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# Electric Current Induced Light Emission From C<sub>60</sub>

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## Abstract

We report the luminescence of C<sub>60</sub> crystals and films due to the passage of an electrical current. The current-voltage behaviour is highly non-linear with light-emission beyond a threshold voltage. The emission spectrum is featureless and resembles black body radiation with an effective temperature on the order of 1700K. We report experiments aimed at distinguishing between electro- and thermo-luminescence.

Keywords: fullerenes, C<sub>60</sub>, luminescence, organic, thin film, single crystal

## 1. INTRODUCTION

Electroluminescent materials are of current interest because of the new applications that are envisaged for modern video displays. Displays based on inorganic electroluminescent materials excited by keV-electrons are being augmented with color displays based on liquid crystal technology.<sup>1</sup> Still, enormous progress can be realized by developing more efficient electroluminescent materials. Organic materials have shown promising properties. Organic materials have been synthesised that electroluminesce over a large portion of the visible spectrum. The organic electroluminescent devices can be separated into two classes: 1) exciton decay in hole conducting polymers<sup>2</sup>, such as PPV and, 2) electron-hole recombination at the interface of electron and hole transporting heterojunctions<sup>3</sup>, such as TAD/ALQ. While remarkable progress has been reported over the last few years in developing and understanding these materials, several problems are encountered besides efficiency, such as environmental instability, charge transfer at the organic conductor/metal electrode interface, and photodegradation. Clearly, new materials with improved properties are required.

Recently it was reported that C<sub>60</sub> single crystals show electroluminescent behavior<sup>4</sup>. As C<sub>60</sub> shows moderately high electron mobility and is stable to molecular exciton formation, it is an excellent candidate for a new electroluminescent material. Evidence for an electroluminescent process was obtained by comparing the luminescence spectrum induced by optical input power and by an electrical current. Here we report our findings that confirm previous results obtained in the visible part of the spectrum. However, we will show that significant deviations between electric and optically stimulated response can be observed in the infrared part of the spectrum. We relate the high intensity luminescence at least in part to local heating and to the formation of fragmented C<sub>60</sub> species which are ultimately converted to amorphous carbon under these extreme conditions.

The optical properties of pristine C<sub>60</sub> have been studied by a number of groups. The symmetry of the C<sub>60</sub> molecule forbids optical transitions between the HOMO h<sub>u</sub> and the LUMO t<sub>1u</sub> orbitals<sup>5</sup>. This

transition is weakly allowed because of vibronic coupling to the higher lying  $t_{1g}$  orbitals. The photoluminescence spectrum exhibits a peak at 1.7 eV<sup>6</sup>. This is significantly smaller than the band gap of pure C<sub>60</sub>, which is about 2.3 eV. This difference has been attributed to molecular exciton formation on the basis of experiments comparing the XPS/BIS spectrum with the self-convoluted Auger spectrum<sup>7</sup>. However, careful comparison of the optical absorption spectrum of samples in various reports shows variations in peak position and intensity among different samples. The purification of C<sub>60</sub> crystals showed that these variations can be attributed to defects in the C<sub>60</sub> lattice<sup>8</sup>. In fact, these authors show that in most samples, the intrinsic luminescence of crystalline C<sub>60</sub> is overwhelmed by that of C<sub>60</sub> molecules in defect states, arising from stacking faults and interstitial vacancies, which cause considerable broadening of the spectrum.

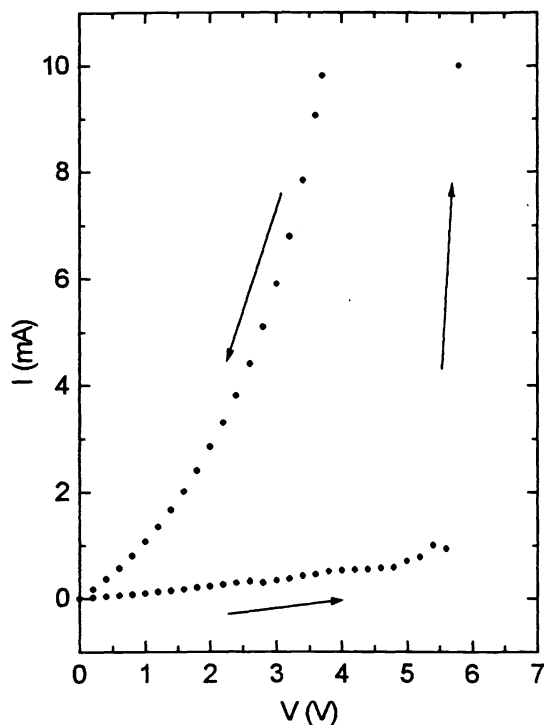
At very low incident power the photoluminescence scales linearly with incident power  $I$ , but levels off to  $I^{1/2}$  at intermediate incident power, indicating a bimolecular relaxation process<sup>9</sup>. However, beyond a certain threshold power, the luminescence increases dramatically, showing a  $I^3$  dependence. The luminescence band at 1.7 eV was shown to shift to lower energies and increase in intensity with increasing laser input power. The luminescence is easily observable with the eye and white in appearance. The photoluminescence is reported to be fully reversible, suggesting that no irreversible chemical photodegradation occurs.

It was reported that concomitant with the luminescence, the photoconductivity behavior changes in character<sup>9</sup>. At low incident power the photoconductivity is thermally activated, but at high incident power the photoconductivity becomes temperature independent. This highly excited state was therefore associated with a metallic state originating from band formation of the excitons. The relationship between the photonic and electrical response was further emphasised by comparing the photoluminescence with the electroluminescence - both showing a narrow maximum at around 1.2 eV, shifted from 1.7 eV at low incident power. This correspondence was taken as evidence that the light emission caused by an electrical current is indeed an electroluminescent process.

In this paper we report experiments aimed at understanding the light emission caused by an electrical current. We show that the correspondence between the photo- and electric current induced luminescence that has previously been reported, is not observed in the infrared part of the spectrum. Concomitant with light emission caused by an electrical current, we provide evidence for a degradation process, as C<sub>60</sub> is converted slowly into amorphous carbon. The light emission originates at the interface between pristine C<sub>60</sub> and amorphous carbon. It is possible that intermediate reaction products (such as highly defective or fragmented C<sub>60</sub> species), at the interface are the strongly luminescent centres.

## 2. EXPERIMENTAL RESULTS

C<sub>60</sub> single crystals were grown in a three zone furnace<sup>10</sup> after two sublimations of pure C<sub>60</sub>. The crystals grow in the cooler central zone at 530 °C, while the two outer zones were held at 580 °C over a period of 3 days. This leads to well-formed crystals a few mm in size, that exhibit shiny facets, often reflecting the hexagonal crystal symmetry (shown later in Figure 3). Four electrical contacts were made to the samples using 75  $\mu$ m platinum wire and silver epoxy. The platinum wire to C<sub>60</sub> contacts are provided with strain relief by a sapphire substrate to make a mechanically rigid sample. This assembly is mounted in a glass tube with electrical feedthroughs for the sample and a SAES getter source, for dispensing controlled amounts of alkali metal. The glass tube is evacuated for one day at 100 °C and then sealed with a torch.



**Figure 1** Current-voltage characteristic of a partially doped C<sub>60</sub> single crystal showing the threshold voltage for luminescence, and hysteretic behaviour.

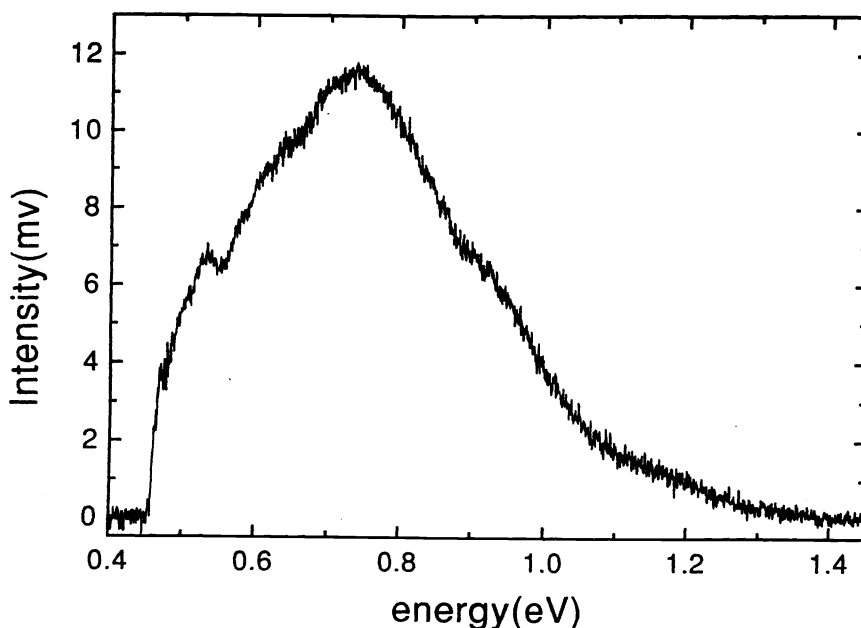
We used two methods to obtain light emission from C<sub>60</sub> single crystals that were both found to be very reliable. Pristine undoped crystals do not emit light under the conditions of our experiments. It proved necessary to first reduce the resistance of the sample. One way is to partially dope the C<sub>60</sub> crystals with alkali metal in an evacuated glass tube. The other way is to deposit a thin (200Å) film of silver over a pristine C<sub>60</sub> crystal, before attaching the contacts and mounting the sample. In the first case, the crystals were repeatedly exposed to alkali vapour from the getter source at 30°C, and then annealed overnight at 60°C to give a 2 point resistance of ~1 kΩ. The intrinsic resistance of a stoichiometric A<sub>3</sub>C<sub>60</sub> crystal of this size is estimated to be less than 1Ω, based on an intrinsic resistivity of about 1mΩcm. This indicates that the light emitting samples are only lightly doped. The silver covered crystals also exhibit a 2 point resistance of ~1 kΩ. Since the silver film should have an intrinsic resistance of ~1Ω, the silver probably dopes the surface of the crystal.

The two point current-voltage characteristics are shown in Figure 1. For a small bias voltage the current increases linearly with voltage, with a slope of the order of ~1 kΩ. However, for larger bias current, the resistance (V/I) decreases by about two orders of magnitude and it is at this threshold that light emission is observed from the sample. After light emission starts, it persists down to low current values, while the sample remains in the high-conductivity state. After turning the current off, the low-conductivity state is recovered, again yielding the hysteresis shown in Figure 1.

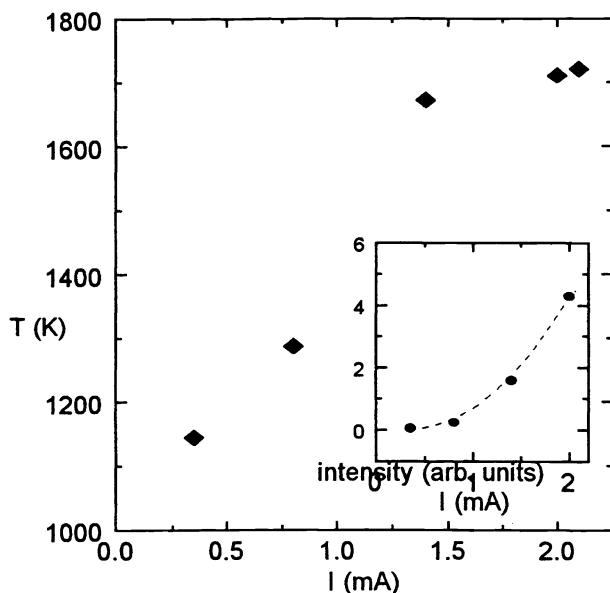
The emission data were obtained using two different spectral set-ups to span the required wavelength coverage. First, the sample emission was imaged through an Aries f250,0.25M spectrometer onto a Princeton Instruments intensified Si diode array for visible emission detection. The IR emission was collected using a Mattson galaxy series FTIR 5000 IR spectrometer which has been configured for emission studies, using both Ge and InSb detectors.

The light emission is not homogeneous over the crystal, but confined to areas in the vicinity of the contacts. The emission is clearly visible in daylight and usually appears white to the eye. The entire spectrum of the emitted light is difficult to collect continuously due to the wide range of emission wavelengths, ranging from the visible to the near IR. The peak of the emission intensity is in the infrared, and can only be detected with an IR sensitive detector. Measurement of the emission with a Si diode, for example, will follow the detector cut-off in the near IR at 1.2 eV. Figure 2 shows the emission collected between 0.5 and 1.5eV using an InSb detector, although the spectrum is not fully corrected one can readily see that it is featureless over the entire frequency range and resembles black body radiation, with the peak in the spectral response corresponding to an effective temperature of  $\sim 1700$  K.

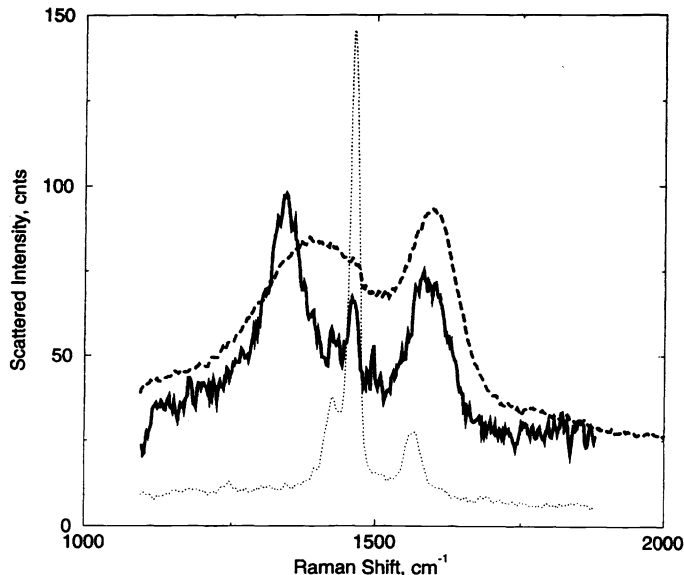
The pristine crystal exhibits shiny facets. Light emission is localized at a narrow spot, usually near the contact, and after prolonged light emission a crevice is observed in the crystal. While thermal effects may be important, this does not prove that the light emission has a thermal origin. Many early organic electroluminescent devices showed burning effects. If the light emission ceases, further emission can often be excited in another part of the sample. After extended periods of light emission deposits were observed on the sapphire mount. It is important to note that highly resistive materials at doping levels closer to pristine  $C_{60}$  crystals do not emit light, even at bias voltages as high as 100V. The resistance of the pristine crystal limits the currents below  $1\mu A$ , which is insufficient to observe light emission. Likewise, highly conducting samples, obtained by doping closer to  $A_3C_{60}$ , do not emit light under the conditions of our experiments. Ohmic dissipation apparently prevents the build up of the



**Figure 2.** Emission spectrum of a partially doped  $C_{60}$  single crystal induced by an electrical current, using Si-diode and an InSb detector. The spectrum resembles black-body radiation with an effective temperature of 1700K.



**Figure 3** Spectrally corrected peak emission of single crystal C<sub>60</sub> for several bias currents. The inset shows the increase in peak intensity with increasing bias current. The line through the data points is a power law dependence consistent with a thermal process.



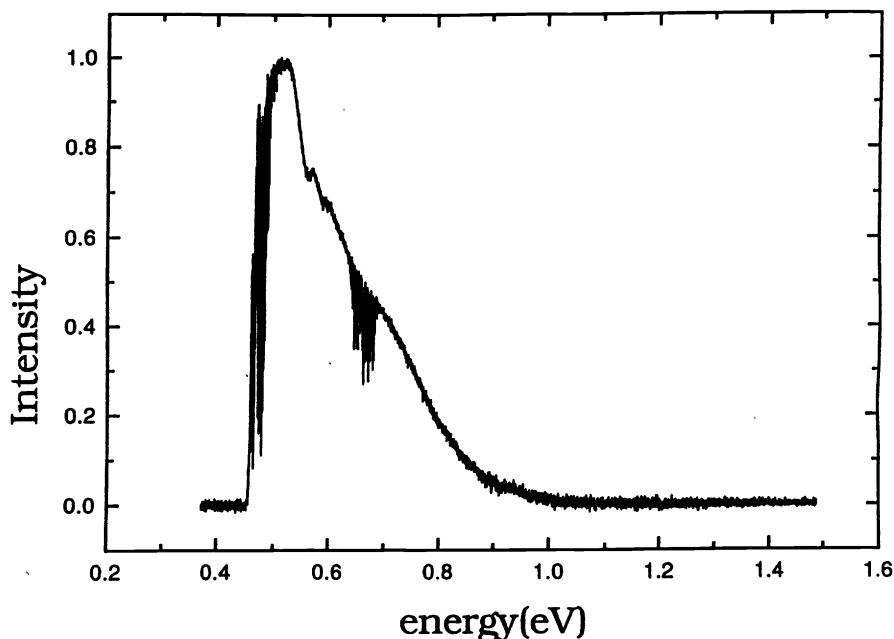
**Figure 4** Microprobe Raman spectrum (spot size 5  $\mu\text{m}$ ) of a crystalline C<sub>60</sub> film that had been emitting light before the current was turned off to allow collection of the spectrum: Pristine C<sub>60</sub> region of film, 50  $\mu\text{m}$  away from the point of luminescence (dotted line). Discolored region of film, 50  $\mu\text{m}$  away from the point of luminescence (dashed line). Point of luminescence (solid line).

required threshold voltage ( $\sim 7$  V) across the sample, which seems necessary to observe light emission.

In Figure 3 we show the emissive response for several bias currents. The spectrally corrected peak emission data for several biases are illustrated, with the inset showing the change in peak intensity as a function of current. Clearly the spectrum shifts to the blue (higher energy), for higher bias currents consistent with a thermal process. Based on the position of the maximum, the effective temperature increases from 1100K to 1700K.

In order to study the luminescent process in more detail, we attempted to duplicate this phenomenon in C<sub>60</sub> films. Crystalline 10 $\mu\text{m}$  thick films were grown on glass substrates using the hot wall technique,<sup>11</sup> with four in-line Cr or Ag electrodes as contacts. The samples were  $\sim 1$ cm wide with a gap between the electrodes of 200  $\mu\text{m}$ . The films were deoxygenated by heating to 240°C under vacuum after mounting in glass sample tubes. Due to the sample geometry, the current was sufficient to stimulate light emission in the pristine (deoxygenated and undoped) films. The films yielded an I-V characteristic very similar to the one shown in Figure 1, with light emission above an excitation voltage of  $\sim 7$ V. The light emission is long-lived (several hours) and occurs in confined bands between the electrodes. When the luminescence intensity decreases after prolonged excitation, the emission spreads to other areas of the gap and ultimately gives rise to discolored bands across the film that are visible under a microscope.

Microprobe Raman spectroscopy showed clear evidence for a chemical conversion. While pristine areas exhibit the well defined Raman line at 1467  $\text{cm}^{-1}$  (originating from the C<sub>60</sub> pentagonal



**Figure 5.** Photoluminescence spectrum of a single crystal of  $C_{60}$  after obtaining the spectra shown in Figure 4. The observed structure is due to the presence of water vapor in the beam sample arm of the spectrometer. The photoluminescence intensity is increased by the current induced light emission.

breathing mode), this peak is absent in the discolored areas which now show a broad Raman spectrum (Figure 4), consistent with that of amorphous carbon (a-C). This spectrum could be reproduced by converting  $C_{60}$  into a-C with very high intensity laser irradiation. A spectrum that was recorded at the interface between  $C_{60}$  and a-C, at a point that was emitting light before turning off the current is also shown in Figure 4. This spectrum is not a superposition of the other two and thus it appears that the emitting regions are composed of material that is intermediate in structure between  $C_{60}$  and a-C.

Chemical modifications were also noted for the single crystals. Because there are no allowed transitions for optical emission, the photoluminescence of pristine crystals is very weak. The luminescence is substantially increased for samples with damage caused by the light emission process. In Figure 5 we show the photoluminescence spectrum observed for the crystal previously used to obtain the data presented in Figure 3. The spectral peak is now too low in energy to be observed with the InSb detector. Clearly the spectral behavior has completely changed in character. However, our data, taken with low incident laser power, contrast with data under high incident power that also reflect a spectral response of black body radiation.<sup>12</sup>

### 3. DISCUSSION

The following important points emerge from our experiments. First, we emphasize the highly reproducible nature of the light emitting process in both crystals and films. The process is long lived and exhibits a turn-on voltage of  $\sim 7V$ . The featureless spectrum, resembling black body radiation, advocates a thermoluminescent process. This explanation is supported by the observation of a-C in the active region, suggesting that  $C_{60}$  is not stable under these conditions. However, there are several pieces

of information that contradict a simple thermoluminescent process. First,  $C_{60}$  sublimates at  $\sim 700\text{K}$ , which might be explained by assuming that it is not  $C_{60}$  but a-C that is the active species at these high temperatures. However, carbon filaments were not observed - instead the a-C consists of micron-sized globular structures. Furthermore, the I-V curve is hysteretic while filament formation would lead to a stable high-conductance state. Also, the process involving a-C alone would require a continuous high-conductance path between the electrodes, in contrast to the locally observed light emission. Nevertheless we attempted to reproduce our results on a-C films. On continuous films the resistance was too low to obtain the required voltage drop across the sample, and no obvious light emission could be seen. In the case of samples with non-connecting paths between the electrodes, no light emission was observed even at excitation of 100V. Occasionally light emission could be generated at electrode positions having  $\sim 1\text{k}\Omega$  impedance. However, the light emission was very short lived (a fraction of a second) and was clearly caused by arcing between two distinct areas of the a-C film. Therefore, we think that a simple thermoluminescent process cannot account for the observations.

The light emission could also be the result of a plasma discharge, with the current exciting a plasma of  $C_{60}$ -like species from the surface. However, the lifetime of the emission process puts an upper bound on the sublimation rate of the order of 1 monolayer per second. This density is many orders of magnitude too low to sustain a plasma discharge.

The consistent value of  $\sim 7\text{V}$  as turn-on voltage for the light emission, the hysteretic I-V curve, and the reproducible nature of the process suggest that the emission is caused by impact ionisation<sup>1</sup>. For such a process a voltage of roughly three times the ionisation potential is required. This will lead to exciton formation at low excitation densities, and at high excitations to fragmentation of the  $C_{60}$  molecule. The resulting  $C_{60}$  fragments can chemi- or electro-luminesce, no longer having forbidden optical transitions because of their high symmetry. Such a local process would result in high effective temperatures, causing a broad spectral response, resembling thermoluminescence. Eventually, the  $C_{60}$  fragments convert to a-C. Such a process is metastable, and requires high excitation either by electrical or optical stimulus. This is consistent with a local phenomenon near the electrodes, since here the largest potential drop can be expected

Such a process might be reproduced by exposing solid  $C_{60}$  to an electron beam. However, no light emission was observed when we exposed  $C_{60}$  films to an e-beam between 10 V and 1 kV. Apparently this experiment cannot attain the high current densities required to observe luminescence (perhaps because of charging effects), leaving the material in the low conductivity state. Similarly, spectroscopic studies have shown that  $C_{60}$  is stable to energetic electrons, as long as the current density is low. Likewise,  $C_{60}$  is stable to low intensity light input, but starts to polymerise at intermediate light intensity<sup>13</sup>, and will convert to a-C at high intensities.<sup>14</sup>

In conclusion, we have observed light emission from  $C_{60}$ , under high current density excitation conditions. The light emission has a broad spectral response with a peak intensity near 0.7 eV. Concomitant with light emission, we provide evidence for a degradation process, as  $C_{60}$  is converted slowly into amorphous carbon. The light emission originates at the interface between pristine  $C_{60}$  and amorphous carbon. It is possible that intermediate reaction products (such as highly defective or even fragmented  $C_{60}$  species), at the interface are the strongly luminescent centres.

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