High-pressure behavior of the crystal structure of the fullerene molecular complex with ferrocene $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$

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High-pressure behavior of the crystal structure of the fullerene molecular complex with ferrocene $C_{60}\cdot\{Fe(C_5H_5)_2\}_2$

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ABSTRACT

The crystal structure of the molecular complex $C_{60}\cdot\{Fe(C_5H_5)_2\}_2$ was studied by single crystal X-ray diffraction (XRD) analysis at pressures up to 5 GPa using the diamond anvil cell (DAC) technique. The XRD data and subsequent structural analysis clearly show that there is no pressure-induced polymerization in fullerene layers in pressure range studied. The reciprocal unit cell volume V_0/V is a smooth and monotonous function of pressure and fits well to the Murnaghan equation of state $(V_0/V)^{B'} = \{1 + P\cdot(B'/B_0)\}$, where V_0 is the volume at ambient pressure, $B_0 = 8.7$ GPa and $B' = 10.5$ are the bulk modulus and its derivative, respectively. Pressure dependence of the shortest distance between the C_5H_5 ring of the ferrocene molecule and the center of the nearest fullerene molecule is linear, while the slope changes at 2.2 GPa indicating on the intermolecular interactions crossover. Other relevant parameter, the Fe-C bond lengths of ferrocene, sensitive to iron charge state, gradually increases. This peculiarity can a sign of pressure-induced partial charge transfer between the donor ferrocene and acceptor fullerene molecules.

1. Introduction

The properties of the donor-acceptor molecular complexes of C_{60} at high pressure were studied in numerous publications.[1–6] Traditionally these studies are aimed at finding the pressure-stimulated charge transfer from donor molecule to acceptor fullerene molecule and/or the fullerene polymerization in C_{60} layers of complexes. Normally, the observations are based on Raman spectroscopy at high pressure. However, more direct, structural evidence is required to conclude that the phenomena take place. In case of the C_{60} fullerite crystals the fullerene polymers, carefully prepared by high pressure/high temperature (HPHT) treatment, have been studied by both XRD crystal structure analysis and Raman spectroscopy, and the typical changes in their phonon spectra have been identified.[7–11] Therefore, Raman spectroscopy is often used for detection of the C_{60} polymerization processes. For example, the most intensive $A_g(2)$ mode of the C_{60} molecule is commonly used for these purpose – this band shifts from 1468 cm^{-1} for single molecule to 1464 cm^{-1}, 1458 cm^{-1}, 1446 cm^{-1} and 1408 cm^{-1} in dimers, linear chains, planar tetragonal and rhombohedral polymers, respectively.[11] In addition, the transfer of one electron from alkali metal to C_{60} molecule in intercalated fullerides also results in downshifting of this mode by about 6 cm^{-1}.[12] It should be noted that irradiation of the fullerite by laser light upon the Raman measurements may also result in photo-induced polymerization. The photopolymerization was observed for the first time in thin films and surfaces of bulk fullerite samples.[13] Later, the laser-induced photopolymerization was observed also in a number of fullerene molecular complexes at ambient conditions.[14,15] In addition, the pressure-stimulated photopolymerization was observed in some other fullerene molecular complexes insensitive to irradiation at ambient conditions.[4,5,16]

In this work, we report the XRD study of the neutral molecular donor–acceptor complex of fullerene with ferrocene – $C_{60}\cdot\{Fe(C_5H_5)_2\}_2$ at pressures up to 5 GPa. Earlier, the Raman study of this complex at high pressure revealed presumably the signs of the pressure-induced charge transfer and polymerization in C_{60} layers.[2] Another Raman study has shown that observed in[2] polymerization is related most likely to the pressure-assisted photopolymerization that was observed also in some other molecular complexes of fullerene.[4,5] In view of this, we have carried out XRD studies of the $C_{60}\cdot\{Fe(C_5H_5)_2\}_2$ complex single crystals at pressures up to 5 GPa aimed at finding the evidences of both charge transfer and polymerization in fullerene layers at high pressure, argued in.[2] We found that the reciprocal unit cell volume V_0/V is a smooth and monotonous function of pressure and fits well to the Murnaghan equation of state $(V_0/V)^{B'} = \{1 + P\cdot(B'/B_0)\}$, where V_0 is the volume at ambient pressure, $B_0 = 8.7$ GPa and $B' = 10.5$ are the bulk modulus and its derivative, respectively. There are none observed structural changes which could indicate on the pressure-induced polymerization in C_{60} layers in the pressure region studied. It should
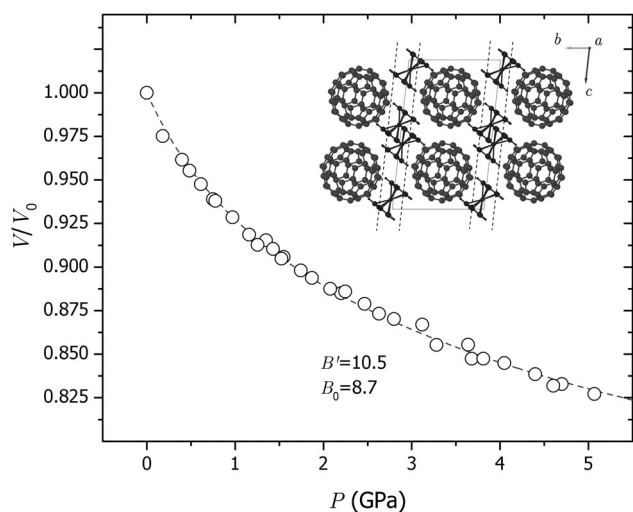
Figure 1. Pressure dependence of the cell volume V/V_0 of the $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ complex at pressure up to ~5 GPa (circles) and it's fit by Murnaghan equation of state (dotted line). Insert: the arrangement of the ferrocene donor and fullerene acceptor molecules in view along a axes.

be noted the fullerene molecules are still far from each other to form the intermolecular covalent bonds. Nevertheless, the pressure dependence of the shortest distance between the ferrocene and fullerene molecules shows peculiarity near 2.2 GPa where the linear dependence changes its slope indicating on the intermolecular interactions crossover. Additionally, our data show that the Fe-C bond lengths gradually increase with pressure, conjugated parameter, the length of the ferrocene molecule, gradually increases from 3.29 Å at ambient pressure to 3.34 Å at 4.5 GPa. Taking into account that the length of the $Fe^{2+}(C_5H_5)_2$ equal to 3.29 Å increases to 3.4 Å for the $Fe^{3+}(C_5H_5)_2$,[17] we suppose that observed peculiarity is due to pressure-induced partial charge transfer from the ferrocene donor to the C_{60} acceptor molecules.

2. Experimental details

The single crystal samples of the donor-acceptor complex $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ were obtained by slow evaporation of toluene solution containing fullerene C_{60} and ferrocene $Fe(C_5H_5)_2$ molecules. The XRD data at high pressure were collected in series of four independent pressure runs with the high-quality single crystals of typical size ~250 μ using the four-circle Oxford Diffraction diffractometer equipped with two-dimensional CCD Atlas S2 and DAC with Boehler type Ia anvils. As a pressure transmitting medium was used the mixture 4:1 methanol/ethanol and the ruby fluorescence technique was employed as pressure calibration tool.[18]

3. Results and discussion

The complex is crystallized in triclinic layered structure in which the close-packed fullerene layers alternate with layers of the ferrocene molecules.[19] Crystal structure analysis taken in this work confirmed the crystal structure above with unit cell parameters $a = 10.060(1)$ Å, $b = 11.311(1)$ Å, $c = 18.514(1)$ Å,
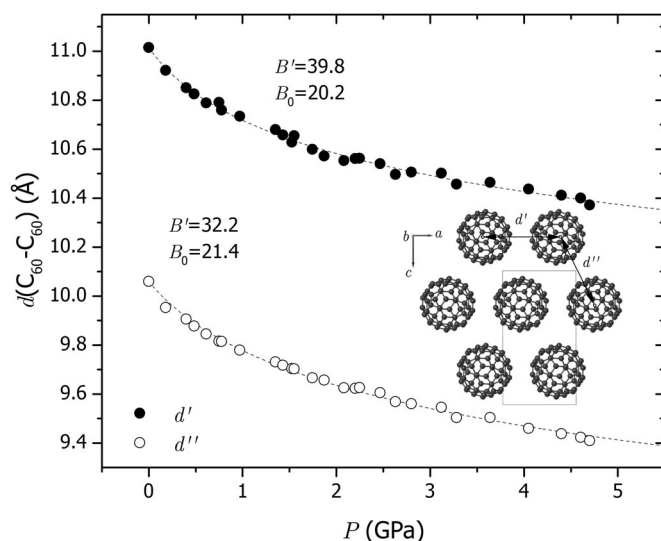

Figure 2. Pressure dependence of the shortest distances between the C_{60} molecules d' (closed circles) and d'' (open circles) and its fit by the Murnaghan equation of state (dotted lines). Inset: in the hexagonal arrangement of the fullerene molecules in view along b axes.

$\alpha = 83.63(1)^o$, $\beta = 89.82(1)^o$, $\gamma = 89.46(1)^o$, $V_0 = 2093.6(2)$ Å^3 at normal conditions. In the fullerene layers, each C_{60} molecule is surrounded by six neighbors with the shortest distances between the centers of molecules $d' = 10.060$ Å (two neighbors) and $d'' = 11.015$ (four neighbors).

Figure 1 depicts the pressure dependence of the unit cell volume of the $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ complex at pressure up to ~5 GPa. The insert shows the arrangement of the ferrocene donor and fullerene acceptor molecules in view along the a axes. The experimental V_0/V behavior is fitted well by Murnaghan equation of state:

$$(V_0/V)^{B'} = \{1 + P \cdot (B'/B_0)\} \qquad (1)$$

whith the $B_0 = 8.7$ GPa bulk modulus and the $B' = 10.5$ derivative. The values of bulk modulus and its derivative are close to those of the C_{60} fullerite in simple cubic phase.[20] The pressure dependence of the cell volume is smooth and monotonous and does not show any peculiarity hinting at phase transition.

Pressure dependence of the shortest distances d' (closed circles) and d'' (open circles) between the C_{60} molecules is fitted well by a two-dimensional analog of the Murnaghan equation of state (1) (Figure 2, dotted lines). The inset in Figure 2 shows the hexagonal arrangement of the fullerene molecules with the depicted d' and d'' shortest distances. The pressure dependence of the d' and d'' is also smooth and does not show any peculiarity in the pressure range investigated. The full structural analysis clearly shows that the fullerene molecules are far enough from each other and do not form interfullerene covalent bonds. We tend to believe that the reported in[2] pressure-induced polymerization observed at pressures from 4 to 5 GPa is due to the effect of laser irradiation upon the Raman measurements. Moreover, the pressure-assisted photopolymerization under laser irradiation was clearly manifested in the recent high-pressure Raman study of this complex.[5] Additionally, our preliminary high-pressure Raman data (not presented in this short communication) also indicate on the pressure-assisted photopolymerization starting at
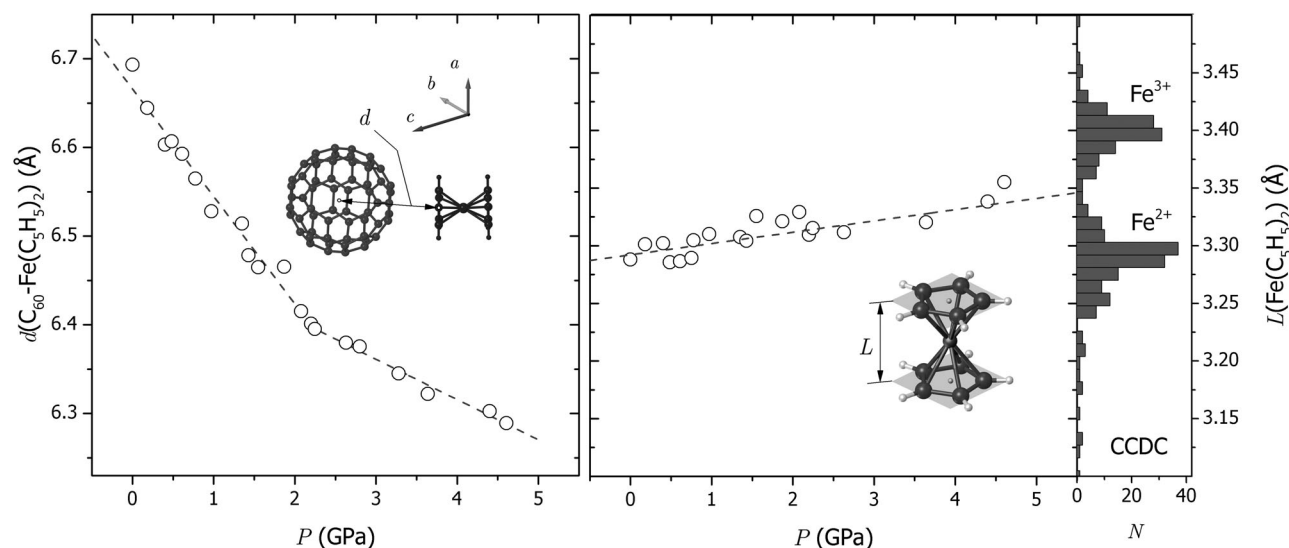
Figure 3. Left panel: pressure dependence of the shortest distance d (open circles) between the ferrocene donor and fullerene acceptor molecules, dotted line - linear fit of experimental data. Right panel: pressure dependence of the ferrocene donor molecule length (open circles), dotted line - linear fit of experimental data. Insets: left – arrangement of the ferrocene donor and fullerene acceptor molecules, right – histogram of the systematized data on the ferrocene molecule length depending on the oxidation state of iron atom (CCDC data base).

~4.5 GPa. Finally, one should remember that the shortest distance between the centers of the C_{60} molecules in various polymeric phases becomes close to 9.06 Å.[21] Note, that the shortest d'' distance between C_{60} molecules in the $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ complex at 5 GPa is 9.4 Å as it measured in this work, i.e., the fullerene molecules are still far from each other to form the intermolecular covalent bonds. Under further pressure increasing d'' distance will gradually decrease, the numerical estimation on the basis of present in-plain compressibility data shows that the value 9.06 Å would be reachable at pressures $P \geq 18.5$ GPa, if any phase transitions do not occur at intermediate pressures.

Figure 3 (left panel) depicts the experimental pressure dependence of the shortest distance d (open circles) between fullerene molecule and nearest cyclopentadienyl ring of ferrocene (see inset), the dotted line is a linear fit of experimental data. The dependence shows peculiarity near ~2.2 GPa where the slope of linear fit abruptly changes indicating on the intermolecular interactions crossover. Additionally, our data show that the Fe-C bond lengths gradually increase with pressure while one would expect the reverse pressure behavior. Conjugated parameter, the length of the ferrocene molecule L, gradually increases with pressure (Figure 3, central inset in right panel). The dotted line is a linear fit of experimental data – $L = 3.29 Å + P \cdot 0.012 Å/GPa$. Thus, the initial length of ferrocene molecule at ambient pressure 3.291 Å increases to 3.344 Å at 4.5 GPa.

We suppose that observed dependence is due to pressure-induced partial charge transfer from the ferrocene donor to the C_{60} acceptor molecules. Indeed, the published crystal structure data demonstrate the change of ferrocene molecule length with the iron valence state. The insert in the right side of panel depicts the systematized data from the Cambridge Structural Database (CCDC)[17] on the ferrocene molecule length depending on the valence state of iron atom. The data are presented in the form of histogram which shows the number of communications vs the reported length of the ferrocene

molecule with two different valences of the iron atom. According to these data, the length of the ferrocene molecule increases from ~3.29 Å for Fe^{2+} to ~3.40 Å for Fe^{3+}. In light of these data the observed dependence above means that the valence of the iron atom in ferrocene donor molecule gradually increases from 2^+ to 3^+ when pressure increases. In other words, the application of high pressure to the $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ complex stimulates the charge transfer from ferrocene donor to fullerene acceptor molecule. Thus, at pressure ~4.5 GPa the partial charge transfer results in intermediate oxidation state of iron atom, whereas the complete transfer of one electron is expected at pressure ~9.1 GPa.

Finally, we have studied the crystal structure of the high quality single crystals of the $C_{60} \cdot \{Fe(C_5H_5)_2\}_2$ complex at pressures up to 5 GPa by XRD using the DAC technique. The unit cell volume V/V_0 is smooth and monotonous function of pressure and fits well to the Murnaghan equation of state $(V_0/V)^{B'} = \{1 + P \cdot (B'/B_0)\}$ with $B_0 = 8.7$ GPa and $B' = 10.5$. No structural indications of the pressure-induced polymerization in fullerene layers were observed in the pressure range under investigation. There are structural data that show in favor of pressure induced partial charge transfer from ferrocene to fullerene molecules.

Acknowledgments

References

[1] Meletov, K. P.; Dolganov, V. K.; Spitsina, N. G.; Yagubskii, E. B.; Arvanitidis, J.; Papagelis, K.; Ves, S.; Kourouklis, G. A. Pressure-Induced Charge-Transfer Phase Transition in Crystalline $C_{60} \cdot C_{10}H_{12}Se_4 \cdot 2(CS_2)$ Molecular Complex Studied by Raman Spectroscopy. *Chem. Phys. Lett.* **1997**, *281*, 360–365.

[2] Cui, W.; Yao, M.; Liu, D.; Li, Q.; Liu, R.; Zou, B.; Cui, T.; Liu, B. 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*, 2643–2650.

[3] Meletov, K. P.; D. V.; 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*, 21–25. DOI: 10.1016/j.cplett.2012.09.050.

[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 $\{Cd(Dedtc)_2\}_2\cdot C_{60}$. *J. Exp. Theor. Phys.* **2015**, *120*, 989–997. DOI: 10.1134/S1063776115050167.

[5] Kato, K.; Murata, H.; Gonnokami, H.; Tachibana, M. Polymerization in Ferrocene-Doped C_{60} Nanosheets Under High Pressure and Light Irradiation. *Carbon* **2016**, *107*, 622–627. DOI: 10.1016/j.carbon.2016.06.042.

[6] Sun, S.; Cui, W.; Wang, S.; Liu, B. Investifation of the Polymerization Mechanism of Ferrocene Doped C_{60} Nder High Pressre and High Temperatre. *Sci. Rep.* **2017**, *7*, 10809–10801-10809-6. DOI: 10.1038/s41598-017-11425-4.

[7] Iwasa, Y.; Arima, T.; Fleming, R. M.; Siegrist, T.; Zhou, O.; Haddon, R. C.; Rothberg, L. J.; Lyons, K. B.; Carter, H. L.; Hebard, A. F.; et.al. New Phases of C_{60} Synthesized at High Pressure. *Science* **1994**, *264*, 1570–1572. DOI: 10.1126/science.264.5165.1570.

[8] Nunez-Regueiro, M.; Marques, L.; Hodeau, J.-L.; Bethoux, O.; Perroux, M. Polymerized Fullerite Structures. *Phys. Rev. Lett.* **1995**, *74*, 278–281. P. DOI: 10.1103/PhysRevLett.74.278.

[9] Rao, A. M.; Eklund, P. C.; Hodeau, J.-L.; Marques, L.; Nunez-Regueiro, M. Infrared and Raman Studies of Pressure-Polymerized C_{60}. *Phys. Rev. B* **1997**, *55*, 4766–4773. DOI: 10.1103/PhysRevB.55.4766.

[10] Senyavin, V. M.; Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; Agafonov, V.; Allouchi, H.; Ceolin, R.; Sagon, G.; Szwarc, H. Spectroscopic Properties of Individual Pressure-Polymerized Phases of C_{60}. *Chem. Phys. Lett.* **1999**, *313*, 421–425. DOI: 10.1016/S0009-2614(99)01050-7.

[11] Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; Senyavin, V. M.; Céolin, R.; Szwarc, H.; Allouchi, H.; Agafonov, V. Spectroscopic Study of Pressure Polymerized Phases of C_{60}. *Phys. Rev. B* **2000**, *61*, 11936–11945. DOI: 10.1103/PhysRevB.61.11936.

[12] Winter, J.; Kuzmany, H.; Soldatov, A.; Persson, P.-A.; Jacobsson, P.; Sundqvist, B. Charge Transfer in Alkali-Metal-Doped Polymeric Fullerenes. *Phys. Rev. B* **1996**, *54*, 17486–17492. DOI: 10.1103/PhysRevB.54.17486.

[13] Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; et al. Photoinduced Polymerization of Solid C_{60} Films. *Science* **1993**, *259*, 955–957. DOI: 10.1126/science.259.5097.965.

[14] Meletov, K. P.; Velkos, G.; Arvanitidis, J.; Christofilos, D.; Kourouklis, G. A. Raman Study of the Photopolymer Formation in the $\{Pt(Dbdtc)_2\}\cdot C_{60}$ Fullerene Complex and the Decomposition Kinetics of the Photo-Oligomers. *Chem. Phys. Lett.* **2017**, *681*, 124–129. DOI: 0.1016/j.cplett.2017.05.065 DOI: 10.1016/j.cplett.2017.05.065.

[15] Meletov, K. P. Photopolymerization in the Fullerene Layers of the Molecular Donor-Acceptor Complex $\{Pt(nPr_2dtc)_2\}\cdot(C_{60})_2$. *Phys. Solid State* **2018**, *60*, 2103–2108. DOI: 10.1134/S1063783418100190.

[16] Kuzmin, A. V.; Konarev, D. V.; Khasanov, S. S.; Meletov, K. P. Crystal Structure and Raman Spectra of Molecular Complex $[Cd(Et_2dtc)]_2\cdot DABCO\cdot C_{60}\cdot(DABCO)_2$ at High Pressure. *Nanosyst: Phys., Chem., Math.* **2018**, *9*, 23–37. DOI: 10.17586/2220-8054-2018-1-33-37.

[17] Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **2016**, *B72*, 171–179. DOI: 10.1107/S2052520616003954.

[18] Jayaraman, A. Ultrahigh Pressures. *Rev. Sci. Instrum.* **1986**, *57*, 1013–1031. DOI: 10.1063/1.1138654.

[19] Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. Preparation and Characterisation of $C_{60}(Ferrocene)_2$. *J. Chem. Soc, Chem. Commun.* **1992**, *24*, 1764–1765. DOI: 10.1039/C39920001764.

[20] A.; 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*, 8329–8336. DOI: 10.1103/PhysRevB.53.8329.

[21] Narymbetov, B.; Agafonov, V.; Davydov, V. A.; Kashevarova, L. S.; Rakhmanina, A. V.; Dzyabchenko, A. V.; Kulakov, V. I.; Ceolin, R. The Crystal Structure of the 2D Polymerized Tetragonal Phase of C_{60}. *Chem. Phys. Lett.* **2003**, *367*, 157–162. DOI: 10.1016/S0009-2614(02)01526-9.