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# Photoluminescence study of the planar polymers of $C_{60}$ at high pressure

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## Abstract

The photoluminescence (PL) spectra of high quality single phase samples of the planar polymers of  $C_{60}$  have been studied as a function of pressure up to 4 GPa. The intensity distribution between the bands and their pressure-induced shifts differ among the pristine  $C_{60}$ , tetragonal and rhombohedral polymeric phases of  $C_{60}$ . The changes in the PL spectra of the planar polymers of  $C_{60}$ , as compared to the pristine material, are discussed in relation to the calculated electronic structure of the  $C_{60}$  polymers. The obtained data can be used to effectively characterize the planar polymeric phases of  $C_{60}$ .

### 1. Introduction

The solid  $C_{60}$  is a semiconductor with a direct energy gap at the X-point of the Brillouin-zone with gap value  $\sim$  1.5 eV [1]. The optical transitions from the lowest excited singlet state of the  $C_{60}$  are dipole forbidden and the fluorescence is related to the vibronically assisted Herzberg-Teller transitions [2,3]. The PL spectrum of the crystalline C<sub>60</sub> at low temperature exhibits fine structure associated with the optical transitions from shallow defect levels [4]. The polymerization of  $C_{60}$  under high pressure and high temperature [HPHT] treatment leads to changes in the crystal structure and therefore to the phonon spectrum of the materials [5,6]. The various polymeric structures are formed by bonding adjacent  $C_{60}$  molecules via the [2+2] cyclo-addition reaction mechanism [7]. The treatment at intermediate pressure and temperature leads to the formation of the planar polymers, which have either a rhombohedral (2D-R) or a tetragonal (2D-T) crystal structure [5,11,12]. The

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decrease of the intermolecular distances, the deformation of the C<sub>60</sub> molecular cage and the lowering of molecular symmetry in the polymers affect significantly their electron energy spectra. Thus, numerical calculations, performed using the local-density (LD) approximation, predict that the 2D-T and 2D-R polymers of C<sub>60</sub> are indirect, low gap semiconductors and their electronic structure differs significantly from that of the pristine  $C_{60}$  [1,8–10]. Experimental optical study of the polymeric phases has revealed some differences of the PL spectrum of pristine C<sub>60</sub> compared to its polymeric forms [13]. Unfortunately, the specimens used in the above study [13] were mainly mixtures of various polymeric phases of  $C_{60}$ . The progress in the synthesis of pure single phase polymeric samples during the last years as well as advances in calculating numerically their electronic structure, makes it necessary for new experimental data, related to the PL spectra of the 2D-T and 2D-R polymers of C<sub>60</sub>.

In this work, we present measurements of the PL spectra of single phase samples of the 2D-R and 2D-T polymers of  $C_{60}$  as a function of pressure up to 4.0 GPa at normal conditions. The pressure dependence

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of the PL bands proves to be a very sensitive tool for the identification and characterization of the polymeric phases of  $C_{60}$ . The comparison of the PL spectra of polymers with that of the pristine  $C_{60}$ , as well as with the results of numerical calculations of the electronic structure, provides an insight in the changes associated with the polymerization of  $C_{60}$  under HPHT treatment.

# 2. Experimental

The 2D-R polymer was obtained by subjecting 99.99% pure C<sub>60</sub> powder to a pressure of  $P \approx 5$  GPa and temperature  $T \approx 773$  K (rhombohedral structure, space group:  $R\bar{3}m$ , a = 9.22 Å and c = 24.6 Å) [5]. The 2D-T polymer was obtained in a similar way by subjecting 99.99% pure C<sub>60</sub> powder at  $P \approx 2.2$  GPa and  $T \approx 820$  K (tetragonal structure, space group: P4<sub>2</sub>mmc, a = b = 9.082 Å and c = 14.990 Å) [14]. The PL spectra were recorded using a JOBIN-YVON THR-1000 monochromator equipped with a CCD liquid-nitrogen cooled detector. The spectral width of the system was  $\sim 0.5$  meV. The 488 nm line of an Ar<sup>+</sup> laser with power  $\sim 2 \text{ mW}$  was used for excitation of the PL spectra. Measurements at high pressure were carried out using the diamond anvil cell of Mao-Bell type [15]. The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [16].

## 3. Results and discussion

The PL spectra of the pristine  $C_{60}$ , 2D-R and 2D-T polymers of C<sub>60</sub> at ambient conditions are shown in Fig. 1a (the spectrum of pristine  $C_{60}$  was taken also at 10 K). In Fig. 1b the Raman spectra of the same samples at the same conditions with those of the PL spectra are also shown. The number of bands, their frequencies and intensities for these materials are uniquely characteristic and the Raman spectra provide assurance that the specimens selected for the PL measurements do not contain inclusions of other polymeric phases [6,17,18]. The PL spectrum of the  $C_{60}$  single crystal at room temperature is rather diffuse but becomes well resolved at 10 K due to the transitions from the shallow defect levels, occupied at low temperatures by localized excitons [4]. The measurements have also revealed a band related with transitions of the free excitons which has pressure coefficient noticeably higher than those related to the localized excitons [19].

The PL spectra of the 2D-R and 2D-T polymers differ considerably from that of the pristine  $C_{60}$ . The differences are related to the onsets of the spectra, the number of bands and the intensity distribution among them. The PL spectrum of the 2D-T polymer consists of two main bands similar to the pristine  $C_{60}$ , but its onset is shifted downwards to lower energy by ~0.14 eV and the intensity distribution between the bands is reversed. On the contrary, the onset of the PL spectrum



Fig. 1. PL spectra (a) and Raman spectra (b) of  $C_{60}$ , 2D-R and 2D-T polymers of  $C_{60}$  at ambient conditions. The spectra of  $C_{60}$  at 10 and 300 K are also included.

of the 2D-R polymer is almost the same with that of the pristine  $C_{60}$ , while the spectrum is better resolved and contains four narrow intense bands. In addition, the PL spectrum of the 2D-T polymer contains two weak shoulders at the high energy side. The positions and pressure behavior of these bands are coincident with those observed in the 2D-R polymer, therefore they are attributed to minute impurity of this phase in the 2D-T phase as we shall discuss below. Note, that the quality of the PL spectra is much better than those reported earlier in Ref. [13].

The most important difference between the polymers and pristine  $C_{60}$  is the pressure behavior of the PL spectra. Fig. 2 shows the PL spectra of the 2D-R polymer at various pressures up to ~3.5 GPa for increasing and decreasing pressure cycles. The most intense spectrum in Fig. 2 is that recorded at normal conditions, whereas the spectra taken at high pressure are less intense due to the aperture limitation of the high-pressure cell. The intensity distribution in the PL spectra is shown as measured. The rapid decrease of the PL intensity near 1.4 eV is related most likely to the spectral cut-off of the CCD detector. When the pressure increases, the bands gradually shift to lower energies and their intensity decreases. The red shift of the optical spectra in the fullerene-based materials is related to the Van-der-Waals interaction [19], while the decrease of the intensity may be, in part, due to the convolution of the CCD cut-off. The pressure coefficients,  $\partial E/\partial P$ , and the positions of the bands at ambient conditions, E, in the PL spectra are shown in Table 1. The pressure coefficients for the bands of the 2D-R polymer are in the region -0.022 to -0.028 eV/ GPa, while the pressure coefficient of the free exciton band of  $C_{60}$  is about -0.086 eV/GPa [19]. The PL spectra of the 2D-T polymer for the increasing and decreasing pressure runs are shown in Fig. 3. The pressure coefficients for almost all bands of the two planar polymers are quite different (see Table 1).

The pressure dependence of the band frequencies of the pristine  $C_{60}$ , 2D-R and 2D-T polymers of  $C_{60}$  is shown in Fig. 4. The circles and squares are related to the 2D-R and 2D-T polymers, respectively, while the stars show the pressure dependence of the free exciton band of  $C_{60}$ . The open (closed) symbols represent data



Fig. 2. PL spectra of the 2D-R polymer at various pressures and room temperature for upstroke and downstroke pressure cycles. The ruby peaks are marked by \*.

Table 1	
Positions and pressure coefficients of the bands in the PL spectra of the pristine C <sub>60</sub> , 2D-R and 2D-T polymers of C <sub>60</sub>	

2D-R polymer <sup>a</sup>		2D-T polymer <sup>a</sup>		Pristine C <sub>60</sub> <sup>b</sup>	
<i>E</i> (eV)	$\partial E/\partial P$ (eV/GPa)	E (eV)	$\partial E/\partial P$ (eV/GPa)	$E_0$ (eV)	∂ <i>E</i> /∂ <i>P</i> (eV/GPa)
1.747 <sup>c</sup>	-0.022	1.746	-0.021	1.669 <sup>c</sup>	-0.086
1.673	-0.025	1.534 <sup>c</sup>	-0.015		
1.622	-0.025	1.437	-0.013		
1.531	-0.028				
0.35 <sup>d</sup>		0.72 <sup>d</sup>		1.5 <sup>d</sup>	

<sup>a</sup> The data were taken at ambient conditions.

<sup>b</sup> The data taken at T = 10 K.

<sup>c</sup> These values are taken as the energy gap values.

<sup>d</sup> Calculated gap values [1,9,10].



Fig. 3. PL spectra of the 2D-T polymer at various pressures and room temperature for upstroke and downstroke pressure cycles. The ruby peaks are marked by \*.



Fig. 4. The pressure dependence of the band positions in the PL spectra of  $C_{60}$ , the 2D-R and the 2D-T polymers of  $C_{60}$  (stars, circles and squares, respectively). Open (closed) symbols represent data recorded for increasing (decreasing) pressure runs.

recorded for increasing (decreasing) pressure runs. Note that the position and the pressure dependence of the high energy shoulder in the PL spectrum of the 2D-T polymer coincide with the first band of the 2D-R polymer. This is an indication that the specimen of the 2D-T polymer contains small inclusions of the 2D-R polymer. The fact, that the Raman characterization of the samples does not show the presence of the other polymeric phase, means that the PL measurements are more sensitive to the purity of the specimens.

The obtained experimental data clearly indicate that the electronic structure of the polymeric phases

is changed with respect to the pristine  $C_{60}$ . According to numerical calculations of the electronic structure, the 2D-R and 2D-T polymers are narrow indirect gap semiconductors with gap values of 0.35 and 0.72 eV, respectively [9,10]. The calculated gap values for the polymers are noticeably smaller than the experimental values extracted from the PL spectra, whereas for the pristine C<sub>60</sub> this discrepancy is smaller. Taking into account that the LD approximation generally underestimates the gap value, it is more relevant to compare the difference between the calculated gap values of the polymers to that of pristine  $C_{60}$  with the corresponding differences among the experimental data. The difference between the calculated gap values for the 2D-R and 2D-T polymers to that of the pristine  $C_{60}$  is 1.15 and 0.78 eV, respectively. These values are not compatible with the corresponding experimental values -0.078 and 0.135 eV. The most intriguing aspect is that the onset of the PL spectrum of the 2D-R polymer is shifted to higher energy with respect to the position of the free exciton band of the pristine  $C_{60}$ . Normally the spectra of polymers should be shifted to lower energies. This is related to the decrease of the intermolecular distances in polymers under high pressure. In fact the situation is more complicated due to the deformation of the fullerene molecular cage which can affect significantly the electronic structure of the polymer. The numerical calculations based on the LD approximation take into account the deformed fullerene molecular cage and the reduced intermolecular distances in the polymeric phases, nevertheless the experimental results are rather far from the calculated data. This may be related to the fact, that the observed PL spectra of polymers may be associated also with direct phonon-assisted

transitions from the local energy minimums at various points of the Brillouin-zone.

The difference in the pressure coefficients of the 2D-R and 2D-T polymers in their PL bands is a characteristic feature despite the fact that their bulk moduli  $B_0$  are very close (28.1 and 29.9 GPa for the 2D-R and 2D-T polymers, respectively) [20]. The compressibility of the 2D-R polymer within the polymeric sheets is almost three times larger than that of the 2D-T polymer, whereas the out-of-plane compressibility is almost the same [20]. The large difference in the pressure coefficients may be related to the difference in the in-plane compressibility of the two polymers. This means that the contribution of the in-plane intermolecular interaction to the electronic structure of planar polymers is more important due to the reduced intermolecular distances than the contribution of the out-of-plane interaction.

In conclusion, we have measured the PL spectra of the planar 2D-R and 2D-T polymers of  $C_{60}$  and found significant differences between them and their pressure behavior. The experimental data prove that the polymerization of  $C_{60}$  leads to considerable changes in the electronic structure of  $C_{60}$ , they are also compatible, in general, with the results of numerical calculations but they are rather far from quantitative agreement. Finally, the PL spectra prove to be a very sensitive tool in the characterization of the  $C_{60}$  polymeric phases.

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