RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 57, NUMBER 6 1 FEBRUARY 1998-II

Temperature dependence of the photoluminescence in polymeric solid C_{60}

U. D. Venkateswaran and D. Sanzi
Department of Physics, Oakland University, Rochester, Michigan 48309

A. M. Rao and P. C. Eklund
Department of Physics and Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506

L. Marques and J.-L. Hodeau
Laboratoire de Cristallographie, CNRS, 38042 Grenoble, France

M. Núñez-Regueiro
EPM-Matformag, CNRS, 38042 Grenoble Cedex 09, France

(Received 3 November 1997)

Photoluminescence (PL) spectra of several polymeric phases of solid C_{60} synthesized under high pressure and high-temperature conditions have been studied in the temperature range between 300 and 15 K. The PL spectra of polymerized C_{60} show significant redshift and broadening relative to the PL spectrum of pristine C_{60}. Results on photopolymerized C_{60} films are also presented for comparison. A peak at 1.75 eV in the room temperature PL spectrum is found to be a characteristic of the rhombohedral phase. This peak is moderately strong at 300 K and disappears below 100 K in contrast to the behavior of other PL peaks, particularly the emission at about the same energy in pristine C_{60}. The 1.75 eV PL peak is absent at all temperatures in the photopolymer and in the orthorhombic phase. Our results show that the room temperature PL spectra and the temperature dependence of the PL can be used to distinguish the various polymeric phases.

[S0163-1829(98)50506-1]

A rich variety of metastable fullerene polymers, with interconnected C_{60} molecules and shorter interfullerene distance compared to pristine solid C_{60}, have been synthesized by several methods.[1] Common methods are irradiation by intense visible or ultraviolet light,[2] alkali-metal doping,[3] and treatment under high pressure and high temperature (HPHT).[4–7] A recently published pressure and temperature phase diagram of solid C_{60} shows that the structure of the fullerene polymers produced by HPHT treatments depend sensitively on the synthesis temperature and pressure.[8] Progressively higher temperatures and pressures produce one-, two-, and three-dimensional links between C_{60} molecules. Reported structures of HPHT polymers include: slightly compacted face-centered-cubic (fcc),[4] one-dimensional (1D) orthorhombic (O),[5] two-dimensional (2D) tetragonal (T),[5] and 2D rhombohedral (R).[4,5] The C_{60} molecules are connected as linear chains in the O phase and as square or hexagonal networks in the T and R phases, respectively.[5] Nuclear magnetic resonance studies[9] have shown that the C_{60} molecules in the R-phase polymer are connected by $2+2$ cycloadditions as proposed originally for photopolymerized C_{60}.[2] Theoretical calculations supporting the structure and stability of O, T, and R phases have also been carried out.[10]

X-ray diffraction[5,11] and vibrational spectroscopy (both Raman and infrared)[12,13] have been used extensively in the characterization of the HPHT polymers. However, not much is reported on the photoluminescence (PL) of these fullerene polymers. In this paper, we report a study of the temperature dependence of the photoluminescence (PL) spectra of pristine and photopolymerized C_{60} films and several phases of HPHT polymerized C_{60}.

C_{60} polymers were synthesized by subjecting microcrystalline C_{60} powder to different high pressure and high temperature treatments in a ‘‘belt-type’’ apparatus.[5] Details of the synthesis parameters have been reported earlier.[14,15] The structure of the polymers were confirmed by simulations of the x-ray diffraction data.[5,8] Powder samples of the polymer were mixed with 20 weight % KBr and pressed into pellets for PL studies.[16] PL was excited with less than 3 mW of 488 nm laser line focused to a size of $\sim 3\ \mathrm{mm} \times 0.5\ \mathrm{mm}$. The PL spectra were recorded using a cooled photomultiplier detector and photon counting electronics. A closed cycle helium refrigerator (Janis Model CCS-150) was used for studying the temperature dependence of the PL.

The comparison of the 15 K PL spectra of pristine and photopolymerized C_{60} films with those of HPHT polymerized phases is shown in Fig. 1. The spectrum labeled R+3D in Fig. 1 is from a rhombohedral sample in which the interplanar distance is about 10% less than that of the 2D R phase, which suggests some degree of three-dimensional (3D) bonding in the R+3D sample. The overall reduction in the PL intensity of the R+3D polymer compared to all other samples is suggestive of the formation of nonradiative centers at the higher pressure and temperature conditions used in the synthesis of this phase. In the case of pristine C_{60}, the main PL peak at ~ 1.69 eV has been attributed to the emission from bulk C_{60} and all other PL peaks to emissions from X traps.[17] The peak at 1.76 eV has been attributed to surface related excitonic X traps[17] in analogy with anthracene. Its intensity is seen to increase[18] for temperatures below 80 K, which is close to the glassy phase transition temperature. The PL features in the polymers are redshifted and broadened relative to those of pristine C_{60}. The HPHT treated polymers show a larger redshift and broadening compared to the photopolymer. The down shifting of PL peak energy in fullerene polymers implies a reduction in the highest occupied mo-

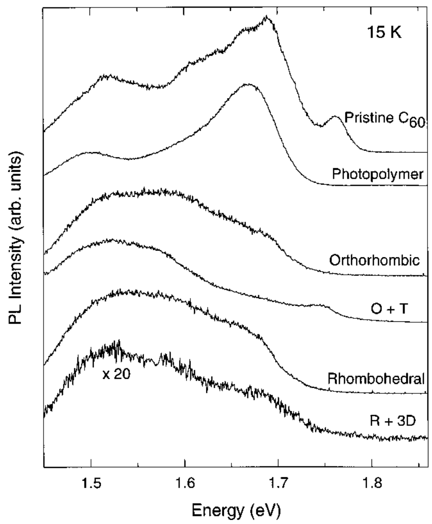

FIG. 1. Comparison of the 15 K PL spectra in pristine and photopolymerized C_{60} films with several pressure-polymerized phases of solid C_{60}.

lecular orbital-lowest unoccupied molecular orbital gap upon polymerization similar to the case of conjugated polymers[19] and helicene series and polyacenes.[20] Recent electronic structure calculations for the R-phase C_{60} polymer also predict a reduction in the energy gap compared to pristine C_{60}.[21] Electrical conductivity measurements on HPHT polymers have shown a decrease in the band gap[22] which is consistent with the overall redshift of the main PL peak (see Fig. 1). As regarding the PL line shape, it is reasonable to assume that the PL lines are inhomogeneously broadened due to the random location of defects or impurities.[23] In C_{60} polymers, a distribution in the size (or the molecular weight) of the polymeric units also contributes to the width of PL lines.

Figures 2(a)–2(e) show, respectively, the normalized PL spectra of pristine and polymerized forms of C_{60} at four representative temperatures. It should be noted that the overall PL intensity increases at low temperatures in all the samples, although the spectra shown in Figs. 2(a)–2(e) have been normalized. A sum of several Gaussian functions has been fitted to these inhomogeneously broadened PL spectra. The experimental data are shown as dots and the resulting fits, which are almost indistinguishable from the data, are shown as solid lines through the data points. The individual Gaussians are also shown below each of the PL spectra. In the case of pristine C_{60} [Fig. 2(a)], the room temperature (RT) PL spectrum is best fit with three Gaussians while the 15 K PL spectrum reveals five distinct peaks which are considerably narrow. The PL spectra of the photopolymer at all temperatures can be resolved into three broad Gaussian peaks [see Fig. 2(b)]. There is an overall broadening and redshift relative to pristine C_{60} especially for temperatures below 100 K. Similar to the photopolymer, the PL spectra of the O-phase polymer [Fig. 2(c)] can also be fit with three broad Gaussians at all temperatures. Two of these peaks are more or less at the same energy (1.5 and 1.68 eV) as in the photopolymer, whereas the middle peak at ~ 1.58 eV is redshifted in the O phase. It should be noted, however, that the PL line shape in the O phase is quite different from that of the photopolymer.

In the case of the R sample [Fig. 2(d)], at RT there are two broad peaks at 1.52 and 1.67, and a relatively narrow peak at 1.75 eV. The first two peaks are at about the same energy as two of the peaks in Figs. 2(b) and 2(c). As temperature is lowered, the 1.75 eV peak decreases in intensity and becomes very weak at 100 K when an additional peak at 1.58 eV develops. The 15 K PL spectra of both the O and R phases are very similar [see Figs. 2(c) and 2(d)]. The O+T sample, which is a 50:50 mixture of the O and T phases, contains four Gaussians at RT and six at 15 K [see Fig. 2(e)]. The line shape and peak positions of the O+T phase PL at 15 K suggest that one can view this spectrum as a combination of those of pristine C_{60} and the O phase. However, there was no evidence for the presence of pristine C_{60} in the O+T sample from the RT Raman work reported earlier.[12] Subtraction of the O phase PL from that of O+T generates several undulations which cannot meaningfully be interpreted as from the T phase. Further work on *pure* T phase is needed for more detailed information about this phase.

The PL peak at 1.75 eV seen in the R phase at RT is specific only to the R phase and is seen most strongly at RT. At low temperatures, the intensity of this peak *decreases* gradually until it disappears around 100 K; its energy position remains the same within the uncertainty of the fitted peak position, at all temperatures between 300 K and 100 K. The R+3D phase (spectrum not shown) also contains a PL peak at 1.75 eV at RT with moderate intensity, which disappears at low temperatures. This observation strengthens the conjecture that the 1.75 eV PL peak at RT is characteristic of the R phase. Although not as pronounced as in the R-phase samples, the PL spectra of O+T phase [Fig. 2(e)] also has a PL peak at ~ 1.75 eV at RT. However, this peak in the O+T sample persists with almost the same intensity at all temperatures down to 30 K and a slight *increase* in intensity is observed at 15 K—a behavior somewhat similar to that seen for the 1.75 eV peak in pristine C_{60}.[18] Thus the RT PL spectra *and* the temperature dependence of the PL can be used to identify the presence of O, R, or T phases in HPHT-polymerized C_{60} samples.

Although the temperature dependence of the 1.75 eV PL peak in the R phase is unusual, its pressure shift (~ 0.03 eV/GPa), as reported earlier,[14] is the same as that of the other PL peaks in the R phase. The temperature behavior of the 1.75 eV PL peak is atypical for excitonic transitions and is suggestive of a stronger electron-phonon coupling for this transition compared to other peaks. It is interesting to note that the Raman spectrum of the R-phase polymer[4,12] contains a strong phonon peak at 1408 cm^{-1}, which is not present in the O or O+T phases. The role of this phonon in the vibronic transitions observed in PL needs to be investigated further. Kozlov and Yakushi[7] have also reported a PL peak at 1.75 eV at RT in the R-phase polymer. They compared this peak with the 1.76 eV peak seen in the low-temperature PL spectrum of pristine C_{60}, that was attributed to surface excitonic emission from X traps[17] and ascribed it to defects related possibly to deformed or partially destroyed C_{60} cages. Our results (presented here and in Ref. 18) show that the temperature dependence of the excitonic X traps in pristine C_{60} is opposite to that of the 1.75 eV peak in the R phase. Therefore, it is reasonable to think that these peaks have different origins in pristine C_{60} and in the R phase despite the close proximity of their emission energy.

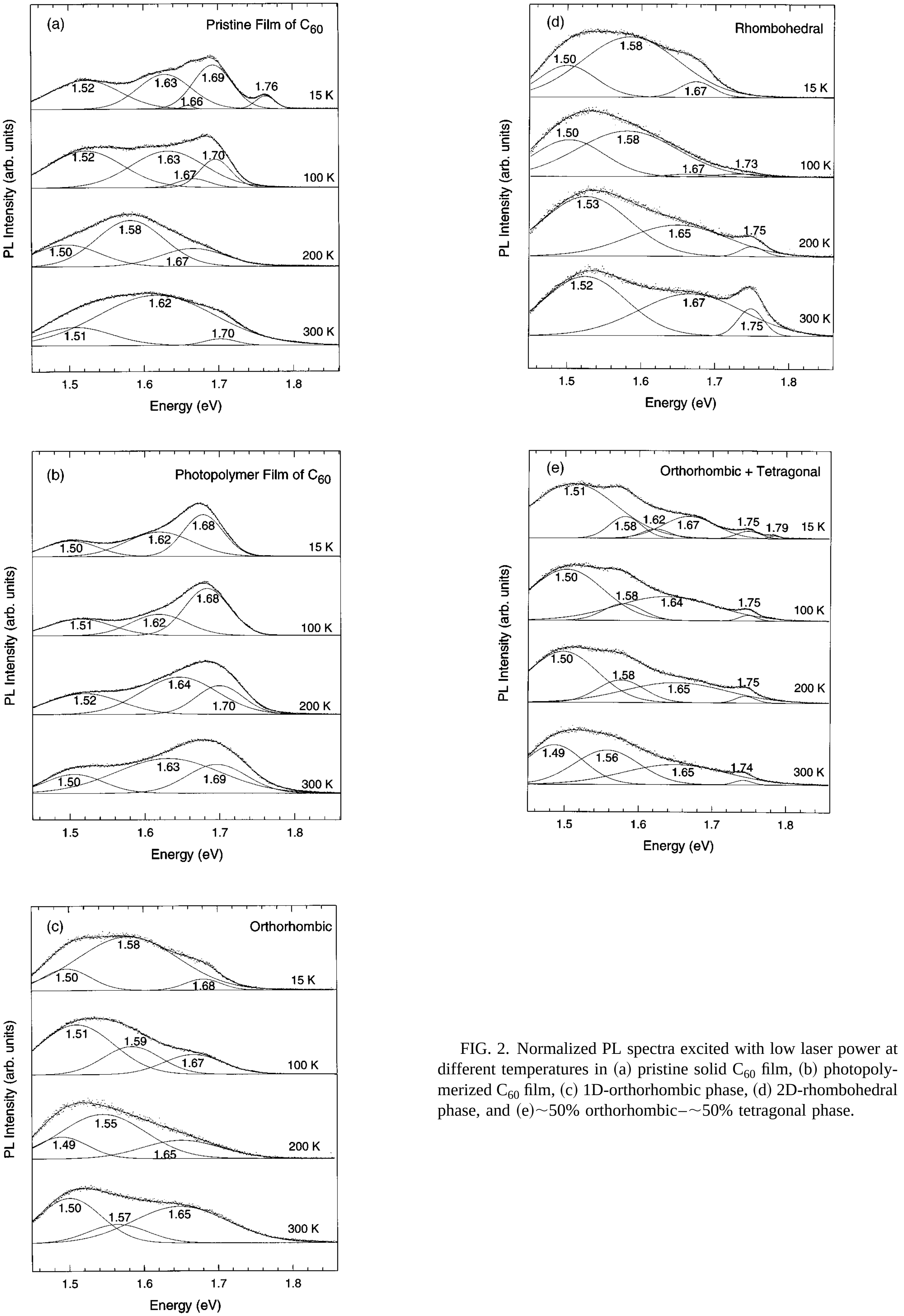

FIG. 2. Normalized PL spectra excited with low laser power at different temperatures in (a) pristine solid C_{60} film, (b) photopolymerized C_{60} film, (c) 1D-orthorhombic phase, (d) 2D-rhombohedral phase, and (e)~50% orthorhombic–~50% tetragonal phase.

In pristine C_{60}, an orientational ordering transition[24] and a ‘‘glassy’’ phase transition[25] occur at ~ 250 K and ~ 90 K, respectively. Since the 1.76 eV PL peak becomes evident below 100 K, it is possible that this peak is associated with some defect related excitonic emission in the glassy phase rather than surface related X traps. In the case of the R-phase polymer, the 1.75 eV peak might be due to some defects in the hexagonal network formed at the high temperature (700 °C) used for synthesis. It is possible that a reordering in the R-phase polymer network at low temperature causes the disappearance of the 1.75 eV peak below 100 K. Temperature-dependent structural studies will be needed to test this possibility. Since the 1.75 eV peak has been observed only in polymers synthesized at temperatures above 400 °C, it is reasonable to think that applying pressure first and then increasing the temperature during synthesis plays a role in creating the emission centers responsible for the 1.75 eV peak. The absence of this peak in the photopolymer and in the O phase that was synthesized at 250 °C suggests that there is a strong influence of the synthesis conditions on the formation and properties of the different polymeric phases.

From the structural and optical spectroscopic studies available on polymerized C_{60}, it is clear that the formation of intermolecular bonds lowers the original icosahedral (I_h) symmetry of the C_{60} molecules. The symmetry reduction can be treated as a perturbation which activates many new vibrational and electronic states. Consequently, in the polymerized structures, new peaks appear in the Raman and IR spectra, and the PL spectra are broadened significantly. Redshifts in the peak frequencies are also observed. The degree of polymerization, as reflected by the redshifts of peak positions and line shape changes in the vibrational and PL spectra, depends on the method and synthesis conditions. A strong Raman mode at 1408 cm^{-1} and a PL peak at 1.75 eV which disappears at temperatures below 100 K are found to be unique to the R-phase polymer.

The work at Oakland University was supported by Cottrell College Science Award No. CC-3293 by Research Corporation and by the OU foundation. The work at the University of Kentucky was supported by NSF Grant No. OSR-9452895.

---

[1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996), Chap. 7.

[2] A. M. Rao, P. Zhou, K.-A. Wang, G. T. Hager, J. M. Holden, Ying Wang, W. T. Lee, Xiang-Xin Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science **259**, 955 (1993).

[3] S. Pekker, A. Jánossy, L. Mihály, O. Chauvet, M. Carrard, and L. Forró, Science **265**, 1077 (1994).

[4] 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).

[5] M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, and M. Perroux, Phys. Rev. Lett. **74**, 278 (1995).

[6] I. O. Bashkin, V. I. Rashchupkin, A. F. Gurov, A. P. Moravsky, O. G. Rybchenko, N. P. Kobelev, Ya. M. Soifer, and E. G. Ponyatovsky, J. Phys.: Condens. Matter **6**, 7491 (1994).

[7] M. E. Kozlov and K. Yakushi, J. Phys.: Condens. Matter **7**, L209 (1995); M. E. Kozlov, M. Tokumoto, and K. Yakushi, Synth. Met. **86**, 2349 (1996).

[8] L. Marques, J.-L. Hodeau, M. Núñez-Regueiro, and M. Perroux, Phys. Rev. B **54**, R12 633 (1996).

[9] C. Goze, F. Rachdi, L. Hajji, M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, and M. Mehring, Phys. Rev. B **54**, R3676 (1996); P.-A. Persson, U. Edlund, P. Jacobsson, D. Johnels, A. Soldatov, and B. Sundqvist, Chem. Phys. Lett. **258**, 540 (1996).

[10] C. H. Xu and G. E. Scuseria, Phys. Rev. Lett. **74**, 274 (1995).

[11] V. A. Davydov, L. S. Kashevarova, O. G. Revin, V. Agafonov, P. Dubois, R. Ceolin, and H. Szwarc, Mol. Mater. **7**, 285 (1996).

[12] A. M. Rao, P. C. Eklund, J.-L. Hodeau, L. Marques, and M. Núñez-Regueiro, Phys. Rev. B **55**, 4766 (1997).

[13] K. Kamarás, Y. Iwasa, and L. Forró, Phys. Rev. B **55**, 10 999 (1997).

[14] U. D. Venkateswaran, D. Sanzi, J. Krishnappa, L. Marques, J.-L. Hodeau, M. Núñez-Regueiro, A. M. Rao, and P. C. Eklund, Phys. Status Solidi B **198**, 545 (1996).

[15] A. M. Rao, P. C. Eklund, U. D. Venkateswaran, J. Tucker, M. A. Duncan, G. M. Bendele, P. W. Stephens, J.-L. Hodeau, L. Marques, M. Núñez-Regueiro, I. O. Bashkin, E. G. Ponyatovsky, and A. P. Morovsky, Appl. Phys. A: Solids Surf. **64**, 231 (1997).

[16] Mixing polymeric C_{60} powder with KBr is a convenient way to study the PL from micron size grains. It has been verified in a separate experiment that the PL spectra of the R-phase polymer remain the same with and without KBr addition both at RT and 20 K.

[17] W. Guss, J. Feldmann, E. O. Göbel, C. Taliani, H. Mohn, W. Müller, P. Haüssler, and H.-U. ter Meer, Phys. Rev. Lett. **72**, 2644 (1994).

[18] U. D. Venkateswaran, M. G. Schall, Y. Wang, P. Zhou, and P. C. Eklund, Solid State Commun. **96**, 951 (1995).

[19] D. D. Bradley and R. H. Friend, J. Phys.: Condens. Matter **1**, 3671 (1989).

[20] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley and Sons, London, 1970).

[21] S. Okada and S. Saito, Phys. Rev. B **55**, 4039 (1997).

[22] T. L. Makarova, A. Ya. Vul, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmannina, and P. Scharff (unpublished).

[23] Y. Wang, J. M. Holden, A. M. Rao, P. C. Eklund, U. D. Venkateswaran, D. Eastwood, R. L. Lidberg, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **51**, 4547 (1995).

[24] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCaulay, Jr., A. B. Smith III, and D. E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).

[25] C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, and J. R. Salem, J. Phys. Chem. **95**, 9 (1991); R. Tycko, R. C. Haddon, G. Dabbagh, S. H. Glarum, D. C. Douglas, and A. M. Mujsce, *ibid.* **95**, 518 (1991).