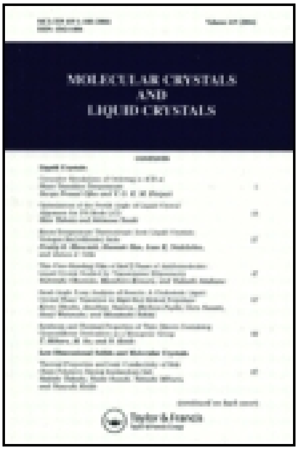

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THE RADIOLUMINESCENCE EXCITATION MECHANISM FOR ORGANIC BULK MATERIALS

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Abstract The radioluminescence excitation mechanism of organic bulk materials is discussed. The study is based on the experimental results obtained for radioluminescence intensity and kinetics of organic crystals, for the cases of α- and γ- excitation.

Keywords: radioluminescence, charge generation, charge recombination, organic crystals, ionizing

INTRODUCTION

The radioluminescence of organic crystals can be attributed to phenomena which take place in unconventional photoactive solids. Really, in contrast to the photoluminescence, the radioluminescence is caused not only by optical properties of the object, but by semiconducting ones as well. The radioluminescence excitation process is going through the stage of charge carrier generation and recombination.[1,2] It is precisely that stage which causes the specific character of the radioluminescence process and defines its low fluorescence yield as well. For the systems which have the fluorescence yield about 0.9 for the case of photoexcitation, such a value does not exceed 0.1-0.03 for the case of radioexcitation and decreases with specific energy loss (dE/ dx) increase.[3] In order to look into this problem the analysis of the radioluminescence excitation process will be performed. It has a sense to study the radioluminescence process, when the ionizing radiation loses the main portion of its energy in the material. Therefore, the radioluminescence study is usually performed for bulk materials.

THEORY

Losses of the ionizing radiation energy E in an organic material result in generation of secondary electrons both of high (δ-electrons) and low energies.[3] The electrons of low energies create high activation density regions (Figure 1), i.e. the regions which contain ionized, excited and chemically activated centers as well as products of their interaction. For an ionizing radiation with high specific energy losses ($dE/dx \geq 10^1$ MeV/cm) such regions are cylindrically symmetrical (tracks), and

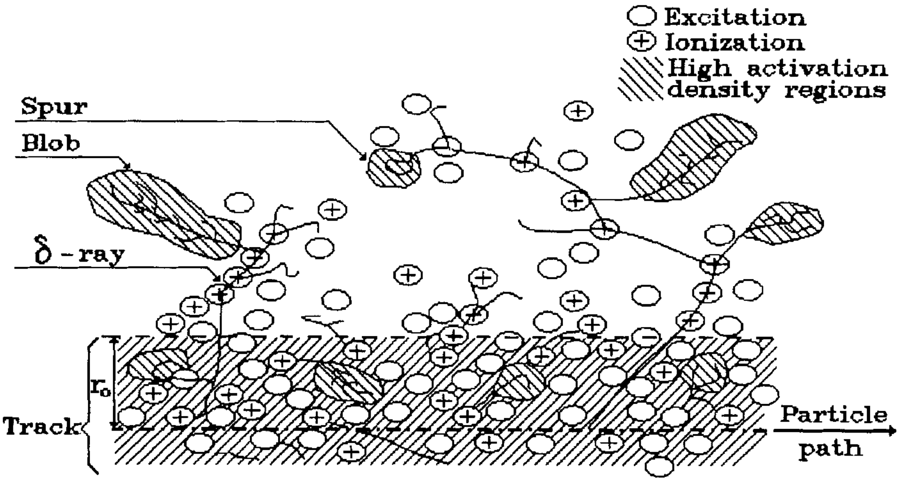

FIGURE 1 Schematic representation of the spatial distribution of excitations induced by charged particle in an organic solid.

for the one with low specific energy losses (dE/ dx $\leq 10^{-1}$ MeV/cm) they are spherically symmetrical (spurs).[4] Into those regions, according to the spin statistics, the ratio of generation probabilities of a singlet (S) and triplet (T) - excited molecule is equal 1:3 during the recombination process of charge states.[3,4] Outside them this ratio is about $1:10^{-6}$ because the S → T transition for a single molecule is unfavourable one. Owing to such a difference in T-state concentration the probability of T-states exchange interaction is high only inside tracks or spurs. The exchanged interactions of T- states result in T-T- annihilation process (Eq. (1)). When the probability of the singlet channel of the T-T-annihilation is high, the slow component of the radioluminescence pulse arises.

$$T + T_1 \Rightarrow \begin{cases} S_1 + S_0 \Rightarrow h\nu + 2\,S_0 \\ T_1 + S_0 \\ \cdots\cdots\cdots\cdots\cdots \end{cases} \qquad (1)$$

In such a case, the energy $h\nu$ of the delayed radioluminescence photons is the same one as for prompt radioluminescence, but the moments of their emission are delayed due to the transport of the lowest T-excited states (T_1) to one another. In Eq.(1) S_1 is the lowest excited singlet state and S_0 is the ground state. Nevertheless, it was considered[5] that the ratio of probabilities of T- and S-state generation into tracks and spurs is less then 3:1. This statement, which contradicts with the spin statistics conditions and with results of electroluminescent experiments,[3] was based on the fact of low light yield in the tracks. Really, after excitation the concentration of ions in such regions is high. Owing to ion field action S_1-states have a high probability of the nonradiative $S_1 \rightarrow S_0$ transition. The $T_1 \rightarrow S_0$ transition is unfavourable due to the different multiplicity of the states. Therefore, when the probability of the T-state generation is not high the quenching of luminescence is simply explained by a monomolecular process.[5] Thus, the calculation of the concentration of the states generated by ionizing radiation, the definition of tracks and spurs dimensions, as well as the study of the conditions of a charge carrier recombination and nonradiative energy losses in them are needed to ascertain the physics of radioluminescence excitation process.

The ratio of the radioluminescence yield in the regions of low and high activation density can be obtained by measuring the shape of the radioluminescence pulse, and especially the shape of its slow component. The radioluminescence slow component pulse - shape can be described in the following form[4]

$$I(t) \sim M(t)\ (1 + t/\ t_D)^{-k} \qquad (2)$$

where t is the time after excitation, $k = m/\ 2$, $m = 3$, 2 and 1 for tree-, two- and one- dimensional diffusion of T-states, respectively. The m-value is determined by a symmetry of high activation density regions as well as an anisotropy of the diffusion coefficients D_T of T-excitons in organic crystals. For the time $t \geq 50$ ns $M(t)$ is a constant. The time constant

$$t_D = r_0^2\ /\ 4D_T \qquad (3)$$

is determined during experimental data processing. The initial radius r_0 (Figure 1) of a track (or spur) cross-section can be obtained by the method described in the previous papers.[4,6] It is possible to calculate the track volume and the density of generated states using the r_0-value and the reference data for the track length. The study of the luminescent emission intensity allows to calculate the portion of states which results in a photon emission.[6] The difference in the results of aforementioned two types of calculations should be caused by the nonradiative energy losses, which distinguish the radioluminescence process. Measurements of the light output N for the cases of different types of excitation (α-particles, photons of γ-radiation, protons, electrons etc.) give the opportunity to verify the previous calculation by using the values

$$\xi_{ij} = \left(\frac{N_i}{E_i} \right) / \left(\frac{N_j}{E_j} \right) \qquad (4)$$

where E_i, E_j are the energies of i-, and j- type of excitation.

EXPERIMENT

The investigation of the radioluminescence pulse slow component, was performed for organic single crystals (SC) of anthracene, stilbene and p-terphenyl (doping with diphenylbutadiene molecules[1]). Samples were in the shape of cub (20x20x20 mm^3). Their sides were paralleled to the crystallographic axes a, b, c'. The radionuclide source ^{241}Am (α-excitation with energy $E_\alpha \sim 5.49$ MeV, dE/ dx $\sim 10^4$ MeV/cm as well as γ-excitation with main energy $E_\gamma \sim 59{,}5$ keV, dE/ dx $\sim 10^{-1}$ MeV/cm) was used. The scale of analyzing device (multichannel amplitude analyzer) had been calibrated in energies of γ-scintillations of NaJ(Tl) single crystal, before the measurements of SC radioluminescence amplitude spectra were performed.

Amplitude spectra of SC radioluminescence were studied for the cases when the source of α-particles (and γ- ray photons) was mounted on the sample and when there

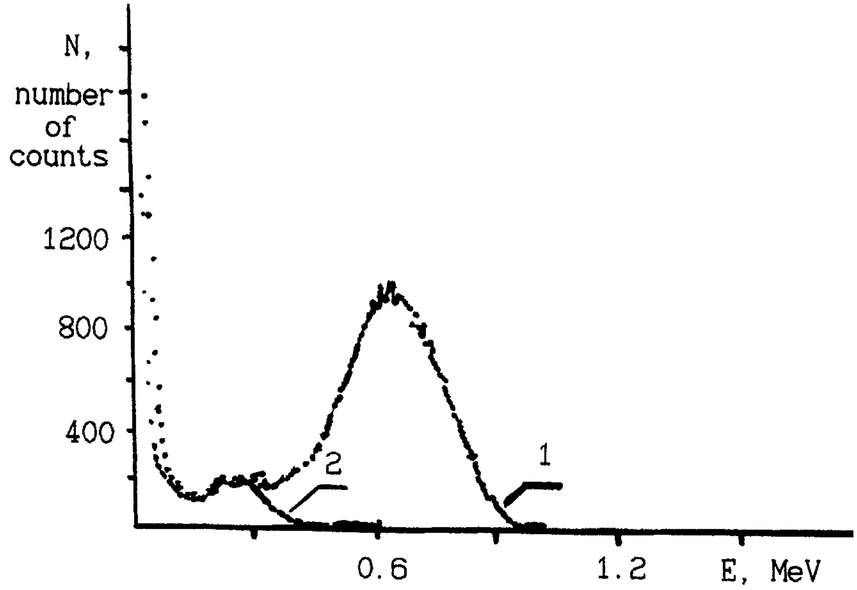

FIGURE 2 The radioluminescence amplitude spectra of the anthracene SC irradiated along c′ axis by α-particles and γ- ray photons as well (curve 1) and by γ- ray photons only (curve 2).
N is the number of counts, E is the energy (the scale of γ- scintillations of NaJ(Tl) single crystal).

was a sheet of paper between them . The measurements with radionuclide ^{241}Am γ- source, in which α- particles were absorbed by special film, have been performed too. In all the cases the low energy peak appeared in the same place of analyzer scale (Figure 2). It allows to identify this peak with registration of SC γ-scintillations (E_γ ~ 59.5 keV). The high energy peak was only observed in the first case. It gives the information about α- scintillations (E_α ~ 5.49 MeV). The values $\xi_{\alpha,\gamma}$ of 0.04; 0.05 and 0.07 have been obtained for the anthracene, stilbene and p-terphenyl SC, respectively. The $\xi_{\alpha,\gamma}$ value increase with the rise of SC light yield. For the stilbene and anthracene SC a light yield anisotropy about 20% was observed. The highest light output were achieved for irradiation along c′ axis, the lowest one for irradiation along b axis.

The study of a radioluminescence light-pulse shape (in the time range 0 - 2.0 μs after excitation) was performed using the single photon method.[1] The difference in the slow component relative intensity for α- and γ-excitation were observed. The Table I shows D_T-values (see Eq.(3)). The r_0-values are about 50 and 100 nm for α- and γ- excitation, respectively.[4]

TABLE I Results of radioluminescence kinetics study for SC of anthracence (A), stilbene (S) and p-terphenyl (T)

Excitation	Axes	A		S		T	
		I[†]	II[‡]	I	II	I	II
α	a	1.8	0.16	0.4	0.23	0.6	0.20
	b	1.5	0.15	0.1	0.21	0.4	0.19
	c′	2.1	0.18	0.4	0.24	0.8	0.20
γ	a,b,c′	2.1	0.03	0.4	0.02	0.8	0.03

[†] I is the D_T, 10^4 cm^2 s^{-1} (Eq.(3))

[‡] II is a relative intensity of the slow component of the radioluminescence pulse.

DISCUSSION

The generation of plasmons with the energy $\varepsilon \sim 20$ eV is the most probable result of ionizing radiation influence on SC.[3] Taking into account that the length of the α-particle track is about 30 μm, one can obtain the initial track volume $V \simeq 2.4 \times 10^{-13} cm^3$. In such a volume $n = 2.7 \times 10^5$ plasmons can appear ($n' = 5 \times 10^4$ plasmons/MeV), and therefore the concentration of the states which are formed in track is about 10^{18} cm^{-3}. It is known,[6] that for an anthracene SC excited by the α - particles from ^{241}Am radionuclide source $(4-5)x10^3$ photons form a radioluminescence pulse and 600-800 photons form its slow component. These data are in a good agreement with ones from Table I. The Table II shows the values N_α, $N_{\alpha S}$, $N_{\alpha F}$ on per - energy unit (1 MeV) basis for the case of α- excitation. Taking into account obtained $\xi_{\alpha,\gamma}$- values, one can calculate the mean number of photons on per- energy unit basis in SC radioluminescence pulse N_γ for the case of γ- excitation as well as the rest of parameters (see Table II) by using values of the relative intensity of radioluminescence pulse slow component (Table I).

Table II The number of photons on per-energy unit (1 MeV) basis (N_i) in the radioluminescence pulse, its slow (N_{iS}) and fast (N_{iF}) components for the anthracene (A), stilbene (S) and p- terphenyl (T) SC in the case of i- type of excitation.

SC	i	N_i	N_{iS}	N_{iF}
A	α	$(7 - 9)x10^2$	$(1 - 1.5)x10^2$	$(5.5-7.3)x10^2$
	γ	$(1.8 -2.3)x10^4$	$(5 - 7)x10^2$	$(1.8-2.2)x10^4$
S	α	$(5.3 -6.8)x10^2$	$(1.3-1.6)x10^2$	$(4 - 7)x10^2$
	γ	$(1 - 1.4)x10^4$	$(1.7-2.2)x10^2$	$(1 - 1.4)x10^4$
T	α	$(8.4-10.8)x10^2$	$(1.7-2.2)x10^2$	$(6.7-8.6)x10^2$
	γ	$(1.2 -1.5)x10^4$	$(3.6-4.5)x10^2$	$(1.2-1.4)x10^4$

The density of charge and excited states in spurs is low.[3] Therefore, it is possible to neglect quenching inside them, and hence to obtain for anthracene SC $N_\gamma \sim (1.8 - 2.3)x10^4$ photons/MeV (Table II). This value is right for the unreal, theoretical case of α- excitation with no quenching too. For such a case $N^*_{\alpha S} \simeq N_\gamma - N_{\alpha F} \simeq (1.7 - 2.2)\text{x}10^4$ photons/MeV, and, consequently, the α- particle must dissipate in track about 94% - 98% of it energy E. In the real situation the number of photons $N_{\alpha S}$ is smaller by a factor of 10^2 and their concentration in track is about $(2.5\text{-}3.3)\text{x}\ 10^{15}\text{cm}^{-3}$. Using D_T- values (Table 1) it is not difficult to show that the mean time needed for two T-states to draw to one another is about 10^{-11}s and 10^{-8}s when the T- states concentration is about 10^{18}cm^{-3} and 10^{16}cm^{-3}, respectively. Thus, in the case of the last concentration the process (1) becomes the diffusion - controlled one.

The ratio between the values $N_\gamma \sim 2\text{x}10^4$photons/MeV and $n' \sim 5\text{x}10^4$plasmons/MeV shows that in the case when a nonradiative decay of the states in the high activation density regions is negligible $n' \sim N_\gamma$. For the case of α-excitation $n' \sim (N_{\alpha S})^2$. Such a ratio (square dependence) is possible only for bimolecular process of interaction of charge as well as excited states, which are generated during a plasmon or superexcited state decay. The nonradiative decay of excited S- states, which are generated in the process (1), in the field of ions results in decrease of the radioluminescence yield. The same quenching mechanism of excited S- states, which are generated immediately in decay process of superexcited states, hardly can substantially influence on the process of the radioluminescence pulse formation. Using the results of the measurements of the SC radioluminescence amplitude spectra, the N_i- values for another SC were obtained. Using the results of the radioluminescence pulse - shape investigation, it is possible to calculate N_{iS} and N_{iF} values. The results, which have been got for stilbene and p- terphenyl SC, are in a good agreement with those, which have been obtained for the anthracene SC (Table II). Corresponding $N^*_{\alpha S}$ values for the stilbene and p- terphenyl SC are equal to $(1\text{-}1.4)\text{x}10^4$ and $(1.1\text{-}1.4)\text{x}10^4$ photons/MeV.

CONCLUSIONS

Low radioluminescence yield of organic crystals is caused by the nonradiative decay process of excited states generated in bimolecular exchange interactions between charge states as well as between T-excited ones. These processes mainly take place during the time $\sim 10^{-11}$s after excitation in the high activation density regions. The effect of these processes becomes stronger when dE/ dx value increases because an energy portion accumulated in the high activation density regions grows. For recoil electrons, which are generated by γ- ray photons (dE/ dx $\leq 10^{-1}$ MeV/cm), and for α-particles (dE/ dx $\simeq 10^{4}$ MeV/cm) the portion of the energy accumulated in these regions is about 10^{-2} and more than 0.9, respectively. Anisotropy of SC radioluminescence light yield is caused by anisotropy of D_T - values (Eq.(3)).

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