Functional Materials 19, No.1 (2012)

Generation and energy exchange of charge states in organic molecular crystalline scintillators

O.A.Tarasenko

Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received December 7, 2011

This paper discusses the physical processes that determine the aspects of generation and energy exchange of charge states, which arise in molecular organic media by an action of ionizing radiations of different types. The semi-empirical description of the primary processes of energy exchange in the track of ionizing particles is analyzed. This description takes into account the primary influence of the polarization processes on the charge states energy exchange and quenching processes. The process of quenching is determined by the very fast initial recombination of the molecular polaron pair. This process, at least, is an order of magnitude faster than the process of diffusion expanding of the track, and its efficiency increases with the density of the recombining pairs. The analysis is based on the results of the measurements of the light yield of stilbene and *p*-terphenyl scintillation detectors as the function of energy for the cases of alpha-, neutron- and gamma excitations. We have studied structurally perfect organic single crystals, hot-pressed polycrystals and composite scintillators. The obtained results testify about the primary influence of the type of ionizing radiation in comparison with the influence of the matter structure.This paper discusses the physical processes that determine the aspects of generation and energy exchange of charge states, which arise in molecular organic media by an action of ionizing radiations. The primary energy loss of a charged ionizing particle in the regions of high density of excitation and the possible causes of this effect are considered.

В работе обсуждаются физические процессы, определяющие особенности генерации и размена энергии зарядовых состояний, возникающих в молекулярных органических средах под действием ионизирующих излучений различных типов. Анализируется полуэмпирическое описание процессов первичного размена энергии в треке ионизирующей частицы. Данное описание учитывает определяющее влияние поляризационных процессов на размен энергии зарядовых состояний и процессы тушения. Процесс первичного тушения определяется очень быстрой рекомбинацией молекулярно-поляронной пары. Этот процесс как минимум на порядок быстрее процесса диффузионого расширения трека, а его эффективность растет с ростом плотности рекомбинирующих пар. Анализ основывается на результатах измерений величины светового выхода органических сцинтилляционных детекторов на основе стильбена и *n*-терфенила как функции энергии при альфа-, нейтронном- и гамма-возбуждении. Исследовались структурно совершенные органические монокристаллы, поликристаллы, полученные методом горячего прессования, композиционные сцинтилляторы. Полученные результаты свидетельствуют в пользу определяющего влияния на изучаемые процессы типа ионизирующего излучения по сравнению с влиянием структуры вещества.

1. Introduction

In contrast to the photoluminescence that occurs under photoexcitation, the mechanism of the radioluminescence is largely determined by the initial conditions of generation of excited states. They, in turn, depend on the conditions of interaction of radiation with matter and the conditions of

formation and exchange of charge states in it [1, 2]. For the same objects excited by light (photoluminescence) or by a particle, the energy of the emitted photons is 10^2–10^4 times less in the case of the radioluminescence. For example, approximately 12 000 photons are created per 1 MeV of the energy of gamma radiation and approximately 965 photons are created per 1 MeV of the energy of an alpha particle (5 MeV) in the scintillation pulse of a ∅50 mm×5 mm stilbene single crystal [3]. Really, the ratio of the energy of scintillation photons in a pulse to the energy of a primary photon of gamma radiation or an alpha particle is approximately equal to $3.81 \cdot 10^{-2}$ or $3.07 \cdot 10^{-3}$, correspondingly. The process of the energy loss, which is specific for the radioluminescence, is known as the "specific" quenching [4]. This effect is stronger for heavier particles and particles of low energies, i.e. the specific energy loss dE/dx of a particle increase with energy E. The process, which reduces the efficiency of the radioluminescence with increasing dE/dx, is sometimes called the "ionization quenching" [5].

The theory of the scintillation process, which existed in the 60–70s of the XX century, in fact, only declared that the processes of generation, transfer and recombination of charge carriers are an important stage of the scintillation process in organic molecular scintillators. To describe the scintillation process it used the theory of the photoluminescence of molecular compounds [6, 7], which was well developed previously. To take into account the particularity of the radioluminescence process the following assumed. The conversion efficiency of excitation energy in the light signal is lower for ionizing excitation than for photoexcitation [4, 8–10].

An improved edition of the radioluminescence theory of organic condensed media was developed in the 80–90s of the XX century [11]. For the first time this theory gave serious attention to the description of generation, transfer and recombination of charge carriers. It showed that above the Debye temperature the process of charge transfer occurs in accordance with the mechanism of the molecular polaron and therefore differs fundamentally from the mechanism of generation and charge transport in inorganic scintillators, which are ionic or covalent systems. At the beginning of the XXI century, it was proved that the charge transport in molecular scintillation crystals is described by the mechanism of the lattice-molecular nearly small polaron [12, 13]. It means that the transfer occurs through the mixed mechanism of thermally-activated hops of the lattice small polaron and intermolecular tunneling of a charge in accordance with the mechanism of the nearly small polaron [14].

Despite a substantial progress in the theory of the radioluminescence of organic condensed media, which has been achieved by the end of the XX century, a situation with the description of the specific quenching, as before, remained a mystery [14]. A large amount of the results, accumulated in the radiation chemistry and physics of track detectors, are practically not used [11, 15–17]. It was not only due to the different research purposes of the radioluminescence, radiation chemistry and track detector studies, but also due to necessity to harmonize the interpretations of the different experiments. The situation was similar to that which occurred when one try to explain the results of a molecular crystal study as an organic semiconductor. Really, for the scintillation process the recombination of surplus electrical charges is the source of creation of molecular excitation and luminescence. It is the way to produce the radioluminescence signal. For the physics of organic semiconductors the recombination of surplus electrical charges is a parasitic phenomenon that reduces the output current of a sample. Similarly, the rapid recombination following the excitation of a matter is a serious complication for the tasks of radiation chemistry. It decreases the accuracy of calculation of the energy required to create a chemical radical and makes uncertain the balance of primary chemicals that occur after the passage of a particle. The study of the reaction products is possible only when these products are stable over time that is longer than the time of the measurements. The rapid process of the primary recombination usually does not leave imprints in track detectors. In this field of investigation, the accurate experiment is that for which the recombination effect becomes minimal. However, the phenomenon of the rapid initial recombination exists, and therefore a careful analysis, based on the experiments with chemical scavengers, is able to distinguish information about this phenomenon [15].

Why is it necessary to study the processes of a track formation, especially, in organic scintillators?

Firstly, it can be associated with the peculiarities of the use of organic scintillators

as detectors of ionizing radiations. For example, the ion-covalent inorganic systems are excellent detectors of gamma radiation [18]. In this case, as well as in the case of excitation by fast electrons when the specific energy loss dE/dx are too low, the influence of the features of formation of the primary radiation track on the characteristics of the scintillation pulse is neglected. When dE/dx is low the tracks are not formed, and the scintillation process can be studied within the so-called "optical" approximation [11] using well-known description, which was developed for the photoluminescence [6, 7]. Organic molecular scintillation systems are mainly used to detect those types of ionizing radiation, for which the formation of the track regions is determinative. Really, organic scintillators have the low effective atomic number. Therefore they, in contrast to inorganic ones, demonstrate a negligible back scattering when detecting charged particles [11, 19, 20]. A fast neutron produces recoil protons in such organic materials with its highest energy equal to the energy of this neutron. This physical process is the basis for fast neutron spectrometry [11, 20, 21]. Therefore organic scintillators are very effective detectors of the above-mentioned types of radiations. Alpha particles, protons, electrons of the low energy, etc. form the track. So, the knowledge of the characteristics of the processes occurring in the tracks of ionizing particles is the key for understanding the results of the studies of the radioluminescence of organic molecular scintillators [1, 4, 8–11, 14].

Secondly, it is the set of properties that defines the fundamental difference between organic and inorganic scintillators. The density as well as the effective nuclear charge is very close for different organic condensed media. It is the result of a predominance of the light atoms of hydrogen and carbon in their molecules [11]. A comparison of the results of studies of various organic scintillators excited by different types of ionizing radiation gives a good possibility to select the results, which are caused by the type of irradiation, rather than the peculiarities of the composition or the structure of the object.

In addition, organic molecular systems have two interesting features related to the problem discussed here. Detectors based on organic scintillators are the most effective for detecting alpha particles and fast neutrons [11, 19–21], that is the ionizing radiations, which are the most hazardous to humans. Thus, the radiation-weighting factor for photons of gamma radiation is equal to 1, while for fast neutrons with energies up to 2 MeV and for alpha particles the value of the radiation-weighting factor increases to 20 [22]. Therefore, the results of such measurements, individually, are of great interest for radiation medicine, biology and ecology. The number of scintillation photons emitted by the organic scintillator proportionally grows with the excitation energy and decreases by the coefficient of the energy loss, including those, which are related to the process of excitation of the scintillator. This allows us to consider organic scintillators as an alternative class of model systems for studying the interaction of ionizing radiation with organic condensed media [1, 11, 14].

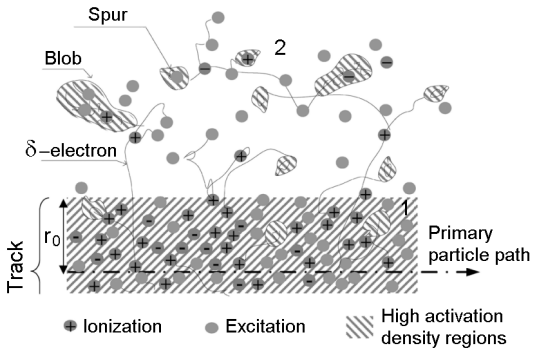

Fig. 1 [8–11]. Schematic representation of the primary processes of excitation induced by a charged particle with the high specific energy loss (*1* is the high activation density region, *2* is the low activation density region).

2. Theory

2.1. Primary particle energy exchange in an organic medium

The interaction of an ionizing particle with a matter can be described in terms of successive "collisions" of the particle with molecules of the matter. These collisions are divided into glancing collisions and knock-on ones. They are, correspondingly, lead to glancing and knockon activations of the molecules of a matter. In the case of the glancing activation for a separate act of energy transfer the resulting energy loss are small and are comparable with the ionization potential of a substance. If the unit energy loss is much greater than the ionization potential, then it is the knock-on activation [15, 16].

Secondary low-energy electrons lose their energy in close vicinity to the path of the

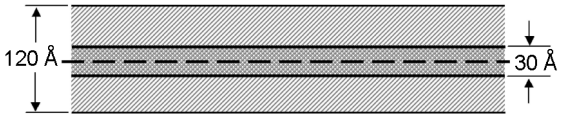

Fig. 2 [25]. A typical fission fragment track in water, showing dense overlap of secondary electrons in the core shell region (shaded).

primary particle. The electrons of higher energies or δ-electrons form their own separate tracks, creating "a halo" of the primary particle track [11, 15, 23, 24].

A value of the specific energy loss, or the linear energy transfer varies from 10^{-2} MeV/cm for photons of gamma radiation up to 10^{3} MeV/cm for alpha particles and can reach higher values for heavy ions [15]. In the case of particles with the high specific energy loss, the local regions of excitation overlap and create the high activation density regions. The primary particle with the high specific energy loss creates the high activation density regions with a quasi-cylindrical symmetry that is the primary track (Fig. 1). The tracks of δ-electrons are separate local regions of the high activation density, called spurs and blobs (Fig. 1). The glancing collisions generate spurs each of which contains one or more pairs of the charge states. High-energy electrons and photons of gamma radiation do not form the high activation density regions.

The knock-out collision of an ionizing particle with a molecule results in direct knock-out of a molecule electron. Usually such the electron has a kinetic energy appreciably different from zero; while in a case of the glancing collision the separate acts of ionization occurs through the intermediate stage of formation of short-lived localized states such as plasmons and superexcited states [5, 11]. Further recombination of uncompensated positive and negative electric charges can lead to molecular excitation, and then, to luminescence.

2.2. Track structure

Knowledge of the regions in which the recombination process takes place is very important to make the correct analysis of the features of energy exchange of the charge states in the track regions and the influence of the polarization mechanisms on this process. It means that not only the information about the size of such the region is necessary, but also a correct interpretation of the track structure produced by an ionizing particle is essential. The track

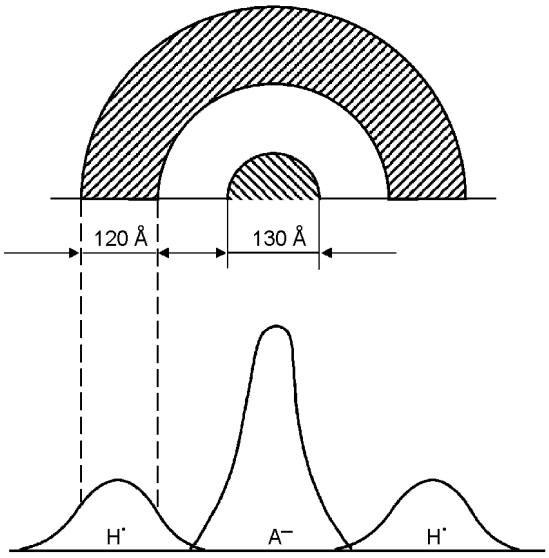

Fig. 3 [28]. Schematic representation of the distribution of atoms H and ion-radicals A^- in a track.

structure means the spatial distribution of acts of the energy loss of an ionizing particle. The complexity of the situation is caused by the difference both in terminology, which different authors use, and in criteria, which are introduced to describe the different types of radiations and materials. In addition, the lack of reliable experimental data concerning the ranges of the secondary electrons with the energies less than 6.5 keV (the average energy of electrons in the reaction of tritium decay) makes the estimations of the external sizes of the track regions more difficult.

Radiation chemistry in most cases considers the track core (see Fig. 2), but not the entire track, as the region of heavily damaged substance with the maximum energy loss of ionizing radiation [15]. This is the region of a latent track, which is partial or complete etched [23–26]. Various models of formation of the track estimate the size of the track core from 3 to 10 nm [15, 23, 25]. The physical core size can be defined as the distance at which the transported energy deposition by secondary electrons just exceeds those due to every other channel. The mean range of secondary electrons determines [15] the size of the core shell of the track. Authors [15, 17] described in detail the results of investigations of the energy distribution of the primary charged particle between track objects (spurs, blobs and short tracks) in a condensed medium.

The process of radiolysis provides additional opportunities to study the track structure in a condensed matter. The track of an ionizing particle is a precursor of the radical track. It is the region where short-lived intermediate products of radiolysis interact with each other and with the environment. Methods of electron paramagnetic resonance [27, 28] can be used to investigate the structure of radical tracks that is to determine the relative spatial distribution of active particles. Such studies can directly demonstrate the inhomogeneous spatial distribution of intermediate products of radiolysis in a condensed matter. Fig. 3, as an example, shows the structure of the radical tracks of beta particles of tritium in a frozen at 77°K 8M sulfuric acid solution. Fig. 3 shows the characteristic size of stabilization of radicals. The size of the region of stabilization of atoms H are determined by a path length of secondary electrons before their thermalization, and the size of stabilization of ion-radicals SO_4^- (A^-) are determined by the Coulomb repulsion of positive charges, up to their stabilization [28].

The study of the delayed radioluminescence pulse shape of organic scintillators is another indirect method for studying the structure of a particle track [11]. This method is based on the assumption that a slow component of the radioluminescence pulse is formed in the process of the diffusion-controlled triplet-triplet annihilation. This approach is valid if the concentration of the triplet states is low [2, 11]. The triplet states occur during the recombination of the charge states in the core shell of the track, and in the peripheral part of the particle track, called the track halo [11, 23].

The description of the process of triplet-triplet annihilation by the prescribed diffusion approach [11, 15] allows us to represent the radioluminescence pulse slow component of organic scintillators in the form [11, 29]:

$$P(t) \sim (1 + t/t_D)^{-l/2} \sim \left(1 + 4\frac{D_T}{r_0^2}t\right)^{-l/2}, \quad (1)$$

In (1) t_D is a time parameter which is defined by the approximation of experimental curves of the radioluminescence pulse slow component, D_T is the diffusion coefficient of triplet states (T_1-states), and r_0 is the parameter, often called as the "initial radius" of the particle track (for time $t_0 = 0$) [8, 9, 11]. Parameter l in (1) gives the number of dimension of the T_1-states diffusion.

The results of the studies [2, 11, 29–31] of the slow component of the scintillation pulse in organic scintillators have shown that l in (1) is close to 2 for excitation by alpha particles or fast neutrons. It means that the energy exchange of T-states is quasi-two-dimensional. In other words, an excitation by ionizing radiation with the high values of dE/dx mainly causes the formation of tracks whose symmetry is close to a cylindrical one. The value of $l = 3$, obtained for the excitation by photons of gamma radiation, testifies that in this case the symmetry is close to spherical one and the separate spurs are mainly formed. These results are in a good agreement with the results of the radiation-chemical studies [15–17, 25, 27], the results of the studies of track structures in solid-state track detectors [23, 24, 26], and agree with the distribution functions of radicals obtained by electron paramagnetic resonance [28].

Despite the lack of real physical meaning the experimental, effective parameter r_0 gives reproducible results in the formal calculation of the diffusion coefficients of T_1-states [11, 30–32], which agree with the analogous values of the diffusion coefficients of T_1-states obtained by the direct measurements under photoexcitation [33].

The results of the measurements of the scintillation pulse shape, as well as knowledge of the diffusion coefficients of triplet excitons from the photoluminescent experiments allowed estimating the initial radius of the track for different types of excitation. In [2, 11, 29–32] were obtained values $r_0 = 50$, 65 and 100 nm for alpha (^{241}Am), neutron (^{252}Cf) and gamma (^{60}Co) excitations, correspondingly.

2.3. Polarization effects and theirs influence on the energy exchange of charge states

The polarization energy that is necessary to create a molecular polaron is about 0.1 eV for a molecular organic scintillation crystal, which consists of initially neutral molecules. This value is by a factor of 10^2 more than the energy of intermolecular interaction that holds molecules together in a crystals lattice [34]. A specific time of the electronic, molecular, and in some cases, the lattice polarization, is shorter than a specific time of electronic excitation energy transfer and relaxation processes.

The relaxation time that is necessary for the electron polarization of neighbouring molecules of an organic crystal can be estimated as $\tau_e \approx 10^{-16}$–10^{-15} s. The average

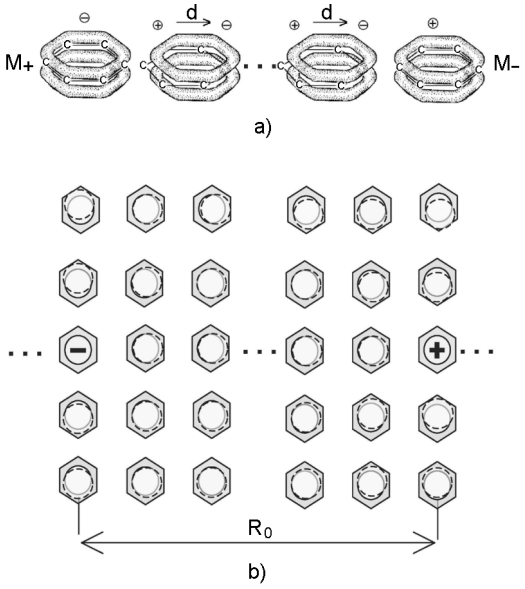

Fig. 4 [35]. Schematic representation of a formation of the electron polarization "shells" around charge states in a hypothetical molecular crystal consisting of benzene molecules.

time τ_h that is necessary for a charge carrier to hop from one molecule to other in organic crystals, usually, is about 10^{-12} s. The necessary and sufficient condition for the electronic polarization to appear in the surrounding of surplus molecule charge in such a crystal is $\tau_h > \tau_e$. A charge carrier moves along with its polarization surrounding. The relaxation time τ_v that is required for intramolecular (vibronic) oscillations is about 10^{-14} c. The condition of a formation of the molecular polaron is $\tau_h > \tau_v$. The representative value of lattice polarization time τ_l is more than 10^{-13} c. Therefore the formation of the lattice polaron is not always possible for these systems, since, in particular, the condition $\tau_h \leq \tau_l$ is often realized only along the crystallographic axis c' [34]. Our preliminary analysis shows that the polarization interaction has a significant or even preponderant effect on the progress of the scintillation process in a molecular condensed medium [14].

Previously proposed theories of the scintillation process in organic condensed media [4, 5, 11], in fact, ignored the effect of polarization interaction on the recombination of charge states, which precedes the formation of excited states and their subsequent radioluminescence. Therefore it is necessary to study this point more carefully.

There are no free electrons of low energies in molecular crystals. If a molecule loses an electron and becomes the positively ionized quasi-ion M_+, then this electron localizes on some other molecule. The negatively ionized quasi-ion M_- appears. Fig. 4(a) schematically shows this situation for a hypothetical crystal of benzene. The molecular π-orbitals of the neighboring molecules have a negative charge, so they attract to the positive quasi-ion M_+, but their skeletons repel from it. The polaron M_p^+ is formed. In the case of the negatively ionized quasi-ion M_- the molecular π-orbitals of the neighboring ionized molecules repel from it, and the skeletons of these molecules attract to it. The polaron M_p^- is formed. Fig. 4(b) schematically represents the situation where the polarons M_p^- and M_p^+ are formed on a certain initial distance R_0. The polarization surrounding r_c in diameter is formed around the molecular quasi-ion. For example, for the organic crystals of polyacenes the distance of the stable polarization surrounding r_c around the surplus charge is equal to 13–16 nm, and such the polarization surrounding can include about 7000 molecules [34]. In the case when the distance R_0 between the polarons M_p^+ and M_p^- is less than this value ($R_0 < r_c$) these polarons form the molecular-polaron pair with one joint polarization surrounding.

Hot (that is still unrelaxed) electrons [33, 34] can be easily created in a molecular scintillator by an ionizing radiation. After that the electron rapidly loses its excess energy in inelastic collisions and generates Frenkel excitons or lattice phonons. Inelastic collisions of an electron lead to its localization and for the case when $\tau_h > \tau_e$ the subsequent behavior of an electron is determined by the electronic polarization. The thermalization time of such electron is not less than 10^{-13} s [36]. Thus, the processes occurring after generation of charge carriers in a time comparable or shorter than 10^{-13} s are the processes involving hot charge states. For a very strong electrostatic field $E \approx 10^6$ V/cm that reaches the values of the local field strength inside the polaron pairs [34], the scattering time τ of charge carriers becomes very small value, estimated as 10^{-14} s. For example, according to the results of the direct calculations of the drift velocity of charge carriers in an anthracene crystal based on the experimental data, it has been obtained $\tau = 8 \cdot 10^{-14}$ s [37]. From this a very important conclusion

follows. A fast primary ($\leq 10^{-13}$ s) recombination of polaron pairs can be initiated by the polarization interactions. It may have its own specifies [12].

3. Experimental

We used organic scintillation detectors based on stilbene and *p*-terphenyl to study the generation and energy exchange of charge states in the track regions. There were structurally perfect organic single crystals [11, 20, 31, 38, 39], polycrystals obtained by the hot pressing [20, 39, 40], composite scintillation materials [3, 21, 39]. The detectors were irradiated by ionizing radiations of the following radionuclide sources: ^{239}Pu–Be (fast neutrons) [21, 41–44], ^{239}Pu and ^{241}Am (alpha particles), ^{22}Na, ^{60}Co, ^{137}Cs, ^{152}Eu, and ^{241}Am (photons of gamma radiation). We used the effect of an attenuation of alpha particles in air to obtain the energy range E_α from ≈1 to 5.3 MeV [45]. To obtain the spectra of recoil protons for the combined source of fast neutrons and photons of gamma radiation ^{239}Pu–Be we used the method of the selective detection of different types of ionizing particles based on the pulse shape discrimination [46]. For the reconstruction of the neutron spectrum from the measured spectrum of recoil protons, we used the procedure described in [29, 44].

The most promising way to study the processes of the primary quenching in the track is the following [1, 14, 29, 41]. In the case of irradiation of an organic scintillator by ionizing radiation with a low specific energy loss dE/dx (for example, photons of gamma radiation) the track is not formed and hence the additional energy loss, associated with the "specific" quenching, are absent. If nonlinearity of a scintillation response is caused only by the specific quenching in the particle track then in this case the light yield must depend linearly on the energy of ionizing radiation. Such a scintillation response will carry information concerning: i) the loss, associated with the efficiency of energy conversion of ionizing radiation into light photons collection, ii) the efficiency of light collection in a scintillator, iii) the loss in a scintillator caused by reabsorption and so on. To put it otherwise it is the specific own losses for a given scintillator. If the same scintillator, under the same conditions as before, is irradiated by the ionizing radiation with a high specific energy losses dE/dx (for example, protons or alpha particles), then in such case

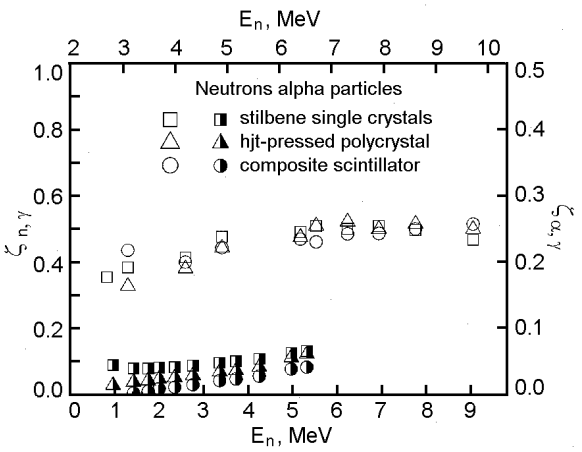

Fig. 5. The $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values (lower and upper family of curves) as a function of the energy of excitation for stilbene detectors. Squares, triangles and circles represent the $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values for a single crystal, a hot-pressed polycrystal and a composite scintillator (grain size from 1.7 to 2.0 mm), correspondingly. Half-filled symbols are from alpha excitation while open symbols are from neutron excitation.

the track is formed. A scintillation response will carry information concerning: i) the cumulative effect of loss for a given scintillator (as in the previous case) and ii) the additional loss caused by the quenching process in the track.

We can use the value of "*i*/gamma"-ratio, $\zeta_{i\gamma}$, as a quantitative estimation of the quenching processes occurring in the track of the particle of *i*-type [1, 14, 29, 41]:

$$\zeta_{i,\gamma} = \left(\frac{P_i}{E_i}\right) \Big/ \left(\frac{P_\gamma}{E_{Comp}}\right), \qquad (2)$$

where P_i and P_γ are the number of scintillation photons generated by radiation of *i*-type and by gamma radiation, correspondingly. In (2) E_i is the energy of radiation of *i*-type of and E_{Comp} is the energy of the edge of the Compton distribution of gamma radiation with energy E_γ.

4. Results and discussion

Values of $\zeta_{i,\gamma}$ (2) for organic scintillators were calculated in [1, 11, 14, 29, 32, 41, 47]. Fig. 5 demonstrates the $\zeta_{i,\gamma}$-values (2) as the function of the energy of neutron ($\zeta_{n,\gamma}$) and alpha ($\zeta_{\alpha,\gamma}$) excitation for a ∅50 mm×5 mm stilbene single crystal, a ∅30 mm×5 mm hot-pressed stilbene polycrystal and a ∅30 mm×20 mm composite

scintillator on the base of crystalline grains of stilbene (grain size from 1.7 to 2.0 mm).

Fig. 5 shows that the difference of $\zeta_{i,\gamma}$-values for the organic single crystal, the polycrystal and the composite scintillator is negligible in comparison with the difference between $\zeta_{\alpha,\gamma}$- and $\zeta_{n,\gamma}$-values those were obtained for the same one scintillator. A fundamental change of the structure of a scintillator can vary the value of the scintillation signal not more than on 20–25 %, but the type of excitation changes the value of the scintillation signal by an order of magnitude.

Thus, the results give the evidence of the formative influence of a type of ionizing radiation as compared with the influence of the structure of a matter. The structure should determine a character of the transport of relaxed charge carriers from molecule to molecule.

4.1. The "one step" model

The above experimental data, with the theoretical estimates (see Section 2.3) became the basis of the "one-step model", proposed in [41]. This model defines as the "step" the expansion of the primary particle track on one average intermolecular distance. The case is considered when the time t_s, which is necessary for such a step, has to be at least by an order of magnitude greater than the duration of the primary quenching t_q. It means that the ratio between the number of acts of the primary ("hot") and the secondary (after track cooling) recombination has to grow with increasing the concentration ν_0 of the primary states, i.e. with growing of the specific energy loss dE/dx.

According to this model, the concentration of charge states ν_0 denote the primary value of dimensionless concentration ν, which is equal to the number of polaron pairs per one molecule. The total concentration of all molecules and quasi-ions is designated as one. All molecules in the track are considered as polarized, i.e. the concentration of polarized molecules is $1 - \nu$. During the time $t_q \le t_s$ the primary concentration of polaron pairs ν_0 suddenly diminishes to the values $\nu << \nu_0$. Therefore it is the process in a "frozen" track area. All changes in ν that last a time $t < t_s$ are not studied versus time. Their total result is only taking into account as a sudden change of ν in the end of a step.

The process of the fast quenching in the "frozen" (non-expansive) track of the ionizing particle with very high dE/dx in the general case can be described in a form [41]:

$$\frac{d\nu(r,t)}{dt} = D\Delta\nu(r,t) - q(\nu)\nu(r,t), \tag{3}$$

where D is the diffusion coefficient of a track expansion and $q(\nu)$ describes the recombination probability of j pairs ($j = 1, 2,...$) of polarons as a joint action. In the "frozen" track, the first term in (3) is equal to zero.

In accordance to definition of $q(\nu)$ the term $q(\nu)\nu$ in (3) can be represented by the following expression:

$$q(\nu)\nu = \{c_1\nu + p_1[1 - \nu]\nu + c_2\nu^2 +$$

$$+ p_2[1 - \nu]\nu^2 + c_3\nu^3 + p_3[1 - \nu]\nu^3 + ...\} =$$

$$= (p_1 + c_1)\left\{1 + \frac{\sum_{j=1}(p_{j+1} + c_{j+1} - p_j)}{p_1 + c_1}\nu^j\right\}\nu, \tag{4}$$

where we take into account the possibility both the direct fast recombination between adjacent polarons (a rate constant p_j), and a random path of polarons, which can forerun their recombination (a rate constant c_j).

A sudden change of ν_0 (the time of quenching $t_q \le t_s$) means that $q(\nu)$ changes discontinuously from a step to a step, but $q(\nu)$ does not vary during a single step, i.e. during the first step $q(\nu) \approx q(\nu_0)$, then:

$$-\frac{d\nu(t)}{dt} \approx q(\nu_0)\nu(t) \approx \tag{5}$$

$$\approx -A(1 + B\nu_0 + C\nu_0^2 + F\nu_0^3 + ...)\nu(t).$$

It was obtained [41] the semi-empirical description of the light yield (or, strictly speaking, the number of photons P) versus the value of the primary concentration of polaron pairs ν_0 (see (6)). Description (6) takes into account that the right side of Eq. (3) is described by (5):

$$P = \frac{S\nu_0}{1 + B\nu_0 + C\nu_0^2 + F\nu_0^3 + ...}. \tag{6}$$

For the same scintillator excited by i-type of radiation $S_i = const/A_i$. The "constant" in S_i-value describes the luminescent properties of a concrete scintillator, namely the influence of the excitation energy transfer,

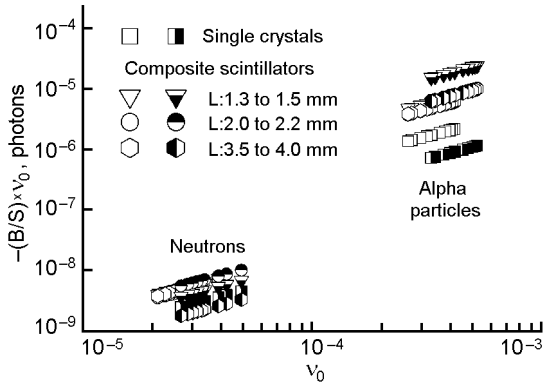

Fig. 6 [41]. Quenching parameter $(B/S)\times\nu_0$ obtained from the measurements of the light yield of organic single crystals and composite scintillators (with grain size L) of stilbene (open symbols) and doped p-terphenyl (half-closed symbols).

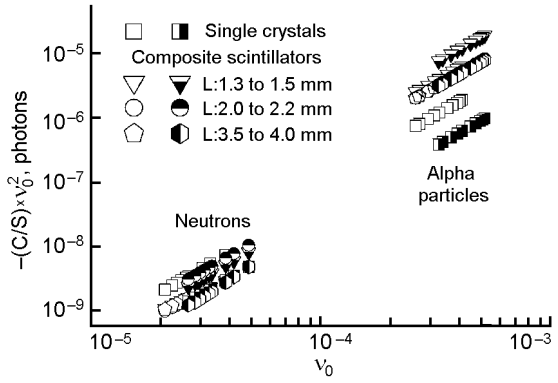

Fig. 7 [41]. Quenching parameter $(C/S)\times\nu_0^2$ versus ν_0 obtained from the measurements of the light yield of the same scintillators as on Fig. 6.

the luminescence of molecules, the processes of light collection and reabsorption. The A-value (5) describes the mean quenching effect in recombination of one polaron pair, whereas the values $B_i\nu_{i0}/S_i$, $C_i\nu_{i0}^2/S_i$, etc. describe the effect of the joint recombination of two, three, etc. polaron pairs on the primary quenching for a concrete scintillator and a type of excitation. According to (4) if the polarization effect is of primary importance then the values B, C, etc. can be negative. To calculate the ν_0-values we used an average energy of a plasmon $\Omega \approx 20$ eV [5, 11, 14, 41]. To calculate a volume V_i of the track of i-type of excitation we took the estimations of the initial track radius r_0 based on the analysis of the delayed radioluminescence pulse shape of organic scintillators (see Section 2.2). The track length was taken as the particle range [45].

Figs. 6 and 7 demonstrate the typical examples of the dependence of $B\nu_0/S$ and $C\nu_0^2/S$ values versus the value of the primary concentration of polaron pairs ν_0 [14, 41]. Figs. 6 and 7 show that the primary quenching in the track is a concentration-controlled process. The negative B-values agree with the statement that the polarization effects have a strong influence of on the recombination of charge states.

The study of the recombination processes in particle tracks requires amplification. An in crease of the concentration of charge pairs in the track regions with increasing the specific energy loss of a particle should lead to a rise of fast and efficient recombination of charge states. However, the intensity of the radioluminescence does not increase, but decreases. Apparent loss increase with growing the density of the states generated in the track of an ionizing particle [14, 41]. The question arises why the effect of quenching increases with increasing the concentration of charge states, or in other words with increasing the probability of their primary recombination.

To try to explain this effect it is necessary to consider in detail the aspects of generation and energy exchange of charge states and excited states in the track of an ionizing particle.

4.2. Aspects of generation and energy exchange of charge states and excited states

It is known [48] that both the maximum energy and the number of secondary electrons, emitted after a collision of the primary particle with a molecule of a matter at the same angle, decreases with increasing the mass of the primary particle of a constant velocity. In the context of the discussed problem, it means that an increasing portion of the energy will be stored in the track. Decreasing of the average velocity of low-energy secondary electrons can promote a rise of the probability of their recombination with the parent ion. An increase of the density of the charge states M_+ and M_-, which create during the time $\tau_e \approx 10^{-16}$–10^{-15} s the polarization surrounding in the region with the characteristic size of 13–16 nm, should lead to a sharp increase of the probability of the recombination of the charge states, which are within this region. This effect will be more sensible when the most part of

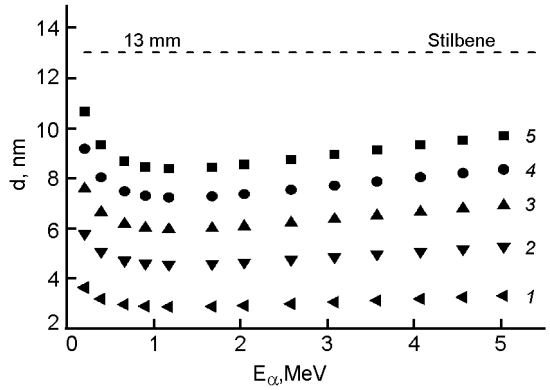

Fig. 8 [41, 49]. The calculated values of the average distance d between the centres of charge pairs (M_+, M_) in the track of an alpha particle with energy E_α for a stilbene single crystal (*1* — r_0 = 10 nm, *2* — r_0 = 20 nm, *3* — r_0 = 30 nm, *4* — r_0 = 40 nm, *5* — r_0 = 50 nm).

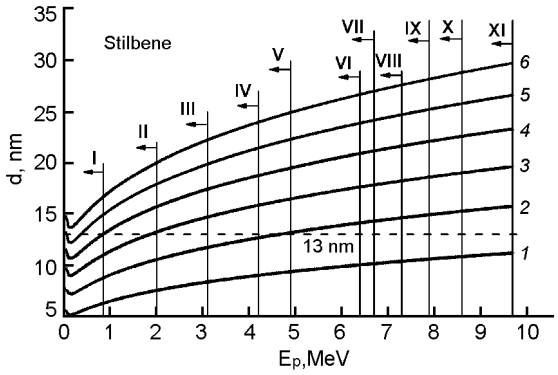

Fig. 9 [41, 49]. The calculated values of the average distance d between the centres of charge pairs (M_+, M_) in the track for the case of excitation of a stilbene single crystal by protons of the following boundary energies: I — 0.85 MeV, II — 2 MeV, III — 3.1 MeV, IV — 4.2 MeV, V — 4.9 MeV, VI — 6.4 MeV, VII — 6.7 MeV, VIII — 7.3 MeV, IX — 7.9 MeV, X — 8.6 MeV, XI — 9.7 MeV (*1* — r_0 = 15 nm, *2* — r_0 = 25 nm, *3* — r_0 = 35 nm, *4* — r_0 = 45 nm, *5* — r_0 = 55 nm, *6* — r_0 = 65 nm).

the track volume will be overlapped by such polarization zones, which accelerate the recombination of charge states of opposite sign.

According to [41, 49], we have estimated this effect for the most applicable scintillation crystals of stilbene and *p*-terphenyl. Figs. 8 and 9 show the results of such calculations for the stilbene single crystal. The average distance d between the centres of charge pairs was estimated as a cube root of the volume occupied by the single pair. This value have been directly compared with the distance of the stable polarization surrounding r_c = 13 nm [34]. For $d > r_c$ polarons do not react upon each other, and the simultaneous recombination of two or more pairs is the event of rare occurrence.

Fig. 8 shows that the average distance between pairs is always less than 13 nm for all considered energies of alpha particles and the cross-section radii of the track. It means that the polarization surrounding not only the polarons in a pair, but neighbouring pairs will overlap and polarization effects will initiate a very fast recombination of the charge states throughout the whole of the track area.

Fig. 9 shows that in most cases under consideration the average distance between pairs is comparable or more than 13 nm in the case of excitation by protons. It means that the polarization surrounding of the neighbouring pairs do not overlap, and charge states in the pair are far enough from each other both not to interact, and not to be involved in the polarization surrounding of another pair. In this case, the influence of polarization effects on the fast recombination of charge states will not be as strong as in the case of the excitation by alpha particles.

Table 1. The total spin of two doublets after their exchange interaction [11]

Spin	+1/2	−1/2
+1/2	1	0
−1/2	0	−1

In the context of a question under discussion it is clear that the specific energy loss will increase sequentially with the energy decrease of the recoil protons, nextly by the transition from the tracks those are generated by protons to the tracks those are generated by alpha particles and then with decreasing the energy of alpha particles. In the same sequence will decrease the calculated value of the average distance d between charge pairs, and hence will increase the probability that the major portion of the particle energy will be used for generation of charge states with simultaneous increasing the probability of their rapid primary recombination.

The recombination of doublet states M_+ and M_ will proceed by the exchange mechanism in the particle track. Table 1 shows the

Table 2. Rate constants γ for the mutual quenching of excites states in some organic single crystals

Single crystal	Rate constants			
	γ_f, cm^3s^{-1}	γ_{rad}, cm^3s^{-1}	γ_{st}, cm^3s^{-1}	γ_{ss}, cm^3s^{-1}
Naphthalene	–	$3.5\cdot10^{-12}$ b), d)	$5\cdot10^{-11}$ b), d)	$1\cdot10^{-10}$ b), d)
Anthracene	"negligible" a)	$2\cdot10^{-11}$ a), b)	$(5\pm3)\cdot10-9$ a), b), d), $(7\pm4)\cdot10^{-9}$ c)	$(1\pm0.5)\cdot10-8$ a), b), c), d)
Tetracene	$1.5\cdot10^{-12}$ a)	$(2.2\pm0.5)\cdot10^{-9}$ a), d)	$2\cdot10^{-7}$ a), d)	$1\cdot10^{-7}$ a), d)
Pyrene	–	$(7.5\pm4.0)\cdot10^{-12}$ d)	–	–

a) Ref. [50], b) ref. [51], c) ref. [52], d) ref. [33].

possible results of such interaction. Three T_1-states eventually are generated per one S_1-state rather than 10^{-6} as it occurs in the low activation density regions [11, 32].

4.3. Possible reasons of "the specific quenching"

The density of S_1-states occurring in the track immediately after it formation is very high. It can be a source of huge loss of the energy in the track regions. Thus, S_1-states have a high probability of disappearing in the process of mutual S–S annihilation, in the process of S–T annihilation, in the process of fission of singlet excitons [50].

$$S_1 + S_1 \xrightarrow{\gamma_{ss}} S_1^* + S_0 \rightarrow S_1 + S_0 + \text{phonons} \quad (7)$$

$$S_1 + T_1 \xrightarrow{\gamma_{st}} S_0 + T_1, \quad (8)$$

$$S_0 + S_1 + \Delta E \xrightarrow{\gamma_f} T_1 + T_1. \quad (9)$$

Table 2 shows the rate constants of the above processes.

Naturally, such processes will reduce the output of radioluminescence photons in the reaction $S_1 \Rightarrow S_0 + h\nu$, which can contribute to formation of the radioliminescence pulse fast component.

An annihilation of singlet excitons at high excitation densities can lead to autoionization (10), which causes the generation of charge states. This mechanism seems reverts the process of the energy exchange in the particle track from the stage of electronic excitation energy exchange back to an earlier stage of the charge states energy exchange [50].

$$S_1 + S_1 \xrightarrow{\gamma_{si}} S_1^* + S_0 \rightarrow e + h. \quad (10)$$

At high excitation densities, the probability of the S–S annihilation (10) that generates charge carriers is 10^3 times higher than the probability of the T–T annihilation that generates charge carriers. The probability of the T–T annihilation with the formation of charge carriers is still low because the energy of two T-states, in most cases, is insufficient to form a charge pair. This suggests that in the regions of the "unfrozen" track there will be the predominant generation of T-states due to both the peculiarities of doublet states recombination, and a high probability of the S–S annihilation leading to a formation of charge carriers and to a loss of S-states. There will be processes that lead to decreasing of the concentration of S_1-states. According to [50], a huge concentration of triplet excitons, until the time of 10^{-9} after excitation, is the most likely source of quenching of singlet states. In addition to the processes (7)–(10), the processes of quenching of S_1-states by charge states will also contribute to decreasing of S_1-states [50]. It is should be noted that the T–T annihilation (11) proceeds efficiently after decreasing the concentration of excited states in the track.

$$T_1 + T_1 \xrightarrow{\gamma_{tt}} \begin{cases} \xrightarrow{\gamma_{rad} = \gamma_{tt} \times f} S_1 + S_0 \Rightarrow h\nu + 2S_0 \\ T_1 + S_0 \\ Q + S_0 \end{cases}. \quad (11)$$

A yield of the singlet channel of the diffusion-controlled T–T annihilation (11) is low ($f \approx 0.4$) [11, 29]. Therefore, for the T–T annihilation (11) in the track region the ratio of the number of light photons to the number of excited molecules that generate these photons is substantially less than for the process of usual luminescent deactivation of S_1-states outside the track. Each of S_1-states located in the low activation den-

sity region with the probability close to a unit can transfer to S_0-state by emitting a light photon. In the case of the low concentrations of triplet states, the process of their loss is unimolecular and the shape of a scintillation pulse can be described by an exponential function of time [2, 11, 29, 32].

5. Conclusions

Thus, the recombination of charge states generated by an ionizing radiation may result in either a luminescence or the energy loss (the quenching).

The preliminary analysis has shown that such a recombination of hot states accelerated by strong polarization interactions must occur in time less than 10^{-13} c. There is the difference between the processes of energy exchange of an ionizing particle which take place in: i) the track halo, ii) the shell of the track core and iii) the track core. In the shell of the track core and in the track core there are additional nonradiative losses due to the primary recombination of hot charge states, which are at small distances from each other. The probability of such loss in the shell of the track core can be significantly lower than in the track core. However, the mechanism of this process is not clear and requires a careful study. It is required a more profound both qualitative and quantitative analysis of the energy balance between: i) the particle energy stored in a molecular scintillation matrix, ii) its distribution in the different regions of the particle track, iii) the energy transfer processes of charge states into the energy of excited states and further into the energy of scintillation photons taking into account all possible channels of the energy loss.

Acknowledgements. I would like to express my gratitude to prof. N.Z. Galunov for stimulation exchange of ideas and helpful comments.

References

1. N.Z.Galunov, E.V.Martynenko, V.P.Seminozhenko, O.A.Tarasenko, *Functional Materials*, **16**, 117 (2009).
2. N.Z.Galunov, N.I.Shishov, Kinetika Zamedlennoy Radioluminestsentsii v Organicheskikh Molekulyarnykh Sistemakh, Univesitet Druzhbi Narodov, Moscow (1991) [in Russian].
3. N.Z.Galunov, B.V.Grinyov, N.L.Karavaeva et al., *IEEE Trans. Nucl. Sci.*, **56**, 904 (2009).
4. J.B.Birks, The Theory and Practice of Scintillation Counting, Pergamon Press, London (1967).
5. M.Pope, C.E.Swenberg, Electronic Processes in Organic Crystals, Clarendon Press, Oxford, (1982).
6. V.M.Agranovich, M.D.Galanin, Excitation Energy Transfer in Condensed Media, North Holland, Amsterdam (1982).
7. V.L.Ermolaev, E.N.Bodunov, E.B.Sveshnikova, T.A.Shakhverdov, Bezyzluchatelnyi Perenos Energii Elektronnogo Vozbuzhdeniya, Nauka, Leningrad (1977) [in Russian].
8. T.A.King, R.Voltz, *Proc. Roy. Soc. Lond. A.*, **289**, 424 (1966).
9. G.Laustriat, *Mol. Cryst.*, **4**, 127 (1968).
10. F.D.Brooks, *Nucl. Instr. Meth. Phys. Res.*, **162**, 477 (1979).
11. N.Z.Galunov, V.P.Seminozhenko, Teoriya i Primenenie Radioluminestsentsii Organicheskikh Kondensirovannykh Sred, Naukova Dumka, Kiev (1997) [in Russian].
12. J.H.Baker, S.V.Budakovsky, N.Z.Galunov et al., in: Dielektriki i Polyprovodniki v Detektorakh Izlucheniy, Institut Monokristallov, Kharkov (2006), p.230 [in Russian].
13. J.H.Baker, N.Z.Galunov, O.A.Tarasenko, *IEEE Trans. Nucl. Sci.*, **55**, 2736 (2008).
14. N.Galunov, O.Tarasenko, *Radiat. Meas.*, **45**, 380 (2010).
15. A.Mozumder, Fundamentals of Radiation Chemistry, Academic Press, San Diego, London, Boston, New York, Sydney, Tokyo, Toronto (1999).
16. J.E.Turner, Atoms, Radiation, and Radiation Protection, WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim (2007).
17. A.M.Mitreev, *Uspekhi Fiz. Nauk*, **172**, 1131 (2002).
18. M.Globus, B.Grinyov, J.K.Kim, Inorganic Scintillators for Modern and Traditional Applications, Institute for Single Crystals, Kharkiv (2005).
19. N.Z.Galunov, I.G.Khomyakova, E.V.Martynenko et al., *Voprosy Atomnoy Nauki i Tekhniki*, **89**, 214 (2006).
20. S.V.Budakovsky, N.Z.Galunov, N.L.Karavaeva et al., *IEEE Trans. Nucl. Sci.*, **54**, 2734 (2007).
21. S.V.Budakovsky, N.Z.Galunov, B.V.Grinyov et al., *Radiat. Meas.*, **42**, 565 (2007).
22. The 2007 Recommend.Intern.Comission on Radiological Protection, Publication 103, Annals of the ICRP, **37**, 1 (2007).
23. E.B.Fisher, R.Spohr, *Rev. Mod. Phys.*, **55**, 907 (1983).
24. A.M.Marenniy, Dielektricheskie Trekovy Detektory v Radiatzionno-fizicheskom i Radiatzionno-biologicheskom Eksperimente, Energoatomizdat, Moscow (1987) [in Russian].
25. A.Mozumder, in: Advances in Radiation Chemistry, Vol.1, Wiley-Interscience, New York (1969), p.1.
26. S.A.Durrani, R.K.Bull, Solid State Nuclear Track Detection Principles, Methods and Applications, Pergamon Press, Harwell, UK (1987).
27. V.M.Byakov, F.G.Nichiporov, Vnutritrekovye Himicheskie Protsessy, Energoatomizdat, Moscow (1985) [in Russian].

28. A.M.Raitzimring, V.M.Moralev, Yu.D.Tsvetkov, *Khimiya Vysokich Energiy*, **9**, 517 (1975).
29. N.Z.Galunov, E.V.Martynenko, *Radiat. Meas.*, **42**, 715 (2007).
30. N.Z.Galunov, L.P.Koval', V.M.Solomonov, N.I.Shishov, *Izv.AN SSSR Ser. Fiz.*, **54**, 485 (1990).
31. N.Z.Galunov, B.V.Grinyov, O.A.Tarasenko, E.V.Martynenko, *J. Korean Assoc. Radiat. Protec.*, **30**, 85 (2005).
32. N.I.Shishov, N.Z.Galunov, *Mol. Mat.*, **3**, 141 (1993).
33. M.Pope, C.E.Swenberg, Electronic Processes in Organic Crystals, Oxford, Clarendon Press (1982).
34. E.A.Silinsh, M.V.Kurik, V.Capek, Elektronnye Protsessy v Organicheskikh Molekulyarnykh Kristallakh. Yavleniya Lokalizatsii i Polyarizatsii, Zinatne, Riga (1988) [in Russian].
35. E.A.Silinsh, Elektonnye Sostoyaniya Organicheskikh Molekulyarnykh Kristallov, Zinatne, Riga (1978) [in Russian].
36. V.A.Andreev, M.V.Kurik, S.Nespurek et al., Elektonnye Protsessi v Organicheskih Molekulyarnykh Kristallakh. Perenos, Zakhvat, Spinovye Effekty, Zinatne, Riga (1992) [in Russian].
37. E.A.Silinsh, A.J.Jurgis, G.A.Shlihta, *J. Mol. Electron.*, **3**, 123 (1987).
38. N.Z.Galunov, in: Abstr.Trans. Intern. Techn. Transfer Conf., Iowa State University, USA (1998), p.124.
39. S.V.Budakovsky, N.Z.Galunov, B.V.Grinyov et al., *Functional Materials*, **16**, 86 (2009).
40. N.Z.Galunov, J.H.Baker, S.V.Budakovsky et al., *J. Luminescence*, **102–103**, 464 (2003).
41. N.Z.Galunov, E.V.Martynenko, *Functional Materials*, **15**, 380 (2008).
42. K.W.Geiger, L.Van der Zwan, *Nucl. Instr. Meth. Phys. Res.*, **131**, 315 (1975).
43. M.E.Anderson, R.A.Neff, *Nucl. Instr. Meth.*, **99**, 231 (1972).
44. E.V.Martynenko, *Functional Materials*, **14**, 238 (2007).
45. O.F.Nemetz, Y.V.Gofmann, Spravochnik po Yadernoi Fizike, Naukova Dumka, Kiev (1975) [in Russian].
46. J.H.Baker, N.Z.Galunov, A.M.Stepanenko, O.A.Tarasenko, *Radiat. Meas.*, **38**, 817 (2004).
47. N.Z.Galunov, B.V.Grinyov, N.L.Karavaeva et al., *IEEE Trans. Nucl. Sci.*, **56**, 904 (2009).
48. K.N.Mukhin, Eksperimentalnaya Yadernaya Fizika. Uchebnik Dlya Vuzov, Vol.1. Fizika Atomnogo Yadra, Part 1. Svoistva Nuklonov Yader i Radioaktivnykh Izlucheniy, Energoatomizdat, Moscow (1993).
49. N.Z.Galunov, N.L.Karavaeva, J.K.Kim et al., in: Conf. Record of 2007 IEEE Nucl. Sci. Symp. Med. Image Conf., Hawaii, USA (2008), p.2469.
50. N.E.Geacintov, M.Binder, C.E.Swenberg, M.Pope, *Phys. Rev. B*, **12**, 4113 (1975).
51. M.Schwoerer, H.C.Wolf, Organic Molecular Solids, WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim (2007).
52. S.D.Babenko, V.F.Benderskii, V.I.Goldanskii et al., *Phys. Stat. Solidi (b)*, **45**, 91 (1971).

Генерація та розмін енергії зарядових станів в органічних молекулярних кристалічних сцинтиляторах

О.А.Тарасенко

У роботі обговорюються фізичні процеси, що визначають особливості генерації та розміну енергії зарядових станів, які виникають у молекулярних органічних середовищах під дією іонізуючих випромінювань різних типів. Аналізується напівемпіричний опис процесів первинного розміну енергії у треку іонізуючої частинки. Даний опис ураховує визначальний вплив поляризаційних процесів на розмін енергії зарядових станів і процеси гасіння. Процес первинного гасіння визначається дуже швидкою рекомбінацією молекулярно-поляронної пари. Цей процес як мінімум на порядок швидше процесу дифузійного розширення треку, а його ефективність росте зі збільшенням густини пар, які рекомбінують. Аналіз грунтується на результатах вимірів величини світлового виходу органічних сцинтиляційних детекторів на основі стильбену та *n*-терфенілу як функції енергії при альфа-, нейтронному- та гамма-збудженні. Досліджувалися структурно досконалі органічні монокристали, полікристали, отримані методом гарячого пресування, композиційні сцинтилятори. Отримані результати свідчать про визначальний вплив типу іонізуючого випромінювання у порівнянні із впливом структури речовини на процеси, які обговорюються.