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THE EXPONENT γ IN THE PHOTOCONDUCTIVITY OF C_{60} FILMS

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We present experimental measurements of the exponent γ, as a function of temperature, of the photoconductivity for C_{60} films. The behavior of γ(T) can not be explained in terms of a Rose's type simple model. Based on a simple model of photoconductivity for C_{60}, we make calculations of γ(T) and compare them to the experimental results. To satisfactorily explain our results, we propose the existence of a peak in the density of localized states within the gap. We also propose that the peak in the density of states presumably has its origin in a Frenkel type exciton band. Copyright ©1996 Elsevier Science Ltd

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In the last few years has been relatively great activity in the study of new allotropic forms of carbon, particularly in the C_{60} and compounds formed with it. Among the many studies concerned with the electronic properties of this system, in which many different techniques had been used, photoconductivity is an interesting property that may give insight about the density of electronic states, and about the processes related with the recombination of carriers. In addition, the study of photoconductivity in C_{60} may provide knowledge which in the future can be used in optoelectronic devices.

Usually in many semiconductors the photoconductivity σ_p follows a law of the form

$$\sigma_p = cI^{\gamma} \tag{1}$$

where I is the intensity of the light incident on the sample, γ is an exponent whose value can depend on temperature, and c is a temperature dependent coefficient. If the sample under study has localized states within the optical energy gap, then γ can be related with the distribution of these states. Rose [1] found that when the localized states are near the conduction band edge and are modeled as an exponential tail of the form $g(E)=g(E_C)e^{(E-E_C)/E_1}$, then γ takes the simple form given by

$$\gamma = \frac{E_1}{(E_1 + kT)} \tag{2}$$

Within the framework of this model one can obtain information about the characteristic value of the density of states E_1, by measuring γ as a function of the temperature. Hamed, et al. [2] made measurements of γ as a function of temperature in C_{60} thin films and found a non-monotonic behavior of γ. They adjusted their experimental results using relation (2) in two regions of temperatures, namely, T < 200 K and T > 260 K. They found two different values for E_1 and argued that this is due to a reduction of the structural disorder for temperatures lower than 260 K; which corresponds to the temperature where the order-disorder structural phase transition exists in C_{60}. At this temperature the system changes from a high temperature orientational disordered fcc phase to a more ordered simple cubic phase [3]. However, close to the temperature at which the phase transition occurs (~250 K) [3], the experimental results of Hamed et al. [2] can not be explained using the Rose's type model for γ.

In this work we will present our experimental results on photoconductivity in C_{60} thin films. We show that in the vicinity of temperature of 260 K the behavior of the exponent γ can not be explained in terms of the Rose's model. According to that results, and mo-

tivated by a previous work on photoconductivity in amorphous silicon [4], we propose instead an alternative explanation of the behavior of γ as a function of temperature based on a different model for the density of states (DOS) within the energy gap.

C_{60} thin films were obtained by thermal evaporation on sapphire substrates at room temperature from C_{60} powder (purity better than 99.5% from MER Corporation). Subsequently, two aluminum strips were evaporated to form Ohmic contacts which are 6.5 mm long and are 1 mm separated. The thickness of the C_{60} films were monitored in situ by a quartz microbalance, and after deposition these were also measured by using a profilometer. Both measurements agree well within experimental error and the typical thickness of the used films were around 4200 Å. The experiments were performed using a closed-cycle helium refrigerator provided with glass windows for optical measurements. We performed two different measurements: in one measurement the illumination was provided with a tungsten lamp and a red filter (centered at λ=620 nm), in the second experiment we used unfiltered white light. A calibrated photodiode was used to measure the light intensity, which varied from $\sim 10^{-3}$ to $\sim$ 1 mW/cm^2 of red light. The range of measurements were from 330 K to 200 K downwards, and stabilized a fixed values of temperatures for periods of time of at least 10 min. The light intensity was varied by steps, and only when a steady state was attained the next step was applied. The photocurrents were measured with an electrometer (Keithley model 619). The minimum temperature measured was limited by the photocurrent that can be measured by the instrument with enough and reliable precision at the minimum light intensity, using a fixed bias voltage of 100 V.

In figure 1 we present the photoconductivity (conductivity under illumination minus dark conductivity) as a function of the inverse temperature for a fixed light intensity using the red filter. Observe that, in the whole range of temperature, the photoconductivity is not a simple activated process. An Arrhenius fit for the data at temperatures higher than 280 K gives an activation energy around 0.26 eV; this may mark a characteristic energy below the conduction band edge involved in the process of the photoconductivity. We will show later that around that energy, a peak in the density of states exist. We should note that an anomalous behavior of the photoconductivity, below ~280 K, has been observed by other workers, but there is no clear explanation for that effect [5, 6]. In the inset of Fig. 1 we plotted the dark conductivity as a function of the temperature, note that a good fit with an Arrhenius model is obtained giving an activation energy of 0.52 eV. This value is within the range recently reported of 0.48-0.61 eV for C_{60} films under different annealing treatments [7].

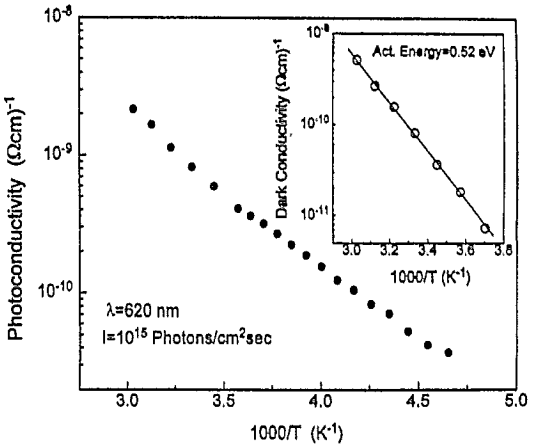

Fig. 1. Photoconductivity against temperature for a constant intensity of illumination using the red filter. In the inset appears the dark conductivity (open circles), the straight line is a fit to the data giving an activation energy of 0.52 eV.

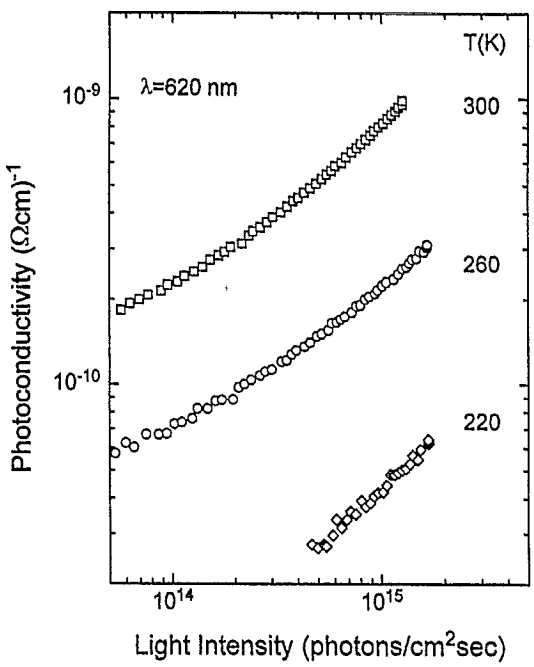

Fig. 2. Photoconductivity versus light intensity for some temperatures using the red filter. The value of the exponent γ was obtained in the region around 10^{15} photons/cm^{2}sec.

In figure 2 we plotted some representative curves of the photoconductivity as a function of the intensity of illumination in a logarithmic scale, for λ=620 nm. We can observe a small curvature in the low light intensities region, mainly for high temperatures (for low temperatures it is difficult to measure the photocurrents

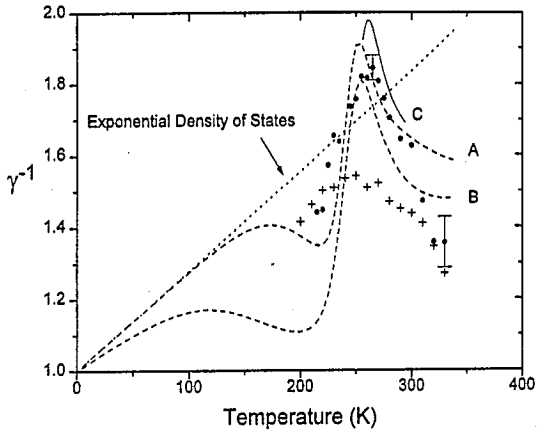

Fig. 3. Experimental results of γ(T) using red light with λ=620 nm (solid circles) and unfiltered white light (crosses) on the same sample. The estimated error for all the solid circles are less or equal than the minimum error bar shown in the figure. The dashed curves labeled A and B correspond to our best approximation to the experimental results for red light. The dotted straight line corresponds to a Rose's type model.

for low intensities, here we only present the regions where the measurements were reliable). In order to calculate the exponent $\gamma(T)$ in the linear region of the log(σ_p)-log(I) curves for each temperature, we choose the interval from ~ $3x10^{14}$ to ~$2x10^{15}$ photons/cm^{2}sec for the light intensities.

In figure 3 we show γ^{-1} vs temperature, where γ was calculated by least square fitting for each temperature. The data obtained on the same sample is shown as solid circles when using the red filter, the crosses correspond to measurements with unfiltered white light. To perform the analysis of our results we have plotted in Fig. 3 γ^{-1}(T). In this plot, the Rose's type model given by Eq.(2) is a straight line in which the slope gives the characteristic energy of the exponential density of states.

We observe that γ^{-1}(T) presents a maximum around 260 K for red light illumination, and around 250 K for white light, with different absolute values in both cases. Nevertheless, the qualitative form of the curves is similar. Accordingly, we can restrict our analysis to the results for monochromatic light. A first look to the results of figure 3 leads to the conclusion that it is impossible to explain the experimental results based on the analysis of a Rose's model. This model is shown in fig 3 by the doted straight line plotted in the same graph.

In order to explain the behavior of γ(T) for the C_{60}, and based in an earlier analysis of photoconductivity for amorphous silicon [4], we propose the existence of a peak in the density of states within the gap for the C_{60}. To calculate γ(T) we now use the model proposed by Kastner and Monroe for the behavior of the steady state photoconductivity [8]:

$$G = b_r n \int_{E_F}^{E_C} g(E) f(E) dE \qquad (3)$$

in this equation G is the optical generation rate, n is the electron density in the conduction band, g(E) is the density of states between the dark Fermi level E_F and the edge of the conduction band E_C, f(E) is the distribution function in the steady state, and b_r is a recombination coefficient which we suppose to be a constant. Equation (3) is valid when electrons dominate the transport in the system, which has shown to be the case for C_{60} [9, 10].

To get information about γ(T) from Eq.(3), we have to propose an explicit form for the DOS within the energy gap. We propose the following form:

$$g(E) = g(E_C) e^{\frac{(E-E_C)}{E_1}} + \frac{b}{(E - E_0)^2 + a^2} \qquad (4)$$

where the first term in the right side of Eq.(4) corresponds to the exponential tail used in the Rose's type model, and the second term is a Lorentzian peak centered at E_0, with its maximum value being b/a^2, and the parameter a represents the full width at half maximum. (we used a Lorentzian peak for simplicity). Although in this model there are many free parameters, we know that the introduction of a peak in the DOS is necessary to reproduce the non-monotonic behavior of γ(T), at this respect some comments are relevant and concern to this point.

Experimental measurements indicate many values for the band gap, E_g, in solid C_{60}. From photoelectron and inverse photoelectron spectroscopy E_g=2.3 eV [11], and from photoconductivity experiments other values have been reported, such as 2 eV [12] and 1.81-1.85 eV [13]. Although the conduction band edge is located around ~2 eV, more structure has been observed in the range from 1.5 to 2 eV. Many authors attribute this structure to a Frenkel type molecular excitons [11, 14–17] with the main line related to the h_u-t_{1u} transition and located around 1.7 eV. We propose that the peak in the DOS is due to an excitonic origin located around 1.7 eV.

To make the calculations we take the following parameters: the valence band edge as the zero in energy, E_C=2 eV, the activation energy measured in this work is E_C-E_F= 0.52 eV, then the dark Fermi level is located at 1.48 eV. Taking the electron mobility μ as ~10^{-3} cm^2/Vsec [18] and using our measurements of the photoconductivities, the electron density $n=\sigma_p/e\mu$ varies from ~ 10^{11}/cm^3 to ~10^{13}/cm^3. Introducing this range of n in Eq. (3) and making graphs of log(G/b_r)

vs log(n) we obtain in the linear region the value of γ for different temperatures. Note that the relation (1) is equivalent to $n \propto G^{\gamma}$ because $G=\alpha\eta I$, where α is the absorption coefficient and η the quantum efficiency.

Beginning with reasonable values for the proposed density of states (Eq. 4), including the position of the peak at 1.7 eV, our best approximation to the experimental results for λ=620 nm are shown in figure 3 as dashed curves labeled A and B. For curve A the value of the parameters are: $g(E_C)=5\times10^{19}$/eVcm^3, E_1=0.03 eV, a=0.013 eV, b=2.5x10^{12} eV/cm^3, and E_0=1.73 eV. For cur= ve B the only changed parameters are E_1=0.04 eV, a=0.018 eV, and b=2.5x10^{14} eV/cm^3. The maximum in the calculated γ^{-1}(T) is very sensitive to the position and magnitude of the peak in the DOS as is shown by the continuous curve labeled C, where the only change respect to the curve A is the position of the peak in the DOS (E_0 = 1.72 eV). We think that the value of the parameters of the DOS used to model the experimental results, might give an idea of the order of magnitude of the true values.

Accordingly to the last calculations, we can make further estimations of other parameters; for example, the recombination coefficient and the recombination time. Let us take T=300 K and I=10^{15} photons/cm^{2}sec, then the corresponding value of the carrier density is ~6x10^{12} cm^{-3}. The calculated values of the ratio G/b_r, for T and n given above, are ~7x10^{26} cm^{-6} and ~4x10^{28} cm^{-6}; for models of the DOS for curves A and B, respectively. On the other side, as $G=\alpha\eta I$, then taking α ~10^4 cm^{-1} at 2 eV (λ=620 nm) [15], and η ~10^{-3} [19]; we finally have an estimation of the order of magnitude of the recombination coefficient of ~1.4x 0^{-11} cm^3/sec and 2.5x10^{-13} cm^3/sec, for models of the DOS A and B, respectively. Equation (3) can be expressed as $G=n/\tau$, where $\tau=1/b_r N$ is the recombination time, and in our case N is the total number of trapped electrons [8] given by the integral in Eq.(3). In our conditions N is basically the area under the peak of the DOS being approximately b/a. These values lead finally to an estimation of the recombination time of the order of 3x10^{-4} seconds, for both models of the DOS. Only for comparison, we write the reported values of the recombination coefficient and the recombination time for undoped amorphous silicon. These values are: b_r is within ~10^{-11}-10^{-10}cm^3/sec at room temperature [20], and τ is between 10^{-2}-10^{-1} seconds [21], at room temperature and for a G value similar to that used in our estimations. Generally speaking, one thing that we can say is that the recombination of carriers in C_{60} is a stronger process than in amorphous silicon, due to a shorter life time τ of the carriers in C_{60}. In other words, for the same value of G, in C_{60} we have less available electrons for conduction ($n=G\tau$), than that in amorphous silicon.

We should note that our model reproduces the Rose's type behavior at low temperatures, as is shown in figure 3, where the doted straight line was calculated in the same way as curves A and B, but where the only contribution to the DOS is the exponential tail with E_1=0.03 eV. Observe that the curve A (with the same value for E_1) approaches asymptotically to the straight line at low temperatures. The reason is that, within the framework of our photoconductivity model, f(E) in Eq.(3) is mathematically similar to a Fermi distribution, but with a quasi-Fermi level (ϕ) whose value depends on temperature and light intensity (through n) in the form: $\phi=E_C-kTLn(N_C/n)$; where N_C is the effective density of states at the conduction band edge [8]. In this scheme, ϕ scans regions in energy close to the conduction band edge at low temperatures, and for higher temperatures it goes to the middle of the gap. For the range of temperatures and light intensities used in our experiments, ϕ moves around 1.7 eV, and this is the reason for which the introduction of a peak in the DOS around that energy is necessary to reproduce our experimental results on γ(T).

Finally, we would like to comment about the difference between the experimental results of γ(T) obtained using monochromatic and white light. With the use of white light many photon energies are taken place in the photoconductive process, and the phenomenon could be more complex than the case with monochromatic light (see for example reference 1). On one side, the photoconductive response is different depending on the photon energy; on the other side, photons with small energies could produce electron transitions within the sub-gap region. Although our experimental results of γ(T) are qualitatively similar, we think that the quantitative differences may be due in part to those effects. This could be the same reason for which the results reported in Ref. 2 are somehow different to this report. Worth mentioning that the substrate temperature for the film deposition used by Hamed, et al. was above room temperature. In addition, recently [17] has been proposed that metastable defects that affect the photoluminescence above 1.7 eV, can be produced by different type of stimuli as irradiation of light, temperature cycles, and growth methods of the solid C_{60}

In summary, we have proposed an alternative model to explain the experimental results of γ(T) in terms of the existence of a peak in the DOS located around 1.7 eV, presumably originated by an exciton band. In this model, some photo-excited electrons in the conduction

band may recombine with a hole to form a Frenkel type exciton. Therefore, these electrons will not contribute to the electronic conduction process; however, under illumination a steady state condition is attained.

We do not discard a possible effect in the photoconductivity of C_{60} due to the change of the structural order around 260 K, as Hamed, et al. proposed [2]. But within the framework of the model used by those authors, $\gamma^{-1}(T)$ would only change in its slope around the transition temperature, and would not have the observed structure . The fact that the anomaly in $\gamma(T)$ appears close to the order-disorder transition temperature, may be only a coincidence because at this temperature the quasi-Fermi level moves around the position of the peak in the DOS, which we propose, is the feature that originates the non-monotonic behavior of $\gamma(T)$.

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