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Sergei Budakovsky [a] , Nikolai Galunov [a] & Igor Krainov [a]
[a] Institute for Single Crystals, Kharkov, USSR
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THE INFLUENCE OF ENERGY EXCHANGE PROCESS OF CHARGE STATES ON RADIOLUMINESCENCE PULSE SHAPE RISE IN ORGANIC SOLIDS

SERGEI BUDAKOVSKY, NIKOLAI GALUNOV, IGOR KRAINOV
Institute for Single Crystals, Kharkov, USSR

Abstract Some violations of the existing radioluminescence theory of organic solids are discussed. These violations were seen in experiments on precise scintillation pulse shape investigations in nano- and subnanosecond ranges. This kind of experimental data made us think about the applicability of the existing radioluminescence theory of organic solids.

INTRODUCTION

The existing radioluminescence theory of organic solids was founded on the work of Birks[1], King and Voltz[2], Laustriat[3] published in the sixties. This theory proceeds from the assumption that the duration of the processes preceding molecular excitation to the lowest excited state, that is, the duration of all processes that take place in superexcited and charge states, is negligible. In this theory radio- and photoluminescence kinetics should be the same, and the shape of radioluminescence pulse fast component should be described by the following functions:

$$i(t) \approx i_0 \exp(-t/\tau) \tag{1}$$

$$i(t) \approx i_0 \exp(-t/\tau) * \exp(-t/\tau_2) \tag{2}$$

$$i(t) \approx i_0 \exp(-t/\tau) * \exp(-t/\tau_1 - q(t/\tau_1)^{1/2}) \tag{3}$$

for single component systems, binary liquid and binary solid systems respectively. The first attempts made by Bengston and Moszynski[4-6] to investigate the precise scintillation pulse shape for binary plastics in the early seventies led them to the equation:

$$i(t) \approx i_0 f_G(t) * \exp(-t/\tau) \tag{4}$$

$$f_G(t) = (\sqrt{2\pi}\sigma)^{-1} \quad (\exp(-(t-m\sigma)^2/2\sigma^2)) \qquad (5)$$

In Eq. (1) - (5): $f(t) * g(t) \equiv \int_0^t f(t-\beta)g(\beta)d\beta$, m = 3,

t is the time after excitation, τ is the decay time constant of the radioluminescence pulse fast component, τ_1, τ_2, σ are the time constants, $q \approx R_0^3 C$, R_0 is the Forster radius, C is the dope concentration, i_0 is the normalization numerical constant. As compared to equation (2), one can get the fast initial pulse rise with its following slowing down for the case of equation (3), and slow initial pulse rise with its following speeding-up for the case of equation (4). In other words, one will observe the additional delay of the moment of photon emission for the case of the equation (4). This delay is described by function (5).

EXPERIMENTAL RESULTS

Bengston and Moszinski[4-6], and some other investigators who verified their results, studied only vinyltoluene plastics. Table I shows also the results of our experiments for precise scintillation pulse shape investigations on plastics and organic single crystals. We also carried out experiments for some toluene liquid scintillators[8,12].

It has been found that the equation (4), modified by Gaussian function (5), is correct for all organic solid scintillators except those in which the process of radiative transport is of primary importance. The sigma value for plastics did not depend on type and concentration of added agents, but was determined by the type of polymer macromolecule and the density of excitation. For organic crystals the sigma value depends on crystal structure perfection just as much as it is connected with the charge carrier and exciton trap concentration. It should be added, that for liquid scintillators no deviation from the equation (2) was observed, which means that in this

TABLE I Results of experiments for precise scintillation pulse shape investigation

Scintillators	$\sigma(5)$ (ns)	Ref
PLASTICS both single and binary component systems		
Base		
styrene	0.26	8-11
vinyltoluene	0.20	4-7
vinylxylene	0.20	8-12
vinylxylene*	0.13	12
ORGANIC SINGLE CRYSTALS		
Stilbene		
The root-mean-square of random orientation of single crystal mosaic structure (minutes of arc)		
25-160	0.18-0.21	8,13
p-Terphenyl Diphenylbutadiene concentration (mol.%)		
No doping	0.38	8
0.042	0.30	
0.083	0.24	
0.415	0.18	

*High density of excitation (tracks were overlapping)

case there is no additional delay of radioluminescence photon emission. The comparison between the fluorescence spectra for the cases of radio- and photoexcitation for all scintillators showed their identity.

DISCUSSION

First of all, we should answer the question: which processes result in the Gaussian function's (5) origin?

As follows from the form of the convolution equation (4), the Gaussian function (5) describes the influence on scintillation pulse rise shape of all the processes that occur after the scintillator was hit by an initial particle and that result in the excitation of luminescence centres. These are the processes that take place when the molecules are in higher energy states, both excited and charged ones. It should be noted, that the Gaussian form of function (5) only testifies to the statistical nature of the processes described, which follows from the central limit theorem. The analysis of the situation discussed has shown that the Gaussian function (5) describes the additional delay of the times of radioluminescence photon emission, and this delay is caused by the delay of molecular excitation in the recombination process of charge states localized on the shallow trap system. Indeed, the duration of other energy exchange processes such as interaction of ionizing emission with organic solids, generation of plasmons and superexcited states, nonradiative inter- and intramolecular energy exchange and nonradiative electron excitation energy transfer are too small. The duration of all these processes does not exceed 10^{-11}s, and consequently they can't cause the additional delay of 10^{-10}s. The charge carrier will have a location time τ_t if it is captured by a trap with depth of:

$$E_t = kT \cdot \ln (\tau_t \cdot \nu) \qquad (6)$$

where k is Boltzman constant, T is the temperature, ν is the attempt-to-escape frequency. Substitution kT = 0.026 eV, $\nu \lesssim 10^{12} s^{-1}$ (Simmons[14], Silinsh[15]) and $\tau_t = 3\sigma$, according to (5), into (6), at the room temperature yields $E_t \lesssim 0.17$eV. So the effect discussed here is caused by the recombination of charge carriers localized on shallow traps.

In this case three following questions arise: What

is the nature of these shallow traps? Why is no additional delay observed for liquids? Why does the additional delay decrease when the excitation density of an organic solid increases?

If the charge carrier motion is defined only by transfer integrals then the corresponding time of charge carrier localization would be about 10^{-14} - 10^{-12}s. In this case, this time exceeds the time of electronic (10^{-16} - 10^{-15}s) and vibronic (10^{-14} - 10^{-13}s) polarizations and a molecular polaron is formed.[15] In the situation discussed, one should expect the formation of a lattice polaron, because the time of charge carrier localization is about 10^{-10}s, which exceeds the lattice polarization time which is about 10^{-12} - 10^{-11}s. Thus a local lattice polarization takes place. It means that a potential well 0.1 eV in depth is formed[15] and that the real structure trap will be deepened by such a depth. Such shallow traps are usually associated with the local trapping centres of a polarization origin which are formed in the regions of local compression and tension of organic crystal individual edge dislocations, and in the regions of structure imperfections of an organic polymer macromolecule.[8,13,15]

For nonviscous liquids, where the duration of processes of migration and recombination of charge states are defined by molecular collisions, that is at times about 10^{-12}s, the above effect of additional delay formation is impossible.

For high excitation density, when the local charge carrier concentration in organic solids increases, the probabilities of charge carrier localization and recombination are defined not only by the type and concentration of traps but also by charge carrier concentration. The probability of recombination increases in this case, and the sigma value in equation (5) should decrease. That is just what has been observed in the experiments.

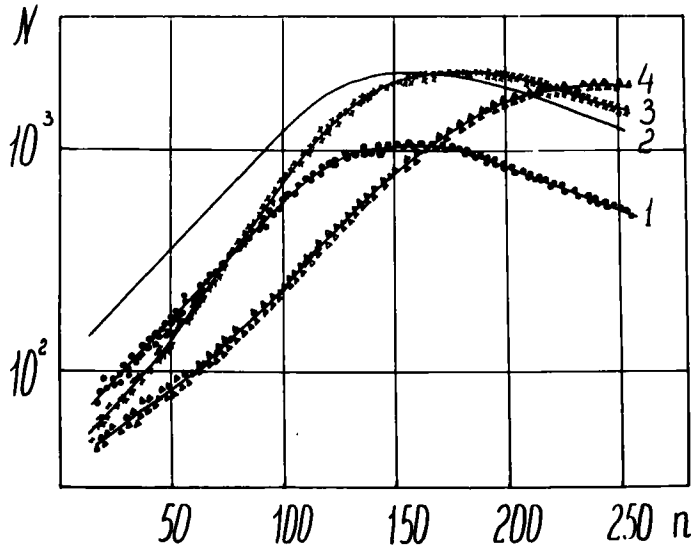

FIGURE 1 The time distribution spectra of the light pulse from binary scintillators 1,2 - for liquid scintillator (0.034 mol./l. PBD in toluene); 3 - for plastic (0.035 mol./mol. PBD in polyvinylxylene); 4 - for single crystal (0.042 mol./mol. diphenylbutadiene in p-terphenyl); N is the number of counts, n is the channel number (the channel width is 10 ps).

The effects discussed are illustrated in Fig.1. It shows the radioluminescence pulse shapes of liquid, plastic and organic crystal binary scintillators. Their decay times are equal and the additional delay of radioluminescence photon emission for plastic and organic crystal could be explained only by the process discussed. This is the experimental result with no data processing.

CONCLUSIONS

The correlation between the process resulting in charge carrier energy exchange in organic solids and their molecular luminescence is neglected in existing radiolumi-

nescence theory.

The analysis of the experimental data reported has shown that the localization of charge carriers on shallow traps of polarization origin results in the additional delay of their recombination, hence of molecular excitation, and consequently these result in the additional delay of photon emission. This delay is described by a Gaussian function owing to the statistical nature of the processes described. The duration of these processes is by more than an order of magnitude, greater than the duration of the electron excitation energy transfer.

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