

Crystal structure and Raman spectra of molecular complex $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ at high pressure

A. V. Kuzmin¹, D. V. Konarev², S. S. Khasanov¹, K. P. Meletov¹

¹Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

²Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow region, Russia

kuzmin@issp.ac.ru

PACS 78.30.Na

DOI 10.17586/2220-8054-2018-9-1-33-37

The crystal structure of the molecular donor-acceptor complex $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ (where dtc is dithiocarbamate, DABCO is diazabicyclooctane) was studied by X-ray diffraction (XRD) at high pressure using the diamond anvil cell (DAC) technique. The pressure dependence of lattice parameters is smooth and monotonous, the bulk modulus and its derivative $B_0 = 7.94$ GPa and $B' = 9.65$ are close to those of pristine C_{60} . Raman spectra of the complex measured at $\lambda_{exc} = 532$ nm showed a peculiarity in the pressure dependence of $A_g(1)$, $A_g(2)$, $H_g(1)$ and $H_g(7)$ modes of the C_{60} molecule near 2 GPa. This peculiarity relates to pressure-assisted photopolymerization in the fullerene layers which is suppressed in Raman measurements at $\lambda_{exc} = 785$ nm showing smooth pressure behavior of phonon modes.

Keywords: high pressure, fullerene complexes, crystal structure, photopolymerization.

Received: 14 June 2017

Revised: 14 September 2017

1. Introduction

The behavior of fullerene complexes at high pressure is of interest due to their layered structure in which the close-packed molecules in the fullerene layers alternate with the layers of the molecular donor. The squeezing of these layers makes intermolecular distances shorter and, hence, increases the overlap between the highest occupied molecular orbitals (HOMOs) of the molecular donor and the lowest unoccupied molecular orbital (LUMO) of the fullerene acceptor that stimulates charge transfer. On the other hand, numerous Raman measurements show that fullerenes can undergo polymerization in molecular complexes at high pressure [1–4]. The Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ complex show time-dependent changes near 2 GPa that look like photopolymerization of pristine C_{60} [4,5]. The photopolymerization of C_{60} can occur in thin surface layers of bulk samples via a [2+2] cyclo-addition mechanism. It requires a suitable mutual orientation of the molecules [6] which can be realized at their rotation or in the process of crystal growth. Unlike disordered photopolymer, bulk polymers synthesized under high-pressure/high-temperature (HPHT) treatment are highly ordered and their crystal structures were identified by XRD to be orthorhombic, tetragonal and rhombohedral lattices [7–9]. C_{60} molecular symmetry lowering leads to the splitting and softening of some phonon bands. As a rule, Raman examination of fullerene polymers is based on the behavior of the $A_g(2)$ PP-mode frequency which decreases from 1468 cm^{-1} for the monomer to 1463, 1458, 1446 and 1408 cm^{-1} for the dimers, linear orthorhombic, planar tetragonal and rhombohedral polymers, respectively [10–12]. Here, we report the XRD and Raman study of the $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ fullerene complex at high pressure. The pressure dependence of lattice parameters is smooth and monotonous, the bulk modulus and its derivative, $B_0 = 7.94$ GPa and $B' = 9.65$, are close to those for pristine C_{60} . The Raman spectra measured at $\lambda_{exc} = 532$ nm show a peculiarity near 2 GPa, which disappears at near infra-red laser excitation 785 nm when photopolymerization in the fullerene layers is suppressed.

2. Experimental details

The crystals of the donor-acceptor complex $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ were synthesized as described in [13]. The structural data were obtained for the single crystals at pressures up to 3 GPa using DAC and a four-circle Oxford Diffraction Gemini-R diffractometer equipped with two-dimensional CCD. The Raman spectra were recorded in back-scattering geometry using an Acton SpectraPro-2500i spectrograph and a LabRam HR micro-Raman setup equipped with a Peltier cooled CCD. The 532 nm and 785 nm laser lines were used for the Raman scattering measurements with laser power up to $\sim 180 \mu\text{W}$ before the DAC while the 4:1 methanol/ethanol mixture and the ruby fluorescence technique were used as pressure transmitting medium and a pressure calibration tool, respectively [14].

3. Results and discussion

The XRD data show that the $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex acquires a tetragonal structure, space group $Pbam$ with unit cell parameters $a = 10.583 \text{ \AA}$, $b = 17.178 \text{ \AA}$, $c = 21.273 \text{ \AA}$, $V = 3867 \text{ \AA}^3$. In the fullerene layers, each C_{60} molecule is surrounded by six neighbors with the shortest distances between the centers of molecules $d = 10.088$ (four neighbors) and $d' = 10.583 \text{ \AA}$ (two neighbors). No C–C bonds were found between the fullerene molecules under ambient conditions. Fig. 1 depicts the pressure dependence of lattice parameters of the complex at pressures up to 3 GPa while the inserts shows the arrangement of molecules in view along a and c axes at a pressure of $P = 0.66 \text{ GPa}$. Circles denote the pressure dependence of cell volume V/V_0 , squares – lattice parameter c/c_0 perpendicular to molecular layers, hexagons – the shortest distance between the fullerene molecules d/d_0 , and dotted lines are fits by Murnaghan equation of state:

$$(V/V_0)^{-B'} = \{1 + P(B'/B_0)\}, \quad (1)$$

where $B_0 = 7.94 \text{ GPa}$ is the bulk modulus and $B' = 9.65$ is its derivative. The values of bulk modulus and its derivative are close to those of the C_{60} fullerite in simple cubic phase [15]. The pressure dependence of lattice parameters is smooth and monotonous. Compressibility within molecular layers is smaller than that in the perpendicular direction that can be ascribed to the layered structure. According to XRD data, there is no phase transition in the pressure range under investigation.

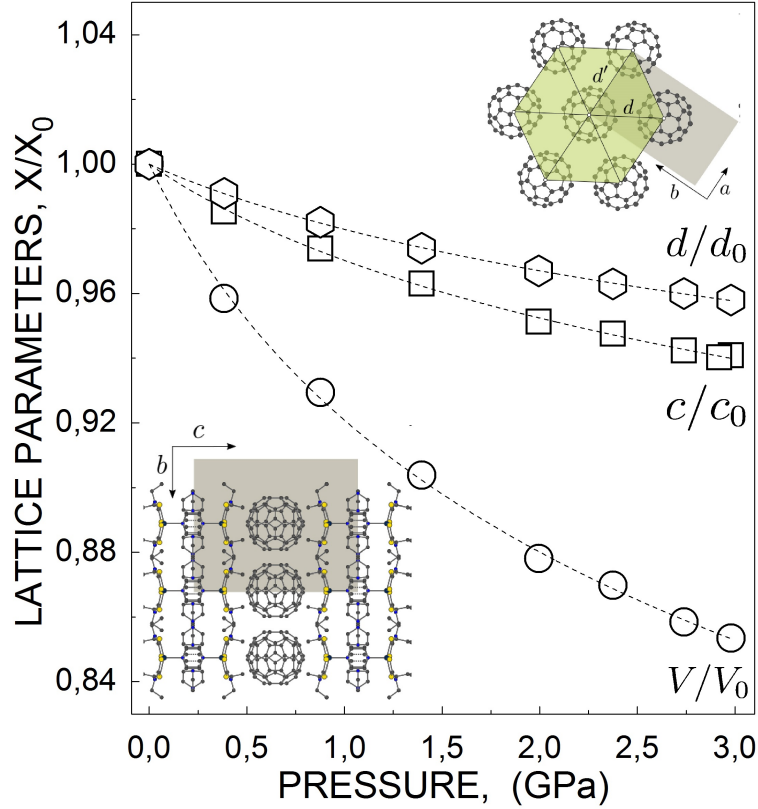


FIG. 1. Pressure dependences of lattice parameters of the $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex and arrangement of molecules in the lattice at $P = 0.66 \text{ GPa}$

Possible polymerization within fullerene layers may be expected at a pressure of $\sim 17 \text{ GPa}$ when the shortest interfullerene distances approach 9.15 \AA which is a typical inter-cage distance in fullerene polymers [8, 9].

Figure 2 shows the Raman spectra of the $[\{\text{Cd}(\text{Et}_2\text{dtc})\}_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex collected at pressure up to $\sim 6 \text{ GPa}$ at $\lambda_{exc} = 532 \text{ nm}$ (left panel) and $\lambda_{exc} = 785 \text{ nm}$ (right panel). The spectra in the left panel were obtained with laser power $\sim 180 \mu\text{W}$ and 300 minutes exposure, whereas spectra series in the right panel was collected with $\sim 34 \mu\text{W}$ laser and 16 min exposure time. The Raman spectra measured at a fixed site of the sample show the phonon modes of the C_{60} molecule due to its dominant contribution to the Raman

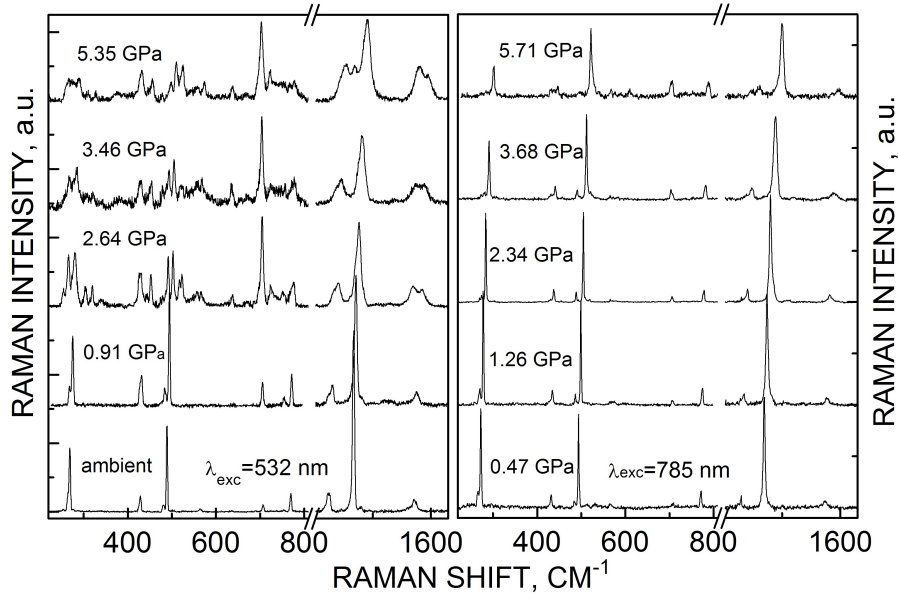


FIG. 2. Raman spectra of the $[\text{Cd}(\text{Et}_2\text{dtc})_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex at different pressures recorded at 532 nm (left panel) and 785 nm (right panel) laser excitations

cross-section of complexes [5]. The spectra at ambient conditions are identical in both panels and demonstrate positive pressure shift whereas their intensity distribution does not depend on exposure time.

The difference in pressure behavior appears near ~ 2 GPa when the phonon bands in the left panel split and broaden, whereas in the right panel, they remain unchanged. Similar time-dependent changes observed earlier in the fullerene complex $\{\text{Cd}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ were attributed to the pressure-assisted photopolymerization [4].

We examined the possibility of pressure-induced photopolymerization in the fullerene layers of the $[\text{Cd}(\text{Et}_2\text{dtc})_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex by using laser excitations at two different wavelengths. The Raman spectra recorded every 15 min ($\lambda_{\text{exc}} = 532$ nm, 180 μW laser power) show fast transformation that occurs in the first Raman scan and further scans do not affect the spectra. Fig. 3 shows evolution of the spectra near the $A_g(2)$ PP-mode recorded consequently every 30 minutes at $\lambda_{\text{exc}} = 785$ nm, laser power 134 μW , and 10 minute exposure at 2.34 GPa (left panel) and 4.3 GPa (right panel) pressure. The spectra at 2.34 GPa are stable whereas at 4.3 GPa, they evolve new components observed near $A_g(2)$ PP-mode and are related to the photo-oligomers of C_{60} . In addition, the five-fold degenerate H_g modes split. The initial spectrum at 4.3 GPa is not yet transformed and resembles the spectra of monomer recorded at 2.34 GPa. This means that spectra in the right panel of Fig. 2 recorded at ~ 34 μW and 16 min exposure can also be related to the monomer.

The pressure dependence of phonon modes is shown in Fig. 4. The open circles and squares mark the frequencies of the $A_g(1)$, $H_g(1)$, $A_g(2)$ and $H_g(7)$ modes recorded at $\lambda_{\text{exc}} = 532$ nm, laser power 180 μW and 300 min exposure, whereas the filled circles refer to the data recorded at $\lambda_{\text{exc}} = 785$ nm, laser power 34 μW and 16 minutes exposure. Solid and dotted lines are linear fits of the experimental data for the $A_g(2)$ and $H_g(7)$ modes and sub linear fits for the $A_g(1)$ and $H_g(1)$ modes. The pressure dependence of the $A_g(2)$ PP-mode frequency measured at $\lambda_{\text{exc}} = 532$ nm exhibits an irregularity near ~ 2 GPa: the pressure coefficient between 2 and 3 GPa is almost zero, whereas outside this region, it is ~ 5 $\text{cm}^{-1}/\text{GPa}$.

A similar peculiarity was observed for the $A_g(1)$, $H_g(1)$ and $H_g(7)$ modes, as well as $H_g(1)$ splits. Extrapolation of the linear fit for the $A_g(2)$ mode to normal pressure gives a value of ~ 1464 cm^{-1} that is the frequency of dimers C_{120} . On the other hand, the data obtained at $\lambda_{\text{exc}} = 785$ nm show smooth and monotonous pressure behavior. Thus, the peculiarity in the pressure behavior of phonon modes relates to pressure-assisted photo-induced polymerization under visible laser excitation which is suppressed under near infra-red laser excitation.

4. Conclusions

The XRD analysis of single crystals of $[\text{Cd}(\text{Et}_2\text{dtc})_2 \cdot \text{DABCO}] \cdot \text{C}_{60} \cdot (\text{DABCO})_2$ complex at high pressure shows a smooth and monotonous pressure dependence of lattice parameters with bulk modulus $B_0 = 7.94$ GPa and its derivative $B' = 9.65$. The pressure dependence of phonon modes in the Raman spectra recorded at $\lambda_{\text{exc}} = 532$ nm shows a peculiarity near ~ 2 GPa which is not observed in the spectra recorded at $\lambda_{\text{exc}} = 785$ nm.

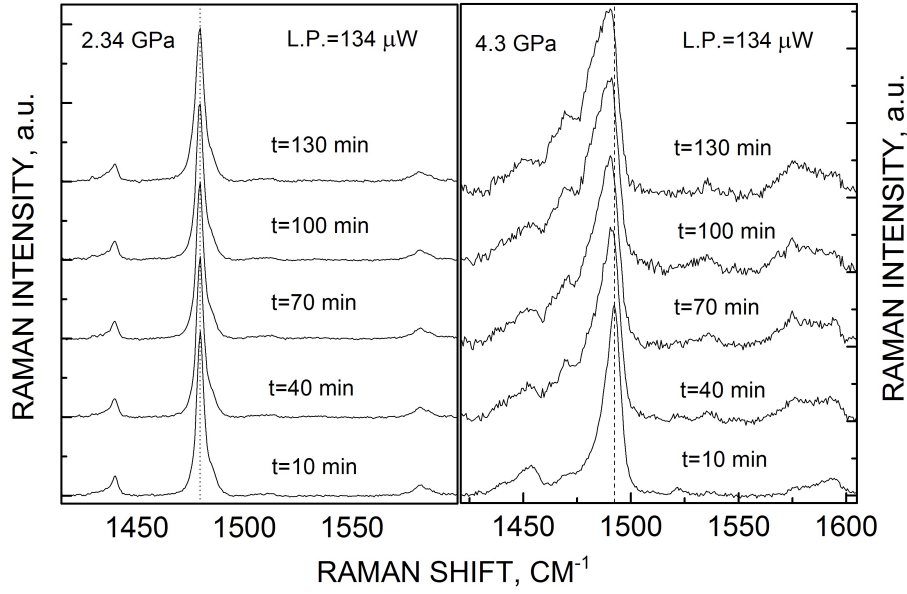


FIG. 3. Time evolution of Raman spectra recorded near the $A_g(2)$ PP-mode at $\lambda_{exc} = 785$ nm and 10 min exposure at 2.34 GPa (left panel) and 4.3 GPa (right panel) pressure. L. P. – laser power

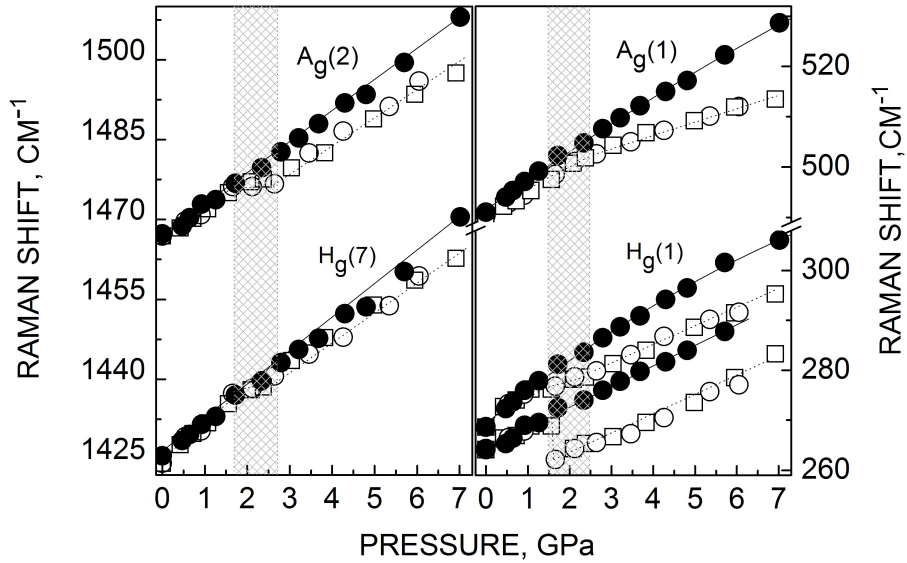


FIG. 4. Pressure dependence of $A_g(1)$, $H_g(1)$, $A_g(2)$ and $H_g(7)$ modes of the $[\{Cd(Et_2dtc)\}_2 \cdot DABCO] \cdot C_{60} \cdot (DABCO)_2$ complex. Open symbols – laser excitation 515 nm, filled symbols – laser excitation 785 nm, solid and dotted lines – fits

This peculiarity relates to the pressure-assisted photo-induced polymerization in the fullerene layers, which is suppressed under near infra-red laser excitation. The absence of photopolymerization at ambient conditions means that close proximity of fullerene molecules is suppressed by the interaction with donor molecules. The most intriguing is high-pressure photopolymerization, which means the emergence of rotation at elevated pressure. Finally, we suppose that the pressure-induced transformations previously observed in numerous Raman studies of fullerene complexes can also be related to the pressure-assisted photo-induced transformations instead of pressure-induced transformations.

Acknowledgements

The main financial support by the Federal Agency for Scientific Organizations is greatly acknowledged. The partial support by the Russian Foundation for Basic Research, grant No. 15-02-01495, and the RAS Presidium Program “Physics of compressed matter” are greatly acknowledged. K.P.M. thanks the Aristotle University of Thessaloniki for hospitality.

References

- [1] Cui Wen, Yao Mingguang, et al. Reversible polymerization in doped fullerides under pressure: the case of $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$. *J. Phys. Chem. B*, 2012, **116**, P. 2643–2650.
- [2] Meletov K.P., Konarev D.V. Raman study of the pressure-induced phase transitions in the molecular donor-acceptor complex $\{Pt(dbdtc)_2\} \cdot C_{60}$. *Chem. Phys. Lett.*, 2012, **553**, P. 21–25.
- [3] Meletov K.P. Phase transitions at high pressure in the fullerene C_{60} molecular donor-acceptor complex $\{Hg(dedtc)_2\}_2 \cdot C_{60}$. *Phys. Solid State*, 2014, **56**, P. 1689–1695.
- [4] Meletov K.P., Konarev D.V., Tolstikova A.O. Phase transitions and photoinduced transformations at high pressure in the molecular donor-acceptor fullerene complex $\{Cd(dedtc)_2\}_2 \cdot C_{60}$. *JETP*, 2015, **120**, P. 989–997.
- [5] Rao A.M., Zhou P., et al. Photoinduced polymerization of solid C_{60} films. *Science*, 1993, **259**, P. 955–957.
- [6] Zhou P., Dong Z.H., Rao A.M., Ecklund P.C. Reaction mechanism for photopolymerization of solid fullerene C_{60} . *Chem. Phys. Lett.*, 1993, **211**, P. 337–340.
- [7] Pusztai T., Oszlanyi G., et al. Bulk structure of phototransformed C_{60} . *Solid State Commun.*, 1999, **111**, P. 595–599.
- [8] Iwasa Y., Arima T., et al. New phases of C_{60} synthesized at high pressure. *Science*, 1994, **264**, P. 1570–1572.
- [9] Nunez-Regueiro M., Marques L., et al. Polymerized fullerite structures. *Phys. Rev. Lett.*, 1995, **74**, P. 278–281.
- [10] Rao A.M., Ecklund P.C., et al. Infrared and Raman studies of pressure-polymerized C_{60} . *Phys. Rev. B*, 1997, **55**, P. 4766–4773.
- [11] Wägberg T., Jacobsson P., Sundqvist B. Comparative Raman study of the photopolymerized and pressure-polymerized C_{60} films. *Phys. Rev. B*, 1999, **60**, P. 4535–4538.
- [12] Davydov V.A., Kashevarova L.S., et al. Spectroscopic study of pressure polymerized phases of C_{60} . *Phys. Rev. B*, 2000, **61**, P. 11936–11945.
- [13] Konarev D.V., Khasanov S.S., et al. Fullerene complexes with divalent metal dithiocarbamates: structures, magnetic properties, and photoconductivity. *Russ. Chem. Bull., Int. Ed.*, 2007, **56**, P. 2145–2161.
- [14] Jayaraman A. Ultrahigh pressures. *Rev. Sci. Instrum.*, 1986, **57**, P. 1013–1031.
- [15] Lundin A., Sundqvist B. Compressibility of C_{60} in the temperature range 150–335 K up to a pressure of 1 GPa. *Phys. Rev. B*, 1996, **53**, P. 8329–8336.