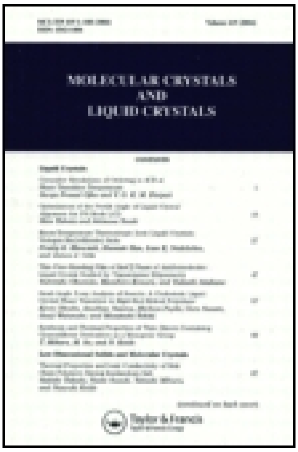

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Nonlinear Optical and Transport Processes in Fullerenes

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NONLINEAR OPTICAL AND TRANSPORT PROCESSES IN FULLERENES

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Abstract Nonlinearities photoluminescence, photoconductivity and resonant Raman measurements of fullerenes at high excitation densities are described and the observations are discussed in terms of an optically induced insulator-metal transition in fullerene crystals. The intensity dependence of the transient photoconductive response is reported to show similar nonlinear behaviour. At low intensities, the response decays exponentially within a time of 15nsec. At increased intensities, a second, delayed component emerges and evolves nonlinearly into a long lived component of lifetime 100-200nsec. The system is fitted with a simple three level model in accordance with a Mott-like transition.

INTRODUCTION

Optical absorption spectroscopy, photoluminescence spectroscopy, Raman spectroscopy as well as transport measurements show strong indications that the solid state packing of C_{60} exerts a minimal perturbation on the properties of the molecule[1,2]. At high excitation densities, however, the properties are seen to undergo dramatic changes[3-5]. In the photoluminescence spectrum of C_{60} crystals the emission maximum shifts from 1.65-1.35eV. The spectral evolution, shown in figure 1, is accompanied by a broadening of the spectrum and a nonlinear increase in both the luminescence output and lifetime. Figure 2 reproduces for example the intensity dependence of the emission intensity. A similar broad red shifted emission is observed as electroluminescence from fullerene crystals above a critical current[6]. Notably, the dependence of the electroluminescence on the current exhibits a nonlinearity similar to that of the photoluminescence. The photoconductive response is seen to undergo similar nonlinear changes at high excitation densities. The magnitude of the response increases with the cube of the input intensity, and, at high intensities, becomes largely temperature independent. The intensity onset of this behaviour appears to be a threshold value indicative of the requirement of a critical excited state density. Such a temperature independence of the conductivity may be characteristic of a metallic-like behaviour and a Mott-like insulator to metal transition is inferred.

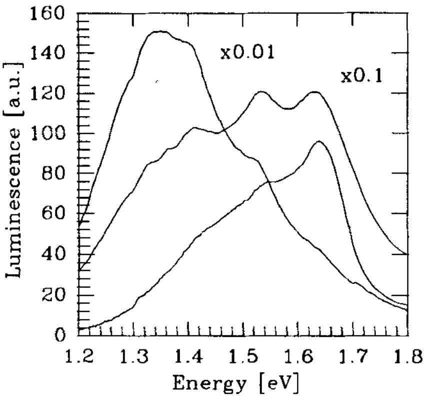

Fig. 1: Luminescence Spectra with increased illumination from 0.1, 0.5 and 3.0mW.

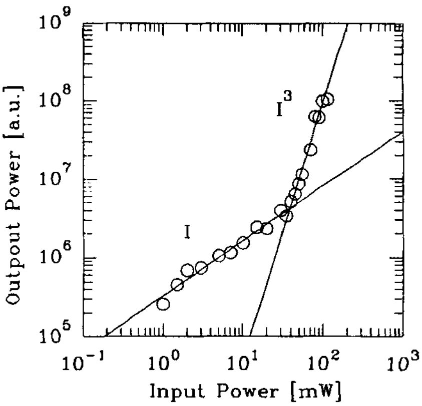

Fig. 2: Dependence of the long lived luminescence on input intensity.

Raman spectroscopy clearly shows that the "highly excited state" is indeed a new phase of the material. The strongest molecular Raman mode is the A_g pentagonal pinch mode[7]. It is seen to shift continuously to lower frequencies with increasing intensity[5]. The dependence is nonlinear, and it can be fitted to a power law of order between two and three. The mode shifting is accompanied by a strong increase in the Raman intensity which fits well to cubic. This nonlinear shifting is fully reversible and the nonlinear characteristics strongly associate it with the nonlinearities observed in the luminescence and photoconductivity.

The effects exhibited by fullerenes under high intensity illumination point towards a departure from the molecular like behaviour of the weakly excited state through the influence of the interaction of molecules in the excited state. Such many body processes have been extensively investigated in inorganic semiconductors[8]. Perhaps the most dramatic effects are exhibited by indirect band-gap materials, in which optical excitations have been observed to exist in the form of electron-hole plasmas or liquids[9] at high excitation densities. The process is driven by electronic exchange and correlation energies and although both are strongly dependent on band structure and anisotropy, it has been shown that their sum is largely independent, enabling a universal description of their contribution[10]. Comparison of the exchange and correlation energies at high excitation densities to the low intensity molecularly localised energies in fullerenes supports the existence of a Mott-like transition at a critical density of ~1x $10^{20}cm^{-3}$ and the increasing prevalence of the sum of the exchange and correlation energies can result in an energy shift of ~150meV, consistent with that observed in the photoluminescence of fullerenes at high intensities[11].

In order to further investigate the nature of the electronic properties of fullerenes at high excitation densities, the transient photoconductive response has been investigated as a function of intensity. In particular it is hoped to gain further insight into the dynamics of the formation and decay of the highly excited state.

EXPERIMENTAL

C_{60} crystals were generated by vacuum sublimation of fullerene powder as described previously[7]. The sample employed was of dimensions ~200x200x200μm^3 and was mounted using silver paste on a substrate with two gold strip lines in an Auston switch geometry of gap width of 100µm. All processing was performed under inert atmosphere, and the sample was mounted in a cryostat which was cooled to liquid nitrogen temperatures.

As excitation source, a cw modelocked Nd^{3+}:YAG laser was used to seed a regenerative amplifier operating at 30Hz. The frequency doubled output, of wavelength 532nm, had pulse width ~70psec and pulse energies of up to 200mJ. The pulses were focused to a spot size on the sample of ~200µm in diameter. The sample was connected to a variable voltage source and the transient response was monitored using a Hewlett-Packard 54111D digitising oscilloscope. For the measurements reported here a voltage of 100V was employed.

RESULTS AND DISCUSSION

The transient photoconductive response was measured over a range of intensities. At low intensities, a weak, rapidly decaying signal was observable as shown in Figure 3 for the example of 1µJ incident pulse energy. The response fits well to a single exponential decay of lifetime 15nsec, the temporal limit of the detection. The response remains single exponential to excitation energies of ~2µJ, whereupon a second, longer lived component emerges which is delayed with respect to the excitation. Figure 4 shows the temporal response of the photoconductive signal at (a)2.8 and (b)3.5µJ. Both the temporal position of the maximum as well as the lifetime of the second component increase with intensity. Furthermore, upon the emergence of the longlived component, the dependence of the integrated photocurrent on intensity becomes superlinear as shown in figure 5. The solid line shows a slope of 3. The progression is cyclable upon decreasing and increasing the intensity.

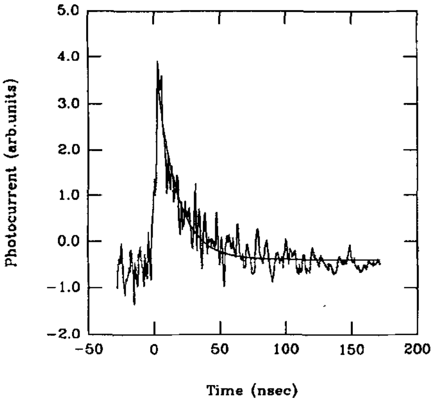

Fig.3 Transient Photoconductive response at 1μJ

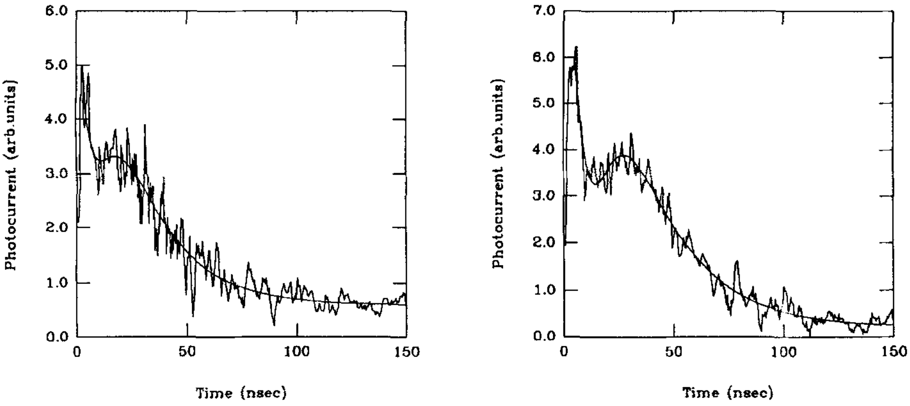

Fig 4 Transient Photocurrent at (a) 2.8 and (b) 3.5μJ

In discussing the nature of the intensity dependence of the photoconductive response described above, it should be noted that a remarkably similar behaviour was observed in $La_2CuO_{4+\delta}$, where δ was near that required for the insulator-metal transition[12]. The process was discussed in terms of an optically induced insulator-metal transition resulting from the shifting of the Fermi level from below a mobility edge into the region of extended states by optical pumping.

In the case of fullerenes, excitation at 532nm is intermediate between the transition to the LUMO, a state (S_1) which is molecularly localised[1,2] and the transition at 440nm to a state (S_2) which has been interpreted as extended

440nm to a state (S_2) which has been interpreted as extended or band-like[13,14]. The state addressed contributes to the photoconductive response until it decays rapidly to the LUMO. Although longlived, any contribution to the photocurrent from this state relies on hopping or tunnelling[15]. Thus, in terms of the photoconductive response, a two level excited state can be constructed. At low intensities, the photocurrent I_{pc} decays at the depopulation rate of S_2 (k_{21}), and thus,

$$I_{pc}(t) \propto S_2(t) = S_2(0)\exp(-k_{21}t) \qquad (1)$$

Assuming the absorption to be linear, I_{pc} is linear in intensity. The nonlinear character of the photocurrent indicates the contribution of a state whose conductivity increases superlinearly with its population. Associating this nonlinearity with that of the photoluminescence[3], a nonlinear dependence of I_{pc} on the population of S_1 may be inferred. Thus I_{pc} takes the form

$$I_{pc}(t) = AS_2(t) + BS_1(t)^n \qquad (2)$$

$$S_1(t) = (k_{21}/k_{10}-k_{21})S_2(0)(\exp(-k_{21}t)-\exp(-k_{10}t)) \qquad (3)$$

and A and B are constants. The solid lines of figures 3 and 4 show fits of such a nonlinear temporal dependence of the photocurrent to the experimental data. Fits to the responses over the range of intensities were performed with all parameters free. Over the range, n varied between 3 and 5. k_{21} remained constant in the range 10-20nsec. Notably, k_{10}, the decay time of the highly excited state increased significantly with intensity. Figure 6 shows the dependence of the fit parameter on intensity. The solid line shows a slope of 2.5, a nonlinearity which is in close agreement with the nonlinearity of the photoluminescence emission lifetime from fullerenes at high excitation densities[3].

The model employed above to describe the nonlinear intensity dependence of the photocurrent and the emergence of a long lived component is primitive and preliminary. k_{21}, as measured here, is limited by the detection and so is not in reality a material parameter. It is assumed to be intensity independent and no explicit nonlinearity of k_{10} is included in the model. Nevertheless, the analysis shows the behaviour to be in good agreement with that observed in the previously described experiments. The interpretation, based on a transition between molecularly localised "excitonic-like" states at low excitation densities, to delocalised states at high intensities is upheld by the model, indicating the importance of intermolecular exchange and correlation energies at high energy densities.

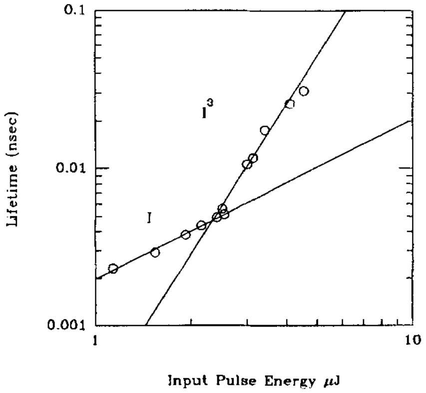

Fig 5 Intensity dependence of of integrated photocurrent

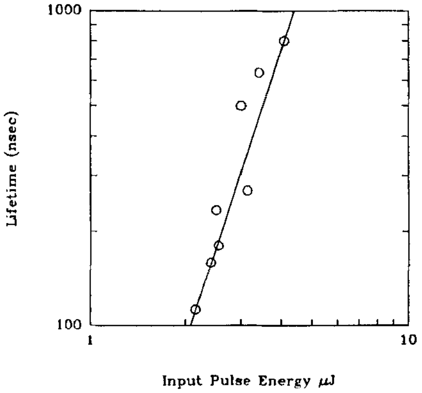

Fig 6 Intensity dependence of long lifetime component.

CONCLUSIONS

Comparison of the optical and transport properties of the solid state of fullerenes to those of the isolated molecule indicate that the electronic properties of the C_{60} molecule are minimally perturbed by the close packing in the solid state. This observation implies that, at least in terms of electronic or optical applications, the material is of little technological interest. Under high intensity illumination, however, both the optical and transport properties of C_{60} undergo dramatic changes. These changes are associated with a Mott-like insulator to metal transition, the result of the onset of intermolecular interactions at high excitation densities. The characteristics of the resultant phase prompt a reassessment of the potential of pristine C_{60} in the solid state.

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