ELECTRON AND HOLE GENERATION IN ANTHRACENE CRYSTALS†

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ABSTRACT

Experimental results regarding electron and hole production in anthracene crystals are reviewed with emphasis on the relevance of these studies to the fundamental question of the nature of the excess electron states in these low mobility crystals. It is pointed out that a number of experiments suggest that above a threshold of about 4 eV in anthracene crystals, electronic transitions involve transitions of an electron from a ground state to a quite broad band rather than to bound states, some of which subsequently autoionize to create carriers, as has been thought to be true in the past. Most of the electrons created in this process apparently immediately recombine with the hole which was simultaneously created because they both have very small mean free paths for energy losing collisions and thus remain trapped in each other's coulomb field. Another experimental test of this hypothesis is proposed. The various types of carrier generation processes which have been observed and which will ultimately be useful in studies of highly excited states in anthracene crystals are reviewed.

INTRODUCTION

The description of carrier transport in low mobility materials is still an outstanding problem in solid state physics and it appears that organic solids can play a very important role in determining what processes are involved. Generally it has been found that carrier mobility in organic crystals is in the low mobility range and in some ways, primarily experimental, organic crystals are simple, clean systems compared to the inorganic crystals in which low mobility transport has been observed. At least in the case of anthracene, high purity single crystals are relatively easily prepared in which electron and hole lifetimes are in excess of 100 μsecs and very extensive measurements have been carried out to experimentally characterize both carrier and energy transport processes.

In this paper studies of carrier production in anthracene will be reviewed with primary emphasis on the relevance of these studies to the fundamental question of the nature of the excess electron states. Before reviewing the carrier generation studies, a brief discussion of our present knowledge of carrier transport in anthracene is presented.

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CARRIER TRANSPORT

During the past ten years there have been extensive investigations of the drift mobility of both electrons and holes in anthracene crystals. It is well established that both carriers have mobilities of the order of 1 cm^2/V sec, that the mobilities are slightly anisotropic and that they depend weakly on temperature[1]. Theoretical calculations in the early sixties using the tight binding approximation provided very good agreement between theory and experiment[2]. It was assumed that the mean free path or mean free time was isotropic and these quantities were used as adjustable parameters. This theory indicated that the bands were extremely narrow, of the order of kT or less, but in spite of the bands being very narrow, the theory did satisfy uncertainty principle requirements. Such experimental data as mobility anisotropy and pressure dependence seemed to support the theory and there were numerous improvements added to the initial paper[3].

In these papers the electron phonon interaction was introduced phenomenologically through the adjustable mean free path or mean free time and no attempt was made to discuss the interaction quantitatively. Subsequently, there have been a number of papers on the electron phonon interaction[4] and, in general, the indications are that the electron phonon interaction is stronger than is consistent with the simple tight binding band calculation and that some form of hopping motion seems to be called for.

A fairly good test of the validity of tight binding band theory was proposed by LeBlanc[5] and Friedman[6]. They pointed out that if the narrow band theory were right an anomalous Hall effect would be observed; the magnitude of the Hall current should indicate a mobility of the order of 5–10 cm^2/V sec and the sign of the current should be reversed. Numerous measurements of a Hall effect have been reported but the results disagree[7].

It has been shown that both electrons and holes do move in bands which are less than kT wide. Hoesterey[8], in a study of trap modulated mobility, showed that quantitative agreement between theory and experiment could be obtained if it was assumed that all the states in the hole band were within kT of the top. Naphthacene molecules were added in known quantities as an impurity in anthracene crystals and the drift mobility of holes studied as a function of both naphthacene concentration and temperature. The naphthacene molecules act as an electron trap 0.43 eV deep. Similarly, it has been found that carbazole acts as an electron trap 0.26 eV deep and that quantitative agreement between theory and experiment can be obtained by assuming that all the states in the electron band are within kT of the bottom of the band[9].

It has also been shown experimentally that both electrons and holes have very short mean free paths, small compared to 100 Å. A number of laboratories have measured the electron-hole recombination coefficient[10, 11] and found it to be about 1×10^{-6} $cm^3 sec^{-1}$. This large value for the recombination coefficient requires that the mean free path of both electrons and holes be small compared to the dimensions of the coulomb potential well, that is, small compared to the distance at which the potential of one carrier in the electric field produced by the other is equal to kT, about 120 Å in anthracene. Langevin[12] pointed out that under these conditions the relative drift

velocities v_d of an electron and a hole when they are a distance r apart is $(\mu_h + \mu_e)\ (e/\varepsilon r^2)$ where μ_e and μ_h are the electron and hole drift mobility, respectively, and ε is the dielectric constant. Therefore, the rate of influx of electrons into a sphere of arbitrary radius r drawn around a hole, and thus the recombination rate constant, is

$$\gamma = 4\pi r^2 v_d = \frac{4\pi e}{\varepsilon}(\mu_h + \mu_e).$$

By substituting 1 cm^2/volt sec for μ_e and μ_h and $\varepsilon = 3$, γ is found to be 1.2×10^{-6} $cm^3 sec^{-1}$, in excellent agreement with the experimental values. Therefore, experimentally it has been shown that the carriers have mean free paths small compared to 100 Å.

Finally, one last experimental observation[13], which may ultimately be very important in determining which theoretical model is correct, is that apparently the drift mobility of carriers in anthracene is independent of applied fields up to fields of 10^5V/cm. This means that even at drift velocities comparable to what the narrow band theory says is the thermal velocity of the carriers, the drift mobility is still about 1 cm^2/V sec. This observation makes it highly unlikely that the narrow band description is valid.

In summary, it has been shown experimentally that electrons and holes in anthracene have drift mobilities on the order of 1 cm^2/V sec and that the mobilities are weakly temperature dependent and independent of field up to 10^5 V/cm. Also, the carriers move in a band of states which is less than kT wide with a mean free path which is small compared to 100 Å. It seems fairly certain that the tight binding band theory is inadequate to explain these observations and that some form of hopping motion needs to be incorporated in the theory although no theory has yet been developed.

CARRIER GENERATION

As might be expected the carrier generation processes in these low mobility, short mean free path molecular crystals exhibit some differences from that of the well understood, high mobility materials and it appears that very careful studies of the carrier generation process will provide new insight into carrier transport processes in these low mobility materials. Excitons play a large role in some of the processes and discussions are in progress regarding the role of highly excited molecular states and geminate recombination, i.e. recombination of an electron and hole before they have had a chance to separate from one another. Typically the quantum efficiency for the various carrier generation mechanisms has been found to be extremely low, of the order of 10^{-4}.

The early photoconductivity work on anthracene involved carrier generation by excitons interacting with impurities on the surface or surface states[1]. Strongly absorbed light created excitons very near the crystal surface and these in turn interacted with the surface. Many puzzling phenomena were and still are observed but generally it has been found that the processes involved are too complex to provide any insight into the fundamental properties of the anthracene crystal.

X-Ray Experiments

Recent work on carrier generation by x-rays in anthracene has provided strong evidence that geminate recombination plays a big role in carrier generation processes[11]. When x-rays interact with semiconductors, it is usually found that the average energy deposited per electron hole pair created is of the order of three times the band gap[14] and in gases, even gases of fairly complex molecules, it is found that of the order of 30 eV are deposited for each ion pair created[15]. In the case of anthracene crystals it was found that on the average 3000 eV were deposited for every electron hole pair created, about one hundred times as much as expected on the basis of the ion yield in gases and more than two hundred times as much as that expected on the basis of experiments conducted on semiconductors. These results, however, have been shown to be consistent with the very large value of the recombination coefficient discussed in the last section[11].

The large value of the recombination coefficient shows that the mean free paths for energy losing collisions for electrons and holes are small compared to the dimensions of the coulomb potential well, i.e. small compared to the distance r_0, at which the coulomb potential energy of one carrier in the field of the other is equal to kT. Therefore, even when an electron is created with sufficient kinetic energy to escape from the coulomb field of the hole left behind, there is a very high probability that it will lose the energy before it has had a chance to escape.

When it is appropriate to describe the motion of a charge carrier with the diffusion equation, that is when the mean free path is small compared to r_0, Onsager[16] has shown that the probability that a diffusing charge carrier will escape from a coulomb potential well is $e^{-r_0/r}$ where r is the distance at which the carrier starts diffusing. He was investigating the creation of ion pairs by high energy radiation in high pressure gases. Onsager also showed that the number of charge carrier pairs created, φ, would depend on the applied field and be $\varphi = A(T)\left[1 + (e^3/2\varepsilon k^2 T^2)E\right]$ where $A(T)$ depends on the initial distribution of diffusing carriers and is a function of temperature but does not depend on the electric field. Higher order terms in E, the applied electric field, have been neglected.

Hummel and Allen[17] have applied this theory in detail to some experimental studies of carrier generation by high energy radiation in hexane and find excellent agreement between theory and experiment. In order to calculate the yield of carriers it is necessary to know the energy spectrum of the electrons created by the radiation as well as the range energy relation and as a result there is considerable uncertainty in this quantity. However, if the yield of carriers is plotted as a function of the applied field, a straight line should result at relatively low fields, if geminate recombination is occurring, and as Onsager pointed out, the slope of this line divided by the yield of carriers at zero electric field should be equal to $e^3/2\varepsilon k^2 T^2$, a quantity which contains no adjustable parameters. Therefore, the field dependence of the carrier yield provides an excellent test for this theory. It is interesting to note that in the studies of ion yields in dielectric liquids[18] the yield of ion pairs is very large in the high mobility liquids, almost certainly indicating that the mean free path is becoming comparable to r_0 so that it is no longer

valid to describe the carrier motion on the scale of a coloumb potential well with a diffusion equation.

Single Photon Experiments

Getting back to anthracene, Batt, Braun and Hornig[19] and Geacintov and Pope[20] have investigated the applicability of geminate recombination to single photon carrier generation processes. It has been shown that single photons of energy greater than 4 eV create free carriers by either a band-to-band transition or a transition to an excited state of the anthracene molecule which can subsequently autoionize. The quantum yield is very low, 10^{-4}, and it was initially thought that this indicated that in an organic molecular crystal like anthracene a direct band-to-band transition was a relatively improbable or forbidden process[21] and that most of the absorbed photons created excitons even when the energy was sufficiently high for a single photon to create a carrier. There have been discussions regarding whether the carriers were created by a weakly allowed band-to-band transition or by autoionization of excitons[22]. The observation of geminate recombination has now added a new dimension to these discussions because it now provides a third possibility.

Batt *et al*[19] and Geacintov and Pope[20] studied the electric field and temperature dependence of carrier generation in the wavelength range where carriers are created by a single photon process. They found fairly good agreement between Onsager's theory and their experimental results, strongly indicating that the carriers are generated in a band-to-band transition and that the low quantum yield arises from geminate recombination. As was pointed out in the discussion of carrier generation by x-rays, the quantum efficiency will depend on the details of where the carriers started diffusing but the electric field dependence, in terms of the slope of a graph of the number of carriers created as a function of electric field divided by the number of carriers created at zero electric field, should have a very specific value. The slope divided by the intercept should be $e^3/\varepsilon k^2 T^2$ and, therefore,

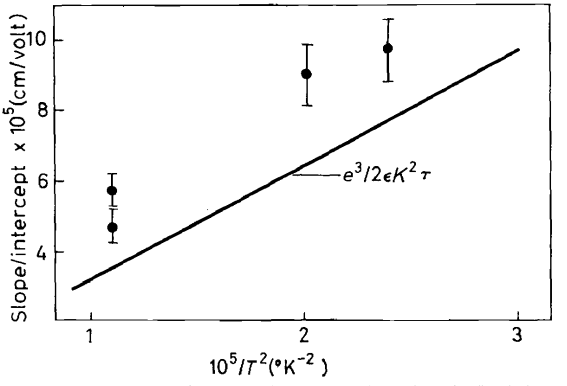

Figure 1. Temperature variation of the carrier generation electric field dependence. The points represent experimental results and the solid line is a theoretical prediction after Batt, Braun and Hornig[19].

should not only have a very specific value but this value should vary as T^{-2}. The agreement between theory and experiment obtained by Batt *et al*[19] is shown in *Figure 1.*

It should be relatively easy to determine experimentally whether or not the low quantum efficiency for carrier generation results from geminate recombination by measuring the fluorescence quantum efficiency as a function of exciting light wavelength in the wavelength range near 4 eV. If geminate recombination is responsible for the low quantum efficiency, the fluorescence quantum yield above 4 eV should drop to about one fourth of its value below 4 eV because it seems unlikely that the singlet character of the molecule ground state would be preserved during the photoionization and carrier recombination process. Therefore, three triplet excitons should be created for every singlet, resulting in one fourth the quantum efficiency. Since it is very difficult to eliminate the possibility of surface quenching of singlet excitons, it would probably be a much more definitive experiment to look for an increase in the number of triplet excitons created by measuring the delayed fluorescence after a pulse of light. Apparently neither of these experiments have been carried out to explicitly check this hypotheses.

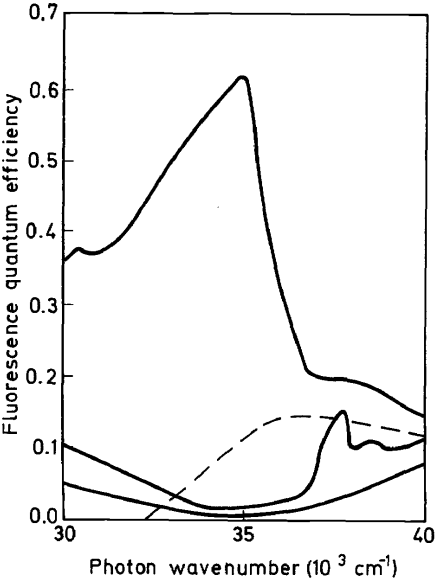

Figure 2. Fluorescence quantum efficiency after Wright[23], upper solid line; extinction coefficient parallel and perpendicular to the *b* axis in the *ab* plane after Bree and Lyons[24], two lower solid lines; and carrier yield after Geacintov and Pope[22], dashed line, versus wavenumber of the incident light.

Wright[23] has measured the fluorescence quantum yield, however, and combining his results with those of Bree and Lyons[24] for the extinction coefficient and Geacintov and Pope[22] for carrier generation as a function of wavelength, results in *Figure 2.* The results are suggestive in the sense that there is a big drop in the quantum efficiency at about the right energy but

not conclusive. Wright interpreted his results on the basis of exciton annihilation at the surface and absorption by a layer of anthraquinone on the crystal surface.

Exciton Ionization

Experiments on anthracene crystals using photons of energy greater than about 3 eV are very difficult because photons with energy greater than 3 eV are absorbed very near the crystal surface and the excitons interact strongly with the surface. A number of second order processes have been observed however and these processes probably will be used to study carrier generation processes in the future when variable wavelength, high intensity lasers become more generally available.

Exciton–exciton annihilation is one second order process which has been considered for years. The existence of the process was questioned for a time but a fairly recent publication[25] appears to present quite definite proof of its existence. It is, of course, not possible to vary the energy of excitation in this process and thus study the nature of highly excited states, but it has been shown that the yield of carriers per exciton–exciton annihilation is very low. Measurements of the exciton–exciton annihilation rate constant[26] have shown that it is about 10^{-8} cm^3 sec^{-1} while the rate of carrier generation[25] by the same process is about 10^{-12} cm^3 sec^{-1}. Thus the quantum efficiency for carrier generation by this process appears to be 10^{-4}, the same as that found for generation by the single photon process.

Another process involving singlet excitons that has been well established is exciton photoionization[27,28]. In studies of carrier generation in anthracene crystals by light from a Q spoiled ruby laser it was found that the number of carriers generated varied as the intensity of the light cubed. It is well known that excitons can be created in anthracene by two photon absorption of ruby laser light and it was hypothesized that carriers were being generated by photons interacting with excitons created by two photon absorption. In order to test this hypothesis an anthracene crystal was irradiated by two pulses of light from a laser separated in time of arrival at the crystal[27] by from 0 to 40 nsec. The two pulses were obtained by sending

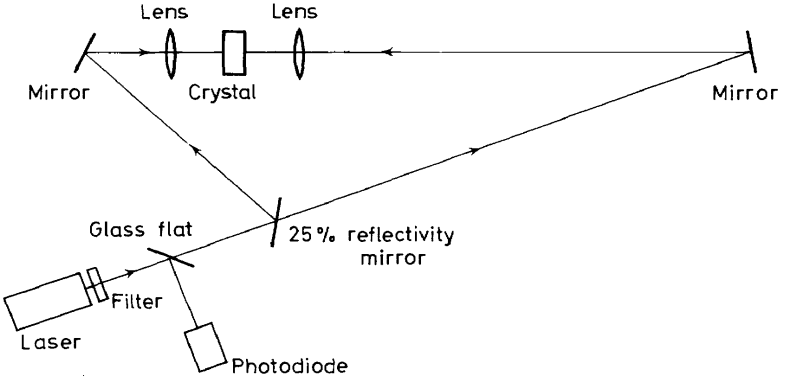

Figure 3. Experimental arrangement used to establish the exciton photoionization process.

the light from the laser through a partially reflecting mirror and the difference in time of arrival was obtained by varying the length of the path one of the pulses took in getting to the crystal. A block diagram of the experimental arrangement is shown in *Figure 3*. The number of carriers created when the two pulses hit the crystal, as well as the number created by each pulse separately, were measured and the experimental results are shown in *Figure 4*.

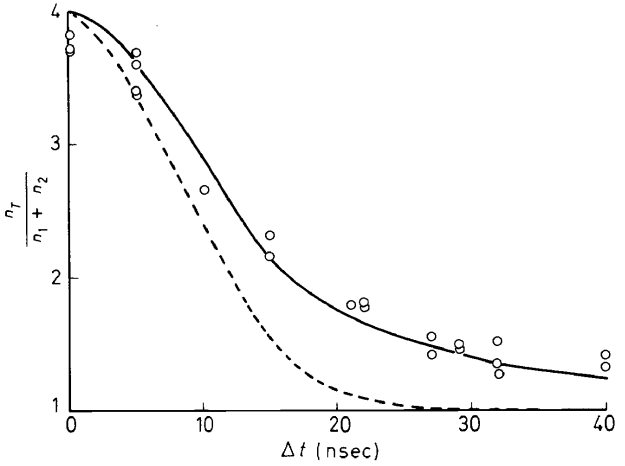

Figure 4. Ratio of the number of carriers, produced by two almost simultaneous light pulses incident on an anthracene crystal, to the sum of the number produced by each pulse independently as a function of the difference in the times of arrival at the crystal of the two pulses. The solid line is the theoretical curve calculated for singlet exciton photoionization and the dashed line is the theoretical curve for three-photon absorption.

The dashed curve indicates the results that would have been expected if no intermediate state were involved, that is if the number of carriers created was just proportional to the integral over time of the intensity of the light cubed. The solid curve was calculated assuming that singlet excitons with a lifetime of 27 nsec were created by two photon absorption and that carriers were created when these excitons were subsequently ionized by another photon. The cross section for exciton photoionization was found to be about 10^{-19} cm^2.

It has also been found that photons from a neodymium laser (1.18 eV) can photoionize excitons but the cross section is about two orders of magnitude smaller than the cross section for ruby laser photons[29] (1.8 eV). In order to carry out this experiment excitons were created by 4250 Å light, obtained by passing the light from a xenon flash tube (about a 2 μsec long pulse) through a monochromator, and while the 4250 Å light was irradiating the crystal, a pulse of photons from a Q spoiled neodymium laser was sent through the crystal. Since the 4250 Å light pulse created carriers by itself, it was necessary to measure both the number of carriers created by the 4250 Å light and the number of carriers created when both light pulses were incident on the crystals. It was assumed that the excess carriers created were created

by exciton photoionization. It was possible to fire the neodymium laser at various times during the flash lamp pulse and measure the number of excess carriers created as a function of the 4250 Å intensity at the time the laser was fired. The experimental results are shown in *Figure 5*. The intensity of the 4250 Å light was about 5×10^{17} photons cm^{-2} sec^{-1} at peak intensity and

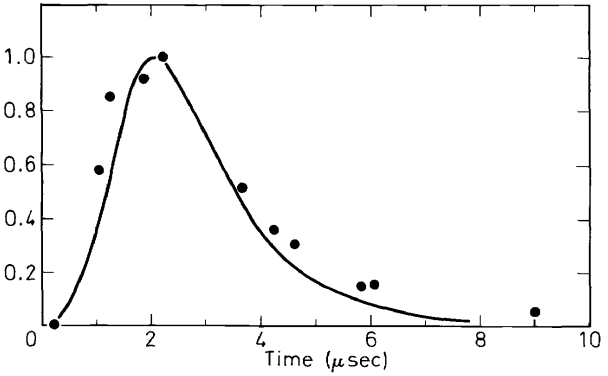

Figure 5. The number of additional carriers created by applying a pulse of light from a neodymium laser to an anthracene crystal during excitation of the crystal with a pulse of 4250 Å light from a flash lamp. The solid curve is the intensity of the 4250 Å light versus time and the solid dots are the number of excess carriers created by the laser pulse. The time at which the laser pulse fired is indicated by the time at which the dot is plotted.

there were about 2×10^{16} photons cm^{-2} in the laser pulse. From this experiment the cross section for photoionization of singlet excitons by neodymium laser photons was found to be about 2×10^{-21} cm^2.

Two Photon Experiments

Strome[30] has recently shown that carriers can also be generated by direct two photon processes. He studied carrier generation in anthracene crystals with photons with energies of 2.07 eV, 2.16 eV and 2.35 eV. At these energies, both the number of singlet excitons and the number of carriers created by the photon pulse were found to depend on the intensity squared. These data were interpreted as evidence for direct two photon transitions.

Strome used a Q spoiled ruby laser to generate anti-Stokes stimulated Raman lines in liquid nitrogen and liquid oxygen to obtain his light pulses. In our laboratory, similar experiments were carried out using frequency-doubled neodymium light (2.35 eV). The intensity dependence of both the fluorescence and the number of carriers created are shown in *Figure 6*. The generation coefficients for carriers and for excitons found in our experiments were 1×10^{-31} cm sec and 8×10^{-28} cm sec, respectively, in excellent agreement with those found by Strome for 2.35 eV photons. It should be noted that in this two photon process there again appears to be a quantum efficiency for carrier generation of about 10^{-4}.

This observation led to an unsuccessful attempt to detect absorption by

excitons[31]. The amount of frequency doubled deodymium laser light transmitted by a 2 cm long anthracene crystal was measured as a function of the intensity of the light. Since the number of excitons created by the light could be calculated from the results of the experiment reported in the previous paragraph, the cross section for photon absorption could be calculated if a saturation in the amount of light transmitted by the crystal could be observed.

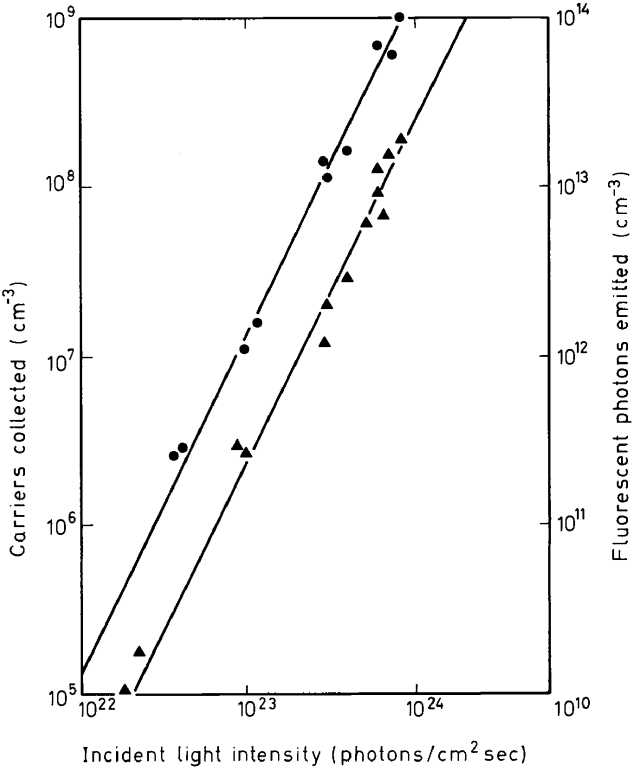

Figure 6. The number of fluorescent photons and the concentration of carriers created in an anthracene crystal by a pulse of frequency doubled neodymium laser light versus the intensity of the light.

Since saturation was not observed, the experimental results, shown in *Figure 7*, only allowed an upper limit of 10^{-17} cm^2 to be set on the cross section for exciton absorption at 5300 Å.

SUMMARY

In anthracene crystals it is known that both holes and electrons have relatively low mobilities, move in a band of states narrow in energy, of the order of kT at room temperature or less and that they both have short mean free paths, small compared to 100 Å. However, the basic mechanism of transport in these crystals has not been established. Early attempts at tight

binding band calculations have given perhaps the most satisfying answers, but in those calculations electron phono interactions were treated phenomenologically and, as investigations into these interactions continue, it appears less likely that a coherent, band theory type approach is adequate.

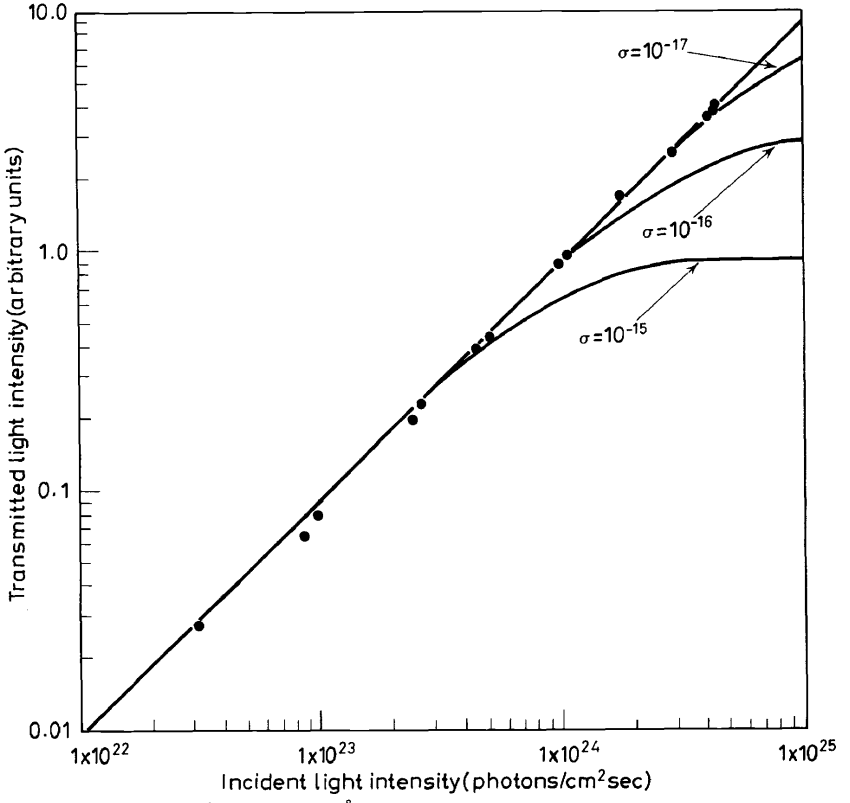

Figure 7. The intensity of light at 5300 Å transmitted by a 2 cm long anthracene crystal as a function of the incident light intensity. The curves labelled $\sigma = 10^{-15}$, $\sigma = 10^{-16}$, and $\sigma = 10^{-17}$ are the theoretical predictions based on the assumption of an exciton absorption cross section of 10^{-15} cm^2, 10^{-16} cm^2, and 10^{-17} cm^2 respectively.

In photoconductivity experiments, band-to-band transitions appear to occur above about 4 eV and no evidence has been found for a narrow band. The quantum efficiency for carrier generation, however, is very low, about 10^{-4}, for all experiments reported for which a quantum efficiency can be determined. There are reasons to believe that this small yield can be explained in terms of geminate recombination, i.e. recombination of an electron with the hole that was created along with the electron before the electron escapes from the coulomb attraction of the hole. In general, the photoconductivity results appear to suggest that above about 4 eV there is something like a wide band of electron states to which transitions can occur.

In anthracene crystals it has been shown that in addition to the standard

one photon carrier generation process, carriers can be generated by exciton photoionization and two photon transitions to highly excited states. With the advent of high power, continuously tunable lasers, these processes could provide the means by which the nature of highly excited electron states in organic crystals are elucidated, and thus, ultimately perhaps, the key to the basic transport mechanism.

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