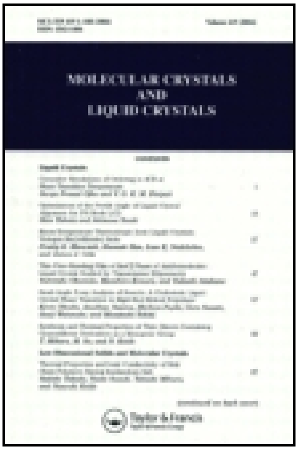

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Excited State Phenomena in Solid State Fullerene

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To cite this article: Hugh J. Byrne , Wolfgang K. Maser , Mathias Kaiser , Lidia Akselrod , Wolfgang W. Rühle , Christian Thomsen , Andreas Mittelbach & Siegmar Roth (1994): Excited State Phenomena in Solid State Fullerene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 49-58

To link to this article: http://dx.doi.org/10.1080/10587259408038210

Mol. Cryst. Liq. Cryst. 1994, Vol. 252, pp. 49–58
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Printed in the United States of America

EXCITED STATE PHENOMENA IN SOLID STATE FULLERENE

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Abstract Photoluminescence, photoconductivity and resonant Raman measurements are performed to investigate the influence of high intensity illumination on the properties of Fullerenes. A highly nonlinear dependence of the luminescence emission efficiency and lifetime is observed on increasing the intensity. This nonlinear increase is associated with a dramatic shift to the red of the emission maximum. The photoconductive response of the fullerenes is also seen to increase nonlinearly with input intensity. Temperature dependent measurements indicate that the nonlinear processes are associated with an insulator-metal phase transition in the material. The transition is reversible and the observed photophysical changes coincide with a reversible shifting of the characteristic fullerene Raman lines to lower energies.

Keywords: fullerenes, photoluminescence, photoconduction, resonant Raman, phase transition

INTRODUCTION

As fully conjugated, molecular organic systems, the fullerenes have attracted much attention for their potential applications as optical and, indeed, nonlinear optical materials[1]. In contrast to other much studied organic conjugated systems, however, the lowest energy electronic transitions in molecular C_{60} are optically forbidden due to the high degree of symmetry of the closed shell electronic configuration[2] leading to a very much reduced optical activity.

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[3-5] rendering the solid state of fullerenes of little interest for optical applications at low excitation densities. In this paper, the response of solid state fullerenes to high excitation densities reported. The properties are seen to undergo dramatic changes which are described and discussed in terms of collective excited state phenomena.

FULLERENES UNDER HIGH EXCITATION DENSITIES

On increasing the input intensity, a dramatic change in the photoluminescence spectrum of C_{60} crystals is observable. Figure 1 shows the evolution of the spectrum over the range $30Wcm^{-2}$ to $1KWcm^{-2}$. The spectral evolution is accompanied by a broadening of the spectrum and a dramatic increase in the luminescence output. Investigations of the temporal decay of the emission indicate that the spectral changes may be associated with the emergence of a long lived emission component. The magnitude of the longlived component increases with the cube of the average input power, in the range $175Wcm^{-2}$ to $1KWcm^{-2}$ as shown in figure 2. Furthermore, within the time window of the measurement (0-10nsec; see refs. 5,6 for details), the decay time of the luminescence, extracted from a fit to a single exponential decay, is seen to increase with intensity, with a dependence of at least squared. The intensity onset of this behaviour appears to be a threshold value and varies with position on the sample by a factor of the order of two. The features of the observed behaviour, including the nonlinear evolution of the emission spectrum, a continuous, nonlinear increase in the luminescence efficiency as well as lifetime, may not easily be accounted for by a model system based on static energy levels. The apparent existence of a threshold intensity for this behaviour is indicative of the requirement of a critical excited state density.

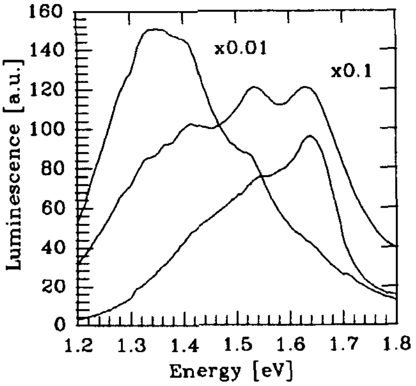

Fig. 1: Luminescence Spectra of C_{60} Crystal illuminated with increased illumination from 0.1, 0.5 and 3.0mW.

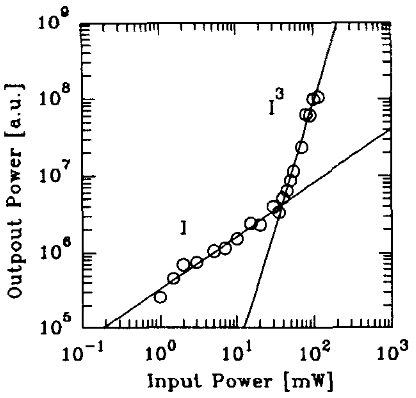

Fig. 2: Dependence of the long lived luminescence on input intensity.

The behaviour observed in the photoluminescence of C_{60} under high intensity illumination is a strong departure from the intramolecular processes observable in solution and in the weakly excited solid state, and, in order to further investigate this phenomenon, the transport properties of the system under high level illumination were investigated. Under low intensity illumination, the photoconductive response of fullerene crystals is linear in intensity[7] and the temperature dependence shows the transport process to be thermally activated, characteristic of a molecular insulator or semiconductor. At elevated intensities, the intensity dependence of the photoconductive response initially reduces to a square root dependence due to the contribution of bimolecular recombination processes[8]. This square root dependence is therefore the first indication of the onset of the interaction of neighbouring excited balls. As is shown in figure 3 this square root dependence is transformed to a cubic dependence upon further increase in intensity. The onset of the cubic dependence of the photoconductive response coincides with the visible onset of the nonlinear

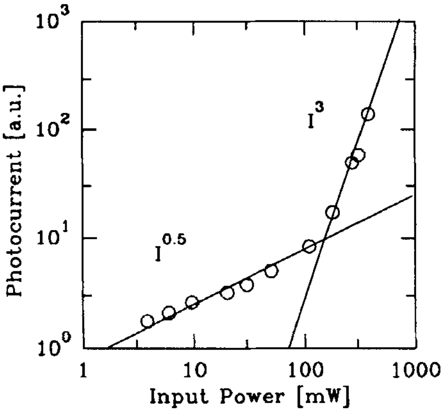

Fig. 3; Intensity dependence of the photocurrent in the fullerene crystal.

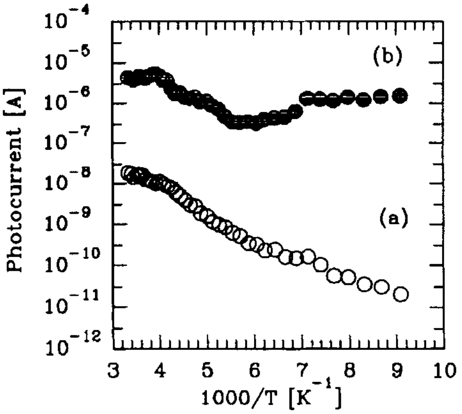

Fig. 4: Temperature dependence of the photoconductivity at (a) low and (b) high illumination conditions.

photoemission process described above and the nonlinear behaviour of the transport properties may, therefore, be associated with the nonlinearity in the optical properties.

The increase of the photoconductive response over two orders of magnitude seen in figure 3 is indicative of a dramatic change in the nature of the photoconductive state. In order to probe the nature of this highly excited state, the temperature dependence of the photoconductive response of highly excited fullerene was monitored. In figure 4(b), the temperature dependence of a crystal illuminated with 300Wcm^{-2} average intensity, an intensity just above the threshold intensity, is compared to that of the same crystal illuminated with 3Wcm^{-2} (figure 4(a)). The measurement was performed by sweeping the temperature and monitoring the high and low intensity response at each temperature. Whereas the low intensity photoconductive response decreases by three orders of magnitude over the temperature range measured, the high intensity response remains constant within an order of magnitude. 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.

The nonlinear behaviour of both the luminescence and transport properties of C_{60} under high intensity illumination are indicative of a transition between a phase which is dominated by molecular processes at low intensities, to one which is more metallic in nature at high excitation densities. 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[9] which is positioned at $1468cm^{-1}$. Although in many samples at room temperature, the mode is seen to degrade to a positioning at $1459cm^{-1}$, with no intermediate, due to a photochemical degradation of the material[10], in the samples studies here, no such degradation was observed. With increasing intensity, however, the mode positioning is seen to shift continuously to lower frequencies. Figure 5 shows the intensity dependence of the mode positioning. Clearly the dependence is nonlinear, and it can be fitted to a power law of order between two and three. The mode reaches a minimum frequency positioning of $1463cm^{-1}$. The mode shifting is accompanied by a strong increase in the Raman intensity as shown in figure 6. The intensity dependence of the Raman intensity 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. In terms of the nature of the Raman spectroscopic changes, both the frequency shift and the increase in intensity are consistent with an increased delocalisation of the π-electrons between the balls[11], consistent with the proposed Mott-transition.

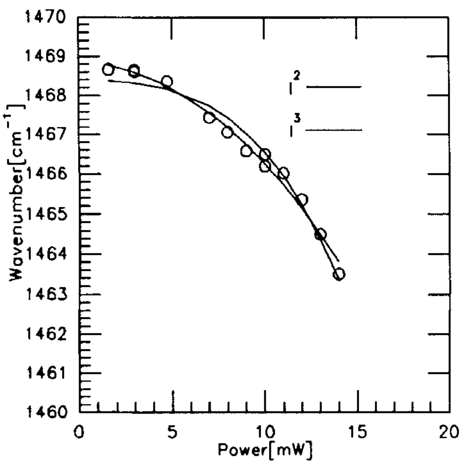

Fig. 5; Intensity dependent shift of Raman pentagonal pinch mode.

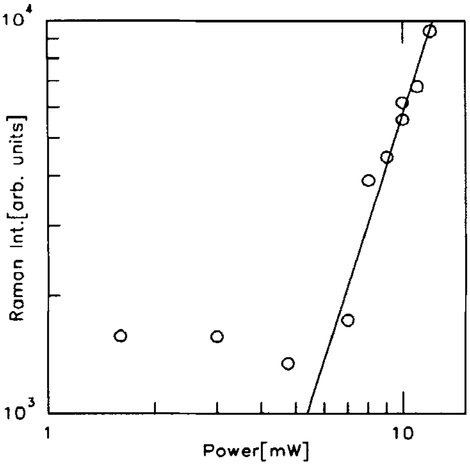

Fig. 6; Increase in Raman intensity with increasing input intensity. Solid line shows a slope of 3.

MANY BODY PROCESSES IN SEMICONDUCTORS

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[12]. Perhaps the mos 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[13]. The most extensive investigations have been carried out on Germanium and Silicon. In both materials, high intensity illumination leads to the emergence of a photoluminescence emission which is red shifted with respect to that of the free exciton[14,15]. As in the case of fullerenes, the dependence of the emission intensity on excitation intensit has been shown to be cubic in both materials[16,17]. The deca kinetics of the red-shifted emission was shown by Westervel et al. to be highly nonexponential, the decay rate increasing with time[18]. Further nonlinear behaviour was observed in the photoconductive response of Ge at high excitation densities [19]. Although not considered in the original work, a cubic dependence of the photocurrent above threshold fits well to the data and the similarities to the behaviour described in figure 3 are remarkable. The many body processes giving rise to the behaviour described come into play when the excited state density dependent exchange and correlation interactions become comparable to the exciton binding energy.

The similarities of the properties of the highly excited state to those of Ge and Si at low temperatures prompt an evaluation of the contribution of correlation and exchange energies in fullerenes. The "exciton" binding energy in fullerenes is ~0.7eV[20]. Band calculations of fullerenes in the solid state yield effective masses of the electron and hole to be 1.41 and 1.1, respectively[21], corresponding to a reduced mass $\mu=0.65$. The exciton Bohr radius is given by $a_o=h^2\varepsilon/\mu e^2$, where ε is the dielectric constant. Taking $\varepsilon=4.3$ [22], the resultant value of $a_o=0.35$nm is consistent with the dimensions of a molecularly localised excited state, analogous to a Frenkel exciton in inorganic semiconductors. The exciton binding energy, given by

$$E_x = \frac{e^2}{\pi\varepsilon_o\varepsilon a_o} \qquad (1)$$

may be calculated to be ~0.5eV and is consistent with the separation of the HOMO-LUMO transition and the first solid state feature, or bandgap, in fullerenes[20,23].

In such a system, the critical, or so-called Mott density, at which the exciton binding energy becomes screened is given by[24]

$$n_c a_o^3 \sim (0.25)^3 \sim 10^{-2} \qquad (2)$$

and may be calculated to be ~$1.4 \times 10^{20} cm^{-3}$. The molecular density is ~$3.6 \times 10^{20} cm^{-3}$, and so this corresponds to an excitation density of ~40%. Both the exchange and correlation energies are strongly dependent on band structure and anisotropy, but it has been shown that their sum is largely independent, enabling a universal description of their contribution in the form[25],

$$E_{xc}(r_s) = \frac{a+br_s}{+dr_s+r_s^2} \qquad (3)$$

where a=-4.8316, b=-5.0879, c=0.0152 and d=3.0426. r_s is the mean distance between excitations. Using the parameters above, the exchange-correlation energy may be calculated as a function of excitation density, and is plotted in figure 7. At a density of $1.4 \times 10^{20} cm^{-3}$, E_{xc} increases above that of the exciton binding energy and, at a density of $4 \times 10^{20} cm^{-3}$, the excess energy has a value of 150meV.

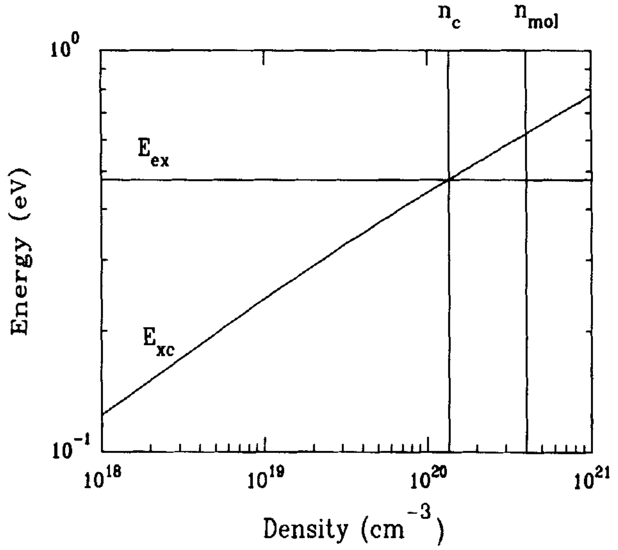

Fig.7; Plot of the sum of exchange and correlation energies as a function of excitation density.

Comparison of the exchange and correlation energies at high excitation densities to the low intensity molecularly localised energies therefore supports the existence of a Mott-like transition at a critical density of ~1x $10^{20}cm^{-3}$ and the increasing prevalence of E_{xc} can result in an energy shift of 150meV, consistent with that observed in the photoluminescence of fullerenes at high intensities. Such a calculation, combined with a comparison of the cubic dependence of both the photoluminescence output and the photocurrent, in fullerenes and both Ge and Si, strongly supports the proposition that the nonlinearities observed are governed by similar interactions.

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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