture and improved the experimental conditions. The pressure was calibrated using the R_1 luminescence line of ruby microcrystals [19].

3. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes in the range of $230\text{--}1750\text{ cm}^{-1}$, measured at pressures below 7 GPa. The initial spectrum is much like that of a fullerene crystal under normal conditions, although there are some minor differences in the positions of bands and distribution of their intensities. Preliminary measurements showed that the spectrum of donor molecules is much richer than that of C_{60} fullerene, but the latter spectrum intensity is greater by about two orders of magnitude. For this reason, the donor phonon modes are not manifested in the spectrum of complexes and it is dominated by the intramolecular modes of C_{60} [20]. This pattern is characteristic of most donor–acceptor complexes of C_{60} fullerene [2–6, 15, 16].

Figure 1a shows the spectra measured with increasing pressure, while Fig. 1b shows the spectra measured with decreasing pressure. The energy interval containing the dominant intense band of the T_{2g} diamond mode ($\Omega = 1332\text{ cm}^{-1}$ at normal pressure) related to the scattering on anvils [21] is omitted, and the background related to diffuse scattering in the pressure-transmitting medium is subtracted. As the pressure is increased, most phonon modes of the complex shift toward higher energies, except for the $H_g(3)$ mode and related split components, which shift toward lower energies. Changes in the Raman spectra are smooth until a level of 2 GPa is approached, above which the spectrum exhibits sharp changes. These are manifested by splitting of degenerate $H_g(2)$ – $H_g(8)$ phonon modes and by softening and splitting of the nondegenerate $A_g(2)$ mode of a C_{60} molecule. The magnitude of splitting and intensity of bands gradually increase as the pressure increases up to 7 GPa, but the subsequent variations are smooth and the structure of spectrum remains unchanged. The splitting of degenerate H_g modes can be related to a decrease in the symmetry of C_{60} molecule upon the formation of covalent bonds between fullerene molecules.

The rupture of double C=C bonds as a result of the cycloaddition reaction decreases the rigidity of the fullerene molecular cage and leads to softening of the $A_g(2)$ mode. The splitting of the nondegenerate $A_g(2)$ mode is not related to a decrease in the symmetry of the C_{60} molecule and can be explained by the simultaneous formation of various C_{60} oligomers with different numbers of covalent bonds per molecule and corresponding degrees of softening of the $A_g(2)$ mode. Note that, in the Raman spectrum of a structurally and compositionally close $\{\text{Hg}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex that also exhibits a phase transition near 2.0 GPa, the $A_g(2)$ mode exhibits no splitting and is only softened to a value characteristic of C_{120} fullerene dimers [20]. When the pressure is decreased from 7.0 GPa to normal, the spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ crystal exhibit reversible variation. At a pressure of about 2 GPa, the splitting of degenerate modes vanishes and the spectrum shows reverse variation to the pattern observed in the initial state (Fig. 1b). When the pressure returns to normal, the spectrum coincides exactly with the initial spectrum, which means that all pressure-induced changes are fully reversible.

The XRD measurements of crystalline $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes were performed in situ during the increase and decrease pressure runs within 6 GPa. The crystals of these complexes possess a microtwinning structure, which complicated structural analysis. The small cross section of the scattering on fullerene molecules and aperture limitations in the high-pressure cell complicate XRD measurements in diamond anvils. The limited accuracy of these measurements does not allow the total structure of complexes to be determined, but the crystal lattice parameters and their pressure dependence can be established

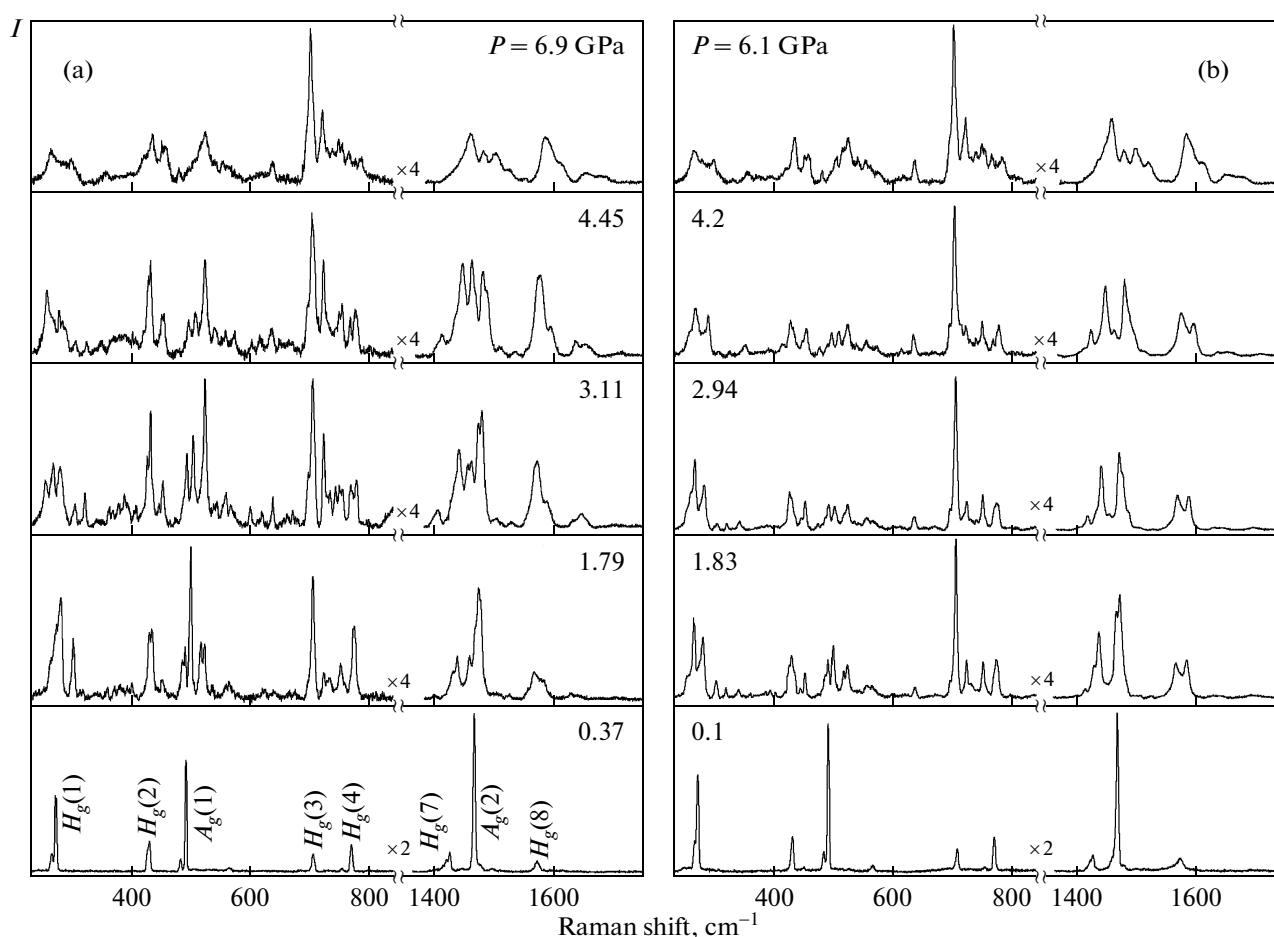


Fig. 1. Room temperature Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes in energy range of $230\text{--}1750\text{ cm}^{-1}$ measured at pressures up to 6.9 GPa in (a) increasing and (b) decreasing pressure runs.

with sufficient precision. In Fig. 2, the open (black) circles show the pressure-induced variations of unit cell parameter a/a_0 (perpendicular to the layers) during increase (decrease) of pressure. The solid line shows the approximation of experimental data by the Murnaghan equation of state:

$$(a/a_0)^{\beta'} = [1 + P(\beta'/\beta_0)]. \quad (1)$$

The experimental data obtained for the increase and decrease of pressure are best described by this equation with the parameters $\beta_0 = 26.1\text{ GPa}$ and $\beta' = 20.4$, where β_0 is a one-dimensional analog of the bulk modulus and β' is the corresponding derivative. These parameter values for the Murnaghan equation are characteristic of molecular crystals with van der Waals interactions and correspond to greater compressibility of complexes.

Squares in Fig. 2 show the pressure dependence of parameter S/S_0 , representing the minimum distance between fullerene molecules in the layer:

$$S = \frac{1}{2} \sqrt{b^2 + c^2},$$

where b and c are parameters of the crystal cell in the lateral directions. Dashed lines show the approximation of these experimental data by the Murnaghan equation of state:

$$(S/S_0)^{\beta'} = [1 + P(\beta'/\beta_0)]. \quad (2)$$

The approximation is constructed separately for the pressure regions before and after the phase transition at 2.0 GPa (the phase transition region is indicated by cross-hatching). The solid curve shows the pressure dependence of S/S_0 calculated by formula (2). In the pressure region of $P \leq 2.0\text{ GPa}$, this line ensures the best fit to experimental data for $\beta_0 = 41.5\text{ GPa}$ and $\beta' = 17.8$. The solid curve in the region of $P \geq 2.0\text{ GPa}$ ensures the best fit to experimental data for $\beta_0 = 86.5\text{ GPa}$ and $\beta' = 18.3$. Dashed curves show the continuation of these dependences outside the corresponding pressure intervals and emphasize a change in the slope upon the phase transition. Thus, after this transition, the value of parameter β_0 exhibits a more than twofold increase equivalent to a one-half smaller compressibility of complexes in the direction along fullerene layers.

The inset to Fig. 2 shows the pressure dependence of the unit cell volume V/V_0 in the regimes of increasing (open symbols) and decreasing pressure (black symbols). Solid and dashed lines show the approximation of experimental data by the Murnaghan equation of state:

$$(V/V_0)^{\beta'} = [1 + P(\beta'/\beta_0)]. \quad (3)$$

The pressure dependence of the cell volume before the phase transition is well described by the values calculated using Eq. (3) for $\beta_0 = 11.9$ GPa and $\beta' = 4.4$, while after this transition, the optimum parameters are $\beta_0 = 25.5$ GPa and $\beta' = 3.4$ (solid lines). Dashed lines show the continuation of these curves outside the indicated pressure intervals and emphasize a change in the character of behavior upon the phase transition at 2.0 GPa with a more than twofold in the bulk modulus.

It should be noted that a change in compressibility upon the phase transition takes place inside the fullerene layers, while the pressure dependence of parameter a (perpendicular to these layers) is smooth. The decrease in compressibility inside fullerene layers is most probably related to the formation of covalent bonds between molecules in these layers. The bulk modulus of complexes after the phase transition ($\beta_0 = 25.5$ GPa) is lower than the values for planar rhombohedral and tetragonal C_{60} polymers ($\beta_0 = 28.1$ and 29.9 GPa, respectively [22]). At the same time, the bulk modulus of complexes in the initial state ($\beta_0 = 11.9$ GPa) is greater than the bulk modulus of a fullerite crystal ($\beta_0 = 9.6$ GPa [23]).

It should also be noted that average distances between fullerene molecules in planar rhombohedral and tetragonal C_{60} polymers are about 9.25 and 9.12 Å, respectively, that is, significantly smaller than the average distance (9.77 Å) between the molecules in fullerene layers of the complex after the phase transition [22]. Thus, the decrease in the compressibility of complexes after the phase transition is most probably related to the formation of covalent bonds between fullerene molecules in these layers. It can be suggested that covalent bonds between fullerene molecules in these layers are formed in a nonregular manner, since a regular polymer network of fullerene molecules in planar polymer crystals of fullerene has a lower compressibility.

Changes in the Raman spectra of complexes under hydrostatic compression are related to phase transitions at high pressure [2–6, 15, 16]. In contrast, laser radiation can also stimulate photoinduced processes similar to the photopolymerization of fullerene (with analogous changes in Raman spectra) in fullerite crystals irradiated by visible light [7, 24, 25]. Therefore, the question is whether laser radiation used to excite Raman spectra can stimulate photopolymerization in fullerene layers of crystalline molecular complexes. In order to check for this possibility, the fullerene complexes under consideration were exposed under normal conditions to laser radiation with wavelength $\lambda =$

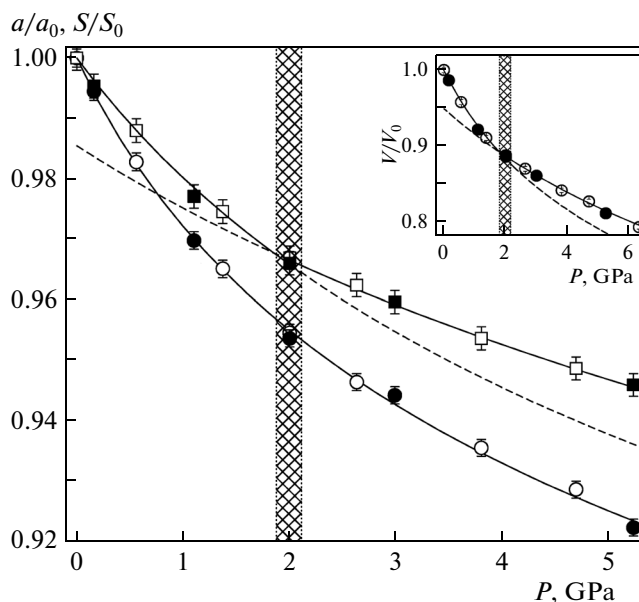


Fig. 2. Pressure dependence of lattice parameters of $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ crystal under increasing pressure (open symbols) and decreasing pressure (black symbols): circles refer to parameter a/a_0 (perpendicular to layers), while squares refer to parameter S/S_0 (minimum distance between fullerene molecules in layer). Inset: pressure dependence of unit cell volume V/V_0 . Solid and dashed curves: approximation of experimental data by Murnaghan equations of state (1) and (2), respectively. Cross-hatched band corresponds to region of phase transition.

532 nm and output power density up to 10000 W/cm². However, no any changes in the Raman spectra of samples were observed. At the same time, in the case of ultimate power of laser radiation, there appeared clear signs of overheating and degradation of fullerene molecules [26]. However, it is known that the application of high pressure can stimulate photopolymerization: in a linear orthorhombic C_{60} polymer, even relatively low pressure leads to the formation of covalent bonds between fullerene molecules of neighboring chains [27].

Then, we must check whether photoinduced transformations at high pressure can take place in fullerene layers of crystalline $\{Cd(dedtc)_2\}_2 \cdot C_{60}$ complexes. In order to do this, a series of Raman spectra were measured at high pressure and laser radiation power density up to 5000 W/cm². These measurements were performed in a broad range of pressures before and after the phase transition, each time in a fresh region of the sample surface. Figure 3a shows the Raman spectrum of fullerene complexes measured in a 230–1650 cm⁻¹ energy range at a pressure of $P = 0.37$ GPa. Figure 3c presents the spectrum measured at a pressure $P = 6.83$ GPa, to which the pressure was increased sequentially at a step of about 1 GPa and the spectra were recorded at all intermediate levels in the same point of the sample (this method was also used to determine the pressure dependence of the Raman spectra pre-

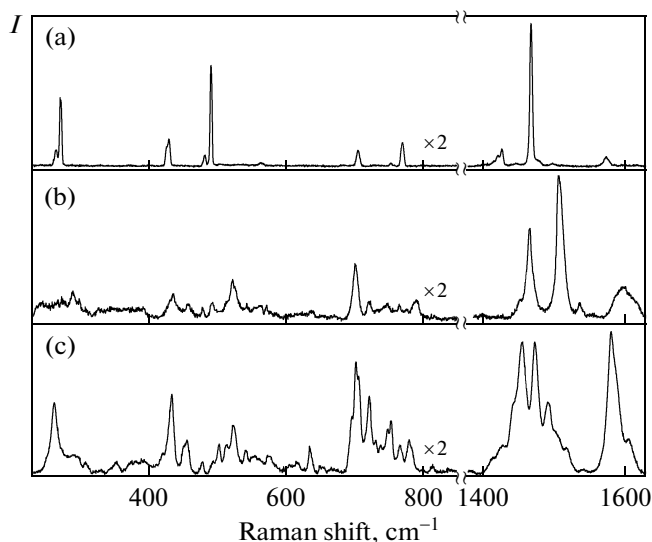


Fig. 3. Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes measured at various pressures in energy range of 230–1650 cm^{-1} : (a) $P = 0.37$ GPa (before phase transition); (b) $P = 6.85$ GPa (without measurements at intermediate pressures); (c) $P = 6.83$ GPa (with measurements at all intermediate pressures with step of about 1 GPa at same point of sample).

sented in Fig. 1). Figure 3b shows the Raman spectrum of another sample measured at the same pressure, but without laser irradiation at intermediate pressures. As can be seen, the spectra in Figs. 3b and 3c are substantially different: the $A_g(2)$ mode in Fig. 3c is split into several components, the numbers of split components in $H_g(3)$ – $H_g(4)$ modes are different, and the intensity distribution between them varies. This difference implies that the laser irradiation of complexes at some pressure can lead to photoinduced transformations similar to those observed in a linear orthorhombic C_{60} polymer [27, 28]. Then, the photoinduced transformations were studied by measuring the Raman spectra in certain time intervals on a sample under continuous laser irradiation. These measurements were performed for four pressure values (1.2, 2.3, 3.6, and 6.3 GPa) and a fixed laser power density of about 5000 W/cm^2 .

Figure 4 shows the Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes measured in certain time intervals on a sample under continuous laser irradiation at pressures of 1.2 (Fig. 4a) and 6.3 GPa (Fig. 4b). The measurements were performed in the regions of the $A_g(2)$ and $H_g(7)$ – $H_g(8)$ modes, which most significantly change in the course of fullerene photopolymerization. As can be seen, no significant changes are observed in the spectra measured upon laser irradiation for various periods of time.

Figure 5 shows series of Raman spectra measured on fresh samples at pressures of 2.3 (Fig. 5a) and 3.6 GPa (Fig. 5b). As can be seen, an increase in irradiation duration t at these pressures leads to sequential

changes in the structure and intensity distribution between spectral bands. Indeed, the $A_g(2)$ mode splits and the intensity of split components increases, while that of the initial component decreases. The splitting of nondegenerate $A_g(2)$ mode in $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes as a result of photoinduced transformations is related to the formation of various photo-oligomers with different numbers of covalent bonds per C_{60} molecule in fullerene layers. The $H_g(8)$ mode also exhibits splitting with the appearance of a new band at lower frequencies, the intensity of which gradually increases. The insets to Fig. 5 show the experimental dependences of the relative intensity of new bands (circles) and their approximation by exponential growth functions. The photopolymer yield depends on the duration of irradiation. The photoinduced transformation accelerates with increasing laser power. The conversion rate also depends on pressure in the 2.0–6.3 GPa interval, outside which no photopolymerization is observed. Fullerene photo-oligomers are formed in a near-surface layer of the fullerene complex crystal with a thickness of about 1 μm , which is equal to the radiation absorption depth. The photo-oligomers are readily detected by Raman spectroscopy, while XRD is not sensitive to these transformations, because the contribution of the indicated surface layer to X-ray scattering is lower than the volume contribution by several orders of magnitude. This result is of independent interest, and we believe that it is worthy of special investigation.

Measurements of the Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes were continued on fresh samples at pressures in the 6.8–17 GPa range to avoid photopolymerization in the intermediate range from 2.0 to 6.3 GPa. These measurements were of interest because average distances between fullerene molecules in their layers at ultimately high pressures approach values characteristic of intermolecular distances in planar C_{60} polymers. It follows from equation of state (2) that in the pressure interval of 14–17 GPa, the minimum distance between fullerene molecules approaches a value within 9.25–9.12 Å characteristic of two-dimensional fullerene polymers. Under this compression, it was possible to expect the formation of covalent bonds and further polymerization in fullerene layers.

Figure 6 shows the pressure dependences of the $A_g(2)$ and $H_g(7)$ – $H_g(8)$ phonon modes of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes, where open and black circles correspond to measurements in the increasing and decreasing pressure runs. Data for the pressure regions below 2 GPa and above 6.3 GPa are indicated by full circles, while half-filled circles refer to the intermediate region. As can be seen, the pressure dependence of all phonons is described by a linearly increasing function of pressure up to about 14 GPa, except for the $H_g(3)$ mode and its split component, whose frequencies exhibit a decrease (not depicted in Fig. 6). At pressures above 14 GPa, the pressure

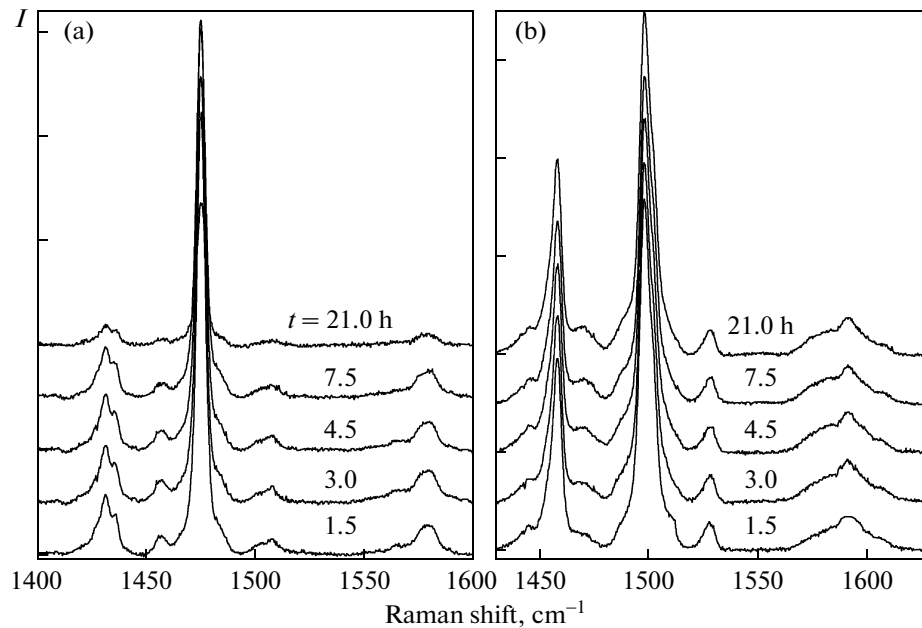


Fig. 4. Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes measured in regions of $A_g(2)$ and $H_g(7)-H_g(8)$ modes at $P = 1.2$ GPa (a) and 6.3 GPa (b) in certain time intervals (indicated at the curves) during continuous exposure to laser radiation at $\lambda = 532$ nm and power density of about 5000 W/cm^2 .

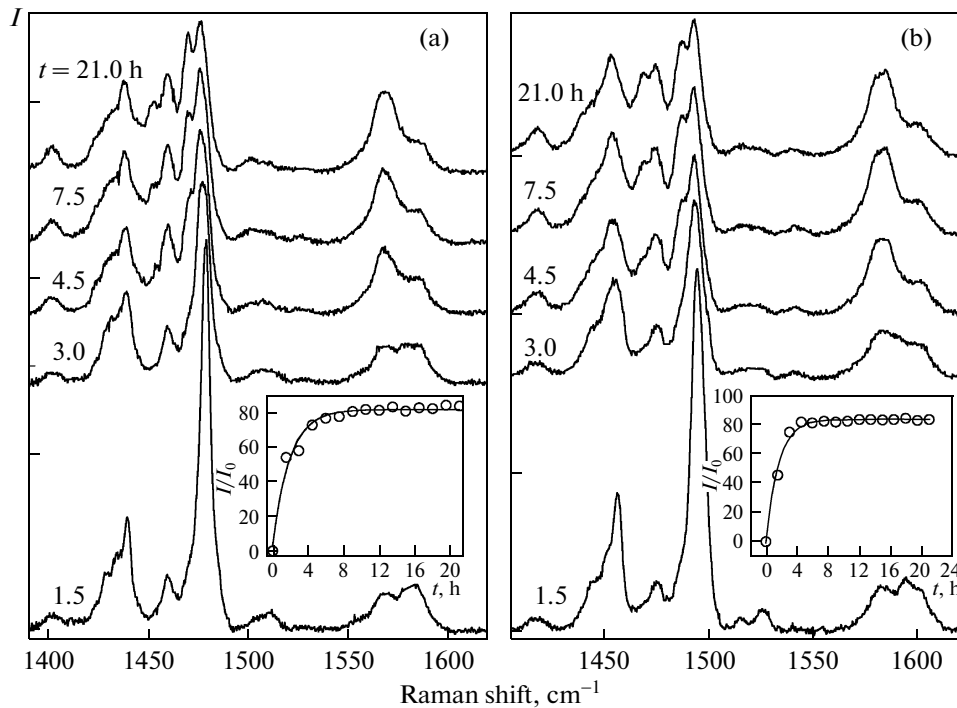


Fig. 5. Raman spectra of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes measured in regions of $A_g(2)$ and $H_g(7)-H_g(8)$ modes at $P = 2.3$ GPa (a) and 3.6 GPa (b) in certain time intervals (indicated at the curves) during continuous exposure to laser radiation at $\lambda = 532$ nm and power density of about 5000 W/cm^2 . Insets show experimental dependences of relative intensity of new bands (circles) and their approximation by exponential growth functions (curves): (a) $P = 81.8-79.6\exp(-t/1.92)$; (b) $83.8-84.8\exp(-t/1.62)$.

dependences of the phonon modes become sublinear but still remain smooth and show no evidence of a phase transition. The pressure shift coefficients dE/dP vary from $0.65 \text{ cm}^{-1}/\text{GPa}$ for the $H_g(3)$ mode to

$5.5 \text{ cm}^{-1}/\text{GPa}$ for the split components of the $A_g(2)$ and $H_g(7)-H_g(8)$ modes. The solid lines in Fig. 6 show the approximate pressure dependences averaged over the experimental data for both increasing and decreas-

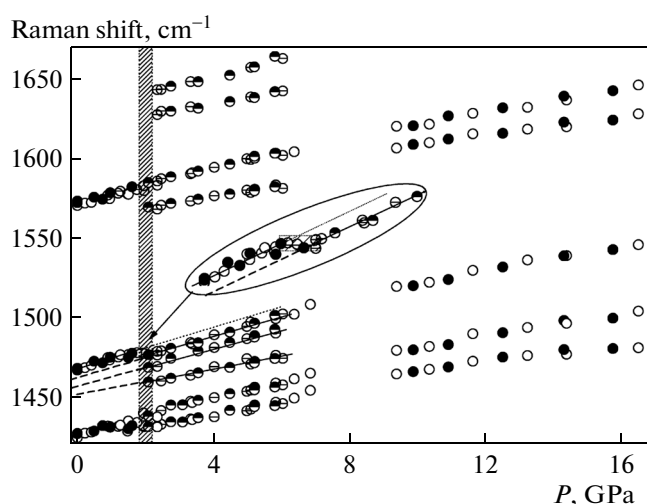


Fig. 6. Pressure dependences of phonon modes of $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes in the 1420–1670 cm^{-1} energy interval at pressures up to 17 GPa. Open (black) circles correspond to measurements at increasing (decreasing) pressure; data in pressure interval of 2.0–6.3 GPa indicated by half-filled circles. Region of phase transition indicated by cross-hatching. Solid lines show approximate pressure dependence averaged over increasing and decreasing pressure runs; dashed lines indicate their continuation. Inset: softening of $A_g(2)$ mode in phase transition region on larger scale.

ing pressure runs, while the dashed lines indicate their continuation. The inset to Fig. 6 illustrates on a larger scale the softening of the $A_g(2)$ mode in the phase transition region of about 2 GPa. The magnitude of softening can be estimated by extrapolating the pressure dependence to normal pressure. This extrapolation yields about 5 cm^{-1} , which is characteristic of fullerene dimers. In addition, the structure of split modes $A_g(1)$ and $H_g(1)–H_g(4)$ in the Raman spectra of complexes after the phase transition is similar to the Raman spectrum of fullerene dimers [29]. It should be noted that softening of the $A_g(2)$ mode also takes place during charge transfer: in the ionic donor–acceptor fullerene complexes and in the intercalated fullerite, this value amounts to about 6 cm^{-1} per electron, but the molecular symmetry does not decrease and the H_g phonon modes do not split [2, 3, 8].

The splitting of the nondegenerate $A_g(2)$ mode in $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes as a result of photoinduced transformations in the pressure interval of 2.0–6.3 GPa after the phase transition is related to the formation of various photo-oligomers with different numbers of covalent bonds per C_{60} molecule in fullerene layers. Since softening of the $A_g(2)$ mode in these oligomers has a different character, the Raman spectrum simultaneously exhibits several bands. The linear approximation of the pressure dependence of split components of the $A_g(2)$ mode continued to normal pressure assumes that the frequencies of these components at normal pressure would be about 1458.6

and 1450 cm^{-1} . These values are close to the frequencies of the $A_g(2)$ mode for linear fullerene polymer chains with four sp^3 bonds per molecule and conjugated linear chains with six sp^3 bonds per molecule, respectively [27].

Thus, the data evidence the formation of covalent bonds between fullerene molecules in $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complexes as a result of the phase transition, after which the Raman spectra of complexes resemble those of fullerene dimers (C_{120}). Another consequence of the phase transition is photopolymerization at pressures within 2.0–6.3 GPa. It should be noted that, unlike C_{120} dimers in fullerite crystals that are stable at room temperature, the hypothetical “dimers” in crystalline molecular donor–acceptor fullerene complexes are unstable and decompose upon pressure release [20]. As is known, the free energy of crystalline C_{60} polymers and dimers is lower than that of fullerite crystals, but these states are separated by such a high energy barrier that large energy consumption is necessary for the formation of the former polymers under conditions of thermobaric treatment. The presence of a barrier also determines their rather high stability at room temperature [30, 31]. The free energy of a rhombohedral C_{60} polymer is 0.13 eV lower than that of a fullerite crystal, while the barrier is 1.76 eV (per molecule). For this reason, obtaining a fullerene polymer requires considerable energy consumption during thermobaric treatment, while its decomposition into monomers requires significant heating [32]. The formation of covalent bonds between molecules in fullerene layers at high pressure and their rupture under normal conditions can be determined by the influence of molecular donor layers, which stabilize the structure of complexes under normal conditions.

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