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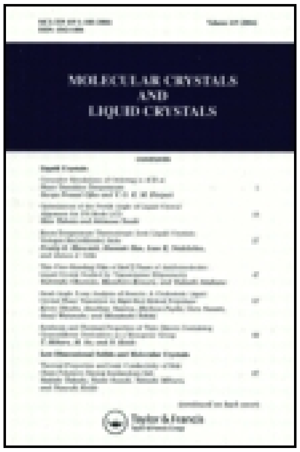

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Remarks on the Process of Carrier Generation in Electron-Bombarded Crystalline Anthracene

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Abstract—Secondary emission results show that the energy needed to create an electron-hole pair by low-energy electron bombardment of anthracene crystals is less than 75 eV, and that the thermalization distance of a secondary is such that initial recombination cannot account for the low yield of one pair per 400 eV obtained by Delany and Hirsch. It is suggested that columnar recombination accounts for at least part of the difference.

Preliminary results of characteristic losses of 41 keV electrons in anthracene are reported. The dominant loss, in the range 14–25 eV, is a solid state effect, tentatively assigned to collective oscillations of the π electrons. The free path for excitation of these oscillations by low-energy electrons should be very short and electron-hole pair creation would proceed largely through ionization of these plasmons.

The small value of the pair-creation energy suggests that radiative recombination inside a column could play a large role in fast scintillation processes in anthracene.

Many details are still not understood in the mechanisms of carrier generation in molecular crystals excited by light or electron irradiation. The electron is generally given initially a substantial amount of kinetic energy, but how or how fast this energy is dissipated is not known. If this dissipation is fast enough, the electron will be thermalized at a short distance of its parent hole, and this might produce a drastic decrease of the net yield. Indeed, the recombination of " cold " carriers (a bimolecular process, whereas initial recombination of an electron with its " parent " hole is monomolecular) is very efficient in anthracene, having a rate constant of the order of $10^{-6}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$. As the dielectric constant is low

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and the mean free paths are very small, the theory developed by Langevin[1] for dense gases applies qualitatively.

If an electron is thermalized at a distance r_0 from its parent hole, the probability that this pair escape recombination is proportional to $\exp(-r_c/r_0)$ where $r_c = e^2/\epsilon\epsilon_0 kT$. In anthracene, where ϵ varies from 3 to 4.2 depending on the crystallographic direction, r_c is between 140 and 200 Å at 300°K. It was proposed by Kepler that r_0 was indeed small enough to account for the small yield observed in anthracene under X-ray excitation,[2] ionizing through the electrons generated by X-rays. In these experiments only one pair is collected for 3.000 eV deposited in the crystal, and Kepler suggested that only secondaries and tertiaries created with a large initial energy were able to escape from the electrostatic attraction of their parent hole, an assumption which had already been made for liquids. This energy was estimated 300–500 eV. Coppage and Kepler also proposed that the yield of the process of photoionization of singlet excitons by 1.8 eV photons was also limited by initial recombination.[3]

We would like here to discuss the conclusions which can be drawn from present experiments on electron-bombarded anthracene, concerning this problem. The following considerations are at present largely qualitative. It is hoped that they will be useful in pointing out new experimental methods, and stimulating the discussion on related problems.

1. Internal yield of cold carriers for medium-energy electron bombardment

In a very careful series of experiments, Delany and Hirsch[4] have shown that the carrier yield for electron-bombardment, when electrons having energies between 10 and 60 keV are used, is of about one pair per 400 eV deposited into the crystal, and is independent of the applied electric field up to about 10^4 V/cm. Onsager considered the role of the field on initial recombination in dense gases.[5,6] His theory predicts that the yield should increase linearly with the field if $r_0 \ll r_c$, that is if initial recombination is very important. It is therefore worth investigating whether the low yield can be explained without invoking initial recombination.

2. Evidence from secondary electrons emission experiments

Some results of secondary emission coefficients of anthracene films deposited upon molybdenum substrate have been published.[7] The energy E_p of the primary electrons was comparable to the energy absorbed in the crystal for one pair collected in.[4] One can hope to get useful information from such measurements.

The relation between the yield δ (number of secondaries emitted per incident primary) and E_p is similar to that obtained with other materials (Fig. 1). Note however the low maximum yield

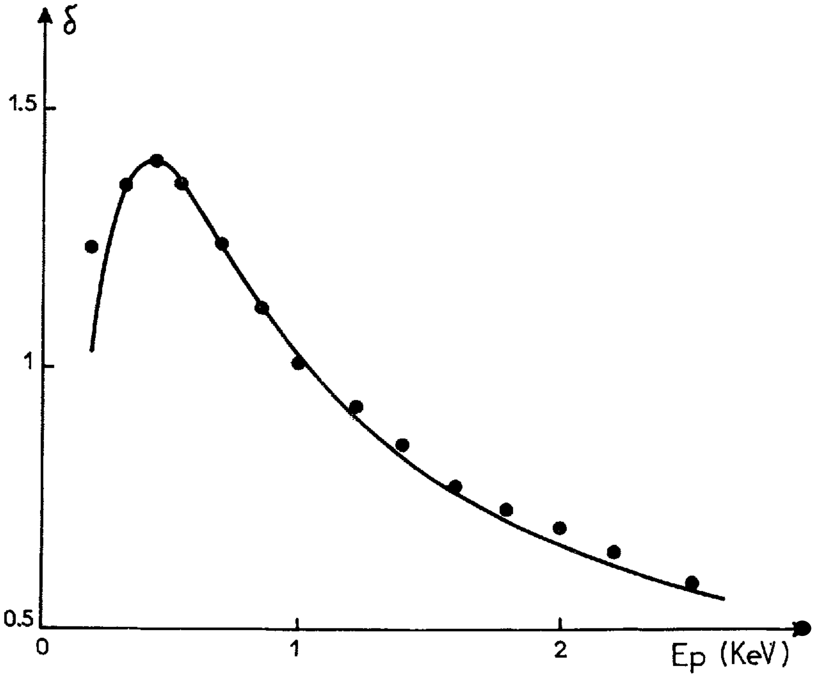

Figure 1. Yield of secondary electrons δ, versus primary energy E_p. The curve is experimental. The points are calculated using $\alpha^{-1} = 70$ Å, $\epsilon/B = 150$ eV and $R = 460 E_p^{1.62}$ (see text).

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$\delta^{(m)} \sim 1.4$ occurring at a primary energy $E^{(m)} \sim 400\,\text{eV}$; $\delta^{(m)}$ in inorganic insulators are generally of the orders of 5 to 10. The yield curve was independent of temperature.

We shall apply the phenomenological theory,[8] which assumes essentially the existence of a range–energy relationship $R = AE_p^n$ for the primaries and an exponential damping of the energy of the secondaries along their path $E_s = E_{0s} \exp(-\alpha x)$. α^{-1} is the mean escape depth of the secondaries. For very slow primaries $R < \alpha^{-1}$; all their energy is absorbed within an escape depth from the surface, and the yield should be $\delta \propto E_p$, increasing with E_p. If the primaries are fast enough, they lose only a small part of their initial energy within a distance α^{-1} from the surface. Experimental evidence shows that, due to momentum randomization, energy dissipation by the primaries is essentially independent from the depth. In this case, the yield for energetic primaries is, from the range–energy relationship quoted above,

$$\delta \cong B/\alpha\epsilon AnE^{n-1} \tag{1}$$

where ϵ is the mean energy used for the creation of a secondary electron. δ is a decreasing function of E_p, and for some intermediate value of E_p, which we call $E^{(m)}$, δ will be a maximum, $\delta^{(m)}$. Relation (1) applies for $E_p \gg E^{(m)}$. B is the probability that a secondary with enough initial energy will be emitted. It is related to the solid angle in which the momentum of the secondary at the surface should lie for the electron to be emitted, which in turn is determined by the, unknown, mean energy of the secondary at the surface. B is therefore a geometrical factor less than 0.5 and generally larger than 0.1.

The experimental results for aromatics actually obey relation (1), with $n = 1.62$ for anthracene, if $E_p > 1000\,\text{eV}$ (Fig. 2). This exponent is very close to that found by Delany, based on data obtained for polystyrene by Ehrenberg and King,[9] for the range–energy relationship of 3–50 KeV electrons $R = 460\,E_p^{1.65}$ where R is in Å if E_p is in keV. Below 1 keV, the penetration depth of the primaries is no more much longer than the escape depth of the secondaries, so that the approximation leading to (1) is no more valid. At low enough E_p, the detailed nature of the energy losses must anyway be included: for instance, if E_p becomes less than the carbon 1*s* electrons binding energy, the scattering by excitation of these electrons is impossible, and the range will be proportionally longer, if these processes were important.

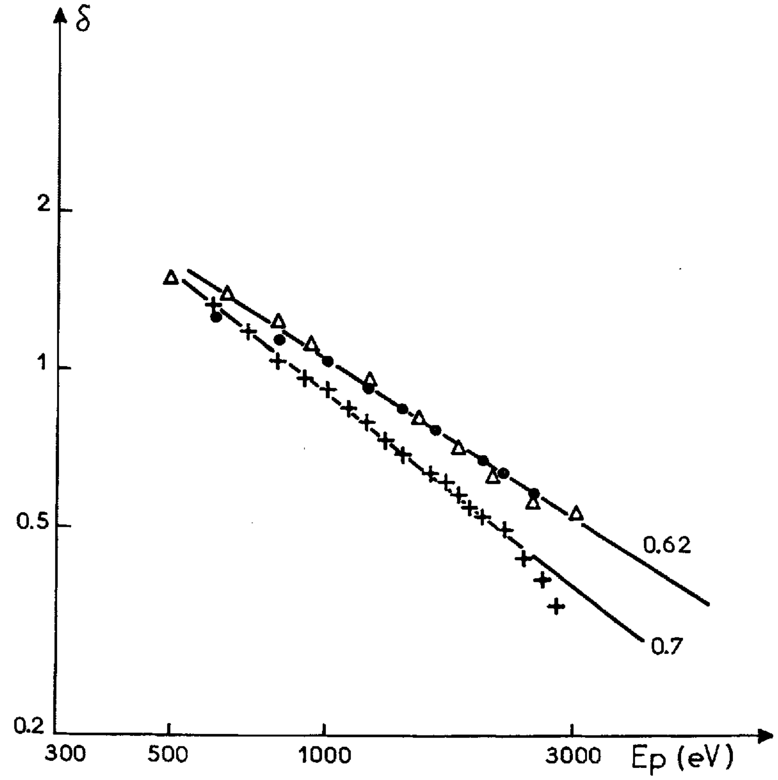

Figure 2. Log–log plot of (EP.)
Experimental points: + phenanthrene; ● anthracene; △ biphenyl.

The phenomenological theory predicts a standard form of the reduced yield curve $\delta/\delta^{(m)} = f(E_p/E_p^{(m)})$. If scattering of primaries is taken into account, the relation is

$$\delta^{(m)} = g(z^{(m)}E_p/E_p^{(m)})/g(z^{(m)}) \tag{2}$$

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where $z^n = R\alpha$ and

$$g(z) = [1 - \exp(-\alpha R)](\alpha R)^{-(n-1/n)} \cdot z^{(m)}$$

is the value where g reaches its maximum $g(z^{(m)})$. When scattering of the primaries is neglected, a relation similar to (2) holds, but with

$$g(z) = \exp[(-z^n)] \int_0^z \exp[(y^n)\, dy]$$

From relation (2), one deduces

$$\alpha^{-1} = A(E_p^{(m)}/z^{(m)})^n$$

$$\frac{\epsilon}{B} = \frac{E_p^{(m)}\, g(z^{(m)})}{z^{(m)}\, \delta^{(m)}}$$

As for anthracene $n = 1.62$, $z^{(m)} = 1.42$ and $g(z^{(m)}) = 0.67$, hence $\alpha^{-1} = 70\,\text{Å}$ and $\epsilon/B = 150\,\text{eV}$.

The actual yield δ is then given by

$$\delta = \frac{BE_p}{\epsilon R\alpha}[1 - \exp(-\alpha R)] = \frac{70E_p}{150R}[1 - \exp(-R/70)] \qquad (3)$$

with E_p in eV and R in Å. The calculated values of δ are plotted on Fig. 1. The agreement with the experiment is very good. The same set of parameters α^{-1} and ϵ/B fits the entire curve from $E_p = 200\,\text{eV}$, where the range of primary is less than the escape depth, to more than 3 keV where the range is of the order of 3000 Å, and where the results here discussed connect smoothly to known results.[9]

Emitted secondary electrons are far from thermalized, as the electron affinity of anthracene crystal is about 1.8 eV. Therefore, initial recombination is, in secondary emission, separated from the other recombination processes involving essentially "cold" carriers. The distance needed for the electron to lose its energy less at least 2 eV, measured straight from the parent hole, not integrated along the path, is about 70 Å, but the distance traveled before complete thermalization will certainly be much longer: the energy of the lowest lying excited electronic state in anthracene, a

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triplet, is 1.8 eV. An electron having less than 1.8 eV kinetic energy will lose energy only by emitting intramolecular vibrations. The efficiency of this relaxation process can at present only be guessed. Choi and Flauss[11] calculated that the corresponding scattering time for a 1 eV electron in benzene is 10^{-14} to 10^{-13} seconds. For an effective mass of one, this corresponds to a free path of several tens of angstroms, and during this process the electron will travel another 50–100 Å from the hole. The cross section for such processes will again become small at kinetic energies below 0.3 eV, and an electron having $4kT$ kinetic energy can lose it only by emitting lattice phonons. The considerable lengthening of the thermalization length due to this range of " subvibrational " kinetic energy has already been recognized by Mozumder and Magee for liquids,[10] it should be even more important in solids.

The role of this " subvibrational " range is shown by the experiments of the Dartmouth group,[12] on the variation with applied field of the quantum yield for ionization of the ground state, by photons in the range 4–5 eV, corresponding to electrons having initially less than 1 eV kinetic energy. If Onsager's theory[5] is applied to these results, one finds r_0 of the order 80–110 Å. Imperfect correction for trapping can only make the true r_0 larger. The behavior of an electron having a given kinetic energy is independent of its previous behavior, these results imply that a secondary electron will travel another 50–100 Å from the hole before being completely thermalized. Hence $r_0 > r_c$ and initial recombination is unable to account for more than a factor of two in the internal carrier yield under electron bombardment.

Conversely, to explain that the energy deposited for one collected pair is 5–10 times more than the creation energy of the pair, would require $r_c/r_0 > 1.6$, or $r_0 < 100$Å, at 300°K which cannot be reconciled with the experimental value of α^{-1}. In addition, as α^{-1} and ϵ/B do not vary with T, if initial recombination is important and Onsager's theory applies r_c/r_0 must be independent of T, hence r_0 should be $\propto T^{-1}$ in this case.

It seems therefore that another recombination process plays a role in limiting this yield (trapping is a too slow process). Surface recombination can be excluded, as[4] electrons are generated as far as 30 μ from the surface. For the sake of simplicity, we shall make a distinction between columnar and bulk recombination: we say that recombination is columnar if an electron has a chance to recombine only with a hole created by the same primary electron, (but not in the same ionization event) and bulk when charge densities are reasonably uniform throughout the excited region. Obviously, there is a continuous transition from the first to the second mechanism. But we shall see that there is, during the first 10^{-11} sec, a very efficient bimolecular recombination inside the same " column ", which cannot be easily avoided by collecting more rapidly the carriers at the electrodes.

3. Possible role of columnar recombination

We shall now reconsider the possibility of columnar recombination as a limiting factor for electron induced conductivity in Delany and Hirsch's experiments.[4] Along the path of the incoming electron, energy is transferred irregularly. In non-polar organic liquids, Mozumder and Magee,[10] in a detailed analysis, consider three kinds of excited region: in the first one, 100 eV or less are transferred by glancing encounters; 100 to 500 eV are deposited in blobs; more than 500 eV in short tracks. As we consider here only relatively low-energy primaries, $E_p < 60$ keV, where 1 MeV electrons, are considered in,[10] we neglect the third class of events. Even then a detailed calculation would be extremely tedious, and useless at the present time. We shall consider that an essential feature of the process is that energy is deposited in the crystal in discrete events, and to get an order-of-magnitude understanding, we assume that the ionization is contained into similar, but not necessarily identical, spherical microvolumes (see below); as the particle loses energy, these volumes become closer, and when the energy of the particle has fallen below a few keV they overlap, forming a unique elongated volume, which we shall take as a circular cylinder.

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In these volumes, there is competition between recombination and diffusion, and we shall roughly estimate their relative influence in the two types of excited regions, cylindrical and spherical.

Consider first the cylindrical track at the end of the path. We shall assume that initial recombination, if present, is an instantaneous process, which leaves in the track at time $t = 0$ a concentration $n(0)$ of electrons and holes in their lowest energy state of small mobility. After initial recombination has ended, the time variation of the number of free carriers is determined by the competition of diffusion and columnar recombination. We characterize diffusion by the relaxation time of this variation, if due to diffusion alone, $t_d = R_0^2/4D$ in cylindrical geometry for small times, even for a source of finite content.[13] R_0 is the radius of the cylindrical track, different, although probably not much, from r_0, and D the carriers diffusivity. In time t_d, the concentration at the boundary of the cylinder would decrease by less than 50% due to diffusion alone. Recombination is characterized by the " instantaneous " lifetime $(Rn)^{-1}$ of the carriers, a function of time. R is the free carriers recombination rate constant.

Assume first a constant ionization density along the track and let θ be the time where $Rn(\theta) = t_d^{-1}$, as $n(\theta)$ is finite, $\theta < t_d$. We neglect diffusion and assume that only recombination takes place before time θ, and inversely that recombination is negligible after θ. Then the total number N_c of pairs which can be collected is $n(\theta)$ times the initial volume of the track

$$N_c = n(\theta)\pi R_0^2\lambda = \frac{4\pi D\lambda}{R} \tag{4}$$

where λ is the length of the track. Note that N_c is independent of R_0.

The ionization density is in fact not constant, but its gradient along the track is less than its gradient normal to the track, so that diffusion along the track may also be neglected. Therefore the final density along the track will be constant and equal to $(Rt_d)^{-1}$, but attained at different times. If somewhere on the track, $n(0)$, considered just after initial recombination, is less than $(Rt_d)^{-1}$, then in the present model no columnar recombination takes place there. If $n(0) > (Rt_d)^{-1}$ throughout, N_c is given by (4). We consider that the track is continuous as soon as the energy of the primary is less than 3 keV, this is consistent with our calculation on the spherical microvolumes (see below). Whatever R_0, it is clearly of the right order of magnitude. We know from the previous paragraph that, for a 3 keV electron, $\lambda \sim 0.3\,\mu$, hence $N_c \sim 10$ pairs. This is the maximum number one should expect for a cylindrical track, when this model applies, as recombination will not be negligible at all after θ, because electrons and hole diffuse together out of the cylinder, and still interact electrostatically. Initial recombination can only make it smaller by lowering $n(0)$ below $(Rt_d)^{-1}$.

Recombination inside an isolated "spherical" microvolume can be treated in the same way, but here we need to know the average initial radius of the microvolume, R_0, that is after initial recombination. We take the same t_d although diffusion is slightly more efficient here. The number of pairs left in each of the spheres after time t_d, N_s, will be:

$$N_s = v_s \cdot n(\theta) = \frac{4\pi R_0^3}{3}\frac{4D}{R_0^2 R} \eqsim 6 \cdot 10^5 R_0$$

If $R_0 \cong 150$ Å, (therefore $t_d \cong 10^{-11}$ sec, or 10 to 100 times the thermalization time of the electron) $N_s \cong 1$. As the recombination still goes on as the carriers tend to diffuse together away, especially if microvolumes are near enough to overlap after some time, N_s is certainly <0.5 and columnar recombination will explain the observed yield, provided the average energy deposited in a single microvolume is >200 eV which seems reasonable. This value of R_0 is compatible with the value of r_0 computed above, and the track of 200 eV electron is short enough, so that the microvolumes may be considered to be spherical, in the first approximation. Any deviation from sphericity would tend to make N_s smaller. In addition, we know that the range of a 3 keV electron is about 3000 Å; its energy is about that deposited

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in 12–15 microvolumes, which therefore will overlap enough to form a cylinder.

These very rough estimations predict the following:

as only a minor fraction of the energy is deposited in the column as soon as $E_p > 3\,\text{keV}$, one expects the total yield per primary to be there proportional to the number of microvolumes, that is, in our oversimplified model to E_p as found in[4]. On the other hand, for $E_p < 3\,\text{keV}$, the yield should reflect the range–energy relationship, and vary as $E_p^{1.62}$, through equation (4), down to the energy where secondary emission becomes important. This range will be difficult to explore experimentally, as the vicinity of the electrode will introduce spurious effects.

as columnar recombination ensures a substantial reduction of the yield, any effect of temperature on the generation process itself will be washed out, except if very prominent, if trapping, bulk recombination and surface effects are avoided in the collection of generated carriers. The temperature dependence of the yield should be given by the temperature dependence of D/R, these parameters referring to free carriers, as trapping, at any temperature, is negligible during columnar recombination (but not always during collection on the electrodes of the remaining carriers), and by the temperature dependence of R_0 if R_0 depends on T.

Experiments are in progress to test these predictions.

4. Estimation of the pair creation energy under electron excitation in aromatic crystals

Some results of secondary emission from films of aromatic molecules other than anthracene have also been published,[14] the results are similar to those for anthracene, and the values for n, $E^{(m)}$ and $\delta^{(m)}$ are comparable. In phenanthrene for instance $n = 1.7$, $E^{(m)} = 360\text{eV}$, $\delta^{(m)} = 1.7$, also $g^{(m)} = 0.66$ and $z^{(m)} = 1.32$. Hence $\epsilon/B \cong 110\,\text{eV}$. Naphtalene and biphenyl give also ϵ/B in the range 100–150 eV. All these results are temperature independent below 0°C. Above 0°C the vapor pressure of the films is too high.

This gives us an upper limit, 50–70 eV, for the pair creation energy. As the valence band is very narrow, a first lower limit is given by the band gap 4–5 eV. Further insight can be given by *characteristic losses experiments.*

Monoenergetic (41 keV) electrons, with a scatter in energy of about 1 eV, were sent through an anthracene single crystal, less than 1 μ thick. The energy spectrum of the electrons transmitted with no angular scattering was recorded (Fig. 3). It is seen that these electrons lose energy mainly by quanta of 14 and 18 eV, with a minor (40 times less) loss at 5.1 ± 0.2 eV and a long tail to higher energy losses. Direct excitation of low lying excited levels has apparently, in these circumstances, a very small probability. The mean energy loss per event is 20–22 eV. The mean free path at 41 keV is in the range 10^3 Å.

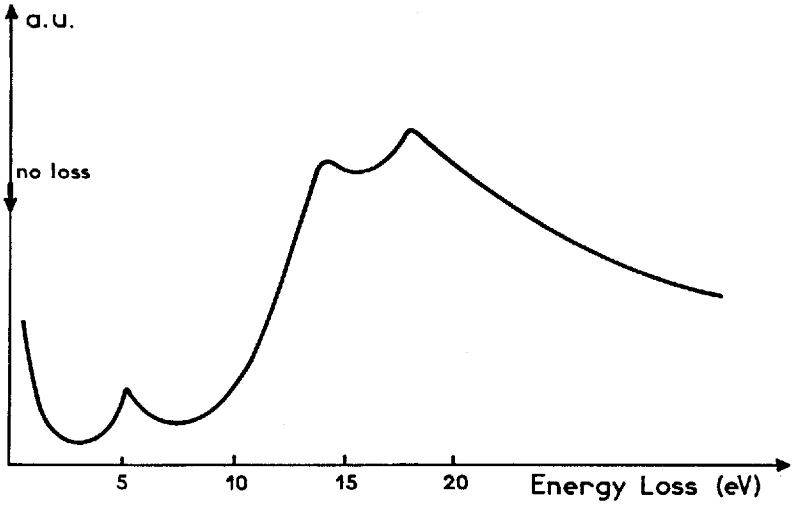

Figure 3. Characteristic losses of 41 keV electrons in anthracene. Crystal thickness: 4000 Å.

The spectrum is very different from that obtained by electron-impact on gaseous benzene where there is a prominent loss at 6.95 eV corresponding to a strongly allowed transition of the isolated molecule to an E state,[15] but is reminiscent of the

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characteristic loss spectrum of 20 keV electrons through polystyrene[16] where there is a small, sharp peak at 6.97 eV, corresponding possibly to the same electronic excitation, and a large, broad peak at 21 eV.

A tentative explanation of the anthracene characteristic losses spectrum would be that the 5.1 eV corresponds to the strongly optically allowed transition to the $^1B_{3u}^+$ state near 2400 Å, and that the larger loss is due to a solid state effect, which might be a collective oscillation of the π electrons. In this case, the electron exciting a plasmon would be scattered by a very small angle, and the relative probability of exciting an exciton could be larger than the observed value. There is no detailed theory of plasmons excitation in filled bands in insulators, but the scattering cross section for this process is likely to vary very rapidly with E_p (as E_p^{-2} for metals). Plasmon excitation would then be a very efficient process for low energy electrons as used in secondary emission experiments (free paths in the range 10–100 Å).

How such a state ionizes is not known. It is not likely to decay in more than one pair (although the secondary electron might be able to ionize another molecule in the crystal). If it does so through a super-excited state, there will even be competition with vibrational relaxation and ionization may well have a yield of less than one, but, according to the secondary emission results, this yield should be larger than 0.2. The average energy deposited in the crystal per pair would therefore be somewhat more than 20 eV. This could be further substantiated by extending the characteristic losses experiments toward lower energies.

5. Finally, a comparison suggests itself with the scintillation yield of anthracene under electron irradiation. It is known that this yield is of about one photon per 60 eV deposited in the crystal.[17] This value, much lower than that found in inorganic scintillations, has been related to energy loss by vibrational relaxation and bimolecular quenching of the excitons. As carrier recombination is known to have a radiative yield of ~0.4,[18] a low value of the pair creation energy might suggest that recombination of free carriers play in the fast scintillation process a more important role than previously thought.

In a recent paper, Perkins studied the fluorescence of anthracene under X-ray irradiation[19] and he concludes too, that the pair creation energy is about 27 eV. The agreement with the value given above and deduced from completely different experiments, is satisfactory

The case of luminescence is a little more involved than that of conductivity, as bimolecular annihilation of the excitons created by bimolecular recombination of the carriers as well as directly, will decrease the scintillation yield, by a mechanism similar to that outlined above for carriers. In a spherical microvolume as considered in Section 3, diffusion and bimolecular annihilation of singlet excitons, will complete: the average number of singlets surviving, if we neglect singlet-triplet interactions, can be roughly estimated as

$$N_s^{(s)} = \frac{4\pi R_0^3}{3} \times \frac{4D^{(s)}}{R_0^2 \gamma_{ss}}$$

and as $D^{(s)}/\gamma_{ss} = 2 \cdot 10^{-3}/4 \cdot 10^{-8} \cong 5 \cdot 10^4\,\text{cm}^{-1}$

$$N_s^{(s)} \cong 8 \cdot 10^5 R_0$$

and in the cylinder

$$N_c^{(s)} = \frac{4\pi D^{(s)}}{\gamma_{ss}} \cong 20$$

as here $t_d \cong 10^{-12}$ to 10^{-11} sec, few excitons will deactivate radiatively during this time.

As only 10^{-3} of the singlet-singlet annihilations is followed by ionization, these will not contribute back to conductivity.

In the case of triplets $D^{(t)}/\gamma_{tt} \gtrsim 10^7\,\text{cm}^{-1}$, and triplet-triplet annihilation *in the column* will be less efficient.

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