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## Photoluminescence of solid $C_{60}$

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**Abstract.** Photoluminescence investigations have been performed on solid  $C_{60}$ ,  $C_{60}/C_{70}$  and  $C_{70}$  samples. The photoluminescence spectra of  $C_{60}$  exhibit a main peak at 1.69 eV and well resolved peaks at 1.65 eV, 1.60 eV and 1.5 eV which we assign to different phonon replicas. The temperature dependence of the photoluminescence spectrum is also investigated. We find that the 1.77 eV emission peak, which appears at low temperature, clearly originates from  $C_{60}$ . The enhancement of this peak seems to be closely related to the amount of  $C_{70}$  existing in  $C_{60}$  samples. In this case  $C_{70}$  acts as an impurity leading to a local distortion of the pure  $C_{60}$  structure.

### 1. Introduction

Recent success in efficiently synthesizing  $C_{60}$  has generated much interest in the physical properties of this new class of molecular crystals [1, 2]. Moreover, the observation of superconductivity in the alkali-metal-doped  $C_{60}$  ( $M_3C_{60}$  phase) has attracted even more attention [3, 4]. As a consequence, in order to understand the unusual properties of this new class of materials, many theoretical calculations as well as experimental investigations have been performed.

The isolated  $C_{60}$  molecule has an icosahedral symmetry ( $I_h$ ) [1] and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is about 1.9 eV [5]. At room temperature,  $C_{60}$  molecules aggregate to form a molecular crystal with rotating molecular units on an FCC Bravais lattice [6]. The  $C_{60}$  crystal is an insulator with an energy gap originating from a narrow valence band (HOMO) and a narrow conduction band (LUMO) at the X point of the Brillouin zone. The computed energy value is 1.5 eV [7]. Exciting an electron from the HOMO to the LUMO level generates an electron-hole pair with strong correlation because it is confined to the volume of the  $C_{60}$  molecule. In the  $C_{60}$  crystal, owing to the weakness of the Van der Waals interactions, this confinement is essentially preserved. As in conjugated polymers, such as polythiophene or poly(para-phenylene-vinylene) (conducting polymers with a non-degenerate ground state), the related elementary optical excitations are polarons-excitons and they may decay radiatively to produce luminescence. Because of the strong correlation, these states are expected to occur below  $E_g$  [8].

Recently, the photoluminescence of  $C_{60}$  has been analysed extensively by different groups [9–14]. The more recent papers especially, report the temperature dependence

of the photoluminescence and discuss possible assignment of the emission peaks [11–14]. However, there are some discrepancies in the conclusions of these studies and, in order to clarify the interpretation of the photoluminescence of  $C_{60}$ , we present a comparison between the photoluminescence spectra measured on pristine  $C_{60}$  (thin film and powder), a  $C_{60}/C_{70}$  mixture thin film (6%  $C_{70}$ ) and  $C_{70}$  (powder).

## 2. Experimental details

### 2.1. Sample preparation

Our fullerene production technique used the standard arc procedure followed by extraction with toluene [2]. The dark red solution obtained was a mixture of  $C_{60}$  and  $C_{70}$  molecules with traces of higher fullerenes. Toluene was removed by evaporation giving a black powder. Pure  $C_{60}$  and 90% rich  $C_{70}$  (called  $C_{70}$  in the following) were collected by alumina column chromatography using pure heptane and pure toluene as eluents [15]. The residual amount of solvent was eliminated by heating the final powder at 200 °C for 2 h under a dynamic vacuum of  $10^{-5}$  Torr. Finally, pristine  $C_{60}/C_{70}$  and  $C_{60}$  powders were deposited in thin films onto silicon substrates by sublimation in a vacuum of about  $10^{-6}$  Torr. The  $C_{60}/C_{70}$  mass ratio in the  $C_{60}/C_{70}$  thin film was estimated from the relative intensity of the Raman lines assigned to  $C_{70}$  and  $C_{60}$  vibrational modes. These intensities were compared with those of Raman spectra carried out on well characterized samples. The ratio was found to be about 1/0.06.

### 2.2. Experimental set-up

Photoluminescence spectra of  $C_{60}$ ,  $C_{60}/C_{70}$  and  $C_{70}$  samples were carried out in the temperature range 5–300 K using a helium flow cryostat. The spectra were obtained in a back-scattering arrangement using a standard Coderg T800 triple-monochromator spectrometer; an argon ion laser with 5154 Å and 4800 Å lines as exciting light source; and C31034 RCA and Centronics 4283 TIR photomultipliers and photon-counting electronics. The instrumental linewidth was fixed to about  $6\text{ cm}^{-1}$ . To prevent laser-induced damage of the samples, the incident power was limited to 10 mW and the incident beam was defocused.

## 3. Results

### 3.1. Low temperature photoluminescence of fullerenes

Figure 1 shows the photoluminescence (PL) spectra recorded at low temperature ( $T = 5\text{ K}$ ) on different samples:

- (a) a thin film of  $C_{60}/C_{70}$  (6%  $C_{70}$ ) (figure 1(a)).
- (b) a thin film of  $C_{60}$  (figure 1(b)).
- (c)  $C_{60}$  powder (figure 1(c)).
- (d)  $C_{70}$  powder (figure 1(d)).

The four spectra exhibit significant differences which we analyse.

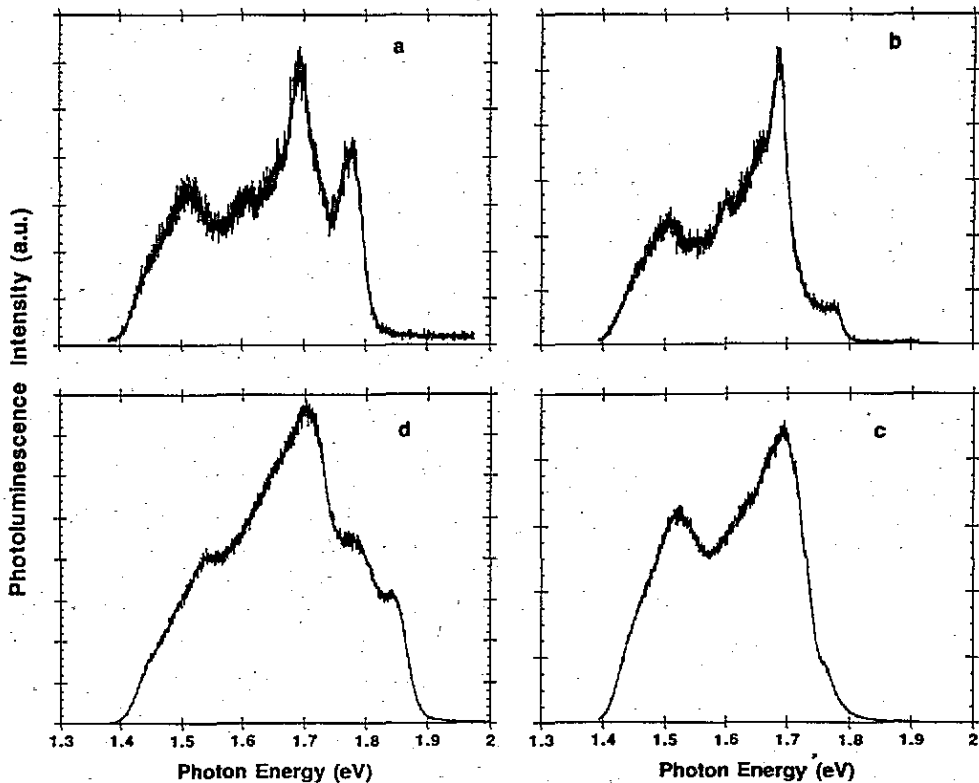


Figure 1. Low temperature photoluminescence ( $T = 10$  K) observed at  $\lambda_L = 5145$  Å for: (a)  $C_{60}/C_{70}$  thin film; (b)  $C_{60}$  thin film; (c)  $C_{60}$  powder; (d)  $C_{70}$  powder.

**3.1.1. The 1.77 eV emission peak.** The low temperature PL spectrum obtained on the  $C_{60}/C_{70}$  thin film shows a strong peak at 1.77 eV (figure 1(a)). In the case of the  $C_{60}$  samples (thin film and powder; see figures 1(b) and 1(c)), this same peak appears but with a smaller intensity.

The PL spectrum ( $T = 10$  K) carried out on a  $C_{60}/C_{70}$  thin film (20%  $C_{70}$ ) using the same excitation energy ( $E_L = 2.41$  eV) has been recently published and the main peak of the PL spectrum in this case was also located at 1.77 eV [9].

The profile of the PL observed in  $C_{60}$  film deposited on a  $CaF_2$  substrate is close to that displayed in [9] with a strong peak at 1.77 eV [10]. In the latter study, a sample dependence of the PL profile is also demonstrated and, consequently, the presence of the 1.77 eV peak can be attributed to the sample's inhomogeneity and/or to an underestimate of the  $C_{70}$  concentration in the samples.

The photoluminescence measured on  $C_{70}$  powder (figure 1(d)) appears in the same spectral region as in  $C_{60}$  but displays a distinctly different fine structure. Two well defined peaks of equal intensities peaking around 1.77 eV and 1.85 eV are observed at low temperature. As the second peak does not appear in the PL of  $C_{60}$ , we strongly believe that:

- the 1.82 eV peak originates from pure  $C_{70}$ ;
- the 1.77 eV peak emission originates from  $C_{60}$ .

To summarize, from the series of results discussed above, we state that the 1.77 eV emission peak, clearly originating from  $C_{60}$ , is correlated with the amount of  $C_{70}$  in the samples under consideration. An initial explanation is to consider that  $C_{70}$  acts as a substitution defect leading to local distortion of the  $C_{60}$  structure with, consequently, the appearance of the 1.77 eV emission.

In order to discuss this statement, we compare our results with those reported in the more recent of the published works [13, 14].

(i) The 1.77 eV line is absent in the PL spectra obtained from a pure  $C_{60}$  thin film on Si substrate in the temperature range 78–300 K [11, 13]. In these experiments, a shoulder at 1.71 eV (with a significant dependence upon the excitation energy) has been observed and assigned to emission arising from traces of  $C_{70}$  [13]. With regard to the shape of the PL curve of  $C_{70}$  (figure 1(d); see also figure 1.D in [14]), this assignment seems to be justified. However, it is important to distinguish between this shoulder and the well defined 1.77 eV peak previously observed in our low-temperature spectra.

(ii) A few months ago, the low-temperature PL spectra, excited with a 5145 Å line, of a  $C_{60}/C_{70}$  composite film (15%  $C_{70}$  concentration), a purified  $C_{60}$  film (4%  $C_{70}$  concentration) and a pure  $C_{70}$  film were published [14]. The authors of this study were the first to state that the 1.82 eV peak originates from the  $C_{70}$  contamination and the 1.77 eV peak originates from  $C_{60}$ . In disagreement with us, they assign the 1.77 eV emission as due to  $C_{60}$  interacting with oxygen. We discuss, in the next part of this paper, this assignment.

**3.1.2. The main peak and the phonon replica.** The PL spectrum obtained for the  $C_{60}$  thin film is shown in figure 1(b). The main peak, observed at 1.68 eV, is very sharp and very well resolved. Two weak sidebands emerge at the low-energy side of the peak, at 1.65 eV (shoulder) and 1.60 eV. The 1.60 eV peak has been observed previously [11–14], while the shoulder at 1.65 eV is only clearly observed in [13]. A precise measurement of the shift with respect to the main peak energy show that these two peaks can be assigned to phonon replicas with energy separations of about  $250\text{ cm}^{-1}$  and  $730\text{ cm}^{-1}$  respectively, associated with Raman modes.

With respect to the energy of the emission peaks in the PL spectrum of the  $C_{60}/C_{70}$  mixture [14], we observe a significant downshift (of about 0.03–0.05 eV) of the peaks in our  $C_{60}$  PL spectrum. The 1.68 eV, 1.60 eV and 1.50 eV peaks are pointed at 1.71 eV, 1.65 eV and 1.55 eV respectively in [14]. The same shift between the PL peaks in a  $C_{60}/C_{70}$  mixture and pure  $C_{60}$  has been also observed by Graham and collaborators [13]. The 1.69 eV, 1.65 eV, 1.60 eV and 1.51 eV peaks in pure  $C_{60}$  are shifted to 1.71 eV, 1.67 eV, 1.62 eV and 1.53 eV respectively in the  $C_{60}/C_{70}$  mixture [13]. Finally, in [14], a peak at 1.46 eV is also observed in the PL of the  $C_{60}/C_{70}$  mixture. We suggest assigning this peak to  $C_{70}$  emission. Indeed a peak close to this value appears in the PL spectrum of pure  $C_{70}$  (the shoulder in figure 1.D in [14] and figure 1(d) of this work).

In [12], with regard to the analogous behaviour of the peaks at 1.60 eV and 1.77 eV, it was claimed that these two peaks belong to the same progression. Our measurements cast doubt on this statement. Indeed, in the PL spectrum of  $C_{60}/C_{70}$  thin film (figure 1(a)), the peak at 1.77 eV is better defined and has a stronger intensity than the 1.60 eV peak.

Finally, the PL spectrum of a  $C_{60}$  thin film shows a peak at 1.5 eV, previously reported in [9–14]. In contrast to all previous works, the 1.5 eV peak appears with

a strong intensity with respect to the other peaks in our PL spectrum. This result is in part related to experimental conditions and more precisely to the flat response of our C31034 RCA photomultiplier in the energy range 1.4–2 eV. In other words the profile of the PL spectrum is not distorted by the response of the PMT used in these experiments. To confirm this statement, a PL spectrum has been recorded on the same  $C_{60}$  thin film using a Centronics 4283 TIR PMT. The response of this PMT is maximum around 2.6 eV and strongly decreases at low energy. This spectrum is displayed in figure 2. This profile is close to the one obtained in [11–14]. This result, then, allows us to compare the previously published results with the present data in the high-energy range and to relate clearly the significant decrease of the 1.5 eV peak intensity to instrumental factors (in particular, the response of the PMT used in the different experiments). Consequently, the strong intensity of the 1.5 eV peak (especially at high temperature) seems to be an intrinsic feature of the PL spectrum. Some authors have assigned this peak to a phonon replica with an energy separation of 0.18 eV close to the frequency of the  $A_g$  Raman mode ( $1468\text{ cm}^{-1}$ ).

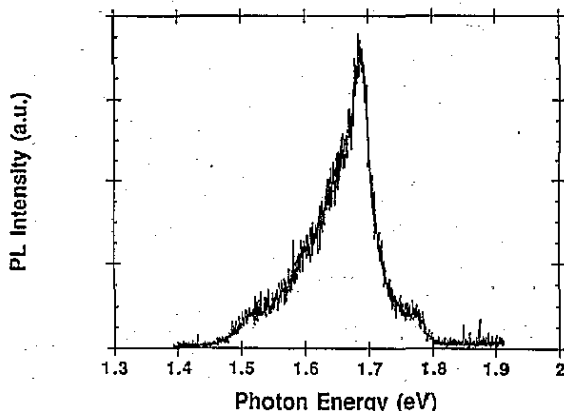


Figure 2. Low-temperature photoluminescence of a  $C_{60}$  thin film obtained with a Centronics 4283 TIR PMT. All other experimental factors (instrumental resolution, incident wavelength and incident laser power) have been kept constant with respect to figure 1(b).

**3.1.3.  $C_{60}$  thin film and  $C_{60}$  powder.** A comparison between the PL spectra obtained for a  $C_{60}$  thin film and  $C_{60}$  powder is given in figure 1(b) and (c). In the  $C_{60}$  powder, the PL is not well resolved and the lines at 1.60 eV and 1.65 eV are not observed. An enhancement of the low-energy peak at 1.5 eV is also found. The relative intensity of this peak with respect to the 1.68 eV peak ( $\rho = I_{1.5\text{ eV}}/I_{1.68\text{ eV}}$ ) is significantly stronger in  $C_{60}$  powder ( $\rho = 70\%$  at  $T = 10\text{ K}$ ) than in  $C_{60}$  thin film ( $\rho = 40\%$  at  $T = 10\text{ K}$ ). All peaks are much broader and slightly shifted to the high-energy side. In particular, the width of the 1.68 eV peak is twice as great. The peak broadening can be viewed as an indication of solid-state effects. On the other hand, by analogy to the behaviour of the PL in conducting polymers [8], the broadening and the shift of the peaks may be correlated with significant inhomogeneity and disorder of the  $C_{60}$  powder. Joint x-ray diffraction and PL experiments performed on the same samples are necessary to make any conclusions on this point.

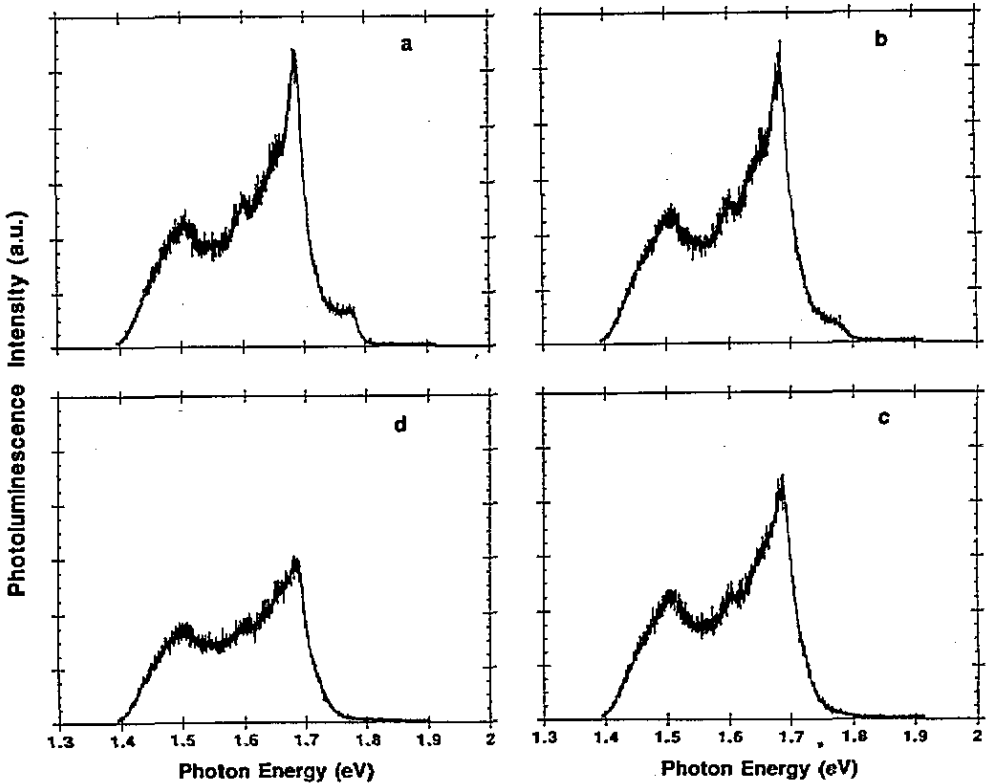


Figure 3. PL spectra of a  $C_{60}$  thin film collected at different temperatures: (a)  $T = 10$  K; (b)  $T = 50$  K; (c)  $T = 100$  K; (d)  $T = 150$  K ( $\lambda_L = 5145$  Å). All spectra have been displayed with the same intensity scale.

### 3.2. Temperature dependence of the photoluminescence of $C_{60}$ thin film

The PL spectra of the pure  $C_{60}$  in the temperature range from 78 K to 300 K have been previously analysed [11–13]. In the present study, in the same temperature range, we have observed the same behaviour of the PL with temperature as described in [11–13]. In summary, the signal increases strongly with decreasing temperature and a slight shift to the high-energy side and a significant narrowing of the peaks are observed. To complete these data, we have focused our attention on the temperature dependence of the PL in the range 5–150 K (figure 3(a)–(d)). The following behaviour can be emphasized: the PL intensity increases monotonically with decreasing temperature. No significant shifts of the peaks are observed in this temperature range; however a broadening of the peaks occurs when the temperature increases. Consequently, the 1.65 eV peak is no longer found and the 1.60 eV peak is not well resolved above 50 K. The ratio  $\rho = I_{1.5 \text{ eV}}/I_{1.69 \text{ eV}}$  increases when the temperature increases, from 40% at 5 K to 60% at 150 K. At high temperature ( $T > 200$  K), the 1.5 eV peak is the strongest one in the PL spectrum. Finally, the peak at 1.77 eV appears only at low temperature (below 90 K). The temperature dependence described above is significantly different from that observed in [14], where the PL goes through a maximum at about 100 K, and decreases strongly for a further reduction of temperature. This quenching of the main line emission is related to the

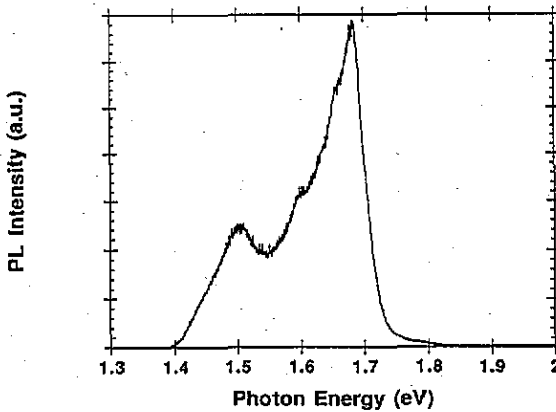


Figure 4. Low-temperature photoluminescence ( $T = 10$  K) at  $\lambda_L = 5145$  Å of a highly purified  $C_{60}$  thin film.

appearance of the 1.77 eV and 1.82 eV emission peaks [14].

#### 4. Discussion

PL provides direct evidence for the formation of a neutral excited state and well resolved peaks can be observed in the experiments performed on thin films. At low temperature, our PL spectrum displays  $250\text{ cm}^{-1}$ ,  $730\text{ cm}^{-1}$  and  $1468\text{ cm}^{-1}$  phonon replicas. We give in table 1 a comparison of the energy of the peaks observed in the different studies devoted to the analysis of the PL of  $C_{60}$ . Our results are close to those of Matus *et al* [14] and Lane *et al* [12]. They essentially cast doubt on the peak assignments proposed by other authors [11–14], especially for the 1.77 eV peak.

Table 1. Comparison of the different peak energies observed in the photoluminescence of  $C_{60}$ . In [14], the peaks are shifted to the high-energy side (see text).

[9] (eV)	[10] (eV)	[12] (eV)	[11, 13] (eV)	[14] (eV)	This work (eV)
				1.82 <sup>a</sup>	
1.76	1.75	1.77		1.785	1.77
			1.71		
1.7	1.7	1.68	1.69	1.71	1.68
			1.65 sh		1.65 sh
		1.59	1.60	1.65	1.60
	1.57	1.50	1.50	1.55	1.50
				1.46 <sup>a</sup>	
	1.41 sh				

<sup>a</sup>:  $C_{70}$  contamination; sh: shoulder.

In our experiments, the emission peak at 1.77 eV, originating from  $C_{60}$ , is clearly enhanced by the presence of  $C_{70}$  in the samples. Our explanation is that  $C_{70}$  acts as an impurity in the  $C_{60}$  structure and locally distorts the structure of  $C_{60}$  leading to a strong activity of the 1.77 eV transition.



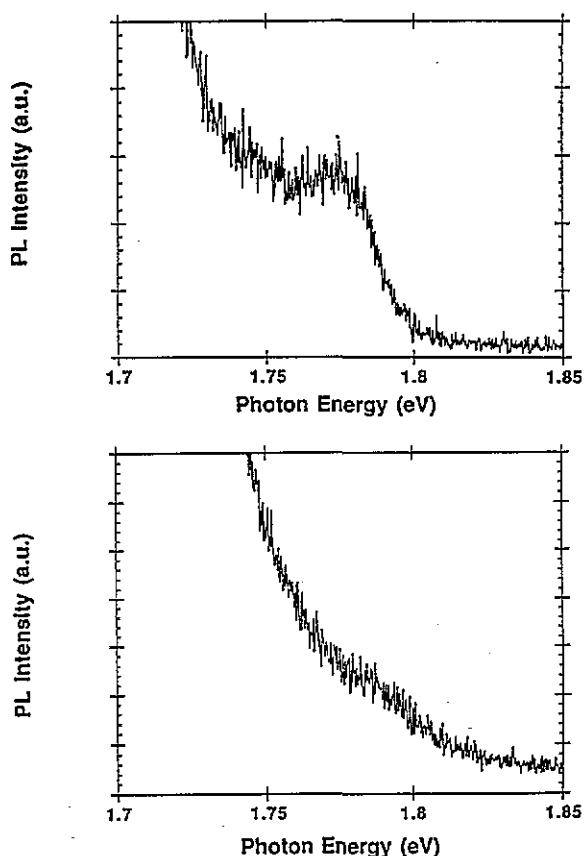


Figure 5. Extent of the PL spectrum in the 1.7–1.85 eV energy range. The two upper spectra have been displayed with the same magnification. Upper curve,  $C_{60}$  thin film (same film as in figure 1(b)); lower curve, highly purified  $C_{60}$  thin film.

This statement is in disagreement with those of Matus and co-workers [14]. These authors, from experiments performed on purified  $C_{60}$  film where the oxygen has been blown off by laser irradiation, observe that the 1.77 eV disappears (see figure 4 of the [14]). Consequently, they claim that the 1.77 eV peak originates from the  $C_{60}$  interacting with oxygen and more precisely from the  $C_{60}^{2+}$  luminescence centre. An argument in favour of this statement is that the vanishing of the 1.77 eV peak in the PL spectrum is correlated with the observation of a peak at around  $1458\text{ cm}^{-1}$  in the Raman spectrum measured on the same sample. This mode was identified as the 'pinch mode' in an 'oxygen free'  $C_{60}$  sample (this mode gives a peak at  $1467\text{ cm}^{-1}$  in  $C_{60}$  in air) [14]. However, in contrast to this last assignment, Ping Zhou and collaborators [18] state that the displacement of the 'pinch mode' from  $1467\text{ cm}^{-1}$  to  $1458\text{ cm}^{-1}$  should be assigned to a phototransformed phase of  $C_{60}$  under laser irradiation and not to oxygen contamination as claimed in [14]. This last result gives another reason to consider with some caution the assignment of the 1.77 eV emission peak as due to a contamination from oxygen.

In order to complete our information about the assignment of the 1.77 eV peak, we have performed PL experiments on highly purified  $C_{60}$  film synthesized at Penn

University. In this sample the  $C_{70}$  concentration is too low to be measured. This film was exposed to air for a long time and the low-temperature photoluminescence spectrum obtained is shown in figure 4. The 1.77 eV peak (figure 4) is not observed. For clarity, we compare in figure 5, with the same magnification, the PL spectra carried out on this film and on the film synthesized in our laboratory (figure 1(b)) in the 1.7–1.85 eV region. In this way, we confirm that the 1.77 eV peak does not originate from the interaction of  $C_{60}$  with oxygen. With regard to the experimental facts stated in this work, namely: (i) for small  $C_{70}$  concentration, the 1.77 eV peak intensity increases with the  $C_{70}$  concentration; (ii) the appearance of the 1.77 eV peak coincides with the quenching of the orientational disorder, we propose to assign the 1.77 eV peak as due to  $C_{60}$  emission enhanced by the presence of  $C_{70}$  impurities. We suggest the following scenario: the presence of a  $C_{70}$  impurity in the  $C_{60}$  lattice leads to a local lowering of the symmetry of the neighbouring  $C_{60}$  molecules of the  $C_{70}$  impurity. At high temperature, due to the orientational disorder of the  $C_{60}$  molecules, this effect is averaged. When the  $C_{60}$  orientational disorder is quenched below 90 K [16], the local distortion induced by the  $C_{70}$  impurity leads to a lowering of the symmetry of the  $C_{60}$  with, consequently, the activation of a new emission line at 1.77 eV. This situation has some analogies with those of isoelectronic impurities in semiconductors [17]. This is an alternative explanation to those proposed in [14].

Finally, these photoluminescence results cast doubt on the value of the gap of solid  $C_{60}$ . They lead to consider  $E_g$  larger than 1.8 eV which is nearer to the value of the HOMO–LUMO transition in the  $C_{60}$  cluster than to the 1.5 eV value calculated for the  $C_{60}$  crystal [6].

## 5. Conclusion

Photoluminescence (PL) experiments have been performed on different samples with variable  $C_{60}/C_{70}$  composition and a significant sample dependence of the PL spectrum has been found. The PL of the  $C_{60}$  thin film exhibits well resolved peaks at 1.68 eV, 1.65 eV, 1.60 eV and 1.5 eV, assigned to phonon replicas. The enhancement of the intensity of the 1.77 eV peak, which clearly originates from  $C_{60}$ , seems to be correlated with the amount of  $C_{70}$  in the samples under consideration, the  $C_{70}$  molecule acting as an impurity which locally distorts the  $C_{60}$  cluster at low temperature. The appearance of this peak (below 90 K) is the PL 'signature' of the quenching of the orientational disorder.

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