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# Pressure-induced transformations in the linear orthorhombic polymeric phase of $C_{60}$

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### Abstract

The pressure-induced transformations in the linear orthorhombic polymer of  $C_{60}$  have been studied by *in situ* Raman scattering. The simultaneous application of pressure and laser irradiation results in fast photo-transformation of the 1D-O polymer at pressures as low as ~0.3 GPa. The pressure dependence of the Raman modes of the photo-transformed polymer shows singularities near ~4 GPa and ~15 GPa, related to reversible phase transition and transformation to a metastable highly disordered phase, respectively. The diffuse spectrum of the disordered phase does not exhibit essential changes for increasing pressure up to 29 GPa. The recovered high-pressure phase transforms to a mixture of pristine and dimerized  $C_{60}$  within ~30 h. © 2007 Elsevier B.V. All rights reserved.

## 1. Introduction

The pristine C<sub>60</sub> forms a variety of polymeric structures due to the great potential of the 30 unsaturated C=C bonds in the fullerene molecular cage. The photo-induced polymerization of the monomeric fcc phase of fullerene  $C_{60}$  was observed for the first time under light illumination with a power density exceeding  $5 \text{ W/cm}^2$  [1]. The covalent bonding between adjacent C<sub>60</sub> molecules via the [2+2] cycloaddition reaction results in the creation of fullerene oligomers  $(C_{60})_n$ , with n = 2-20, associated with the sp<sup>3</sup>like coordination of some C atoms in the fullerene cage [1-3]. The treatment of C<sub>60</sub> under various conditions of high pressure and high temperature (HPHT) leads to the formation of dimers, linear polymeric chains, planar and/ or three-dimensional polymeric networks that show distinct changes in the crystal structure and optical spectra [4–9]. The changes in the Raman and IR spectra are related to the deformation of the  $C_{60}$  molecules resulting in the

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lowering of their symmetry, which leads to the splitting and/or softening of the bands.

The crystal structures of the HPHT C<sub>60</sub> polymers have been identified as the linear orthorhombic (1D-O), planar tetragonal (2D-T) and rhombohedral (2D-R), and threedimensional face-centred cubic (3D-fcc) [4,5,10]. The relatively small number of sp3-like coordinated C atoms in linear and planar polymers of C<sub>60</sub> leaves open the possibility for further polymerization, in particular by application of uniaxial pressure perpendicular to the polymeric sheets of the planar and/or to the polymeric chains of linear polymers of C<sub>60</sub> [11,12]. Experimental in situ Raman and Xray studies of the 2D-T polymer at high pressure have revealed an irreversible transition above 20 GPa to an ordered high-pressure phase, related to its three-dimensional polymerization [13,14]. The in situ Raman studies of the 2D-R polymer at high pressure have revealed an irreversible transition near 15 GPa to a disordered phase [15], related most likely to chaotic bonding of molecules belonging to adjacent polymeric sheets. Recently, in a high pressure study of the C<sub>60</sub> crystalline polymeric phases, we have reported an irreversible transformation of the 1D-O polymeric phase of C<sub>60</sub> under simultaneous application of

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pressure and laser irradiation [16]. This transformation was associated with the pressure-assisted photopolymerization that occurs even at normal pressure, whereas the simultaneous application of high pressure and laser irradiation drastically increases the photopolymerization rate [17]. The Raman spectrum of the photo-transformed 1D-O polymer differs from those of known planar polymers of  $C_{60}$  [16]. The recent X-ray powder diffraction study has shown also that, under simultaneous application of pressure and X-ray irradiation, the 1D-O polymer transforms to a phase, characterized by conjunction of adjacent linear polymeric chains [18].

We report the study of the pressure behavior of the photo-transformed 1D-O polymer of  $C_{60}$  at pressure up to 29 GPa and at room temperature by means of *in situ* Raman scattering. The pressure dependence of the phonon frequencies could reveal possible pressure-induced phase transitions and/or irreversible transformations related to further polymerization of the material.

# 2. Experimental

Samples of the initial 1D-O phase were prepared from sublimed 99.98% pure C<sub>60</sub> powder at 1.2 GPa at 573 K in a 'toroid'-type device. The preliminary X-ray analysis has confirmed that the samples have the orthorhombic packing of linear polymeric chains (space group  $P_{mnn}$ : a = 9.098 Å, b = 9.831 Å, and c = 14.72 Å). The samples used had dimensions of ~100 µm and have been selected from the batch material by means of micro-Raman probing for their intense, clear and spatially uniform Raman spectra, typical of the 1D-O polymeric phase [9,19]. Raman spectra were recorded in back-scattering geometry using a triple monochromator (DILOR XY-500) equipped with a CCD LN cooled detector system. The system utilizes an OLYMPUS microscope with objective of  $20 \times$  magnification and a spatial resolution of ~8 µm. The spectral width of the system was ~3 cm<sup>-1</sup>. The 514.5 nm line of an Ar<sup>+</sup> laser with beam intensity in the range 0.1–1 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out using a Mao-Bell type cell [20] with 4:1 methanol–ethanol mixture as pressure medium while ruby fluorescence provided the calibration [21].

#### 3. Results and discussion

The Raman spectra of the photo-transformed 1D-O linear orthorhombic polymer of C<sub>60</sub> at various pressures and at room temperature are shown in Fig. 1. The left panel of Fig. 1 represents the data recorded upon pressure increase whereas the right panel represents the data for pressure release. The spectral region around the strong triply degenerate  $T_{2g}$  mode of diamond, appearing at 1332 cm<sup>-1</sup> at ambient pressure [22], is excluded. The background, which is somehow increasing with pressure, has been subtracted from the spectra. The initial Raman spectrum of the photo-transformed 1D-O polymer of  $C_{60}$  consists of a large number of narrow and well-resolved bands and has more complicated structure than the Raman spectrum of the 1D-O polymer of C<sub>60</sub>. It resembles the Raman spectra of the planar 2D-R and 2D-T polymers but differs in the number of peaks and their positions [16].

As the pressure increases, the Raman peaks shift to higher energies and their bandwidth gradually increases. The broadening of the Raman bands is further enhanced above 10 GPa due to the solidification of the pressuretransmitting medium. It is known that the methanol-etha-



Fig. 1. Raman spectra of the photo-transformed 1D-O linear orthorhombic polymeric phase of  $C_{60}$  at room temperature and various pressures: left panel – spectra recorded upon pressure increase, right panel – spectra recorded upon pressure decrease.

nol mixture is fully hydrostatic up to 10 GPa while in its glassy form could support pressure gradients of up to 0.4 GPa at extreme pressures [23], therefore we expect shear components in the order of this gradient. The most important pressure effects are related to the changes in a number of Raman active modes, their pressure coefficients and intensities. The relative intensities of the Raman modes in the 700–1100  $\text{cm}^{-1}$  region gradually increase with respect to other modes. Significant changes were observed near  $\sim 15$  GPa when the Raman spectrum loses its fine structure in all frequency regions and becomes very diffuse. This transformation was preceded by a rapid decrease in the intensity of the modes related to  $A_g(2)$  'pentagonal pinch' (PP) mode of the pristine C<sub>60</sub> and a relative increase in the intensities of the  $H_g(8)$  and  $G_g(6)$  modes. The broad Raman features in the spectrum of the high-pressure phase above ~15 GPa can be tracked back to the photo-transformed 1D-O polymer of C<sub>60</sub> and seems to incorporate the corresponding group of the well resolved Raman bands of this phase. Despite the similarities in the diffused Raman bands, the spectrum of the high-pressure phase differs significantly from that of the amorphous carbon with respect to the number of peaks as well as to their location. Comparing the Raman spectrum of the high-pressure phase to that of the high-pressure phase of the 2D-T polymeric phase of  $C_{60}$  [13,24], we observe that the former does not contain peaks in the high energy region, like the  $1840 \text{ cm}^{-1}$  peak observed in the later phase. In addition, the new phase shows spatially uniform Raman response over all the surface of the sample, as it was documented by probing various places in the sample, a behavior which differs drastically from the 2D-T polymeric phase of  $C_{60}$ [13]. Note, that the broad Raman features of the high-pressure phase in the photo-transformed 1D-O polymer of  $\bar{C}_{60}$ resemble the Raman features of the disordered high-pressure phase in the 2D-R polymer, which was also observed at pressure above ~15 GPa [15]. Upon pressure decrease the broad Raman bands of the disordered phase shift to lower energies without any observable changes in their intensity distribution (right panel of Fig. 1). The high-pressure phase remains stable upon total release of pressure.

The pressure dependence of the Raman mode frequencies of the photo-transformed 1D-O polymer of C<sub>60</sub> in the energy regions  $240-620 \text{ cm}^{-1}$  and  $1380-1680 \text{ cm}^{-1}$  are shown in Figs. 2 and 3. The phonon frequencies were obtained by fitting Voigt peak functions to the experimental data after background subtraction. In the high-pressure phase, the frequencies were defined with somewhat lower accuracy because of their diffuse nature. The Raman mode frequencies of the initial 1D-O polymer are also marked in the figure. The phonon frequencies obtained upon pressure increase cycle coincide in the two pressure runs within the accuracy of our measurements. As it can be seen from Figs. 2 and 3, the pressure-induced shift of the majority of Raman modes is linear and positive, with exception of a few modes, which display small negative pressure shifts. The magnitudes of the pressure coefficients vary between



Fig. 2. Pressure dependence of the Raman frequencies of the phototransformed 1D-O polymer in the region  $240-620 \text{ cm}^{-1}$ . Circles and squares represent data taken upon two different pressure runs up to 12 GPa and 29 GPa, respectively. Stars denote the Raman frequencies of initial 1D-O polymer at normal conditions. The open (solid) symbols represent the increasing (decreasing) pressure cycles. Dashed vertical lines near ~4 GPa and ~15 GPa mark the pressure where changes are observed.

 $-0.4 \text{ cm}^{-1}/\text{GPa}$  and  $+7.0 \text{ cm}^{-1}/\text{GPa}$  for the 561 cm<sup>-1</sup> and 1442 cm<sup>-1</sup> modes, respectively. The pressure dependence of all Raman modes is reversible with pressure at least up to ~12 GPa, the highest pressure reached during



Fig. 3. Pressure dependence of the Raman frequencies of the phototransformed 1D-O polymer in the region 1380–1680 cm<sup>-1</sup>. Circles and squares represent data taken upon two different pressure runs up to 12 GPa and 29 GPa, respectively. Stars denote the Raman frequencies of initial 1D-O polymer at normal conditions. The open (solid) symbols represent the increasing (decreasing) pressure cycles. Dashed vertical lines near ~4 GPa and ~15 GPa mark the pressure where changes are observed.

the first experimental pressure run (open and closed circles in Figs. 2 and 3). The dashed lines near  $\sim$ 4 GPa and  $\sim$ 15 GPa indicate the pressure range where the changes in the pressure dependence of Raman frequencies take place. The pressure coefficients and the number of Raman bands change abruptly at  $\sim 4$  GPa. The slopes of the low energy Raman modes change near ~4 GPa from  $8.4 \text{ cm}^{-1}/\text{GPa}$  to  $2.2 \text{ cm}^{-1}/\text{GPa}$  and from  $2.7 \text{ cm}^{-1}/\text{GPa}$ to  $0.04 \text{ cm}^{-1}/\text{GPa}$  for the 288 cm<sup>-1</sup> and 333 cm<sup>-1</sup> modes, respectively. For the high frequency modes, the pressure coefficients change from  $3.2 \text{ cm}^{-1}/\text{GPa}$  to  $6.2 \text{ cm}^{-1}/\text{GPa}$ and from  $7.0 \text{ cm}^{-1}/\text{GPa}$  to  $4.0 \text{ cm}^{-1}/\text{GPa}$  for the 1429 cm<sup>-1</sup> and 1442 cm<sup>-1</sup> modes, respectively. In addition, the 1559 cm<sup>-1</sup> band splits near  $\sim$ 4 GPa and the pressure coefficients of the split components are different, namely  $4.9 \text{ cm}^{-1}/\text{GPa}$  and  $4.5 \text{ cm}^{-1}/\text{GPa}$  for upper and lower components, respectively. The splitting of the  $1559 \text{ cm}^{-1}$  mode and the changes in the pressure slopes of a number of modes along with the reversibility of these effects upon pressure release below 12 GPa, may be the indication of a structural phase transition that takes place near  $\sim$ 4 GPa. As to the changes taking place near  $\sim$ 15 GPa, they are related to an irreversible transformation. The disappearance of the majority of the phonon modes, the changes in the pressure slopes, the drastic broadening of Raman bands and the irreversible behavior upon pressure release are unambiguous evidence of an irreversible transformation to a highly disordered state.

After pressure release, the recovered sample was tested by means of micro-Raman probing in order to check its stability. Fig. 4 shows the Raman spectra of various phases of the 1D-O polymer of  $C_{60}$  in the frequency region 1350–  $1780 \text{ cm}^{-1}$ , where the basic changes in the Raman response take place. The Raman spectrum of the initial photo-transformed 1D-O polymeric phase is shown in Fig. 4a. This spectrum differs essentially from that of the initial 1D-O polymer of C<sub>60</sub> shown in Fig. 4e. The Raman spectrum of the high-pressure phase of the photo-transformed 1D-O polymer immediately after pressure release is shown in Fig. 4b, whereas the Fig. 4c and d shows the Raman spectra of the high-pressure phase at various sites of the sample  $\sim$ 30 h after pressure release. These spectra indicate that the high-pressure phase is metastable and demonstrates a rather fast transformation to a phase whose spectrum (Fig. 4d) resembles the spectrum of the initial 1D-O polymer of C<sub>60</sub> and is typical of a mixture of pristine and dimerized  $C_{60}$ . Nevertheless, the frequency of the  $A_g(2)$  PP-mode in Fig. 4d is shifted to higher energies and has similarities to the spectra of various annealed polymeric phases that are typical of a mixture of pristine and dimerized  $C_{60}$ [13,25]. This transformation of the recovered material was observed at normal conditions without any special heating of the sample except that of the excitation beam during the Raman probing [26]. The behavior of the recovered high-pressure phase of the photo-transformed 1D-O polymer differs from that of the high-pressure phase of the 2D-R polymer, which is more stable and transforms



Fig. 4. Raman spectra of various phases of the 1D-O linear orthorhombic polymer of  $C_{60}$  in the frequency region 1350–1780 cm<sup>-1</sup>, recorded at normal conditions. (a) The photo-transformed 1D-O polymeric phase. (b) The recovered 'high-pressure' phase immediately after pressure release. (c and d) The Raman spectra of the recovered 'high-pressure' phase at various sites of specimen recorded at ~30 h after pressure release. (e) The Raman spectrum of initial 1D-O linear orthorhombic polymer. The vertical line at 1462 cm<sup>-1</sup> marks the frequency of the PP mode of a mixture of pristine and dimerized  $C_{60}$ .

to a mixture of pristine and dimerized  $C_{60}$  only under sample annealing at 600 °C [15].

The changes in the pressure dependence of the Raman frequencies of the photo-transformed 1D-O polymer of  $C_{60}$  at ~4 GPa, give rise to suspicions for a possible structural phase transition. This may be related to minor changes in the packing of the conjunct linear polymeric chains. However, to make sure that the singularities observed in the high-pressure Raman study are associated to a phase transition, an X-ray study of the crystal structure is necessary. Recent high-pressure X-ray powder study [18] of the linear orthorhombic polymer of  $C_{60}$  has not revealed clear changes in the diffraction patterns near  $\sim$ 4 GPa, still this study was not conclusive since the lowresolution along with the small number of peaks could not permit further refinement, nevertheless we hope that the announced synchrotron radiation experiments may clarify this situation.

The increase of pressure to  $\sim 15$  GPa causes the wellresolved Raman spectrum of the photo-transformed 1D-O polymer to transform to a diffuse one that is typical of a disordered phase. The rapid decrease of the A<sub>g</sub>(2) PPmode intensity and the enhancement of the neighboring  $H_g(8)$  and  $G_g(6)$  modes in the pre-transitional pressure regime is reminiscent of analogous behavior exhibited by these modes in the 2D-T and 2D-R polymeric phases of C<sub>60</sub> before their further polymerization under high pressure [13,15]. Taking into account that the PP-mode is associated with the in-phase stretching vibrations of the C=C bonds, the decrease of its intensity may be related to the destruction of a number of these bonds and the subsequent creation of covalent links between molecules belonging to adjacent polymeric planes or chains. Albeit pressure decreases preferentially the distance between the linear polymeric chains rather than the cage distance in the chain, the interchain bond formation is not always easy. The  $C_{60}$ molecular cages belonging to adjacent polymeric chains may not have relative orientations optimal for the formation of new covalent bonds. Therefore, we may expect that the new bonds are formed in a random way due to some distortion in the molecular orientations. As a result, the new high-pressure phase exhibits a degree of disorder characterized by a random polymerization. Similarly, in the case of 2D-R polymer the diffuse Raman spectrum of the high-pressure phase is also related to a disordered polymeric phase of C<sub>60</sub> characterized by random covalent bonding between molecules belonging to adjacent 2D-polymeric planes of the initial rhombohedral phase. Note that this behavior differs significantly from that of the 2D-T polymeric phase of C<sub>60</sub>, in which the pressure-induced shortening of the intermolecular distances, accompanied by the optimal orientation of molecules, leads to a high degree of regularity in the formation of the out-of-plane covalent bonds.

In conclusion, the photo-transformed 1D-O polymer of  $C_{60}$  undergoes probably a structural phase transition at ~4 GPa, whereas further increase of pressure to ~15 GPa causes a transformation to a metastable phase with a diffuse spectrum typical of a disordered phase. After pressure release, this phase relaxes to a mixture of pristine and dimerized  $C_{60}$ . We assume that a new high-pressure phase is formed by random creation of covalent bonds between  $C_{60}$  molecules belonging to adjacent polymeric chains due to some distortion in the molecular orientation. This conclusion is supported by the retention of the fullerene molecular cage in the high-pressure phase as well as by the similarity in the pre-transitional behavior with that of the 2D-T and 2D-R polymeric phases of  $C_{60}$ .

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