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K. P. Meletov^a

^a Institute of Solid State Physics RAS, Chernogolovka, Moscow Region, 142432, Russia

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Phase transitions at high pressure in the donor–acceptor complexes of C₆₀ studied by Raman spectroscopy[†]

K.P. Meletov*

Institute of Solid State Physics RAS, Chernogolovka, Moscow Region 142432, Russia

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In this study, the Raman spectra of the molecular donor–acceptor complex {Cd(dedtc)₂}C₆₀ (fullerene with cadmium diethyldithiocarbamate) were measured at pressure of up to 8 GPa. The phonon modes of the C₆₀ molecule dominate in the Raman spectra, whereas the molecular donor modes are absent probably due to the small cross-section of Raman scattering. The Raman peaks split and soften near 2.5 GPa, indicating the phase transition associated with the inter-fullerene covalent bonding. The high pressure phase is stable as the pressure increases up to ~8 GPa, while with decreasing pressure it reverts to the initial monomer phase near 2 GPa.

Keywords: phase transition; Raman scattering; fullerene molecular complexes; diamond anvil cell

Introduction

The donor–acceptor complexes of C₆₀ are extensively studied with respect to their structure and physical properties [1]. Fullerene complexes have been synthesized with different classes of donor molecules, such as aromatic hydrocarbons, tetrathiafulvalenes, amines, metalloporphyrins, metallocenes and others [2]. Different organic donors form a wide family of compounds with fullerene, which have both neutral and ionic ground states. The behavior of the donor–acceptor complexes of fullerene at high pressure is of great interest due to the possible formation of polymeric networks between fullerene molecules and/or pressure-induced charge transfer from the organic donor to the fullerene acceptor in the case of a neutral ground state. At high pressure, the reduction of inter-fullerene distances in donor–acceptor complexes could create covalent inter-cage bonds in the directions of relatively short intermolecular distances. On the other hand, the overlap of the highest occupied molecular orbital of the molecular donor and the lowest unoccupied molecular orbital of the fullerene acceptor rises with pressure. This may cause charge transfer, particularly in the case when the molecular complex at ambient conditions is rather close to the ionic state.

The X-ray diffraction study of the ionic ground-state donor–acceptor complexes of C₆₀ has revealed the formation of fullerene (C₁₂₀)^{2−} dimers bonded by one or two single bonds [3,4]. The Raman spectra of the molecular donor–acceptor complex {C₁₀H₁₂Se₄(CS₂)₂}C₆₀ (C₁₀H₁₂Se₄,

*Corresponding author. Email: mele@issp.ac.ru

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tetramethyl-tetra-selenafulvalene) at high pressure show an irreversible phase transition at 5 GPa accompanied by the splitting and softening of the fullerene phonon modes [5]. Recently, the high pressure study of the fullerene complex $C_{60}\{Fe(C_5H_5)_2\}_2$, $\{Fe(C_5H_5)_2 - \text{ferrocene}\}$ has revealed signs of charge transfer accompanied by the reversible polymerization of the fullerene sub-lattice at ~ 5 GPa [6]. Besides, the reversible changes in the Raman spectra of the molecular donor–acceptor complex $\{Ni(nPr_2dtc)_2\}(C_{60})_2$, observed in the pressure region 0.5–2.5 GPa, may be related to the charge transfer and/or the formation of fullerene dimers [7]. The ability of C_{60} to form inter-cage covalent bonds is due to the existence of 30 unsaturated double C=C bonds in the fullerene molecule. Pristine C_{60} polymerizes under light illumination [8], alkali metal doping [9,10] and high pressure/high temperature treatment [11,12]. Inter-cage bonds formed via four-membered rings by the $[2 + 2]$ cyclo-addition reaction result in the lowering of the C_{60} molecule symmetry accompanied by the splitting and softening of the phonon modes [8]. An important probe of C_{60} polymers is the behavior of the $A_g(2)$ pentagonal pinch (PP) mode related to the in-phase stretching vibration, which involves tangential displacements of carbon atoms with contraction of the pentagonal rings and expansion of the hexagonal rings. The PP mode frequency downshifts due to the lowering of the intramolecular average bond stiffness as the number of inter-cage bonds per fullerene molecule increases.

In this article, we report the Raman study of the pressure-induced transitions in the molecular donor–acceptor complex $\{Cd(dedtc)_2\}C_{60}$ at pressure of up to 8 GPa. The phonon modes of the C_{60} molecule split and soften near 2.5 GPa, reflecting the transformation of the fullerene sub-lattice. The high pressure phase is stable with the increasing of pressure up to 8 GPa, while further decrease of pressure down to ~ 2.0 GPa results in the recovering of the initial phase.

Experimental details

The samples of the donor–acceptor complex $\{Cd(dedtc)_2\}C_{60}$ were obtained by the evaporation of a solution containing fullerene acceptors and cadmium diethyldithiocarbamate donors by the technique described in [1]. The X-ray data of the $\{Cd(dedtc)_2\}C_{60}$ complex show that it acquires a monoclinic structure (space group $P2_1/c$). The parameters of the unit cell are $a = 16.368(3)$, $b = 17.056(2)$, $c = 10.6650(15)$ Å, $\beta = 100.058(14)^\circ$ and $V = 2931.63$ Å³. The compound has the composition $\{Cd(dedtc)_2\}C_{60}$ and exhibits a layered structure. The C_{60} molecules of the close-packed fullerene layers are arranged in a nearly hexagonal way. Six C_{60} molecules surround each C_{60} molecule in the layer with the shortest distances between the centers of the fullerene molecules, 10.058 (four neighbors) and 10.665 Å (two neighbors). Since the 10.058 and 10.665 Å distances are shorter than the van der Waals (vdW) diameter of the C_{60} molecule, multiple vdW C...C contacts are formed between the fullerenes that are 3.30–3.68 Å long. No C–C bonds are found between the fullerenes and, therefore, the fullerene sub-lattice of the complex is monomeric at ambient conditions (see the inset in Figure 1(a)).

The Raman spectra from the well-faceted crystals of the $\{Cd(dedtc)_2\}C_{60}$ complex that were ~ 50 μm in diameter were recorded *in situ* in back-scattering geometry using a micro-Raman setup comprising an Acton SpectraPro-2500i spectrograph and a CCD Pixis2K detector system cooled down to -70°C . The 532-nm line of a YAG CW diode-pumped laser was focused on the sample by an Olympus 50× objective in a ~ 10 -μm-diameter spot due to slight defocusing. The laser line was suppressed by a super-notch filter with optical density OD = 6 and bandwidth ~ 160 cm⁻¹, while the beam intensity before the diamond anvil cell (DAC) was ~ 0.7 mW. The measurements of the Raman spectra at high pressure were carried out using a Mao-Bell type DAC. Methanol/ethanol mixture (4:1) was used as a pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [13].

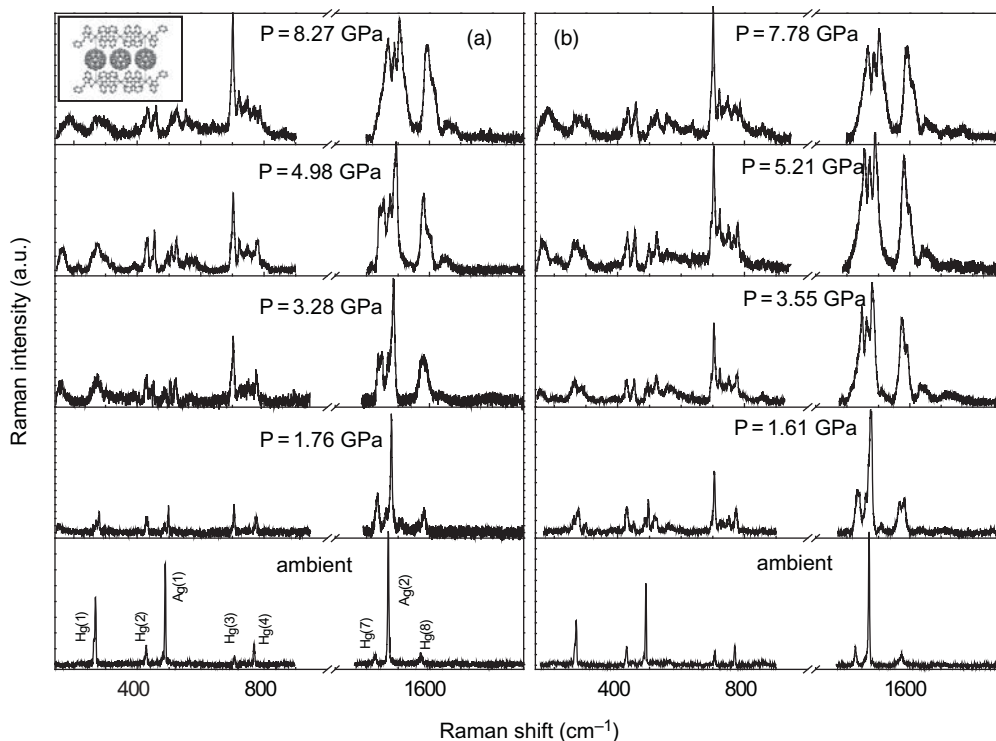


Figure 1. The Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex in the frequency range $140\text{--}1900\text{ cm}^{-1}$ at pressure of up to 8 GPa. (a) The spectra recorded under increasing pressure and (b) the spectra recorded at decreasing pressure, inset—the arrangement of the fullerene and cadmium diethyldithiocarbamate molecules along the b -axes of the primitive cell.

Results and discussion

The Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex, in the frequency range $140\text{--}1900\text{ cm}^{-1}$ and at pressure of up to 8 GPa, are shown in Figure 1. Figure 1(a) depicts the spectra recorded upon the increase of pressure, while Figure 1(b) shows those recorded upon the decrease of pressure. The spectral region around the strong triply degenerate T_{2g} mode of diamond, appearing at 1332 cm^{-1} at ambient pressure, is excluded [14]. The background is subtracted from the experimental spectra. The inset in Figure 1(a) shows the arrangement of the fullerene and cadmium diethyldithiocarbamate molecules along the b -axes of the primitive cell. The phonon modes associated with the C_{60} molecule dominate in the Raman spectrum, which coincides with that of the fcc C_{60} monomer, whereas the modes of the molecular donor are absent, probably due to their relatively small Raman scattering cross-section. As the pressure increases, the majority of the Raman peaks shift to higher energies except for some modes that show a negative pressure shift. The pressure behavior is smooth up to 2.5 GPa where all the Raman modes split and their intensity distribution changes. It is interesting that aside from the splitting of the degenerate H_g modes, the non-degenerate $\text{A}_g(1)$ and $\text{A}_g(2)$ modes split too. Further increase of pressure up to 8 GPa does not lead to significant changes in the Raman spectra, except for a gradual redistribution of the mode intensities. The most important changes are the decrease of the $\text{A}_g(1)$ mode intensity and the increase of the $\text{H}_g(3)$ and $\text{H}_g(7)$ mode intensities, as well as the increase of the split $\text{A}_g(2)$ mode intensity. The splitting of the degenerate modes is most likely related to the creation of the inter-fullerene covalent bonds similar to those of the C_{60} polymers [8,11,12]. On the other hand, the splitting of the PP mode for the three components that are shifted to lower energies indicates

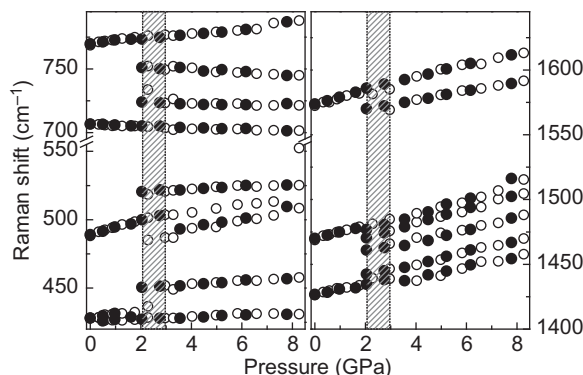


Figure 2. The pressure dependence of the Raman mode frequencies of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex at pressure of up to 8 GPa. Left panel—the phonon modes in the energy region 420–795 cm^{-1} , right panel—the phonon modes in the region 1400–1645 cm^{-1} . The open and closed symbols represent the data for increasing pressure and decreasing pressure, respectively. The shaded area shows the pressure region of the phase transition.

the presence of fullerene molecules with a different number of inter-cage covalent bonds per fullerene molecule. Note that the ionic donor–acceptor complexes of the fullerene show no splitting of the fullerene modes, but only softening of the $A_g(2)$ PP mode. Thus, the observed features in the Raman spectrum of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex after the phase transition are definitely not related to the charge transfer.

The Raman spectra of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex recorded upon the decrease of pressure (Figure 2(b)) demonstrate a smooth behavior down to ~ 2 GPa, where the reverse transformation to the initial phase takes place. The Raman spectrum after pressure release is identical to the initial one at ambient conditions. Therefore, the transformation observed under high pressure is reversible and the Raman spectrum after pressure release is typical of the C_{60} monomer.

The pressure dependence of the Raman mode frequencies of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex is shown in Figure 2. The left panel presents the Raman frequencies in the range of 420–795 cm^{-1} and the right panel presents those in the 1400–1645 cm^{-1} range. The open (closed) symbols represent the data for the increase (decrease) of pressure. The pressure shift of almost all the modes is positive except that of the $H_g(3)$ mode and its split components that exhibit a negative shift. The phonon modes in the initial and high pressure phases demonstrate a linear pressure dependence; the pressure coefficients dE/dP vary between $-1.4 \text{ cm}^{-1}/\text{GPa}$ for the split component of the $H_g(3)$ mode and $5.4 \text{ cm}^{-1}/\text{GPa}$ for the $H_g(7)$ mode. The shaded area shows the pressure region where the changes in the pressure behavior of the Raman modes take place. These changes are associated with the splitting of the Raman modes, the softening of the split components of the PP mode and the redistribution of the mode intensities. It is of interest that the pressure dependence of the split components of the $A_g(2)$ mode extrapolated to ambient conditions implies that the ambient pressure frequencies of these components are 1469, 1459 and 1450 cm^{-1} . The first frequency is typical of the C_{60} monomer, while the second and third frequencies are related to the linear chains with four inter-cage bonds [15] and to the conjugated linear chains with six inter-cage bonds per fullerene molecule, respectively [15,16]. Taking into account the short inter-fullerene distances in the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex at ambient conditions, we believe that the observed changes in the Raman spectra of the high pressure phase are related to the inter-fullerene covalent bonding.

Finally, the pressure behavior of the Raman spectra in the molecular donor–acceptor complex $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ clearly demonstrates the reversible pressure-induced phase transition near 2.5 GPa. The Raman features of the high pressure phase are related to the inter-fullerene covalent bonding that may result in the formation of oligomeric and/or polymeric structures in the

fullerene sub-lattice. To clarify the structural aspects of the observed pressure-induced phase transitions, we will be undertaking an X-ray diffraction study of the $\{\text{Cd}(\text{dedtc})_2\}\text{C}_{60}$ complex at high pressure.

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