Electronic Spectra of the Crystalline Polymers of C_{60}: Photoluminescence Study at High Pressure

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Specific details of the electronic spectra of perfect crystalline polymers of C_{60} were studied by means of the photoluminescence spectra measurements at normal conditions and at high pressure up to 4 GPa. The structure of the photoluminescence spectra, the intensity distribution between the principal bands and the pressure-induced shift of the bands differ considerably among the pristine C_{60}, linear orthorhombic and planar tetragonal and rhombohedral polymeric phases of C_{60}. Unlike the planar polymers of C_{60}, the linear orthorhombic polymer exhibits irreversible changes in the photoluminescence spectrum under simultaneous application of high pressure and laser irradiation. The changes observed in the photoluminescence spectra of the planar polymeric phases of C_{60}, as compared to the pristine material, are discussed in relation to the corresponding changes in the calculated electronic structure of the pristine C_{60} and its polymeric phases. The observed photoluminescence spectral structure along with the pressure behavior of the photoluminescence spectra are very sensitive to the structure of the polymers as well as to the C_{60} cage deformations and can be used to effectively characterize the various polymeric phases of C_{60}.

Keywords: Fullerenes, High Pressure, Photoluminescence, Polymers.

1. INTRODUCTION

The optical transitions to the lowest excited singlet state of the C_{60} molecule (symmetry $^1T_{1g}$) are dipole forbidden, whereas the first allowed transition to $^1T_{1u}$ state has noticeably higher energy.[1] Thus the fluorescence of the C_{60} molecule is related to the vibronically assisted Herzberg-Teller transitions which is the main reason why the fluorescence quantum yield is relatively small: about 10^{-5} in solution and 7×10^{-4} in solid.[2–4] The solid C_{60} is a semiconductor with a direct energy gap at the X-point of the Brillouin-zone with energy value in the range 1.5–1.8 eV as it follows from the numerical calculations of the electronic structure and optical absorption spectra measurements.[5, 6] The fluorescence quantum yield of the solid material is higher due to the presence of impurities and defects in the crystalline state. The photoluminescence (PL) spectrum of the single crystal of pristine C_{60} at low temperature is well-resolved, exhibiting fine structure associated with the optical transitions from shallow defect levels, the so-called X-traps.[7]

The polymerization of C_{60} under high pressure and high temperature [HPHT] treatment leads to drastic changes in the crystal structure as well as in the phonon spectrum relative to the pristine material.[8, 9] The electron energy spectra of the polymeric phases differ considerably from that of the pristine material, this has been predicted in a number of numerical calculations of the electronic structure of the planar rhombohedral and tetragonal polymers of C_{60}.[5, 10–12] The pristine C_{60} forms a variety of polymeric structures due to the great potential of the 30 double C=C bonds in the fullerene molecular cage for polymeric bond formation. These covalent polymeric bonds are formed via the $[2 + 2]$ cyclo-addition reaction followed by the formation of four-membered rings between adjacent fullerene molecules, resulting in deformation of the fullerene molecule cage and an appreciable decrease of the intermolecular distance.[13] The structure and the dimensionality of HPHT crystalline polymers depends strongly on the pressure (P) and temperature (T) treatment conditions. Thus, at lower P and T the C_{60} molecules form linear polymeric chains having orthorhombic crystal structure (1D-O) and/or dimers and higher oligomers. At intermediate P and T the C_{60} molecules form planar polymeric layers, which have either a rhombohedral (2D-Rh) or a tetragonal (2D-T) crystal structure, while at higher P and T, they form face centered cubic structures, which are based on three-dimensional cross-linked

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polymerization.[8, 14–16] This polymerization of C$_{60}$ is associated with the destruction of a number of double C=C bonds and the creation of intermolecular covalent bonds associated with sp^3-like fourfold coordinated carbon atoms within the fullerene molecular cage. Their number increases from 4 to 8 and to 12 per each cage for 1D-O, 2D-T, and 2D-Rh polymeric phases, respectively and it is expected to increase further in the 3D-polymeric phases. The decrease of the intermolecular distances, the deformation of the fullerene molecule cage and the lowering of the molecular symmetry in polymeric phases of C$_{60}$ affect significantly the electron energy spectrum with respect to the pristine C$_{60}$ molecule. Thus, numerical calculations, performed using the local-density approximation, predict that the tetragonal, and rhombohedral polymeric phases of C$_{60}$ are indirect low gap semiconductors and their electronic structure differs significantly from those of the pristine C$_{60}$.[1, 10–12] The early experimental optical study of the C$_{60}$ polymers has revealed some important changes in the PL spectrum of pristine C$_{60}$ related to its polymerization.[17] Unfortunately, the specimens identified as orthorhombic and tetragonal polymers were mainly a mixture of various planar polymeric phases of C$_{60}$.[17] The progress in the synthesis of perfect single phase samples of the linear and planar polymers of C$_{60}$ during the last years as well as in calculating numerically their electronic structure, makes it necessary for new experimental data, especially related to the luminescence spectra of the pure 2D-T and 2D-Rh polymeric phases of C$_{60}$.

In this work, we present measurements of the PL spectra of perfect crystalline samples of the 1D-O, 2D-Rh, and 2D-T polymeric phases of C$_{60}$, at normal conditions and as a function of pressure up to 4.0 GPa. The comparison of the PL spectra of the linear and planar polymers with those of the pristine C$_{60}$, as well as with the results of numerical calculations of the electronic structure, provide an insight in the changes associated with the polymerization of C$_{60}$ under HPHT treatment. The pressure dependence of the PL bands proves to be a very sensitive tool for the identification and characterization of various polymeric phases of C$_{60}$.

2. EXPERIMENTAL DETAILS

Samples of the 1D-O polymer were prepared from sublimed 99.98% pure C$_{60}$ 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 2D-Rh polymer was obtained by subjecting 99.99% pure C$_{60}$ powder to a pressure of $P \approx 5$ GPa and temperature $T \approx 773$ K. The X-ray analysis, after the high-pressure treatment, confirmed that the crystal structure of the polymer is rhombohedral (space group: $R\bar{3}m$ $a = 9.22$ Å and $c = 24.6$ Å).[8] The 2D-T polymer was obtained in a similar way by subjecting 99.99% pure C$_{60}$ powder at $P \approx 2.2$ GPa and $T \approx 820$ K. The X-ray analysis of the samples after the HPHT treatment confirmed that the crystal structure of the polymer is tetragonal (space group: P4$_2$mmc $a = b = 9.082$ Å and $c = 14.990$ Å)[18] while the Raman analysis showed the typical spectrum of the 2D-T polymer of C$_{60}$. The samples used for the optical PL measurements have been characterized by means of preliminary micro-Raman and were selected from the batch material on the basis of their intense, clear, and spatially uniform Raman spectrum, typical of the 1D-O, 2D-Rh, and 2D-T polymeric phases with no detectable inclusions of other polymeric phases.[19, 20]

The PL spectra were recorded using a single monochromator JOBIN-YVON THR-1000 equipped with a CCD liquid-nitrogen cooled detector system. The spectral width of the system was ∼0.5 meV. The 488 nm line of an Ar$^+$ laser were used for excitation of the luminescence spectra. The laser power was kept at 2 mW measured directly in front of the high-pressure cell. The spectra were recorded with a spatial resolution of ∼20 μm by the use of microscope arrangement. Measurements of the PL spectra at high pressures were carried out using the diamond anvil cell (DAC) of Mao-Bell type.[21] The 4:1 methanol–ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration.[22]

3. RESULTS AND DISSCUSSION

The photoluminescence spectra of the pristine C$_{60}$, 1D-O, 2D-Rh, and 2D-T polymeric phases of C$_{60}$ at ambient conditions are shown in the Figure 1(a), while in Figure 1(b) the Raman spectra of these materials, at the same conditions with those of the PL spectra, are shown. The Raman spectra of the various polymeric phases, as characterized earlier, show significant differences between the pristine C$_{60}$, 1D-O, 2D-Rh, and 2D-T polymers of C$_{60}$ in the number of the phonon bands, their frequencies as well as their intensity distribution. The spectra in Figure 1(b) show typical features that are characteristic of these materials and provide assurance that the specimens selected for the photoluminescence measurements do not contain detectable inclusions of other polymeric phases.[9, 19, 23] The PL spectrum of C$_{60}$ single crystals, at normal conditions, consists of two broad peaks. The diffuse spectrum becomes well resolved when recorded at liquid helium temperature. The narrow bands associated with optical transitions from shallow defect levels are located near the bottom of the conduction-band and occupied by localized excitons[7] at low temperatures. The measurements at low temperature and high pressure have also revealed a band related with the transitions of the free excitons. The intensity of this band increases with pressure and its pressure coefficient is noticeably higher than those related to the localized excitons.[24]
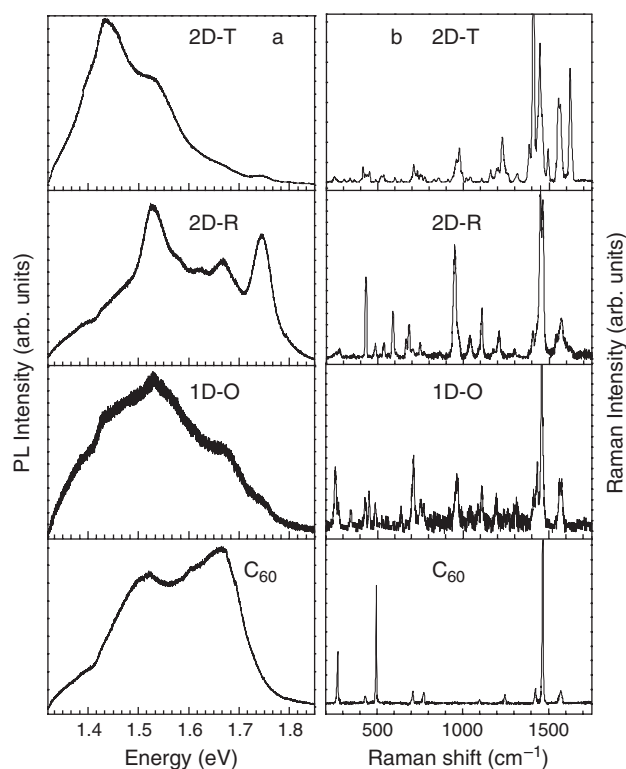
Fig. 1. Photoluminescence spectra (a) and Raman spectra (b) of the pristine C_{60}, 1D-O, 2D-Rh, and 2D-T polymeric phases of C_{60} at ambient conditions.

The PL spectrum of the linear 1D-O polymer is also diffuse but its structure differs from that of the pristine C_{60} in both the number of peaks and the intensity distribution among them. The planar polymers of C_{60} show additional changes in their PL spectra in comparison to the corresponding pristine C_{60} and 1D-O polymer recorded at normal conditions.[25] The differences refer to the onsets of the spectra, their structure, and the number of bands as well as to their intensity distribution. The PL spectrum of the 2D-T polymer consists of two main bands similar to that of the pristine C_{60}, but its onset is shifted to lower energy by ~0.14 eV and the intensity distribution between these bands is reversed. In addition, the PL spectrum of the 2D-T polymer contains two very weak bands at the high energy side, their positions and pressure behavior are coincident with bands observed in the 2D-Rh polymer, therefore are attributed to minute impurity of this phase in the 2D-T phase as we shall discuss below. On the contrary, the onset of the PL spectrum of the 2D-Rh polymer is almost the same with that of the pristine C_{60}, while the spectrum is better resolved even at room temperature and contains four relatively narrow intense bands. Note, that the quality of the PL spectra is better than those reported earlier[17] that is related, in our opinion, to higher purity and better crystallinity of the polymeric specimens used in the present study.

The important difference between the PL spectra of the two planar polymers to that of the pristine C_{60} refers to
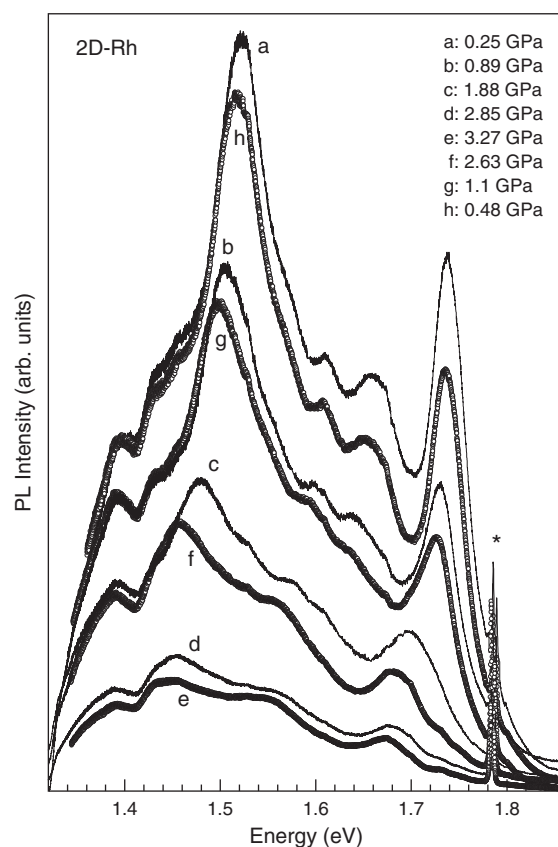
Fig. 2. Photoluminescence spectra of the 2D-Rh polymeric phase at various pressures and room temperature for increasing (solid line) and decreasing (open circles) pressure cycles. The peaks marked by the $*$ are the ruby luminescence bands.

their pressure behavior. Figure 2 shows the PL spectra of the 2D-Rh polymer at various pressures up to ~3.3 GPa for increasing and decreasing pressure cycles. Solid lines show the spectra related to the increasing pressure cycle while the spectra related to the decreasing pressure cycle are shown by open circles. The intensity distribution in the PL spectra is shown as measured: it is not corrected for the spectral response of the CCD detector. Thus, the rapid decrease of the PL intensity below 1.4 eV is related to the spectral cut-off of the CCD detector. When the pressure increases, the bands gradually shift to lower energies and the intensity of the PL spectrum decreases. The red pressure shift in the optical spectra of the fullerene-based materials is typical for solids with van der Waals intermolecular interaction,[6, 24] while the decrease of the PL intensity at the low energy part of the spectra most probably is due to the cut-off of the CCD detector. On the contrary, the pressure-induced decrease of the PL intensity at the high energy part of the spectra, which is a common feature for the pristine C_{60} and its polymeric phases, has another origin. It is associated, in our opinion, with the decrease of the fluorescence quantum yield that may be related to the pressure-induced enhancement of the singlet-triplet conversion. The proximity of the singlet and triplet electronic

Table I. Energy E_0 and pressure coefficients $\partial E/\partial P$ of the principal bands in the PL spectra of the pristine C_{60}, 2D-Rh, and 2D-T planar polymeric phases of C_{60}.

C_{60}[a]		2D-Rh[b]		2D-T[b]	
E_0 (eV)	$\partial E/\partial P$ (eV/GPa)	E (eV)	$\partial E/\partial P$ (eV/GPa)	E (eV)	$\partial E/\partial P$ (eV/GPa)
1.669^a	-0.086	1.747^c	-0.022	1.746	-0.021
		1.673	-0.025	1.534^c	-0.015
		1.622	-0.025	1.437	-0.013
		1.531	-0.028		
1.5^d		0.35^d		0.72^d	

[a]The data for the free exciton band in the PL spectrum were taken at $T = 10$ K.[24]
[b]The data for the PL spectra were taken at ambient conditions.
[c]These values, corresponding to the higher energy band in the PL spectra of the two polymeric phases and pristine C_{60}, are taken as the experimental energy gap values (see discussion).
[d]Calculated gap values.[5, 11, 12]

states in the C_{60} molecule[1] results in the relatively high phosphorescence of the fullerene that reduces the quantum yield of fluorescence. The energy gap between the singlet and triplet electronic states in the molecular solids decreases with the increase of pressure. This results in the enhancement of the singlet-triplet conversion, in the consequent decrease of the fluorescence and the increase of the phosphorescence intensities, respectively.

The pressure coefficients, $\partial E/\partial P$, for the various bands in the PL spectra of the 2D-Rh polymer, as well as the positions of the bands at ambient conditions E, are shown in Table I. The pressure coefficients for the various bands of the 2D-Rh polymer are in the region –0.022 eV/GPa to –0.028 eV/GPa. For comparison, the pressure coefficient of the free exciton band in the PL spectrum of the pristine C_{60} is about –0.086 eV/GPa.[24] The PL spectra of the 2D-T polymer at high pressure up to 2.5 GPa for the increasing (solid lines) and decreasing (open circles) pressure cycles are shown in Figure 3. The pressure behavior of the PL spectra is similar, in general, to that of the 2D-Rh polymer, but the pressure coefficients for the main bands of the 2D-T polymer are considerably smaller (see Table I). Note that the pressure dependence of the PL spectra for both planar polymers is reversible with pressure and all details of the spectra, that is, structure, band positions, and intensities of the PL spectra, are restored after pressure release.

The PL spectra of the 1D-O polymer for increasing (solid lines) and decreasing (open circles) pressure cycles are shown in Figure 4. The intriguing feature, in the pressure behavior of the 1D-O polymer, is the irreversibility of the transformation in the PL spectra during the increasing-decreasing pressure cycle. The structure of the PL spectra after pressure release differs from that of the initial material. The difference is most pronounced at the high-energy part of the PL spectrum, which resembles, after pressure release, somehow the spectrum of the 2D-Rh polymer. It is important to note, that irreversible transformation was also observed earlier in the high-pressure Raman study of the 1D-O polymer.[26] It was found that the 1D-O polymer is
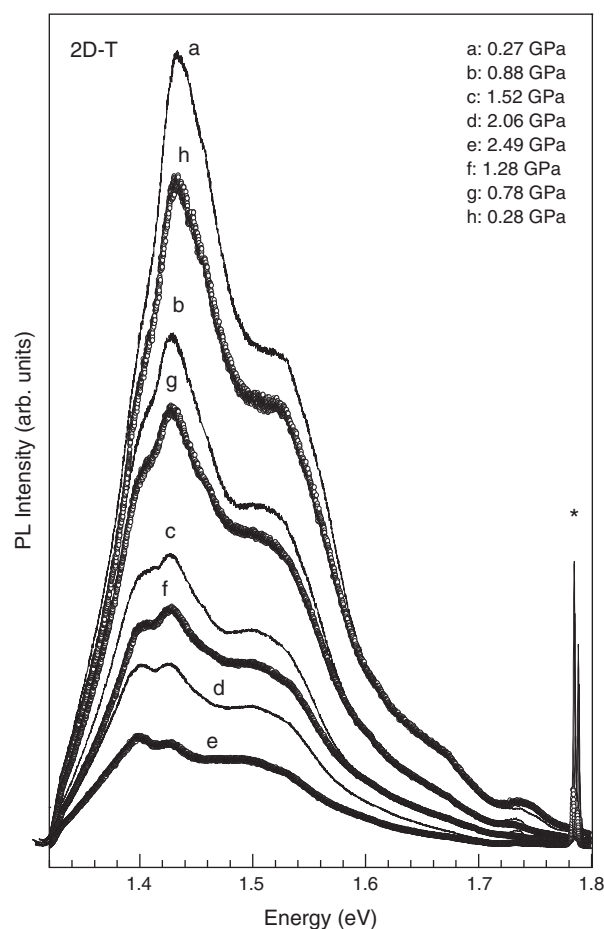
Fig. 3. Photoluminescence spectra of the 2D-T polymeric phase at various pressures and room temperature for increasing (solid line) and decreasing (open circles) pressure cycles. The peaks marked by the * are the ruby luminescence bands.

not stable with respect to the simultaneous application of high pressure and laser irradiation, which results in the pressure-assisted photo-induced polymerization of material at pressure even as low as 0.3 GPa.[26] Note that the 1D-O polymer at normal conditions is stable with respect to moderate laser irradiation intensity; therefore, the role of high pressure in the pre-orientation of the linear polymeric chains is crucial for the pressure-assisted photo-induced polymerization.
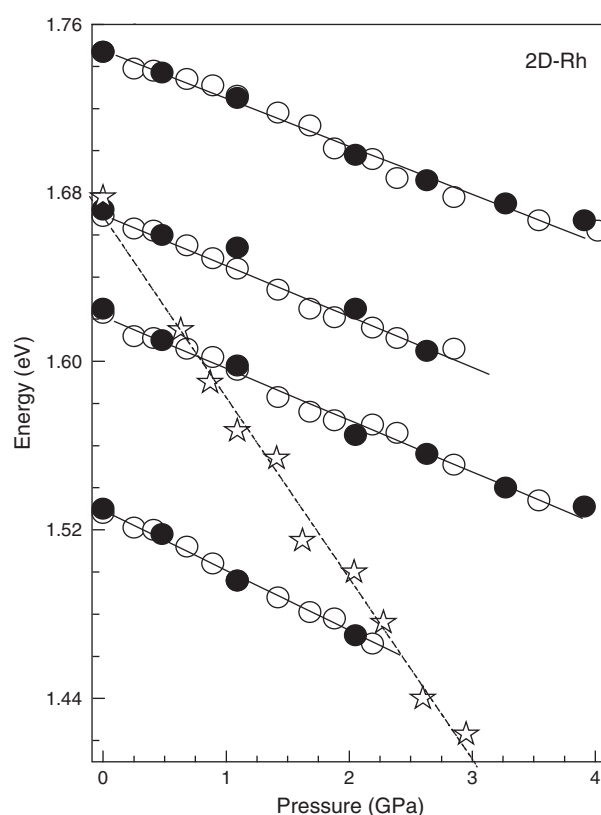
The pressure dependence of the band positions in the PL spectra of the 2D-Rh polymer is shown in Figure 5. The open (closed) circles refer to the increasing (decreasing) pressure cycles, respectively, while the stars show the pressure dependence of the free exciton band of the pristine C_{60}. The solid and dashed lines are linear fittings of the experimental data related to the bands of the 2D-Rh polymer and pristine C_{60}, respectively. Figure 6 shows the pressure dependence of main bands in the PL spectrum of the 2D-T polymer. The open (closed) symbols refer to the increasing (decreasing) pressure cycles; the stars show the same pressure dependence of the free exciton band. The solid and dashed lines are the linear fittings
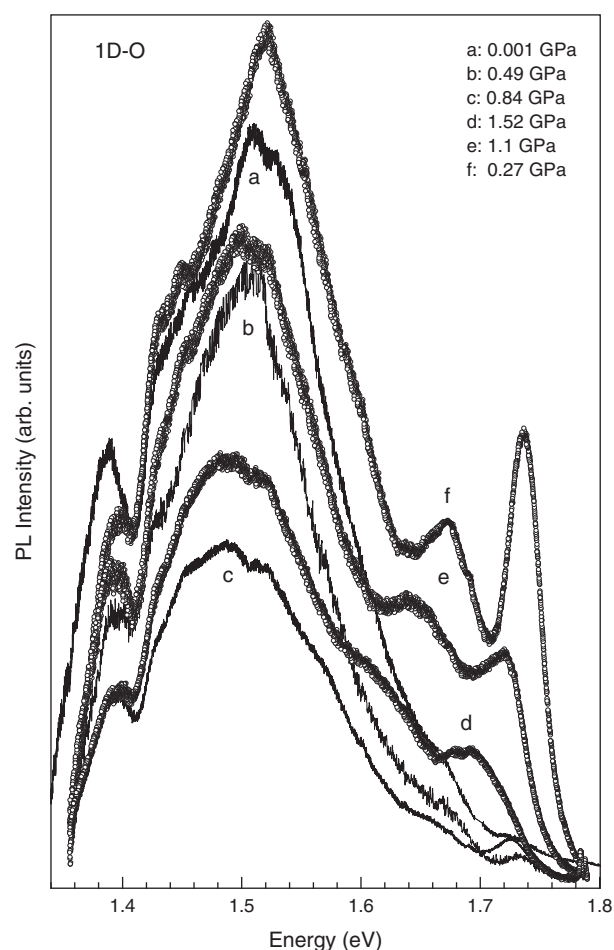
Fig. 4. Photoluminescence spectra of 1D-O polymeric phase at various pressures and room temperature for increasing (solid line) and decreasing (open circles) pressure cycles.

Fig. 5. Pressure dependence of the band positions in the PL spectra of the 2D-Rh polymer. Open (closed) symbols represent data recorded for increasing (decreasing) pressure cycles; stars show the pressure dependence of the free exciton band in the PL spectra of the pristine C_{60}.[24] Solid and dashed lines are linear fitting of the data for the 2D-Rh polymer and pristine C_{60}, respectively.

of the experimental data related to the bands of the 2D-T polymer and pristine C_{60}, respectively. Note that the slopes of the pressure dependencies differ for almost all bands of the two planar polymers except for the high-energy band. The initial position and the pressure dependence of this band coincide in the spectra of the 2D-Rh and 2D-T polymers, while its pressure coefficient $\partial E/\partial P = -0.022$ eV/GPa, being the same for the two polymers, differs from those of the other two bands of the 2D-T polymer (see Table 1). This is an indication that the specimens of the 2D-T polymer contain small inclusions of the rhombohedral polymer, which result in the appearance of the weak first band at $E = 1.747$ eV in the PL spectra. The fact, that the preliminary 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 characteristics of the PL spectra of the planar polymeric phases of C_{60} and the data related to the pressure dependence of the PL bands are clear indications that the electronic structure in these polymeric phases is changed with respect to the pristine C_{60}. Numerical calculations

of the electronic structure predict that the planar 2D-Rh and 2D-T polymers are indirect gap semiconductors with gap values of 0.35 eV and 0.72 eV for the rhombohedral and tetragonal polymeric phases, respectively.[11, 12] On the contrary, pristine C_{60} is a direct-gap semiconductor with gap energy $\sim$1.5 eV as it follows from the LDA numerical calculations.[5] The calculated gap values are noticeably smaller than the experimental values determined from the PL spectra of the polymeric phases (Table I). This discrepancy tends to be smaller for the pristine C_{60} in which the difference between the calculated and the experimental determination is smaller than those corresponding to the polymeric phases. The LDA approximation generally underestimates the energy gap value, so it seems to be more relevant to compare corresponding differences of calculated gap values versus experimentally determined gap values[11] of the polymers to that of pristine C_{60}. The differences of the calculated gap values for the rhombohedral and tetragonal polymers to that of the pristine C_{60}, are 1.15 eV and 0.78 eV, respectively, while the corresponding experimental values are –0.078 eV and 0.135 eV. These last values are significantly lower than the former. Furthermore, the most intriguing aspect in the PL behavior is
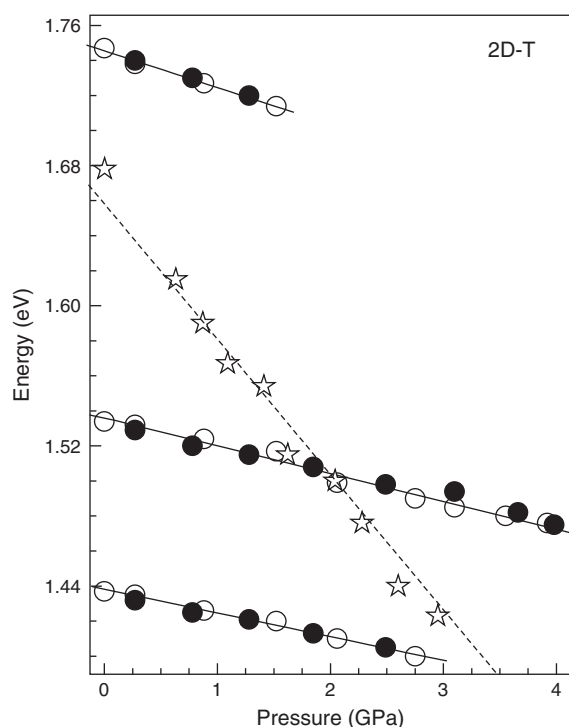
Fig. 6. Pressure dependence of the band positions in the PL spectra of the 2D-T polymer. Open (closed) symbols represent data recorded for increasing (decreasing) pressure cycles; stars show the pressure dependence of the free exciton band in the PL spectra of the pristine C$_{60}$.[24] Solid and dashed lines are linear fitting of the data for the 2D-T polymer and pristine C$_{60}$, respectively.

that the onset of the PL spectrum of the 2D-Rh polymer is shifted to higher energy with respect to the position of the free exciton band of the pristine C$_{60}$. Normally the electronic spectra of the polymers should be shifted to lower energies: this is related to the decrease of the intermolecular distances in polymeric phases in comparison to those of the pristine C$_{60}$ 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 in LDA approximation take into account the deformed fullerene molecule cage and the reduced intermolecular distances in the polymeric phases, nevertheless the experimental results of the present work are rather far apart from the calculated data.[11, 12] A possible reason for this discrepancy may be related, in particular, with the structure of the experimental PL spectra of polymers which represent mainly the direct phonon-assisted electronic transitions due to their relatively large intensity with respect to the indirect ones.

The most important feature in the pressure behavior of the PL spectra is the noticeable difference in the pressure coefficients of the 2D-Rh and 2D-T polymers despite the fact that their bulk moduli B_0 are very close (the values of B_0 are 14.4, 28.1, and 29.9 GPa for the pristine C$_{60}$, 2D-Rh, and 2D-T phases, respectively).[14,27] According to the X-ray diffraction measurements at high pressure

the compressibility of the planar polymers differs for the directions perpendicular and parallel to the polymeric sheets.[27] In particular, the compressibility of the 2D-Rh 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.[27] The large difference in the pressure coefficients of two polymers may be related to the difference in the in-plane compressibility of polymers. This means, in our opinion, that the contribution of the in-plane intermolecular interaction to the electronic structure of planar polymers is more important than the contribution of the out-of-plane interaction.

In conclusion, we have measured the PL spectra of the linear 1D-O polymer, 2D-Rh and 2D-T planar polymeric phases of C$_{60}$ and have found significant differences between them. These differences along with the difference in their pressure behavior provide the experimental proof that the polymerization of C$_{60}$ results in considerable changes of the electronic structure of the pristine C$_{60}$. The experimental data are qualitatively 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 polymeric C$_{60}$ phases.

References and Notes

1. F. Negri, G. Orlandi, and F. Zerbetto, *Chem. Phys. Lett.* 144, 31 (**1998**).
2. G. Herzberg and E. Teller, *Z. Phys. Chem. B* 21, 410 (**1933**).
3. Y. Wang, *J. Phys. Chem.* 96, 764 (**1992**).
4. P. A. Lane, L. S. Swanson, Q.-X. Ni, J. Shinar, J. P. Engel, T. J. Barton, and L. Jones, *Phys. Rev. Lett.* 68, 887 (**1992**).
5. S. Saito and A. Oshiyama, *Phys. Rev. Lett.* 66, 2637 (**1991**).
6. K. P. Meletov, V. K. Dolganov, O. V. Zharikov, I. N. Kremenskaya, and Yu. A. Ossip'yan, *J. Phys. (France)* 2, 2097 (**1992**).
7. W. Guss, J. Feldman, E. O. Göbel, C. Taliani, H. Mohn, W. Müller, P. Häussler, and H.–U. ter Meer, *Phys. Rev. Lett.* 72, 2644 (**1994**).
8. Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, *Science* 264, 1570 (**1994**).
9. K. P. Meletov, J. Arvanitidis, E. Tsilika, S. Assimopoulos, G. A. Kourouklis, S. Ves, A. Soldatov, and K. Prassides, *Phys. Rev. B* 63, 054106 (**2001**).
10. C. Hui and G. E. Scuseria, *Phys. Rev. Lett.* 74, 274 (**1995**).
11. S. Okada and S. Saito, *Phys. Rev. B* 55, 4039 (**1997**).
12. S. Okada and S. Saito, *Phys. Rev. B* 59, 1930 (**1999**).
13. A. M. Rao, P. Zhou, and K.-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X.-X. Bi, P. C. Eklund,

D. S. Cornett, M. A. Duncan, and I. J. Amster, *Science* 259, 955 (**1993**).

14. B. Sundqvist, *Adv. Phys.* 48, 1 (**1999**).
15. M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, and M. Perroux, *Phys. Rev. Lett.* 74, 278 (**1995**).
16. V. V. Brazhkin, A. G. Lyapin, and S. V. Popova, *JETP Lett.* 64, 11936 (**2000**).
17. U. D. Venkateswaran, D. S. Sanzi, J. Krishnappa, L. Marques, J.-L. Hodeau, M. Nunes-Regueiro, A. M. Rao, and P. C. Eklund, *Phys. Stat. Sol. (b)* 198, 545 (**1996**).
18. T. Wågberg, A. Soldatov, and B. Sundqvist, Private Communication, unpublished.
19. V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. M. Senyavin, R. Céolin, H. Szwarc, H. Allouchi, and V. Agafonov, *Phys. Rev. B* 61, 11936 (**2000**).
20. R. Moret, P. Launois, T. Wågberg, and B. Sundqvist, *Eur. J. Phys. B* 15, 253 (**2000**).
21. A. Jayaraman, *Rev. Sci. Instrum.* 57, 1013 (**1986**).
22. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.* 44, 1 (**1937**).
23. K. P. Meletov, G. A. Kourouklis, J. Arvanitidis, K. Prassides, and Y. Iwasa, *Phys. Rev. B* 68, 094103 (**2003**).
24. K. P. Meletov and V. D. Negrii, *JETP Lett.* 68, 248 (**1998**).
25. K. P. Meletov and G. A. Kourouklis, *Chem. Phys. Lett.* 403, 338 (**2005**).
26. K. P. Meletov, V. A. Davydov, A. V. Rakhmanina, V. Agafonov, and G. A. Kourouklis, *Chem. Phys. Lett.* 416, 220 (**2005**).
27. S. Kawasaki, A. Yao, Y. Matsuoka, S. Komiyama, F. Okino, H. Touhara, and K. Saito, *Solid State Commun.* 125, 637 (**2003**).

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