ATOMS AND MOLECULES

V.YA. DEGODA, I.M. MOROZ

Taras Shevchenko National University of Kyiv, Faculty of Physics
(4, Academician Glushkov Ave., Kyiv 01601, Ukraine; e-mail: inna.moroz1990@gmail.com)

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KINETIC MODEL FOR SPATIAL DISTRIBUTION OF ELECTRON EXCITATIONS IN LIQUID PHOSPHORS

A model of luminescence in liquid phosphors under X-ray excitation has been proposed. The corresponding spatial distributions for electronic excitations and local heating are obtained. They are described by Gaussian functions, the parameters of which are related to the kinetic energy of an X-ray quantum and the medium characteristics. The explanation to a low quantum yield of luminescence in liquid phosphors under the X-ray excitation in comparison with a high quantum yield at the photoluminescence is given. It is shown that the major losses in this case occur at the stage of electronic excitation migration from the solvent to phosphor molecules.

K e y w o r d s: luminescence, photoluminescence, spatial distribution of electronic excitations, liquid phosphors.

1. Introduction

Scintillators are phosphors, in which light flashes or scintillations arise under the action of ionizing radiation. Two types of phosphors are distinguished: organic and inorganic (crystalline) [1, 2]. As liquid scintillators, solvents with a primary additive (a luminescent substance) and a secondary one (a shifter), which shifts the luminescence toward longer wavelengths, are used. Typical luminescent additives in scintillators are n-terphenyl ($C_{18}H_{14}$), PBD ($C_{20}H_{14}N_{20}$), butyl PBD ($C_{24}H_{22}N_{20}$), and PPO ($C_{15}H_{11}NO$). As a secondary additive, POPOP ($C_{24}H_{16}N_{20}$) and others are used. Popular solvents for liquid scintillators are toluene, xylene, benzene, phenylcyclohexane, triethylbenzene, and decalin [3].

A specific feature of liquid scintillators is a short fall time, which is of an order of tens of nanoseconds. Liquid scintillators have some advantages in comparison with crystalline ones. First, additives sensitive to any specific form of irradiation can be introduced into them; e.g., liquid scintillators as ionizing radiation counters [3]. Second, liquid scintillators can be fabricated with any volume and any shape

required for experiments. Third, they remain homogeneous even at large sizes, which is almost impossible for crystals. The luminescence properties of liquid scintillators are governed by the properties of phosphor molecules. The concentrations of the primary and secondary additives are much lower than the concentration of solvent molecules (less than several grams per liter). Despite those advantages, the yield of X-ray luminescence in liquid phosphors is always less than in powders, ceramics, polycrystals, and single crystals [1–4].

The major aim of the work is to determine the processes responsible for a low luminescence quantum yield at the X-ray excitation in liquid phosphors, bearing in mind that the same phosphors have a quantum yield close to unity at the photoexcitation.

2. Mechanisms of X-Ray Luminescence Excitation in the Medium

In the general case, exciting radiation has to be absorbed in order to excite a medium. The dependence of the exciting radiation absorption is described by the Bouguer–Lambert–Beer law [5, 6]

$$J = J_0 \exp(-\alpha x), \tag{1}$$

where J_0 is the intensity of incident electromagnetic radiation, J the intensity of exciting radiation at the depth x in the medium, and α the total coefficient of electromagnetic wave damping in the medium. The magnitude of damping coefficient equals the sum of coefficients for every process that occurs in the medium. The mechanism of interaction between gamma or X-ray quanta and the medium differs from a similar process for charged particles, because the former have no electric charge and no rest mass. Electromagnetic quanta can only be absorbed or scattered in the medium. In all processes when X-ray or gamma quanta interact with the medium, the energy and momentum conservation laws are obeyed simultaneously. It should also be borne in mind that the momentum of even a high-energy quantum is much less than that of an electron or atom at their vibrational motion.

Processes of four types are distinguished when analyzing the interaction of electromagnetic radiation with a medium [7, 8]:

• photoabsorption of quanta, which can be accompanied by the Auger effect,

• coherent (Rayleigh) scattering,

• noncoherent scattering (the Compton effect),

• formation of electron-positron pairs.

Coherent scattering does not excite the liquid phosphor. Noncoherent scattering (the Compton effect) does, but the energy obtained by the phosphor is by orders of magnitude lower in comparison with the photoabsorption case. Since the formation of electron-positron pairs has a considerable energy threshold, which exceeds the energy of X-ray radiation, this process is not realized. Hence, when exciting the liquid phosphors by an electromagnetic field, the major contribution to the interaction with the medium is given by the photoabsorption, whereas the other processes of luminescence excitation in liquid phosphors can be neglected. If the medium is excited by a flux of X-ray quanta, than, with regard for the values of absorption coefficients for them (<1000 cm^{-1}), one can easily be convinced that, even at a powerful X-ray excitation, the events of X-ray quantum absorption can be considered independently of one another.

The photoabsorption gives rise to the generation of a high-energy photoelectron and either another free electron (the Auger effect) or characteristic fluorescent X-ray radiation. The high-energy photoelectron, by moving in a liquid phosphor, loses its energy by generating the electronic excitations and heat. The energy transfer from this electron to the medium takes place through a considerable number of its collisions with medium atoms. Those collisions can be classified into the following types, depending on the impact parameter of an incident photoelectron with respect to the atom [10, 11, 14]:

• elastic collisions, which are characterized by low energy losses ΔW by the photoelectron at every interaction event ($\Delta W < I$, where I is the potential of liquid phosphor excitation or the energy gap width in semiconductors);

• inelastic collisions, which are characterized by high energy losses at every interaction event ($\Delta W > I$) accompanied by the electronic excitation of molecules in the medium.

In both cases, the collisions of a high-energy photoelectron with an atom or a molecule in the medium result also in the heat generation according to the energy conservation law.

In nuclear physics, the ionization losses by high-energy particles at their interaction with the medium are analyzed with the use of the Bethe–Bloch equation. In the SI system [8, 12], it looks like

$$-\frac{dE}{dx} = \frac{ne^4}{8\pi\varepsilon_0^2 mv^2 B}, \tag{2}$$

where

$$B = Z\left[\frac{\ln\left(2mc^2\beta^2\right)}{I(1-\beta^2)} - \beta^2 - \frac{C}{Z} - \delta\right] \tag{3}$$

is the stopping power factor for the medium, n is electron concentration (cm^{-3}), I is average ionization potential (eV), Z is atomic number of the medium, $E = \frac{mv^2}{2}$ is the kinetic energy of the particle, ε_0 the dielectric constant, e the electron charge, and β the relativistic correction. Since the photoelectron energy in the X-ray range is low, the relativistic correction can be neglected in Eqs. (2) and (3). At low energies, the shell correction $\frac{C}{Z}$ and the correction for the medium polarization δ are also neglected, which considerably simplifies the Bethe–Bloch equation.

While developing a basic model of the kinetic X-ray luminescence theory, the main difficulty is the fact that all trajectories of high-energy photoelectrons that arise at the absorption of X-ray quanta differ from one another similarly to the trajectories

of motion of molecules in a gas. In order to obtain one photoelectron trajectory from the infinite set of possible trajectories, the Monte-Carlo method is used [13]. This method is based on the probabilistic approach to the solution of problems in statistical physics. Therefore, while considering the X-ray luminescence excitation, a generalizing concept of the "average spatial distribution of electronic excitations" has to be introduced for a spatial distribution of charge carriers. As a result, the trajectory of every particle should not be considered separately. A considerable number of X-ray quanta (more than 10^6) are always used in X-ray luminescence researches. Therefore, the averaging is carried out in this case over a large number of local excitation regions. It is for this average spatial distribution of electronic excitations that the kinetic model can be developed. If this model produces results that agree with the experiment, the applied approach is valid.

Therefore, leaving the Monte-Carlo method beyond the calculation scheme, we propose the following procedure that allows the character of particle motion in a medium to be described (Fig. 1). Let a high-energy electron move in a medium and sporadically collide with atoms or molecules. As a result, the electron loses its kinetic energy. We assume that the particle almost does not lose energy at elastic collisions, whereas the inelastic collisions are characterized by considerable energy losses. An energy of about $W \approx 3I$ is required to generate one electronic excitation [10, 14, 15]. Actually, we consider uniform losses of the kinetic energy by a photoelectron along its path in the medium. The number of corresponding inelastic collisions $N_0 \gg 1$. Therefore, the initial kinetic energy of a photoelectron can be divided into N_0 identical intervals. In each of them, the photoelectron loses the energy W, and one electronic excitation is generated.

In order to determine the probability to find the photoelectron in the space at the moment when it loses the energy W, the diffusion equation can be used. The general form of this equation for a homogeneous medium looks like

$$\frac{\mathrm{d}n(r,t)}{\mathrm{d}t} = \nabla\big[D\nabla n(r,t)\big], \qquad (4)$$

where $n(r,t)$ is the concentration of particles in the medium. The solution of this equation gives a value for the concentration of particles in the space at a
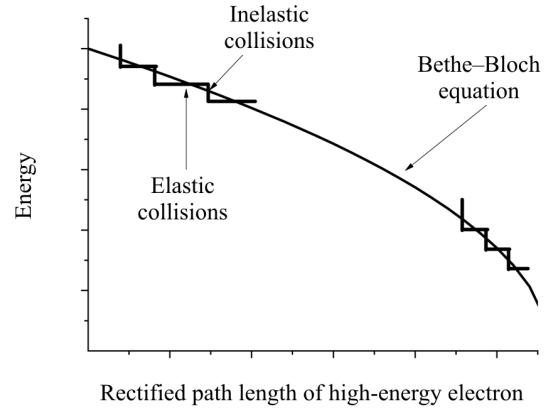
Fig. 1. Schematic representation of the energy variation of a photoelectron at its motion in the medium

given time moment. To find a solution of the diffusion equation, the initial condition is required: at $t = 0$, the initial concentration is determined by the dependence $n(r, t = 0) = n_0 f(r)$, where n_0 is the total number of particles. Then the probability to find one particle at the time moment t at the distance r is determined by the formula $\frac{n(r,t)}{n_0} = p(r,t)$. Hence, the diffusion equation determines, in effect, the probability density to find the particle at a definite spatial point at a definite time moment.

We assume that the photoelectron coordinate at the initial time moment (when an X-ray quantum is absorbed) is equal to zero, $r = 0$. This is the required initial condition for the diffusion equation in the spherical coordinate system. For the probability to find the particle in a homogeneous medium taking only the radial particle motion into account, we have

$$\begin{cases} \dfrac{\mathrm{d}p(r,t)}{\mathrm{d}t} = D(t)\Delta p(r,t), \\ p(r,0) = \delta(r), \end{cases} \qquad (5)$$

where r is the distance from the start point in the spherical coordinate system, i.e. from the place, where the X-ray quantum was absorbed.

Diffusion (4) and Bethe–Bloch (2) equations make it possible to determine the statistical spatial distribution of excitations generated by the photoelectron in the liquid phosphor. Owing to the photoelectron thermalization, we obtain a small region near the point of X-ray quantum absorption, where electronic excitations and heat are generated simultaneously. This local region will be cooled down in time.

For the description of this process, the heat conductivity equation can be used if the generation region is large enough to be described with the use of macroscopic parameters.

The processes of excitation transfer in a liquid phosphor are governed by the properties of its components, i.e. the properties of the solvent and phosphor molecules. The concentration of phosphor molecules in the phosphor is much lower than the concentration of solvent molecules. In general, the processes of excitation transfer between molecules are described by the Förster–Dexter theory and were studied in detail by V.M. Agranovich (see works [14, 16–19]). In the general case, phosphor molecules can be excited owing to the excitation transfer from the solvent or through the direct excitation transfer at the absorption of an optical quantum, which is called photoluminescence. In fact, any photoluminescence research includes the direct excitation of phosphor molecules, whereas, in X-ray researches, the excitation transfer from solvent molecules to phosphor ones are considered. Therefore, it is always necessary to compare X-ray luminescence and photoluminescence spectra. A consecutive detailed analysis makes it possible to determine which mechanism can be responsible for a low yield at the X-ray luminescence against a high quantum yield at the photoexcitation. In other words, it is necessary to understand the contribution of each component of the process (generation, migration, luminescence) while analyzing the experimental data of X-ray luminescence researches.

3. Generation of Electronic Excitations

In order to calculate the probability density to find a particle at the given time t at the distance r, it is necessary firstly to determine the total number of excitations generated in the medium. The absorption of one X-ray quantum in the condensed medium at the photoelectron thermalization gives rise to the generation of N_0 excitations. The specific number is determined by the following phenomenological dependence [14, 15]:

$$N_0 = \frac{h\nu_x}{3I}, \tag{6}$$

which includes the X-ray quantum energy $h\nu_x$ and the potential of solvent molecule excitation or ionization I. Knowing the total average magnitude of excitation

and the initial energy of a photoelectron, it is possible to obtain an analytical formula that approximates the solution of the Bethe–Bloch equation (2). With regard for the mean-value theorem [14], this formula looks like

$$\int\limits_0^x \mathrm{d}x = \frac{\int_0^E(x)\ \mathrm{d}E}{\frac{e^4 n}{8\pi\varepsilon_0^2}\ln\frac{4E}{3I}} \approx \frac{E_0^2 - E(x)^2}{2A}. \tag{7}$$

For the total rectified path length travelled by a high-energy electron (x_0) at the photoelectron thermalization, we obtain

$$x_0 = \frac{E_0^2 - W_0^2}{2A} \approx \frac{E_0^2}{2A}, \quad A = \frac{e^4 n \ln N_0}{8\pi\varepsilon_0^2}. \tag{8}$$

This formula coincides with the Thomson–Whiddington equation. Using Eq. (7), the approximate analytical dependence of the photoelectron energy on the travelled path length can be written in the form

$$E(x) = E_0\sqrt{1 - \frac{x}{x_0}}. \tag{9}$$

It can be used to describe the variation in the kinetic energy of a photoelectron at its passage through a medium (see Fig. 1).

Since the kinetic energy of a high-energy electron gradually decreases at inelastic collisions with molecules in the medium, the diffusion coefficient D also changes during the thermalization. In order to take the photoelectron thermalization into consideration, it is necessary to consider the dependence of the diffusion coefficient on the thermalization time. In the general case, the diffusion coefficient is determined by the formula

$$D = \frac{1}{3}L(t)v(t), \tag{10}$$

where $L(t)$ is the mean free path, which is defined as the distance between two inelastic scattering events (i.e. the generation of an electronic excitation), and $v(t)$ is the photoelectron velocity, which decreases in this model in a step-like manner in the course of photoelectron thermalization, but remains constant in this energy interval.

Using dependence (9) for the variation of the particle energy and the formula $v(t) = \sqrt{2E[x(t)]/m}$ for the particle velocity, we can obtain the dependences

$x(t)$ and $v(t)$:

$$v(x) = \left(\frac{2E_0}{m}\right)^2 \left(1 - \frac{x}{x_0}\right) = v_0 \left(1 - \frac{x}{x_0}\right)^{1/4},$$

$$v(t) = v_0 \left(1 - \frac{t}{t_0}\right)^{1/4}, \quad \text{де} \quad v_0 = \sqrt{\frac{2E_0}{m}},$$

$$t(x) = \int\limits_0^x \frac{\mathrm{d}x}{v(x)} = \frac{4x_0}{3v_0}\left[1 - \left(1 - \frac{x}{x_0}\right)^{3/4}\right],$$

$$x(t) = x_0 \left[1 - \left(1 - \frac{t}{t_0}\right)^{4/3}\right],$$

where $v_0 = \sqrt{\frac{2E_0}{m}}$. The total time of the photoelectron thermalization t_0 is determined from the condition $x \to x_0$, so that we have $t_0 = \frac{4x_0}{3v_0}$. The dependence $L(x)$ or $L(t)$ is obtained from the condition that the photoelectron loses the energy $W \approx 3I$ and generates one electronic excitation along this distance:

$$L(x) = \frac{2W_0 x_0}{E_0}\sqrt{1 - \frac{x}{x_0}},$$

$$L(t) = \frac{2W_0 x_0}{E_0}\left(1 - \frac{t}{t_0}\right)^{2/3},$$

where $L_0 = \frac{2W_0 x_0}{E_0} = \frac{2x_0}{N_0}$. Hence, the analytical dependences for the diffusion coefficient are

$$D(x) = D_0 \left(1 - \frac{x}{x_0}\right)^{3/4},$$

$$D(t) = D_0 \left(1 - \frac{t}{t_0}\right),$$

where $D_0 = \frac{\sqrt{2}}{3}\frac{W_0 E_0^{3/2}}{Am^{1/2}}$. The obtained dependence $D(t)$ is used, while solving the diffusion equation (5).

The diffusion equation is solved with the help of the variable separation method. In this case, we obtain two equations for the time and spatial variables. The general solution of the diffusion equation (5) corresponding to the initial condition has the following form in the spherical coordinate system:

$$p(r,t) = 2\pi D_0 t_0 \left[1 - \left(1 - \frac{t}{t_0}\right)^2\right]^{-3/2} \times$$

$$\times \exp\left\{-\frac{r^2}{2\pi D_0 t_0\left[1 - \left(1 - \frac{t}{t_0}\right)^2\right]}\right\}. \tag{11}$$

This is an analytical formula for the probability density to find a high-energy electron at the distance r from the center at the time moment t in the course of thermalization.

Since every inelastic scattering event generates one electronic excitation, the total distribution of excitations generated by a photoelectron in the medium can be found by summing up the probability density to find the particle at the moment t over i up to N_0:

$$N_0(r) = \sum_{i=0}^{N_0} p(r,t).$$

The moments of the electronic excitation generation, t_0, can be found from the condition that the photoelectron loses the energy W in each interval from t_i to t_{i+1}: $E(t_i) = E_0 - iW_0$. Then we may write down $t_i = t_0\left[1 - (1 - iW_0/E_0)^{3/2}\right]$, and the final expression for the spatial distribution of the electronic excitation density reads

$$N_0(r) = \sum_{i=0}^{N_0} \frac{\exp\left\{-\frac{r^2}{D_0 t_0\left[1 - \left(1 - i\frac{W_0}{E0}\right)^3\right]}\right\}}{\left\{2\pi D_0 t_0\left[1 - \left(1 - i\frac{W_0}{E_0}\right)^3\right]\right\}^{3/2}}. \tag{12}$$

The dependences $N_0(r)$ at various energies of X-ray quanta calculated in the case of the absorption in water (H_2O) are depicted in Fig. 2. Hence, for the generation stage of the kinetic X-ray luminescence theory, we have a procedure to calculate the initial distribution $N_0(r)$ of the electronic excitation density in a medium, provided that one X-ray quantum is absorbed.

The sum of Gaussians in Eq. (12) is not a simple analytical function. Therefore, let us estimate the volume, in which electronic excitations are generated. The spatial distribution can be characterized by the relative number of excitations that are generated in a sphere of radius r:

$$R(r) = \frac{\int\limits_0^r N_0(r)4\pi r^2 \mathrm{d}r}{N_0}. \tag{13}$$

Despite the fact that the dependence $N_0(r)$ is a sum of Gaussians, it can be described rather well by a single Gaussian. The calculated dependences $R(r)$ and their counterparts obtained, when $N_0(r)$ is approximated
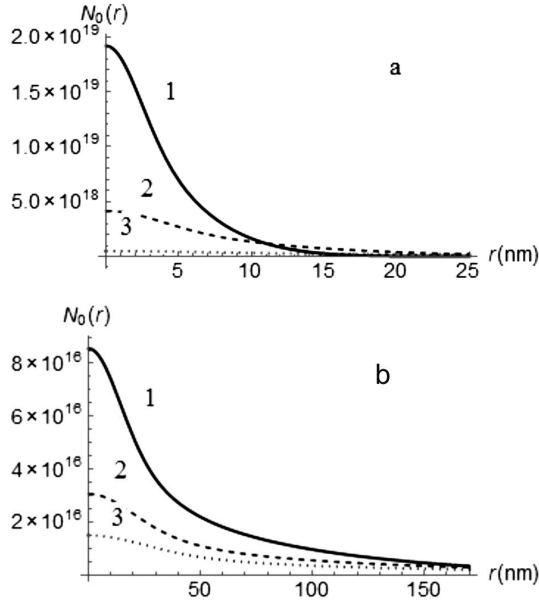
Fig. 2. Spatial distributions of electronic excitations in water ($n = 0.334 \times 10^{24}$ cm^{-3}, $I = 12.59$ eV) for various initial excitation energies (*a*) $E = 1$ (*1*), 2 (*2*), and 5 keV (*3*); and (*b*) $E = 10$ (*1*), 15 (*2*), and 20 keV (*3*)
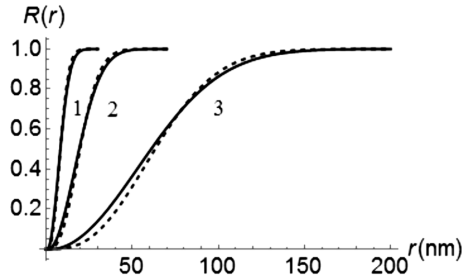
Fig. 3. Calculated distributions of generated excitations (solid curves) and their approximations (dashed curves) for X-ray quantum energies of 1 (*1*), 2 (*2*), and 5 keV (*3*)

by a single Gaussian, are depicted in Fig. 3 for various energies of X-ray quanta.

Note that the functional dependences of the function $N_0(r)$ are described well enough by the approximating function

$$N_0(r) = \frac{N_0}{(2\pi)^{3/2} r_g^3} \exp - \left\{ \frac{r^2}{2r_g^2} \right\}. \tag{14}$$

This function is also suitable for higher X-ray quantum energies. It is characterized by the quantity r_g, which is a phenomenological parameter depending on

the medium characteristics:

$$r_g = \frac{11\pi\varepsilon_0^2 \sqrt{h\nu_x^3 I}}{2e^4 n \ln (h\nu_x/3I)}. \tag{15}$$

A comparison of the obtained formula for r_g with the rectified path length x_0 in liquid phosphors shows that the obtained generation radius is 20–30 times smaller. However, it should be noted that the quantities $r_g (h\nu_x)$ and $x_0 (h\nu_x)$ depend differently on the energy of X-ray quanta (see Eqs. (8) and (15), respectively).

The proposed calculation scheme gives the spatial distribution of the electronic excitation generation at the absorption of one X-ray quantum. The model is characterized by only one parameter r_g, which is determined by the medium characteristics (electron concentration and ionization potential at the place, where the generation occurs) and the X-ray quantum energy.

4. Cooling of Excitation Region

The braking of a high-energy electron in the medium simultaneously generates electronic excitations and heat in it. Therefore, the heat relaxation has to be determined. To calculate a spatial distribution of the temperature in the excitation and cooling regions, we suppose that the total excitation energy obtained from an X-ray quantum is directly transformed into heat. This heat is released within a rather short time interval and in a small enough volume around the point $r = 0$, where the X-ray quantum was absorbed. Actually, at the braking (thermalization) of a high-energy electron within the generation period, the distribution of released heat in space has, to some extent, a random character, which is associated with a stochastic character of high-energy electron scattering. Similarly to the case with electronic excitations, the average spatial distribution of the temperature has to be found. To obtain and analyze the functional dependence of the temperature on the coordinate, the heat equation written in the spherical coordinate system is used:

$$\frac{\partial T}{\partial t} = a^2 \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial t} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial T}{\partial \theta} \right) + \right.$$

$$\left. + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 T}{\partial \varphi^2} \right], \tag{16}$$

where $a^2 = \frac{\lambda}{c\rho}$ is the thermal diffusivity, λ the thermal conductivity, c the specific heat capacity, and ρ the density of the medium. We note that all parameters in this equation are macroscopic. In the case of isotropic heat propagation, this equation can be made simpler by transforming it into an equation for the temperature as a function of two variables, $T(r,t)$. The solution of the heat equation (16) under the condition that the heat ΔQ is instantly released at the point $r = 0$ (at $t = 0$, its distribution looks like the δ-function) equals

$$\Delta T(r,t) = \frac{\Delta Q}{(4\pi a^2 t)^{3/2} c\rho} \exp\left\{-\frac{r^2}{4a^2 t}\right\}, \qquad (17)$$

where $\Delta T(r,t) = T(r,t) - T_0$, T_0 is the initial temperature of a specimen, and $\Delta Q = h\nu_x$. Note that the values of thermal diffusivity lie in a narrow interval $a^2 = (0.62 \pm 1.4) \times 10^{-7}$ m^2/s for a wide class of liquids [19, 20].

Since heat is generated simultaneously with electronic excitations, the spatial temperature distribution in the medium after absorbing one X-ray quantum should be taken into account. Then the solution of the heat equation acquires the form

$$\Delta T(r,t) = \frac{\Delta Q}{(\pi(4a^2 t + 2r_g^2))^{3/2} c\rho} \exp\left\{-\frac{r^2}{4a^2 t + 2r_g^2}\right\}, \qquad (18)$$

where the radius of the electronic excitation generation region is determined by formula (15).

The temperature distributions calculated making allowance for the local heating of liquid phosphors at the absorption of one X-ray quantum are shown in Figs. 4 (for water) and 5 (for toluene). They illustrate the evolution of the corresponding spatial temperature distributions in the region of electronic excitation generation.

The calculations of the electronic excitation region radius, r_g, at the absorption of one X-ray quantum with various energies in liquids gave values larger in comparison with the case of absorption in solids. This difference can be explained by the influence of the medium density, which is less in liquids.

Evidently, the temperature is maximum at $r = 0$:

$$\Delta T(r = 0, t) = \frac{\Delta Q}{\left(\pi\left(4a^2 t + 2r_g^2\right)\right)^{3/2} c\rho}.$$
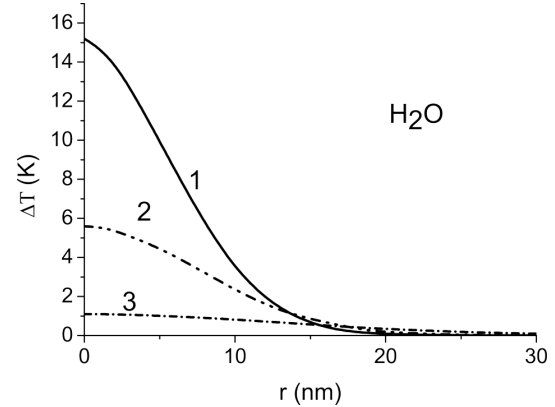
Fig. 4. Spatial distributions of the temperature in water in the region of X-ray quantum absorption ($h\nu_x = 1$ keV) at various cooling times $\Delta t = 0.1$ (*1*), 1 (*2*), and 5 ps (*3*)
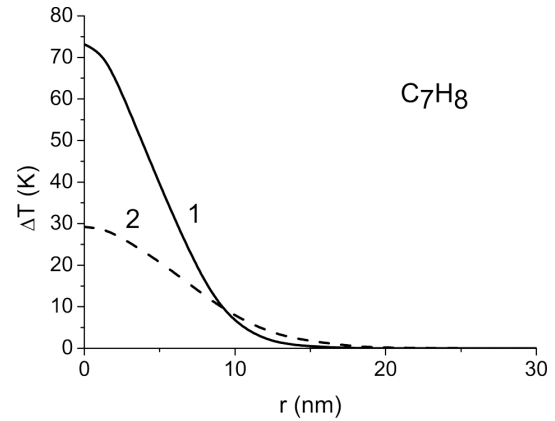
Fig. 5. The same as in Fig. 4, but for toluene. $\Delta t = 0.1$ (*1*) and 1 ps (*2*)

The cooling dynamics of the central parts of excitation regions for water and toluene is illustrated in Fig. 6. The local temperature decreases following a hyperbole with an exponent of 3/2. So, even if the liquid became heated up rather strongly, it cools down to the initial temperature ($\Delta T_{\max} < 1$ K) very rapidly (within tens of picoseconds). The luminescence kinetics of excited luminescent centers is described by an exponential dependence, with the average lifetime of excited phosphor molecules being considerably longer than the characteristic time of local region cooling. This circumstance allows the local heating in the region of X-ray luminescence excitation to be neglected.

Generally speaking, the concept of probability density to find a photoelectron in space used in the frame-
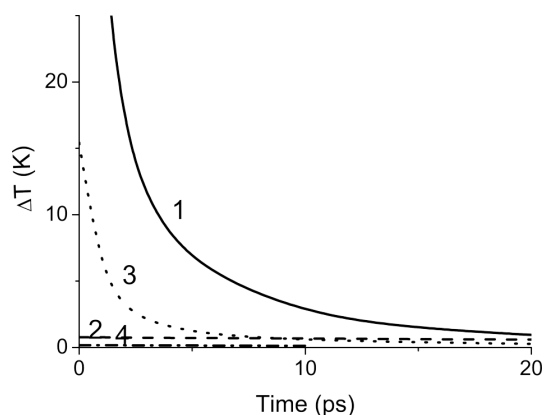
Fig. 6. Cooling of the central part of the excitation region ($r = 0$) after the absorption of an X-ray quantum with an energy of 1 or 5 keV: in water (curves *1* and *2*, respectively) and toluene (curves *3* and *4*, respectively)

work of diffusion theory allows one to considerably simplify calculations of the initial distribution of electronic excitations and determine the size of the region of their generation.

The only shortcoming of the considered model for the generation of electronic excitations by X-ray quanta is the monoenergetic character of photoelectrons adopted at the calculation of the spatial distribution of electronic excitations. Actually, owing to the photoabsorption by different ionic shells, the generation of photoelectrons with corresponding energies is accompanied by the emission of characteristic X-ray radiation, which is effectively absorbed in the surrounding environment. Those factors only slightly enlarge the local region of electronic excitation distribution and elevated temperature. The further migration of electronic excitations and the cooling of a local region results also in the expansion of this local region. Therefore, the method proposed for the calculation of the spatial distributions of electronic excitations and heat adequately describes this process, and its shortcomings do not insert principal inconsistencies into the calculation scheme.

Hence, the generation of electronic excitations in liquids does not differ in principle from that in crystals. Since the intracenter quantum yield of phosphor molecules is very high, the low intensity of the X-ray luminescence in molecules of liquid phosphors can be explained by only a single factor: this is the migration of generated electronic excitations to phosphor molecules.

5. Conclusions

In this work, a kinetic model of X-ray luminescence in liquid phosphors at the absorption of one X-ray quantum is proposed. The model involves the spatial distribution of generated electronic excitations at the absorption of one X-ray quantum in a solution. The spatial distributions are obtained for the generation of electronic excitations and the local heating. It is shown that the distributions can be described by Gaussians with parameters depending of the X-ray quantum energy and the medium parameters.

A shortcoming of the proposed model for the generation of electronic excitations at the X-ray irradiation of a liquid phosphor consists in that only monoenergetic photoelectrons are taken into account, while calculating the spatial distribution of electronic excitations. Actually, besides the generation of photoelectrons with the corresponding energy, the accompanying characteristic X-ray radiation is also emitted due to the photoabsorption by various ionic shells. However, this shortcoming does not substantially affect the adequacy of the model with respect to real physical processes running in liquid phosphors at the X-ray quantum absorption.

In addition, the migration of electronic excitations to phosphor molecules is found to be the main origin of the low yield of X-ray luminescence in liquid phosphors.

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В.Я. Дегода, I.М. Мороз

КІНЕТИЧНА МОДЕЛЬ ПРОСТОРОВОГО
РОЗПОДІЛУ ЕЛЕКТРОННИХ ЗБУДЖЕНЬ
В РІДИННИХ ЛЮМІНОФОРАХ

Р е з ю м е

Для рідинних люмінофорів запропонована модель рентгенолюмінесценції при поглинанні одного рентгенівського кванта. Для такої моделі одержано просторовий розподіл генерації електронних збуджень та локального нагрівання, які описуються гаусіанами з параметрами, що визначаються енергією рентгенівського кванта та характеристиками середовища. Робота присвячена вивченню процесів, які зумовлюють низький квантовий вихід люмінесценції при рентгенівському збудженні в рідинних люмінофорах, в той час, як ці люмінофори мають близький до одиниці квантовий вихід при фотозбудженні. Встановлено, що основні втрати згенерованих збуджень при рентгенівському опроміненні відбуваються на етапі міграції електронних збуджень від розчинника до молекул люмінофора.