Generation and Recombination of Holes and Electrons in Anthracene*

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The generation of electrons and holes in anthracene crystals by x rays from a 600-kV pulsed x-ray source was studied. The average energy deposited per electron-hole pair created W was found to be 3×10^3 eV. The number of carriers generated was independent of temperature from -25 to 25°C and depended linearly upon the x-ray intensity. At high intensity, recombination effects become important and the electron-hole recombination coefficient was found to be $(3\pm1)\times10^{-6}$ cm^3 sec^{-1}. The value of the recombination coefficient is shown to be in good agreement with a theoretical value calculated on the basis of a very small mean free path for electrons and holes, and the large value of W is explained in terms of this model. These results imply that only a very small fraction of electron-hole pairs produced by a low-energy process such as a band-to-band transition would appear as free carriers in anthracene, and provide a possible explanation for the commonly observed exponential temperature dependence of photoconductivity.

INTRODUCTION

VERY little use has been made of high-energy x rays in the production and study of charge carriers in organic crystals even though some of their properties appear to make their use very desirable. For example, it is relatively easy to obtain x rays which readily penetrate laboratory size crystals. The carriers resulting from such x rays are uniformly distributed throughout the volume of the crystal. In contrast the carriers resulting from ultraviolet light are created primarily very near the surface of the crystal because the extinction coefficient of the light which exhibits a significant quantum efficiency for carriers production is quite high.[1,2] For some experiments a uniform distribution is quite desirable.[3] Also, with x rays, a large amount of energy is available per photon so that it might be expected that the effects of temperature on the number of carriers generated would be minimized. It is generally found that photoconductivity produced by ultraviolet light is a strong function of temperature,[4] making low-temperature experiments difficult or impossible.

The dc photoconductivity produced by x rays in anthracene has been investigated by Hartmann.[5] In this paper, the results of a pulsed x-ray photoconductivity study are reported. The emphasis is on a study of the carrier generation and recombination processes and the interpretation of the results leads to important conclusions regarding the process of carrier production by ultraviolet light.

EXPERIMENTAL TECHNIQUE

In the experiments reported in this paper, anthracene crystals were irradiated with 0.1 μsec pulses of x rays with a maximum photon energy of 0.6 MeV and an average energy of approximately 0.25 MeV. Filtering provided by a copper screen-room wall eliminated all photons below approximately 50 keV. The energy spectrum of the x-ray pulse has been analyzed by Bouchard.[6]

The sample holder and other experimental apparatus were very similar to those used previously.[1] The same configuration was used for studies involving both light and x-ray excitation thus requiring that the electrodes be conducting glass (for light excitation) with the front electrode very thin (for use with x-ray excitation). The sample holder was evacuated to approximately 10^{-4} Torr for these studies to eliminate possible erroneous signals which result from ionization of the air surrounding the crystal.

The intensity of x rays incident to the sample was varied by changing the distance of the sample from the x-ray source. The x-ray pulse shape and energy spectrum therefore remained constant.

The energy deposited in the anthracene crystal was measured with a silicon *p-i-n* diode[7] and an integrating circuit. The calibration of the diode had been checked against film dosimeters and a thermoluminescence dosimetry system. After measuring the energy deposited in the silicon diode, only a small correction is needed to obtain the energy deposited in anthracene. The ratio of the energy deposited per gram of anthracene to that deposited per gram of silicon was calculated from tabulated values of the absorption coefficient[8] and the x-ray spectrum[6] and was found to be 0.86.

The anthracene crystals used were grown in this laboratory by the Bridgeman technique. The starting

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[1] R. G. Kepler, Phys. Rev. **119**, 1226 (1960).

[2] V. V. Eremenko and V. S. Medvedev, Fiz. Tverd. Tela **2**, 1572 (1960) [English transl.: Soviet Phys.—Solid State **2**, 142 (1961)]; J. W. Steketes and J. deJonge, Philips Res. Rept. **17**, 363 (1962).

[3] It is possible to generate electron and hole pairs in the interior of an anthracene crystal with ultraviolet light (see Ref. 23) but the concentration achievable is either very low or not uniform. Recent experiments with Q-spoiled ruby lasers (see Ref. 21) show they will be useful in this regard.

[4] D. M. J. Compton, W. G. Schneider, and T. C. Waddington, J. Chem. Phys. **27**, 160 (1957); J. Kommandeur, G. J. Korinek, and W. G. Schneider, Can. J. Chem. **35**, 998 (1957); B. Rosenberg, J. Chem. Phys. **29**, 1108 (1958).

[5] H. K. Hartmann, Z. Angew. Phys. **14**, 727 (1962).

[6] G. H. Bouchard, Sandia Laboratory Report No. SC-R-524, 1962 (unpublished).

[7] See R. W. Kuckuck, R. Bernesent, M. R. Zatzick, and C. P. Jupiter, Trans. IEEE **NS-12**, 111 (1966); L. Koch, J. Messier, and J. Valin, Trans. IEEE **NS-8**, 43 (1961).

[8] E. Storm, E. Gilbert, and H. Israel, Los Alamos Scientific Laboratory Report No. LA-2237, 1957 (unpublished).

material was Eastman Kodak H480 anthracene which had been zone-refined. In these crystals the lifetime of the holes and electrons was sufficiently long that it was possible to collect all of the holes and electrons created provided that recombination was negligible. Using x-ray excitation, the carriers are created uniformly within the bulk of the crystal. Since the electrodes on the crystal are blocking electrodes, the resulting photocurrent pulse is the sum of triangular shaped current components caused by drift of holes and electrons to the surface of the crystal. This fact is illustrated in the typical photocurrent pulse shown in Fig. 1. The experimental curve is a very good fit with the sum of the expected current components. The value of the drift mobility for holes and electrons was found to be 0.7 $cm^2\ V^{-1}\ sec^{-1}$ and 0.35 $cm^2\ V^{-1}\ sec^{-1}$, respectively; values which agree well with published[9] values obtained using light excitation.

At the high intensities necessary for the recombination studies, possible space charge effects have to be considered. With 1400 V applied to the crystal, the largest expected space charge would be only 8% of the applied voltage if the amount of the charge collected is considered and electrode cancellation effects are neglected. However, samples exposed to repeated pulses of x rays with no attempt to remove space charge between pulses showed no measurable decrease in the photocurrent signal. There was a waiting period of approximately three minutes between pulses.

EXPERIMENTAL RESULTS

At very low x-ray intensities, where carrier recombination can be neglected, the average amount of energy deposited per electron-hole pair created is found by measuring the total number of carriers created for a known energy deposition. The total number of carriers created is obtained from the area under a current pulse such as that shown in Fig. 1. In a typical experiment 1.9×10^7, electron-hole pairs are generated in a crystal approximately 5 mm in diam and 1.27 mm thick for an energy deposition of 5.6×10^{10} eV, giving an energy deposition of 3000 eV per electron-hole pair created. The actual volume of the crystal was determined by weighing the crystal and dividing the weight by the density. This value has been obtained for several different crystals and with several slightly different experimental arrangements. The number of carriers generated varies linearly with x-ray intensity. Typical experimental results are shown in Fig. 2. The initial value of photocurrent rather than the area under the photocurrent pulse was used in these measurements to avoid the effects of recombination which occur at high intensities. Within experimental error, the number of carriers generated was independent of temperature over the range −25 to 25°C. The experimental results, shown

[9] R. G. Kepler, in *Organic Semiconductors*, edited by J. Brophy and J. Buttrey (The Macmillian Company, New York, 1962), p. 1.

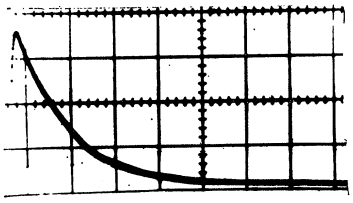

FIG. 1. A typical pulse of current versus time. Each major division on the horizontal scale corresponds to 10 μsec.

in Fig. 3, although independent of temperature are not inconsistent with an activation energy of 0.05 eV as reported by Hartmann[5] but are inconsistent with 0.16 eV, the value observed with optical excitation.[4]

At high x-ray intensities, the carrier density became large enough to allow measurement of the electron-hole recombination coefficient. In order to compare experiment with theory, it has to be noted that although the carriers are generated uniformly within the crystal, the volume in which recombination can take place decreases with time since the carriers are swept out by the applied electrical field. The volume in which recombination can take place, V_r, varies with time in the following manner

$$V_r = V[1-(\mu_h+\mu_e)E_t/d]$$

where V is the crystal volume, d is its thickness, μ_h and μ_e are the hole and electron mobilities and E is the applied electric field. This expression is valid only for time t in the range from 0 to $d/(\mu_h+\mu_e)E$. The time $t_s=d/(\mu_h+\mu_e)E$ corresponds to the time required to separate the electron and hold distributions. Inside the recombination volume the time dependence of the concentration of carriers is given by $dn/dt=\gamma n^2$ where γ is the recombination coefficient and n is the concentration of electrons or holes, these concentrations being equal. The carrier density in the recombination volume is therefore $n=n_0/(1+n_0\gamma t)$ where n_0 is the initial concentration.

The total number of electrons or holes which re-

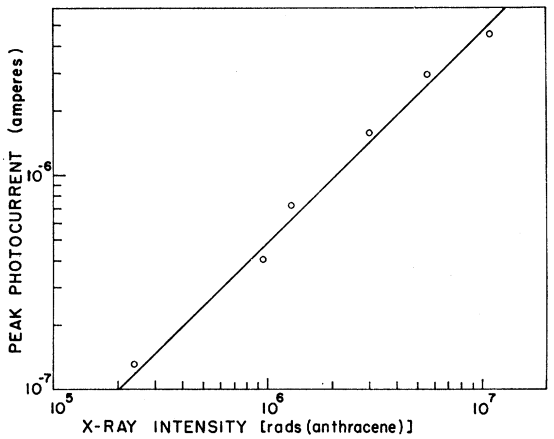

FIG. 2. X-ray intensity dependence of the number of carriers generated by a pulse of x rays. The line drawn represents a linear intensity dependence. One rad is equal to 100 ergs of energy deposited per gram of material.

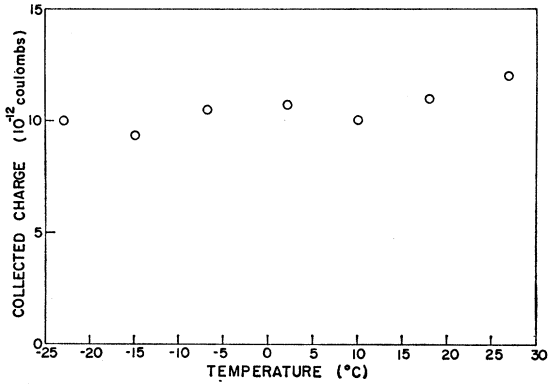

FIG. 3. Temperature dependence of the number of carriers generated by a pulse of x rays.

combine in a given pulse is then

$$N=\int_0^{t_s}\gamma n^2 V_r dt.$$

This equation is readily integrated using the expressions derived for t_s, n and V_r to yield

$$N=n_0V[1-(1/t_s n_0\gamma)\ln(1+t_s n_0\gamma)].$$

This expression has been used to determine the amount of charge collected in a given pulse as a function of the energy deposited in a crystal. The results of an experiment with 1400 V applied to the crystal are shown in Fig. 4. The four theoretical curves shown are for $\gamma=0$, 2, 3, and 4: in units of 10^{-6} cm^3 sec^{-1}. The variation of the amount of charge collected with energy deposited at different applied electric fields is shown in Fig. 5. The solid curves were calculated assuming $\gamma=3\times10^{-6}$ cm^3 sec^{-1}. On the basis of these results it is believed that $\gamma=3\pm1\times10^{-6}$ cm^3 sec^{-1}. This value agrees favorably with that obtained recently[10] using different techniques.

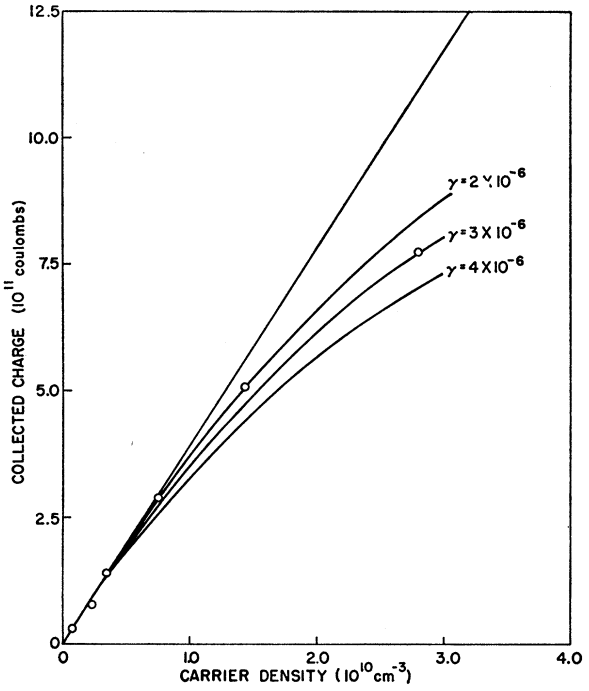

FIG. 4. Total charge collected versus initial carrier density. The solid lines are theoretical curves calculated assuming that the electron hole recombination coefficient $\gamma=0$, 2, 3 and 4×10^{-6} cm^3 sec^{-1}. The voltage applied to the crystal which was 1.27 mm thick was 1400 V.

DISCUSSION OF RESULTS

In 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[11] and in gases, even gases of fairly complex molecules, it is found that of the order of 20–30 eV are deposited for each ion pair created.[12] Therefore, it is quite surprising to find that in anthracene approximately 3000 eV are deposited for every electron-hole pair created and the remaining section of this paper is devoted to an attempt to explain this large value and to consider the consequences of the explanation on other experimental observations.

Recombination Coefficient

We believe that the large value of W and the large value of the recombination coefficient are related. Therefore, let us first discuss the value of the recombination coefficient. Very roughly, recombination involves two steps; the electron and hole have to get close enough to one another so that they could become trapped in each other's Coulomb field and then they have to lose sufficient energy to become trapped. Classically an electron becomes trapped in a Coulomb field if its kinetic energy is less than its potential energy in the field. Therefore, if an electron gets closer to a hole than a critical radius r_0 defined by $\frac{3}{2}kT=e^2/\epsilon r_0$ the probability that it is trapped and eventually recombines with the hole increases markedly. In this expression k is Boltzmann's constant, T is the absolute temperature, e is the electric charge and ϵ is the dielectric constant of the material. In a theory on ion recombination in gases, Thompson[13] assumed that recombination will take place if a collision occurs in which one of the ions loses an energy of the order of or greater than kT when the ions are less than r_0 apart. If the mean free path for an energy losing collision is λ, the probability that a collision will occur while traversing a sphere of radius r_0 is $4r_0/3\lambda$ since the average distance across a sphere is $\frac{4}{3}r_0$. The number of spheres per unit density that a

[10] W. Helfrich and W. G. Schneider, Phys. Rev. Letters **14**, 229 (1965); M. Silver, Bull. Am. Phys. Soc. **11**, 269 (1966).

[11] See for example F. E. Emery and T. A. Rabson, Phys. Rev. **140**, A2089 (1965); C. Bussolati, A. Fiorentini, and G. Fabri, *ibid.* **136**, A1756 (1964).

[12] H. W. Fulbright, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XLV, p. 11.

[13] H. S. W. Massey, and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), Chap. X.

particle of velocity v will encounter per unit time is $\pi r_0^2 v$ and therefore Thompson's recombination-rate constant is $(4\pi v/3\lambda)r_0^3$.

This theory is valid only if $\lambda \gg r_0$ because as λ approaches the value of r_0 it is no longer true that the rate of passing through spheres of radius r_0 per unit density is equal to $\pi r_0^2 v$. Langevin[13] has proposed a theory for recombination in gases which is appropriate if $\lambda \ll r_0$. He pointed out that the relative drift velocity v_d of a positive and a negative ion when they are a distance r apart is $(\mu_+ + \mu_-)(e/r^2)$ where μ_+ and μ_- are the drift mobilities of the positive and negative ions, respectively. Therefore the rate of influx of positive ions into a sphere of arbitrary radius r drawn around a negative ion, and thus the recombination rate constant is $4\pi r^2 v_d = 4\pi e(\mu_+ + \mu_-)$. This theory can be applied to electrons and holes in solids just by including the effect of the dielectric constant.

Essentially the same result can be derived in a different manner which makes the connection with Thompson's theory much more apparent. When $\lambda \ll r_0$ the probability of an energy losing collision while inside a sphere of radius r_0 is one so we only have to determine the rate at which electrons enter a sphere of radius r_0 around a hole. Chandrasekar[14] has shown that this rate per unit concentration of holes and electrons is $4\pi D r_0$ if the motion of the electron relative to the hole can be described by a diffusion coefficient D when they are farther than r_0 apart and if the electron cannot escape after it has entered the sphere. This expression applies only if $\lambda \ll r_0$. From the Einstein relation $D=(kT/e)\mu$, and since $r_0 = 2e^2/3\epsilon kT$, it is found that $4\pi D r_0 = 8/3\pi(e\mu/\epsilon)$ which is the same as Langevin's result except that a factor of 8/3 was obtained rather than 4.

Recombination coefficients as large as that predicted by the Langevin formula are not usually observed,[15] however it does appear that electron capture by α centers in KBr agrees with the Langevin theory at low temperature.[16] In anthracene it is probable that the mean free path for carriers is less than 100 Å[17] so that it seems likely that the Langevin theory might apply. The dielectric constant of anthracene[18] is of the order of 3 and therefore r_0 is about 120 Å. If we take $\mu_+ + \mu_- \approx 2$ $cm^2\ V^{-1}\ sec^{-1}$ and $\epsilon = 3$, the recombination coefficient according to Langevin's theory should be 1.2×10^{-6} $cm^3\ sec^{-1}$. This value is in reasonably good agreement with the experimental value of 3×10^{-6} $cm^3\ sec^{-1}$ and and therefore the small mean free path is indirectly confirmed.

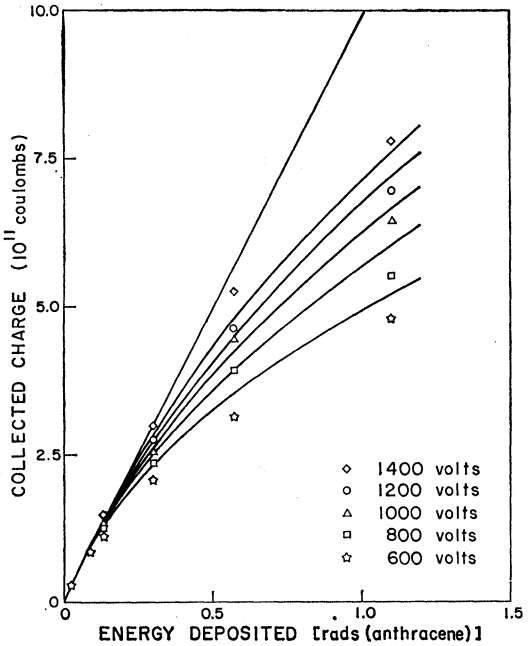

FIG. 5. Total charge collected as a function of x-ray intensity with different voltages applied to the crystal. The straight line is the result expected for no recombination. The curved lines are theoretical lines and were calculated for the different applied voltages assuming that the recombination coefficient is 3×10^{-6} $cm^3\ sec^{-1}$.

Carrier Generation by X Rays

In view of these results, it appears that only those electron-hole pairs which are created in such a way that they end up more than about 120 Å from one another will actually appear as free carriers. With high-energy x rays, it is easy to see that some of the electrons are created with sufficient range. Range here refers to the distance an electron travels in the process of losing its excess energy. The primary process for interaction of x rays of the energy used in this experiment with anthracene is Compton scattering and, considering the x-ray photon spectrum, it can be shown that the average Compton electron will have an energy of about 6×10^4 eV. The range of an electron of this energy is about 50 μ.

The number of Compton electrons created was calculated using the photon-energy spectrum[6] and the cross section for Compton scattering[8] and it turned out to be about a factor of ten smaller than the number of carriers created. Therefore, if this model is right, each primary Compton electron will have to produce about 10 secondary electrons with sufficient energy that their range is greater than 120 Å. It is difficult to talk about ranges (R) as short as 120 Å but if one does extrapolate from higher energy data it is found that $R \sim 120$ Å when $E = 500$ eV.[19] Monte Carlo calculations[20] indicate that

[13] S. Chandrasekar, Rev. Mod. Phys. **15**, 1 (1943). The appropriate derivation begins on p. 60.
[15] M. Lax, Phys. Rev. **119**, 1502 (1960).
[16] R. S. Crandall, Phys. Rev. **138**, A1242 (1965).
[17] O. H. LeBlanc, J. Chem. Phys. **35**, 1275 (1961).
[18] The principal indices of refractions are 1.55, 1.77, and 2.04 [I. Nakada, J. Phys. Soc. Japan **17**, 113 (1962)] and it appears that the dielectric constant will be determined only by the molecular polarizability. Therefore the dielectric constant should be equal to the square of the index of refraction.
[19] M. J. Berga and S. M. Seltzer, Natl. Acad. Sci.—Natl. Res. Council, Publ. **1133**, 264 (1964).
[20] D. O. Schneider, and D. V. Cormack, Radiation Res. **11**, 418 (1959).

a 50-keV electron in the process of slowing down would create approximately 10 secondary electrons with energy in excess of 300 eV and therefore this model predicts the right order of magnitude for the number of carriers produced by high-energy x rays.[21]

Therefore, it appears that when carriers are produced by high-energy x rays, only those electrons which are given sufficient energy to go a distance greater than r_0 become free carriers. Only a very weak temperature dependence is expected on this basis, consistent with the experimental observations, since only the minimum energy required to produce a free carrier would vary with temperature.

Carrier Generation by Light

When optical photons are used to create carriers it is not possible to give an electron sufficient energy to go more than a distance r_0 by brute force as in the case of x rays. It appears that the only chance an electron has to get free of the Coulomb field of the hole left behind is if it does not suffer any collisions while it travels the distance r_0. If an electron has a mean free path λ the probability that it will travel a distance r_0 without suffering a collision is $e^{-r_0/\lambda}$. Therefore, it appears that only the fraction $e^{-r_0/\lambda}$ of those electron-hole pairs produced by low-energy photons will appear as free carriers.

It has often been observed in photoconductivity experiments that the photocurrent varies exponentially with temperature.[4] Usually it appeared that the exponential temperature dependence might be associated with an extrinsic process occurring at the surface of the crystal but in a recent experiment using a Q-spoiled ruby laser to generate carriers,[22] it was found that this temperature dependence was associated with an intrinsic carrier-generation mechanism. Although an activation energy is usually calculated from the experimental results and a value of about 0.16 eV found, there is nothing which requires interpretation in terms of an activation energy. The experimental observations could just as well be described by pointing out that the photocurrent varies exponentially with temperature as $e^{-T_0/T}$ where T_0 is a characteristic temperature.

It is easy to see that the considerations described above would lead to this type of behavior. Since r_0 is proportional to $1/T$, $e^{-r_0/\lambda}$ would look like $e^{-T_0/T}$ provided λ was relatively independent of temperature. If we equate r_0/λ to T_0/T and use the fact that $kT_0 \sim 0.16$ eV, it is found that at room temperature r_0/λ is approximately 6, a very reasonable value.

These considerations therefore indicate that the exponential temperature dependence is related to the probability that the carriers will become free after a band-to-band transition and that the characteristic temperature T_0 is determined primarily by the carrier mean free path, being equal to $2e^2/3\epsilon k\lambda$. At room temperature only about 0.5% of the carriers created by a band-to-band transition in anthracene would actually become free carriers and this percentage would vary exponentially with temperature.

If these considerations are correct, it would mean that the experimental rate constant recently determined by Silver *et al.*[23] for carrier creation by exciton-exciton interactions should be multiplied by a factor of 200 before comparing it with the theoretical value obtained by Choi and Rice[24] and hence it now appears that there is little agreement between theory and experiment.

CONCLUSION

In conclusion, it appears possible to explain the very large amount of energy deposited per electron hole pair created when high-energy x rays are used to create electron-hole pairs. The model is the same as that used to explain the very large value of the electron-hole recombination coefficient and results primarily from an assumption that the mean free paths for electrons and holes in anthracene are less than 100 Å. Extension of these considerations to carrier generation by relatively low-energy photons indicates that the exponential temperature dependence of photoconductivity might also be explained by the same mechanism and comparison of theory with experiment indicates a mean free path of about 20 Å.

ACKNOWLEDGMENTS

The assistance of W. H. Buckalew with some of the energy-deposition problems and the technical assistance of F. C. Peterson are gratefully acknowledged.

[21] A yield of approximately 10 electron-hole pairs for each 50-keV electron incident on an anthracene crystal has recently been reported [J. L. Delaney and J. Hirsch, Solid State Commun. **4**, 107 (1966)] providing additional confirmation for this model.

[22] F. N. Coppage and R. G. Kepler, Bull. Am. Phys. Soc. **11**, 268 (1966); Mol. Cryst. (to be published).

[23] M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters **10**, 12 (1963).

[24] S. Choi and S. A. Rice, J. Chem. Phys. **38**, 366 (1963).