X-Ray Induced Currents in Anthracene and Tetracene

I. Turiel and H. Kallmann *

Radiation and Solid State Laboratory Physics Department, New York University
New York 10003

(Z. Naturforsch. **24 a**, 1347—1352 [1969]; received 16 June 1969)

Herrn Prof. Dr.-Ing. H. Gobrecht *zum 60. Geburtstag gewidmet*

A new method which avoids making measurements or applying an external voltage while the X-rays are on, was used in investigating the ionization process by X-rays in organic crystals (tetracene and anthracene). The following results were obtained: The X-ray induced current is linear with electric field strength over a large range of field strengths and saturates at field strengths above 10^4 V/cm; it is proportional to the intensity of irradiation and to the thicknes of the sample for the same field strength; about 1500 eV are required to produce one charge pair in anthracene and 400 eV in tetracene. It was also found that the saturation field strength is independent of the X-ray intensity (the intensity was varied by a factor of ten). From these results it was concluded that recombination occurs mostly between the electron and the hole from which it was separated. It was also found that a large X-ray irradiation (8×10^5 ergs absorbed) produces trapping sites in the bulk of the crystal which trap charges and thus produce some bimolecular recombination.

The barrier method[1] has been used to determine X-ray induced currents in organic crystals. It allows the determination of charge production by X-rays after removal of the X-rays and the external field, avoiding external ionization currents and the use of a vacuum chamber. The charge separation can even be effected without a concomitant external field, by making use of an internal field confined to the bulk of the crystal.

The crystal to be investigated is sandwiched between an electrode and a thin insulating barrier such as mylar. The mylar exhibits negligible conductivity compared to the crystal under light or X-ray irradiation. Movable charges are produced by X-rays in the bulk of the crystal. If an electric field lies across the crystal, charges of one sign which have not recombinaed accumulate at the crystal-mylar interface. These charges have been shown to persist at the barrier, in the dark and without an external field applied, for several days[2] (persistent internal polarization). The accumulated charge can be released by irradiating the crystal with X-rays or light of the proper wavelength, which produce free charge carriers which move in the internal field in such a way so as to recombine with the previously accumulated charge. (It has been found that no net space charge is stored in the bulk of the crystal under the X-ray excitation used in these experiments.) Two methods of measuring X-ray induced currents have been employed.

(1) X-rays and an external field are applied concomitantly for a given time period. Only after their removal, the charge which was accumulated at the crystal-mylar interface during the X-ray irradiation is measured by the light release method. That is, it is released by light produced charge carriers while one side of the sample is grounded out and the other side is connected to an electrometer. The resulting current pulse is a measure of the accumulated charge. By repeating this procedure for different periods of X-ray irradiation, one obtains the accumulated charge as a function of polarizing time. The initial slope of this rise curve of polarization gives the X-ray induced current at whatever external field was applied during polarizing. This method circumvents measuring the X-ray induced current during irradiation and thus avoids external ionization currents and the effects of stray X-ray radiation on measuring equipment. Charges are accumulated and released only at the crystal-barrier interface.

(2) An alternate method which avoids the application of X-rays during the presence of an external field is the following: The barrier is charged to a known charge accumulation Q by light. After removal of the external field, an electric field exists

---

Sonderdruckanforderungen erbeten an Prof. Dr. H. Kallmann, 8000 *München*, 81 Electrastraße 13
* — jetzt München.

[1] S. M. Matthews, I. Turiel, M. Furst, and H. Kallmann, Rev. Sci. Instr. ,**30**, 910 [1958].

[2] J. Freeman, H. Kallmann, and M. Silver, Rev. Mod. Phys. **33**, 553 [1961].

only in the interior of the crystal which has a known strength and is opposite in direction to the external field applied during light polarizing. It persists for a long time in the dark because of the very slow decay of the charge stored at the barrier. However, under ionization of the crystal by X-ray irradiation, the internal field moves the X-ray produced charges towards the barrier and reduces the stored charge. The remaining charge accumulation Q', is then measured by the above-described light release method. The amount of charge released, $(Q - Q')$, during the X-ray application, equals the amount of charge produced by X-rays and collected by the internal field. The reduction in polarization for various periods of time gives a so-called X-ray decay of polarization. It was found that it is almost identical with the polarizing rise curve. In the case of the decay curve, however, only an internal field limited to the crystal collects the X-ray produced charges. From the observation that both curves are similar to each other for thin as well as for thick anthracene crystals, it is concluded that the external field and external ionization did not influence our measurements. This is so because only the charge collected at the crystalbarrier interface is measured.

For small electric field strengths the X-ray induced current was found to be linear with voltage, approaching saturation at high enough fields. The saturation current, i_{sat}, gives the total number of charge pairs αI, created per sec and per cm³ by I, the X-ray energy absorbed per sec and per cm³, according to Eq. (1):

$$i_{\text{sat}} = A e \alpha I d \tag{1}$$

where d is the crystal thickness and A is the area of the crystal within which the electric field is effective in separating charge pairs. $1/\alpha$ is the energy necessary to create one charge pair.

Anthracene Experiments

Thin single crystals ($\sim 30\ \mu$) grown by sublimation and also 1 and 2 mm thick single crystals supplied by the Harshaw Company were investigated. For all crystals studied the X-ray induced current was found to be proportional to the absorbed X-ray intensity, and to the thickness of the crystal for equal field strengths. This was true even at small field strengths well below the saturation field strength. It also depended linearly on electric field strength until saturation began. All crystals investigated showed saturation at electric field strengths between 1.0×10^4 V/cm and 2.2×10^4 V/cm. Typical curves obtained are shown in Fig. 1 for a 1 mm thick crystal with an absorbed energy of 236 erg sec^{-1} cm^{-3} and 118 erg sec^{-1} cm^{-3}. Saturation, for this crystal, occurs at about 10,000 V/cm for X-ray intensities varying over a factor of ten. For an absorbed energy of 236 ergs sec^{-1} cm^{-3}, the saturation current density of the above crystals is 14.6×10^{-10} A/cm² and $1/\alpha$ is equal to 1610 eV per charge pair. The X-ray tube voltage was 60 kV for all experiments.

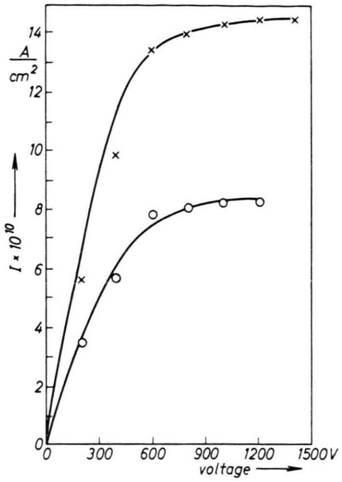

Fig. 1. X-ray current density vs. voltage, 1 mm (I) anthracene. × — × $I = 236$ erg sec^{-1} cm^{-3}, ○ — ○ $I = 118$ erg sec^{-1} cm^{-3}

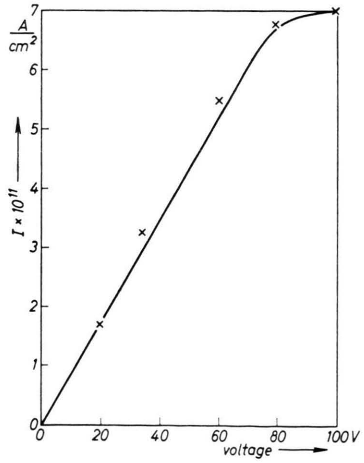

Fig. 2. X-ray current density rs. voltage, 36 μ anthracene crysta, $I = 328$ erg sec^{-1} cm^{-3}.

Crystal	Electrode type and area	Barrier area cm^2	Effective volume cm^3	I_{sat} A/cm^2	Intensity erg sec^{-1} cm^{-3}	E_{sat} V/cm	e.V. charge pair
Anthracene							
1 mm I	Al, 0.4 cm^2	0.4	0.04	14.6×10^{-10}	236	1.0×10^4	1610
1 mm J	Al, 0.4 cm^2	0.4	0.04	18.3×10^{-10}	236	2.0×10^4	1330
36 μ	Water, 0.44 cm^2	0.06	9×10^{-4}	7×10^{-11}	328	2.2×10^4	1680
25.3 μ	Water, 0.10 cm^2	0.10	2.5×10^{-4}	4.16×10^{-11}	266	—	1660
20 μ	Water, 0.28 cm^2	0.10	3.8×10^{-4}	4×10^{-11}	266	2×10^4	1350
Tetracene							
25 μ	Water, 0.28 cm^2	0.28	7×10^{-4}	2.2×10^{-10}	328	5.2×10^4	370

Tab. 1. Saturation currents and fieldstrengths and energies nuessary for creation of one inopair.

In Fig. 2, X-ray induced current vs. voltage is plotted for a 36 μ crystal. It is seen from this curve that at a field strength of about 2.2×10^4 V/cm the current saturates. The X-ray induced current at a field below the saturation value, 5000 V/cm for example, is seen to be much smaller than in the 1 mm thick crystal. This will be discussed below. In Table 1, data for several crystals are tabulated. In some crystals the barrier area, A_{B} (the area of crystal in contact with the mylar barrier), was less than the electrode area, A_{e} (the area of the crystal in contact with the electrode). For these crystals the volume through which charges were moved by the electric field to the crystal-barrier interface, was less than the full crystal volume. Therefore in Eq. (1) the crystal volume $A\,d$ was replaced by an average volume $\frac{1}{2}(A_{\text{e}} + A_{\text{B}})d$, which is also listed in Table 1. The 25 μ anthracene crystal cracked before the saturation field strength could be measured.

Tetracene Experiments

Experiments were also performed on thin single crystals of tetracene grown by sublimation. It was again found that the X-ray induced current was proportional to the absorbed X-ray intensity. In Fig. 3, X-ray induced current vs. voltage is shown for a 25 μ crystal. The current is linear with voltage initially and is seen to saturate at a field strength of 5.2×10^4 V/cm. $1/\alpha$, the energy necessary to create a charge pair, was found to be equal to 370 eV. The experiments with tetracene were performed using only the internal field created by a previous polarization of the crystal by light.

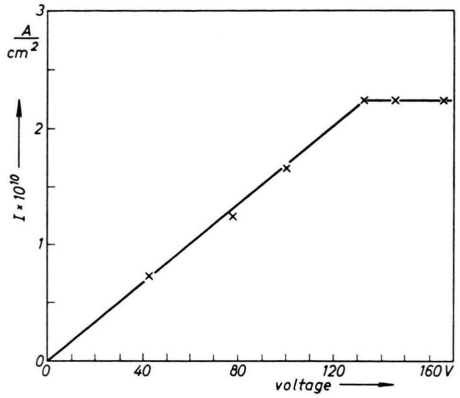

Fig. 3. X-ray current density vs. voltage, 25 μ tetracene crystal, $I = 328$ erg xec^{-1} cm^{-3}.

Discussion

For currents much smaller than i_{sat}, most of the charges recombine before being drawn to the surfaces[3]; otherwise the current would not increase proportionally to the voltage. The nature of this recombination can be deduced from the experimental results. Since the current is linear with the X-ray intensity even at low field strengths, a second order bimolecular recombination according to a relation of the form

$$\beta\, n\, p = \alpha\, I \tag{2}$$

does not take place. This formula implies that electrons of a density n recombine with free or trapped holes of density p produced in a different ionization track and thus the current would be proportional to the square root of the intensity. This was not observed. Further, according to the above mechanism, an increase in recombination with larger X-ray intensity would increase the field strength E_{sat} necessary to collect all charges produced. E_{sat} was, however, independent of the X-ray intensity. Finally from Figs. 1 and 2 it is seen that X-ray induced currents can not be described by a con-

---

[3] J. Birks, The Theory and Practice of Scintillation Counting, Macmillan Co., New York 1964.

ductivity equation of the form

$$i = ne\mu EA \qquad (3)$$

in which n is a charge density determined by (2). If this were true, for $i \ll i_{\text{sat}}$ the current densities i/A would be equal in crystals of differnt thicknesses under the same X-ray intensity and the same electric field strength. This was not so as can be seen from Figs. 1 and 2. (Thick tetracene crystals were not investigated.)

According to these figures, at a field strength of 1000 V/cm the X-ray induced current density is 2.2×10^{-10} A/cm^2 when 118 erg sec^{-1} cm^{-3} are absorbed in the 1 mm thick crystal and only 3×10^{-11} A/cm^2 when 328 erg sec^{-1} cm^{-3} are absorbed in the 36 μ crystal, which gives a current density of 1×10^{-11} A/cm^2 for an energy of 118 erg absorbed per sec and per cm^3, since the X-ray induced current was found to be linear with intensity. Thus, for the same X-ray intensity and field strength the current density is 22 times larger in the 1 mm thick crystal in the 36 μ crystal and is approximately proportional to chickness. (The 1 mm crystal is about 28 times thicker than the 26 μ crystal.) This is at variance with Eq. (3) which would give equal current densities for equal field strengths.

From these three observations it is concluded that recombination between charges originating in different tracks (Eq. 2) does not occur. That Eq. (2) does not hold also follows from the following computation. If one would describe the current density j by Eq. (3), then one would obtain a density of charges for a 1 mm thick crystal and for $E = 10^3$ V/cm of $n \cong 10^6$ charges/cm^3. Substituting this value into Eq. (2) and setting $p = n$ results in a value for β of 10^{-2} cm^3/sec. This is much larger than the otherwise known value of the recombination coefficient (10^{-6} or 10^{-7} cm^3/sec). One can understand that no recombination between charges of different tracks can take place under our conditions from the following consideration also.

For 1000 V/cm the transit time of a charge through a crystal of 1 mm thickness is 10^{-4} sec. During this time with an absorbed energy of 236 erg sec^{-1} cm^{-3}, about 6×10^4 primary electrons of an average energy of about 24 keV are produced in a 1 mm thick crystal of 1 cm^2 area. (Negligible photon energy is transferred to Compton electrons as compared to the primary electrons [photoelectrons] at the X-ray energies used.) Thus these tracks of primary electrons have an average separation of $(6 \times 10^5)^{-3} \cong 1.2 \times 10^{-2}$ cm. Since the track length is only 10^{-3} cm, an electron from one track will hardly ever cross another track before it is removed from the crystal by the field. For larger field strengths and thinner crystals this becomes less probable.

Since one observes that the current is proportional to the field strength, one must assume another type of recombination in which the number of charges contributing to the current is proportional to the field strength and may be assumed to be $N_0 \cdot E/E_{\text{sat}}$ where N_0 is the number of charge pairs produced in the sample per sec and equals $A\alpha Id$ as is seen from Eq. (1). Thus, of all the ion pairs formed only a fraction proportional to E remains free. Most of them recombine at once. Two mechanisms for such processes exist. The electron can recombine with a hole created in the same track or it can recombine with the hole from which it was separated. Both mechanisms would result in a current $i = N_0 e \cdot E/E_{\text{sat}}$ for $E < E_{\text{sat}}$ and $i = N_0 e$ for $E \geqq E_{\text{sat}}$. This description also explains the observation that the current increases linearly with thickness and intensity since N_0 is proportional to the crystal thickness and to the X-ray intensity for constant E. Under such a type of recombination, the density n of electrons and p of holes are not constant throughout the crystal, rather n is zero at the negative electrode and equals $\alpha Id/\mu E_{\text{sat}}$ at the positive one; for holes it is just the reverse.

Recombination of an electron with a hole created in the same track is small as the following consideration shows. Since 1530 eV are necessary to produce one charge pair in anthracene, each primary electron produced on the average about 16 ion pairs in one track. The range of the primary electrons, l_{R}, is about 10^{-3} cm in our case. Therefore, the average distance between charge pairs in the ionization track is about 10^{-4} cm. With a field strength of 10^3 V/cm, the maximum amount of time a charge remains in the range of the track is $l_{\text{R}}/\mu E \cong 10^{-6}$ sec, for most tracks it will be smaller. Since the width of the track is about 10^{-4} cm due to the diffusion of the charges, the carrier density is 10^{12}/cm^3 in the track. Therefore, the recombination time $1/\beta n$ is equal to 10^{-5} sec, and is longer than the maximum time the charges remain in the track. The diffusion length l was calculated from $l = \sqrt{2D\tau}$ where the diffusion coefficient D equals $\mu kT/e \cong 3 \times 10^{-2}$ cm^2/sec and $\tau \sim 10^{-6}$ seconds. Thus recombination with a charge in the same track seems to be an improbable process even at field strengths 20 times smaller than the saturation field strength. We conclude that the recombination which does take place is a recombination of an electron with its own hole from which it was separated (called geminate recombination)[4]. This type of recombination was also observed under light excitation in tetracene[5].

On could observe a pseudo first-order dependence of the current in X-ray intensity if there were a sufficiently high density of trapped holes (or electrons) with which a free electron (or hole) could recombine. However, if trapping were that extreme, one would not expect to find the observed ohmic voltage-current relation. Furthermore, it is possible by heavy X-ray irradiation to create sufficient traps to induce an $I^{1/2}$ dependence for the current. Since a heavy X-ray irradiation was required to produce the $I^{1/2}$ dependence, we conclude that under the weak X-ray irradiation, the density of trapped carriers was too low to show a pseudo first-oder carrier-trap recombination process.

If no external field is present, probably very few electrons will be ultimately separated from the positive charge from which they were originally separated and diffuse through the crystal. Most will recombine with the positive charge. The external field interferes with this recombination process. The electron may be separated from its own positive charge before it can be localized in its neighborhood in a charge-transfer state. The measured saturation field strength is the field strength which prevents the localization of the vast majority of the charges. For a separation distance of 10^{-6} cm, between the two charges, the saturation field strength approaches the attractive coulomb field strength between them. This would indicate that a large portion of the charges reaches this distance after separation. It would be of great interest in this connection to investigate the shape of the current-voltage curve in more detail and to see how saturation is approached.

In the table, data are given for several crystals. All the crystals except one displayed similar saturation field strengths; only one crystal, (I, 1 mm) showed a saturation field strength which was one-half of that observed for other crystals; but the number of charges produced by the same absorbed energy was almost the same as for other crystals. The reason for this difference in E_{sat} was not determined. The last column indicates that about 1500 eV are required to produce one charge pair in anthracene and this value does not depend on crystal thickness as expected. The fluctuations in the last column of the table are within the range of accuracy of these experiments. These values show that ionization in solid anthracene is a much less efficient process than ionization in a gas. About 30 eV are necessary to produce an ion pair in most gases. In anthracene the energy consumption for ionization is only 0.35% compared to 30% for a gas. KEPLER and COPPAGE[6] determined that it takes about 3000 eV to produce a charge pair in anthracene. However, the currents they measured were not saturation currents and therefore recombination effects may have increased the value they obtained for the energy necessary to create a charge pair.

The small ionization efficiency observed in condensed anthracene under high energy irradiation is probably connected to PLATZMAN's[7] superexcited states which have energies considerably larger than the minimum energy required for ionization. These states are also called pre-autoionizing states[8]. Autoionization results because of an interaction between degenerate bound and continuum states. The pre-autoionizing states can decay in two way; one way is via autoionization and the other is by way of intra or intermolecular vibrational dissipation of excitation energy. These latter processes are known to be very efficient in polyatomic molecules[9]. The relative probabilities of these non-radiative vibrational transitions and of the autoionization transitions will determine the efficiency of charge carrier formation. A polyatomic molecule has $(3n-6)$ modes of vibration, where n is the number of atoms in each molecule. For anthracene n is 24, therefore there are 66 vibrational modes. In the condensed phase there are additional modes of vibration (lattice modes). Thus in a condensed system, energy can be dissipated in many more ways than in a diatomic gas molecule and ion pair production is less probable.

---

[4] L. ONSAGER, J. Chem. Phys. **2**, 599 [1934]. — N. GEACINTOV and M. POPE, J. Chem. Phys. **45**, 3884 [1966]. — M. POPE, J. Chem. Phys. **47**, 2197 [1967]. — M. POPE and J. BURGOS, Mol. Cryst. **3**, 215 [1967].

[5] N. GEACINTOV, M. POPE, and H. KALLMANN, J. Chem. Phys. **45**, 2639—2649 [1966].

[6] R. KEPLER and F. COPPAGE, Phys. Rev. **151**, 610 [1966].

[7] R. PLATZMAN, Radiation Res. **17**, 419 [1962].

[8] U. FANO, Phys. Rev. **124**, 1866 [1961].

[9] G. W. ROBINSON and R. P. FROSCH, J. Chem. Phys. **38**, 1187 [1963].

Further if in this process a free electron is produced in solid anthracene, it will rapidly lose its energy to surrounding molecules and may form a charge-transfer (CT) state. This CT state may decay to the ground state or be thermally ionized. The importance of autoionization and CT states has been previously described[4].

Of great importance for the full understanding of the processes of how these charges are produced and how they are separated from each other would be an investigation at low temperature, even below liquid nitrogen temperature. In this temperature range the thermal effects will be reduced compared to those of the external field. Thus, the diffusion of the charges during their drift time would decrease.

Finally we wish to comment briefly on the effect of prolonged X-ray irradiation. Such irradiation (8×10^5 erg absorbed) produces a new recombination process, as is evidenced by the observation that now a sublinear dependence of the current on X-ray intensity was observed and that a higher saturation field strength was required. This additional recombination is apparently due to an increase in trapped charges. Charges produced in one track become trapped and can then recombine with a charge of another track which was produced at a later time. That new trapping sites are produced by such prolonged X-ray irradiation is also evidenced by the experiments with light polarizing. They clearly show that the charge produced at one surface by excitons cannot pass through the crystal as unimpeded as before such irradiation. This reduction in uv and X-ray induced currents was also observed by Hartmann[10]. If only small X-ray energies were applied, the trapping of charges inside the crystal was negligible, as was shown in special experiments. A charge passes through the crystal so fast that trapping is rather improbable.

Acknowledgement

We would like to thank Dr. M. Pope of the Department of Chemistry at New York University for many helpful suggestions.

---

[10] H. Hartmann, Z. Angew. Phys. **14**, 727 [1962].