Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Creation and Evolution of Excited States in Anthracene Crystals Bombarded by Electrons

G. Klein [a]

[a] Centre de Recherches Nucléaires, Laboratoire de Physique des Rayonnements et d'Electronique Nucleaire, 67037, Strasbourg Cedex, France

Version of record first published: 28 Mar 2007.

To cite this article: G. Klein (1978): Creation and Evolution of Excited States in Anthracene Crystals Bombarded by Electrons, Molecular Crystals and Liquid Crystals, 47:1-2, 39-49

To link to this article: http://dx.doi.org/10.1080/00268947808083730

Mol. Cryst. Liq. Cryst., 1978, Vol. 47, pp. 39–49

Printed in Holland

Creation and Evolution of Excited States in Anthracene Crystals Bombarded by Electrons

G. KLEIN

Centre de Recherches Nucléaires, Laboratoire de Physique des Rayonnements et d'Electronique Nucleaire, 67037 Strasbourg Cedex, France

(*Received January 16, 1978*)

A qualitative description of the kinematics of excited states in anthracene crystals bombarded by electrons is given. It is compared with experimental results concerning scintillation decay curves, and magnetic field effects on the prompt and delayed components of the scintillation.

INTRODUCTION

The creation and evolution of excited states in anthracene crystals bombarded by electrons is studied by analysing the time dependence of the scintillation.

The light emission, which is a radiative transition from the first excited singlet state (S_1) to the ground state (S_0) is a result of a sequence of elementary processes which we review in this paper. They can be summarized as follows: the primary excited states (excitons, plasmons, charge carriers) are created by the primary and secondary electrons in a broad energy range at about 20 eV. Afterwards, in a time ranging from 10^{-15} sec to 10^{-12} sec these highly excited states decay by radiationless transitions (autoionization, electronic and vibrational relaxation, charge carriers recombinations) to the lowest singlet (S_1) and triplet (T_1) excitons. In the last time scale, from 10^{-12} sec to 10^{-5} sec occurs the light emission, the diffusion of the excitons and bimolecular annihilations. The light emission of the singlet excitons resulting from the decay of the primary excited states is the "prompt component" of the scintillation. Most of these singlets arise from isolated primary excitations, therefore their decay is monomolecular, and exponential. The radiationless decay of the isolated high energy excitations is in competition with the triplet pair production which is known to be magnetic field dependent.[1,2] The "delayed component" of the scintillation arises from singlet excitons created

by annihilation of two triplet T_1 excitons which is also a magnetic field sensitive process.[3,4] These bimolecular reactions happen in the tracks of low energy secondary electrons.

KINEMATICS OF EXCITED STATES IN ANTHRACENE CRYSTALS BOMBARDED BY ELECTRONS

The creation of the primary excited states by the electrons and the first radiationless transitions (autoionization, electronic and vibrational relaxation) are independent of the nature of the incident ionizing particle. A description of these processes is given in a previous paper[4] dealing with the scintillation induced by α particles. The important differences between α and β excitation are the bimolecular reactions (electron-hole recombination, exciton–exciton collisions) which depend on the excited states concentrations or on the linear energy transfer (LET) of the ionizing particle.

Most energy losses of the primary or secondary electrons correspond to the creation of plasmons of about 20 eV, or electron-hole pairs.[4,5] The very low energy electrons (less than 10 eV) loose their energy by creating singlet as well as triplet excitons.[1,2] Thus, neglecting intramolecular vibrational excitations, the primary excited states are plasmons, excitons T_1, S_1, S_2 and charge carriers.

The lifetime of the plasmon is very short (10^{-15}–10^{-16} sec).[6] As the plasmon energy (≈ 20 eV) is far above the ionization potential (≈ 6 eV), the main decay process is autoionization. The resulting secondary electrons have often enough kinetic energy to form triplet T_1 or singlet S_1, S_2 excitons. Therefore, for each plasmon we get one electron-hole pair and often one singlet or triplet exciton. Below the ionization potential, the decay from high energy excitons (S_2, S_3) to lower energy excitons is possible by internal conversion (rate constant $\approx 10^{14}$ sec^{-1}) followed by exciton–phonon dissociation.[7] The intramolecular vibrations (phonons) and the singlet exciton are independent quasi-particles in anthracene crystals[8] and the exciton diffuses away from the phonon in a time comparable to the exciton hopping time ($\approx 10^{-14}$ sec).

The charge carriers recombination which takes place in the next time scale (10^{-13}–10^{-12} sec) depends on the concentration of excited states: primary or secondary electrons having energies of more than about 5 keV loose energy in regions which are far enough from each other, so that no interaction between them is possible; they can be considered as isolated.[9,10] The excited states (plasmons, excitons, charge carriers) created by electrons of less than 5 keV are near enough from each other, so that they form a track of a roughly cylindrical shape ("short track") where exciton–exciton interactions and non geminate electron-hole recombinations are possible.[9,10] For electrons of less than 500 eV the track ("blob") is better approximated by a spherical shape.[9,10] In

tracks of low energy electrons (100 eV to 5 keV), like in α particle tracks, there are high concentrations of singlet and triplet excitons. In isolated regions where the deposited energy is 20 eV or less, it is possible to get one electron-hole pair and perhaps one T_1 or S_1 exciton[1,2] which results in the formation, after recombination, of one singlet S_1 or two singlets S_1 or two triplets T_1 within a very small radius. As these processes are fast ($\leqslant 10^{-12}$ sec) compared to the spin procession, the total spin is conserved, and it is impossible to get only one isolated triplet exciton T_1, and the total spin of the triplet pair (T_1, T_1) is necessarily a singlet state at short times.

The creation of defects by photochemical processes under β irradiation is one order of magnitude less important than under α particle irradiation.[4] Therefore, it will have no measurable effect on the β particle scintillation and will not be considered here.

The kinematics of the T_1 and S_1 excitons in the last time scale (10^{-12}–10^{-5} sec) will be studied now. The isolated singlet or triplet excitons pairs dissociate or annihilate in a time of 10^{-9} sec or less.[11,12] Therefore, the singlet excitons originating from isolated primary excited states of less than 20 eV, decay monomolecularly after 10^{-9} sec and result in the exponential "prompt component" emission (lifetime 25 nsec). The schematic diagram of the triplet pair production is given in Figure 1. S_n is a high energy singlet state, (e, h) an electron-hole pair, the star meaning the presence of kinetic energy. Reactions (1) and (2) are the β particle excitation, reaction (3) is the coherent spin state evolution, (4) the triplet pair annihilation, (5) the triplet pair dissociation by diffusion and reaction (6) the photon emission. The superscripts 1, 3, 5 are the spin multiplicities. The triplet pairs are created in a singlet total spin state $^1(T_1, T_1)$ which is coupled to quintet states by the triplet fine structure interaction which is magnetic field sensitive. The recombination process (4) is spin conserving and proportional to the squared singlet amplitude of the triplet pair. Therefore, this process and the subsequent light emission which contributes also to the prompt component are magnetic field dependent. These magnetic field effects were widely studied in fission experiments.[1,2,13]

Isolated regions where the deposited energy increases above 20 eV contain an increasing number of excitons. Therefore, in these regions bimolecular

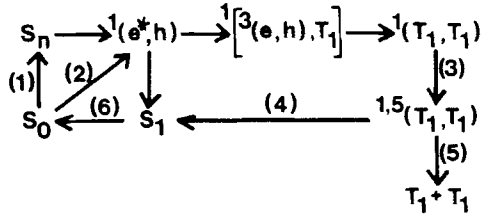

FIGURE 1 Kinetic scheme of the triplet pair production from highly excited singlet states.

quenching of singlet excitons decreases significantly the prompt component intensity[15] and the scintillation yield.[14] Concomitantly a delayed component is appearing due to triplet–triplet annihilation.[15] At electron energies between 100 eV and 5 keV, "blobs" and "short tracks" are formed. As the energy increases, the LET decreases, and the prompt component quenching decreases, as was shown experimentally in Ref. 15. In the region of high concentrations of excited states there is no spin correlation between electrons and holes which recombine and between two triplet excitons which annihilate to contribute to the delayed component. Therefore, in these regions like in α particle tracks,[4] no magnetic field effect on the prompt component is expected, and the effect on the delayed component is an effect on the well known triplet–triplet fusion process.[16]

EXPERIMENTAL AND RESULTS

The scintillation decay curves were measured using the single photoelectron sampling method.[17] The experimental set up is the same as in Ref. 4. The high energy electrons were supplied by a ^{90}Sr ^{90}Y source. In the magnetic field effect experiments the crystal was 5 mm thick and the source in contact with the crystal, so that the whole energy of the electrons was absorbed, and the bending of the electron paths in the magnetic field had no effect on the measured scintillation yield.

The scintillation decay curve of the anthracene crystal bombarded by electrons was measured from 0.5 nsec to 40 μsec and is shown in Figure 2. The measured risetime (from 10% to 90% of the maximum intensity) is 1 nsec and is attributed to the time jitter of the photomultiplier pulses. The prompt component decay is exponential, and the corresponding time constant 25 nsec is the singlet S_1 lifetime.

The magnetic field effect on the scintillation prompt component is characteristic of a triplet pair production, whereas the effect on the delayed component is characteristic of the triplet–triplet fusion process. We measured the relative variations of the light intensities upon magnetic field application: $\Delta i/i = [i_H(t) - i_0(t)]/i_0(t)$, where the subscripts H and 0 correspond to measurements with and without magnetic field. On Figure 3 is shown the magnetic field effect on the scintillation, $\Delta i/i$ as a function of time in the resonance conditions ($|\mathbf{H}| = 4000$ Gauss, $\mathbf{H}_\wedge b = 23°$ in the crystal (a, b) plane). The magnetic field effect on the integrated intensities $\Delta I(0:100)/I(0:100)$ and $\Delta I(230:330)/I(230:330)$ were investigated. In these expressions $I(t_1 : t_2) = \int_{t_1}^{t_2} i(t)\,dt$. In the first time interval (0 : 100 nsec) the prompt component is predominent, but the delayed component is not negligible (see Figure 3). In the time interval (230 nsec : 330 nsec) the light is only a part of the delayed

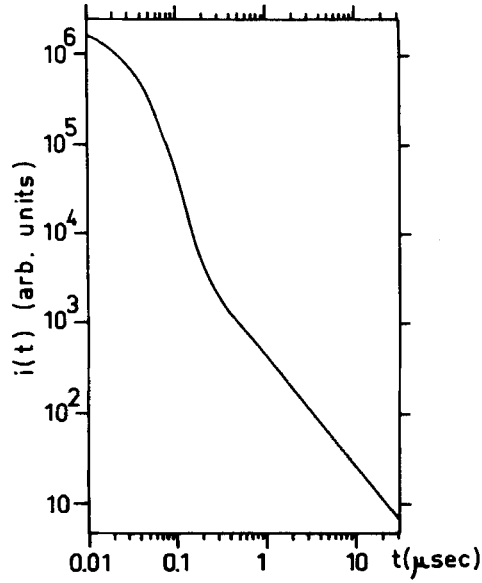

FIGURE 2 Scintillation decay curve of anthracene crystals bombarded by electrons.

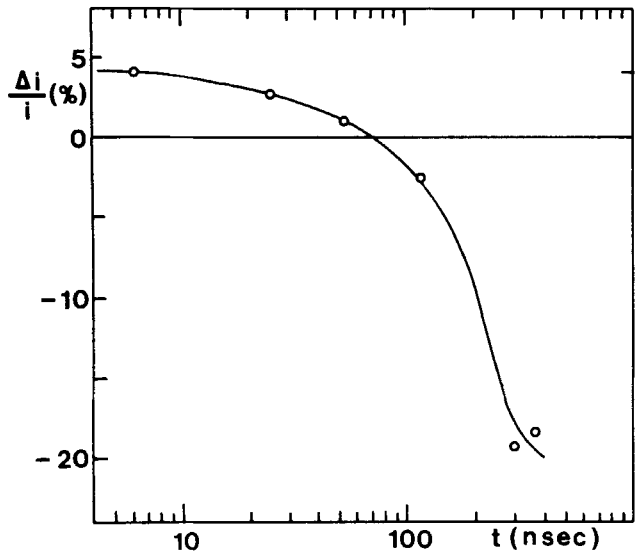

FIGURE 3 Magnetic field effect on the scintillation intensity in the resonance conditions: |H| = 4000 Gauss: $\mathbf{H}_{\wedge} b = 23°$ in the crystal (a, b) plane.

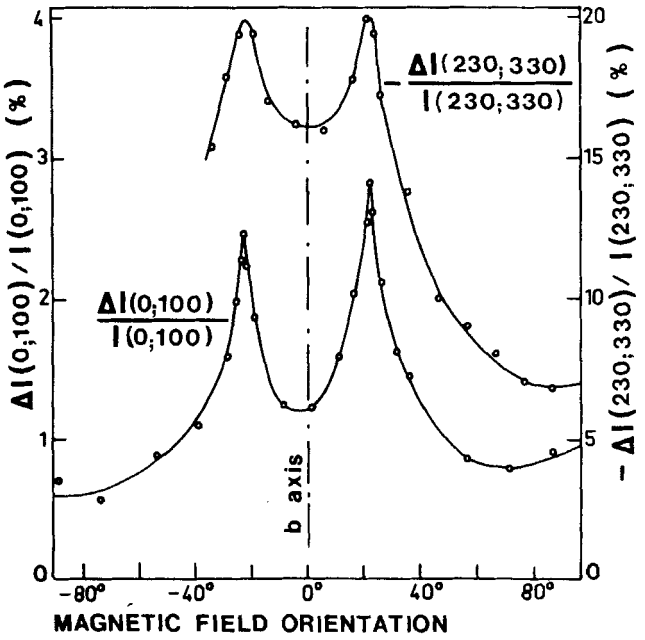

FIGURE 4 Magnetic field effect on the integrated scintillation intensities in the time intervals (0 : 100 nsec) and (230 : 330 nsec) as a function of the orientation of the 4000 Gauss magnetic field in the crystal (a, b) plane.

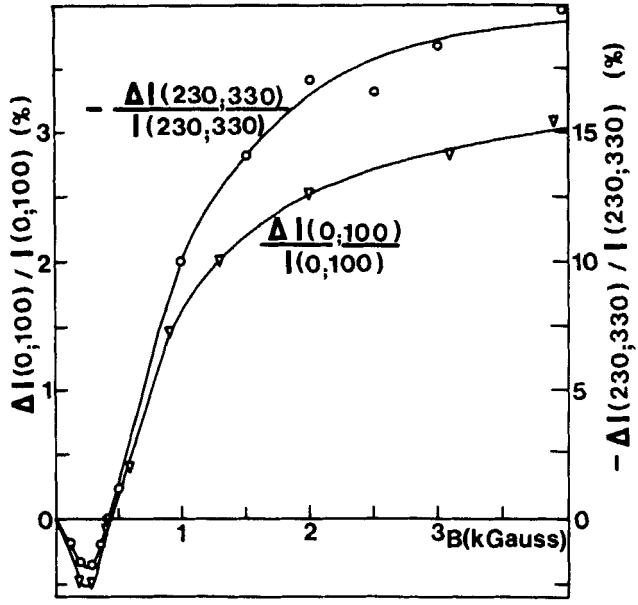

FIGURE 5 Magnetic field effect on the integrated scintillation intensities in the time intervals (0 : 100 nsec) and (230 : 330 nsec), as a function of the magnetic field strength. **H** is in a resonance direction of the (a, b) plane.

component. The anisotropies of

$$\Delta I(0{:}100)/I(0{:}100) \quad \text{and} \quad \Delta I(230{:}330)/I(230{:}330)$$

as a function of the magnetic field orientation in the crystal (a, b) plane are reported in Figure 4 for a magnetic field intensity of 4000 Gauss. The influence of the magnetic field strength is shown in Figure 5 where the magnetic field was in a resonance direction of the (a, b) plane ($\mathbf{H}_\Lambda b = 23°$).

DISCUSSION

The descriptions of the excited states creation and evolution in anthracene crystals excited by high energy electrons are always oversimplified. The spatial distribution of the excited states is too inhomogeneous and intricate. Therefore, complete calculations of the kinematics and of the scintillation decay curves like in α particle tracks[4] are impossible here.

The scintillation exponential decay between 0 and 100 nsec corresponds partly to the radiative decay of the isolated singlet excitons S_1. However, the contribution of the "blobs" and "short tracks" to the prompt component is not negligible. A prompt component was found in the scintillation of *p*-terphenyl crystals excited by electrons of more than 500 eV.[15] Even with electrons of 100 eV and 280 eV a prompt component was measured which decays non exponentially and rapidly by bimolecular quenching like in α particle tracks.[15] This part of the prompt component originating from "blobs" and "short tracks" is quasi-exponential in anthracene crystals after 5 nsec because of the selfabsorption like in α particle tracks.[4] Therefore, there is little difference in the decay of these two parts of the prompt component. The main difference between them is the magnetic field effect. The production of S_1 excitons in isolated regions is in competition with the triplet pair production and is magnetic field sensitive,[1,12,13] whereas in "blobs" and in "short tracks," like in α particle tracks the part of the prompt component is not magnetic field dependent because of the random electron-hole recombination which yields triplet excitons without any spin correlation. The corresponding triplet–triplet annihilation is contributing to the delayed component.

The magnetic field effect in the resonance conditions is $+4\%$ in the beginning of the scintillation where the delayed component is negligible (see Figure 3). In anthracene crystals excited by U.V. light, the magnetic field effect on the fluorescence intensity and the yield of triplet pair production increase with increasing incident photon energy.[1] At 10 eV the magnetic field effect is $+8\%$ which is much more than the $+4\%$ measured with β particles excitation, where the primary excited states mean energy is still higher (≈ 15 eV). Two reasons can explain this. Firstly, the existence of a part of the scintillation prompt component which is not magnetic field dependent, as stated above. Secondly, at higher energies (15 eV or more) the two triplet excitons created by

ion recombinations can be in two different (a, b) planes, or several intermolecular distances from one another, thus decreasing the triplet–triplet recombination probability and the magnetic field effect.

The spikes of the anisotropy of the magnetic field effect on the prompt component of the scintillation are much more narrow than those of the delayed component with excitation β, α or red light. The width at 90% of the maximum of the spike is as low as 2.5° in the best experimental conditions, whereas this width becomes 10° for the delayed component. Moreover, the minimum of the magnetic field effect in the b axis direction is deeper for the prompt component than for the delayed component. These differences were discussed partly in two papers[24,25] but no satisfactory explanation was given.

The delayed component is attributed to S_1 excitons created by triplet–triplet annihilation. The triplet excitons are originating in "blobs" and "short tracks," from random electron-hole recombinations and from direct collisions of electrons of a few eV energy. The LET of low energy electrons are still low enough so that, in "blobs" and "short tracks" the triplet concentration decreases mainly by diffusion out of the track and little by bimolecular annihilation. In these conditions the delayed component of the scintillation decreases with time like $t^{-1.5}$ in tracks of spherical symmetry, and like t^{-1} in tracks of cylindrical symmetry.[18] The experimental decay (Figure 2) of the delayed component is like $t^{-1.25}$, which means that in anthracene crystals irradiated by β particles there are "blobs" of spherical symmetry and "short tracks" of cylindrical symmetry which contribute equally to the delayed component. The same conclusion was obtained in Ref. 15.

The delayed component for a "blob" can be calculated using some simplifications: a secondary electron of 500 eV produces 13 triplet excitons (an average value of 40 eV for 1 triplet[4]) along a path of 150 Å which we suppose to be perpendicular to the crystal (a, b) plane. Let us suppose that the triplet excitons concentration $n(r, z, t)$ is initially a gaussian function:

$$n(r, z, 0) = n(0, 0, 0) \exp(-r^2/r_0^2) \exp(-z^2/z_0^2)$$

where t is the time, and r, z the cylindrical coordinates, the z axis being the electron path, and the origin being at the center of the "blob." $n(0, 0, 0)$ is the triplet concentration at $t = 0$, $r = 0$, $z = 0$. The parameter r_0 may be taken 50 Å, which is the thermalization range of an electron produced by ionization or autoionization.[20] The parameter z_0 will be taken 75 Å which is the half of the secondary electron range. The evolution of $n(r, z, t)$ is given by:

$$\frac{\partial n(r, z, t)}{\partial t} = \mathbf{D}\nabla^2 n - \gamma n^2 \tag{1}$$

where $\mathbf{D}$ is the triplet diffusion tensor whose components are $D_{ab} = 1.5 \times 10^{-4}$ cm^2 sec^{-1} in the crystal (a, b) plane and $D_c = 1.2 \times 10^{-5}$ cm^2 sec^{-1}

perpendicularly to the (a, b) plane.[27] γ is the overall bimolecular annihilation coefficient of the reaction

$$T_1 + T_1 \xrightarrow{\gamma_s} S_1 + S_0 \longrightarrow 2S_0 + \text{photon} \qquad (2)$$
$$\searrow^{\gamma_T} \quad T_1 + S_0$$

where $\gamma = 2\gamma_S + \gamma_T = 2 \times 10^{-11}$ cm^3 sec^{-1}.[21] In the time scale we studied, the monomolecular triplet exciton decay may be neglected. The concentration $n(r, z, t)$ can be calculated from Eq. (1), using the prescribed diffusion method:[18, 22]

$$n(r, z, t) = g(t) n^0(r, z, t)$$

where

$$n^0(r, z, t) = n(0, 0, 0)(1 + t/t_{ab})^{-1}(1 + t/t_c)^{-1/2} \times \exp\left[-\frac{r^2}{r_0^2(1 + t/t_{ab})}\right] \exp\left[-\frac{z^2}{z_0^2(1 + t/t_c)}\right]$$

is the solution of Eq. (1) when $\gamma = 0$, and

$$[g(t)]^{-1} = 1 + \frac{\gamma N t_{ab}}{(2\pi)^{3/2} r_0^2 z_0 R} \log \frac{[(1 + t/t_c)^{1/2} - R][1 + R]}{[(1 + t/t_c)^{1/2} + R][1 - R]} \qquad (3)$$

with $t_{ab} = r_0^2/4D_{ab}$, $t_c = z_0^2/4D_c$, $R = (1 - t_{ab}/t_c)^{1/2}$. N is the initial total number of triplet excitons in the "blob" ($N = 13$ as stated above). The integrated delayed light intensity between 0 and time t is:

$$I_d(0: t) = \alpha N(1 - g(t)) \qquad (4)$$

where $\alpha = \gamma_S/(2\gamma_S + \gamma_T) = 0.18$.[23] The total integrated intensity of the delayed component of the 500 eV "blob" calculated from equations (3) and (4) is: $I_d(0: \infty) = \alpha N \times 0.33$, which means that only 33% of the triplet excitons disappear by bimolecular annihilation. The remaining 67% triplets escape by diffusion out of the track. This is different from the α particle track of cylindrical symmetry where the escape by diffusion is not possible,[4] and all triplet excitons are destroyed by triplet–triplet collisions.

The effect of the orientation and strength of the magnetic field on the scintillation delayed component (Figures 4 and 5) is the same as that on the delayed fluorescence induced by the direct triplet state excitation ($S_0 \rightarrow T_1$).[16] Therefore, the scintillation delayed component in anthracene crystals can be attributed to the triplet–triplet fusion reaction. The relative variations $\Delta I_d/I_d$ can be calculated approximately as a function of the variations $\Delta\gamma_S/\gamma_S$ for a "blob" of 500 eV. In this case, the integrated intensity between 230 nsec and

330 nsec, according to Eqs. (3) and (4) is:

$$I_d(230:330) = \alpha N \times 0.00300.$$

In the resonance conditions $\Delta\gamma_S/\gamma_S = -0.2$.[16] The corresponding variation of γ are $\Delta\gamma/\gamma = 2\alpha\Delta\gamma_S/\gamma_S = -0.072$. The relative variations of $\alpha = \gamma_S/\gamma$ are

$$\frac{\Delta\alpha}{\alpha} = (1-2\alpha)\frac{\Delta\gamma_S}{\gamma_S}\Big/\left(1+2\alpha\frac{\Delta\gamma_S}{\gamma_S}\right) = -0.138.$$

According to Eqs. (3) and (4) and to the values of $\Delta\gamma/\gamma$ and $\Delta\alpha/\alpha$, the relative variations $\Delta I_d(230:330)/I_d(230:330) = -0.175$. This calculated magnetic field effect of -17.5% is slightly lower than the experimental value of -20% (Figures 4 and 5). The difference can be due partly to the poor accuracy of the experimental measurements and to the oversimplification of the track description. The other cause of the difference can be that the triplet pair production from the primary singlet excited states is partly inhibited by a magnetic field in the resonance conditions, decreasing the initial triplet excitons concentration and the delayed component intensity. This effect which was not taken into account in the calculations of the delayed component is not possible in "blobs" where the electron-hole recombination is a random process (as stated above). It can be ignored in isolated regions where the two created triplets do not contribute to the delayed component. But it is efficient in tracks of low LET particles (beginning of "short tracks") where the primary excited states can be considered as isolated, but not the triplet excitons of longer diffusion length.

The calculated magnetic field effect on the total integrated delayed component in the resonance conditions, according to Eqs. (3) and (4) is $\Delta I_d(0:\infty)/I_d(0:\infty) = -0.18$. The measured magnetic field effect on the total scintillation intensity, in the resonance conditions is $\Delta I/I = +0.02$. The corresponding calculated value is:

$$\Delta I/I = (1-F)\Delta I_d(0:\infty)/I_d(0:\infty) + F\Delta i(t=0)/i(t=0)$$

where F is the fraction of the total scintillation intensity corresponding to the prompt component. Using the values $\Delta I_d(0:\infty)/I_d(0:\infty) = -0.18$ and $\Delta i(t=0)/i(t=0) = +0.04$, the calculated value of F is $F = 0.9$. The same value can be obtained by decomposition of the scintillation decay curve (Figure 2) into a prompt exponential component and a delayed component, and by comparison of their integrated values.

The discussion on the scintillation delayed component cannot be considered as general for all organic scintillators. For example, in *p*-terphenyl crystals and in liquid scintillators the delayed electron-hole recombination cannot be omitted in the analysis of the scintillation delayed component.[2,26]

References

1. G. Klein and R. Voltz, in *Molecular Spectroscopy of Dense Phases*, Proceedings of the 12th European Congress on Molecular Spectroscopy, Elsevier, Amsterdam (1976).
2. G. Klein and M. J. Carvalho, *Chem. Phys. Lett.*, **51**, 409 (1977).
3. N. E. Geacintov, M. Binder, C. E. Swenberg, and M. Pope, *Phys. Rev.*, **B12**, 4113 (1975).
4. G. Klein, *Mol. Cryst. Liq. Cryst.*, **44**, 125 (1978).
5. H. Venghaus, *Z. Phys.*, **239**, 289 (1970).
6. R. Voltz, International Discussion on Progress and Problems in Contemporary Radiation Chemistry, Proceedings of the 30th Czechoslovak Annual Meeting (1970).
7. E. I. Rashba, *Sov. Phys. JETP*, **27**, 292 (1968).
8. E. F. Sheka, *Sov. Phys. Uspekhi*, **14**, 484 (1972).
9. A. Mozumder, *Advances in Radiation Chemistry*, vol. 1 (Eds. M. Burton and J. L. Magee), Wiley-Interscience, New York, 1969.
10. A. Mozumder and J. L. Magee, *Radiat. Res.*, **28**, 203 (1966).
11. A. Suna, *Phys. Rev.*, **B1**, 1716 (1970).
12. G. Klein and R. Voltz, *Int. J. Radiat. Phys. Chem.*, **7**, 155 (1975).
13. W. M. Moller and M. Pope, *J. Chem. Phys.*, **59**, 2760 (1973).
14. T. R. Fisher and D. Kohler, *Rev. Scient. Instrum.*, **43**, 471 (1972).
15. C. Fuchs and F. Heisel, *Radiat. Phys. Chem.*, **10**, 163 (1977).
16. R. C. Johnson and R. E. Merrifield, *Phys. Rev.*, **B1**, 896 (1970).
17. L. M. Bollinger and G. E. Thomas, *Rev. Scient. Instrum.*, **32**, 1044 (1961); J. A. Miehe, G. Ambard, J. Zampach, and A. Coche, *IEEE Trans. Nucl. Sc.*, **NS-17(3)**, 115 (1970).
18. T. A. King and R. Voltz, *Proceedings Roy. Soc. A*, **289**, 424 (1966).
19. R. Voltz, in *Actions Chimiques et Biologiques des Radiations* (Ed. M. Haissinsky), Masson, Paris, **13**, 1 (1969).
20. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **64**, 3573 (1976).
21. P. Avakian and R. E. Merrifield, *Mol. Cryst. Liq. Cryst.*, **5**, 37 (1968).
22. A. Kuppermann and G. G. Belford, *J. Chem. Phys.*, **36**, 1412 (1962).
23. R. P. Groff, R. E. Merrifield, and P. Avakian, *Chem. Phys. Lett.*, **5**, 168 (1970).
24. G. Klein, Thesis, Strasbourg (1977).
25. G. Klein, *Chem. Phys. Lett.*, in press.
26. J. Klein and R. Voltz, *Phys. Rev. Lett.*, **36**, 1214 (1976).
27. V. Ern, *Phys. Rev. Lett.*, **22**, 343 (1969).