Simulation of Development
of the Solid State Chain Reaction

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In this work simulation of the kinetics of the explosive decomposition process in silver azide crystals was done. The non local behavior of the chain propagation stage was taken into account. The finite sizes of the sample and the laser radius, the energy transfer through the lattice, which causes the reagents' redistribution, were also taken into account. Optimal area of the crystal for the reaction to develop is the centre of the radiation zone.

Keywords: simulation, difference scheme, model of the chain reaction, explosive decomposition, energy transfer, energetic materials, silver azide.

Моделирование развития твердофазной цепной реакции

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Работа посвящена моделированию кинетики процесса взрывного разложения кристаллов азида серебра при нелокальном характере стадии развития цепи. Моделирование процесса учитывает конечные размеры образца, радиус инициирующего импульса, перенос энергии химической реакции по кристаллической решетке, который приводит к перераспределению концентраций реагентов в кристалле. Оптимальной областью для развития твердофазной цепной реакции является центр облучаемой области.

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1. Introduction

The main purpose of the simulation of the physical and chemical processes is the simultaneous examination of the chemical transformations and the physical processes, among these the main are the diffusion of the reagents and energy transfer [1, 2]. Determination of the mechanisms of the initiation, propagation and development of the energetic materials' explosive decomposition has a wide applied meaning, as long as the inadvertent occurrence of the equipment based on the explosives causes significant material damage [3, 4]. The importance of the study lies in the necessity of development of the optical detonators [5] based on the initiating and high [6, 7] explosives. There are two ways to describe the explosive decomposition process – thermal [8] and chain model [9]. In terms of the thermal model it is supposed that the material decomposes according to the one-stage reaction [10], the constant of this stage has the Arrhenius dependence on the temperature. In terms of the chain model the self accelerated mode is due to the reagent multiplication [11]. A lot of the experimental data on the silver azide explosive decomposition, initiated by the Nd:Yag laser, were explained in terms of the chain model. The aim of this work is to simulate the kinetics of generation, propagation of the reaction taking into account non-local behavior of the propagation stage and the finite radius of the initiating pulse, phenomenological model of the process that was proposed [12].

2. Explosive decomposition model of the silver azide

According to the phenomenological model of the silver azide's explosive decomposition the energy of the chain reaction might transfer along the crystal lattice and causes the e-h pairs' generation. The intensity of the reagents' generation is maximal in immediate vicinity of the reaction area and then decreases exponentially [13]:

$$2h \xrightarrow{\quad k_2 \quad} N_6^{2+} \xrightarrow{\quad k_1 \quad} 3N_2 + 2h + (h + e) \cdot \exp\left(-|\Delta x| / r_0\right),$$
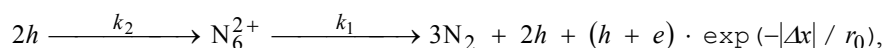
where k_1 – constant of the decomposition of N_6-complex, k_1 – constant of N_6-complex generation. Propagation stage is the interaction of two radicals N_3^0 (h), localized in neighbor points of lattice. The constant of the reaction of N_6 formation was estimated taking into account Coulomb repulsion, Debye screening and tunneling, and its value was equal to $k_2 = 0.5 \cdot 10^{-11}$ cm^{-3}s^{-1} [14]. N_6-complex decomposes with molecular nitrogen formation (N_2); the stage constant is $k_1 = 3 \cdot 10^7$ s^{-1} [15]. Released energy is accumulated by the electron and vibrational degrees of freedom of the nitrogen molecule. In terms of the model of the dipole interaction with the electron system of the crystal the constants of deactivation were estimated for the cases of e-h pairs' formation ($k_e \sim 10^9$ s^{-1}) and energy transfer to a band hole ($k_v \sim 10^{-12}$ cm^{3}s^{-1}) [15]. Deactivation of the nitrogen molecules causes the active particles generation – propagation stage takes place not only in the reaction area, but also outside it with probability $\sim \exp(-x/r_0)$. r_0 was calculated using the experimental data 50 ± 10 μm [16]. Intensity of the generation stage depended on the illumination inside the sample [17], and was not taken into account in the context of the work.

Simulation of the process of the energy transfer was made taking into account the real geometry of the sample – in cylindrical coordinate system using the difference scheme [18]. For the calculations
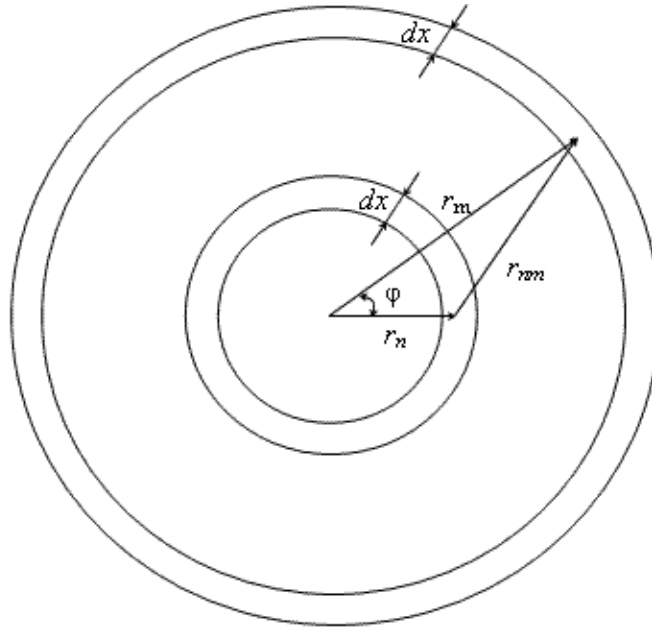
Fig. 1. Layout view of the reaction area in a cylindrical coordinates to estimate the efficiency of the reagents' generation in cell *n* due to the reaction in cell *m*

the sample was divided into kn cells with the same cross dimensions dx (Fig. 1). The reaction in cell n influences the speed of generation of the active particles (chain carriers) in all cells of the crystal, mathematically this might be described as an action of the functional on the function of concentration. In this work the functional was taken in form of square matrix $k_n \cdot k_n$. The elements of the matrix, which relate the intensity of the chain carriers' generation in cell n with the speed of the chemical reaction in cell *m* (S_{nm}), were calculated by using the following procedure. The following conventional signs were used: Y_n – number of holes in cell *n*, *A* – concentration of N_6 complex, S_n – area of cell *n*. Let us estimate how the reaction speed in cell *n* influence the reaction speed in cell *m*. The distance between cells *n* and *m* might be calculated as:

$$r_{mn} = \sqrt{r_m^2 + r_n^2 - 2r_m r_n \, cos \, \varphi} \quad , \quad .$$

$$r_n = dr\left(n - \frac{1}{2}\right) \qquad r_m = dr\left(m - \frac{1}{2}\right)$$

(1)

Speed of chain carriers' generation in any cell *n* because of the reaction of N_6 decomposition in cell *m* might be calculated using the following expression:

$$S_{nm} = T_m \, x_{nm},$$

(2)

where x_{nm} – speed of the chain carriers' generation in cell *n* due to the reaction in cell *m*, T_m – normalizing factor.

While the distance from the reaction area increases the energy decreases inversely as the square of the distance, and it decreases in *e* times while the distance is equal to r_0 because of the absorption.

The entire cylindrical segment with radius r_n contains $A_n r_n dx d\varphi$ particles, so the number of particles generated in cell m:

$$Y_{mm} = \frac{A_n e^{-\frac{r_{mn}}{r_0}}}{2\pi r_0 r_{nm}} dx r_n d\varphi \,,$$ (3)

where Y_{mn} is quantity of the chain carriers, generated in cell m per unit time due to the reaction in cell n. For the layer containing cell m:

$$x_{nm} = 2\int_0^\pi dY_{m\grave{o}}\, d\varphi \,,$$

$$S_{nm} = 2T_m \int_0^\pi \frac{e^{-\frac{r_{mn}}{r_0}} Y_{mn}}{2\pi r_0 r_{mn}} d\varphi \,.$$ (4)

While $n=m$ value of S_{nm} becomes infinite, what is why the piecewise function was used:

$$f = \begin{cases} f_1(m), & m \subset [1, n-1] \cup [n+1, k_n] \\ f_2(m), & n = m \end{cases}$$

According to the model the total value of the chain carriers, generated in cell n because of the reaction in cell m, equal to Y_{mn}, i.e. one act of transformation generates one e-h pair. Coefficient T_m was estimated using the following normalization:

$$T_m = \frac{r_m}{\sum r_n \int_0^\pi \frac{e^{-\frac{r_{mn}}{r_0}} \beta_n}{2\pi r_0 r_{mn}} d\varphi} \,.$$ (5)

Concentration of the chain carriers generated in cell m:

$$p_{nm} = \frac{B_{nm}}{S_m} = \frac{2\int_0^\pi dB_{nm} d\varphi}{2\pi r_m dr} \,.$$ (6)

Calculation of matrix S_{mn} was done in a spatial program, calculation of its components preceded the solution of the equation set, describing the kinetics of the decomposition process. S_{nm} is square $(k_n \times k_n)$ matrix. Fig. 2 and 3 show the section of the matrix for the different values of n ($n_1 = 100$ and $n_2 = 25$). Maximal value of the y-coordinate corresponds to the cell, along which the section was made. It is obvious that the diagonal elements have the maximal values, as long as these elements correspond to the probability of e-h pairs' generation in the same cell where the reaction takes place.

Asymmetry of the elements of matrix S_{nm} is explained by the fact that the recombination of the reagents in the neighborhood of the surface is faster than in the crystal bulk. If the considering cell is
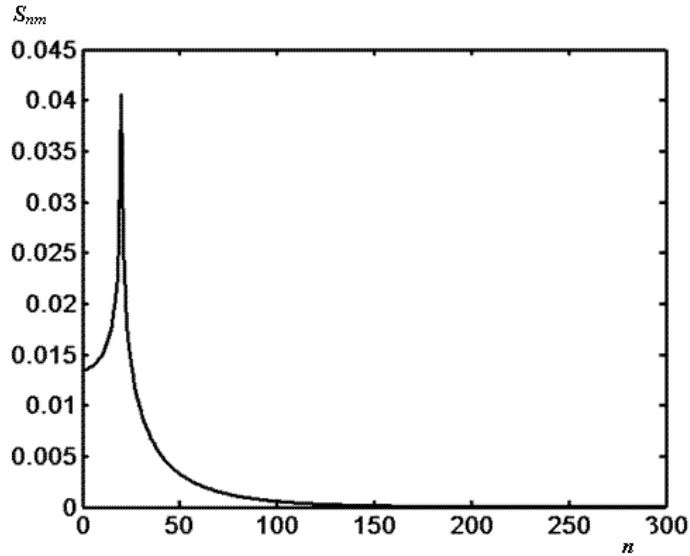
Fig. 2. Probability of the e-h pair generation in cell n because of the reaction in cell $m = 25$
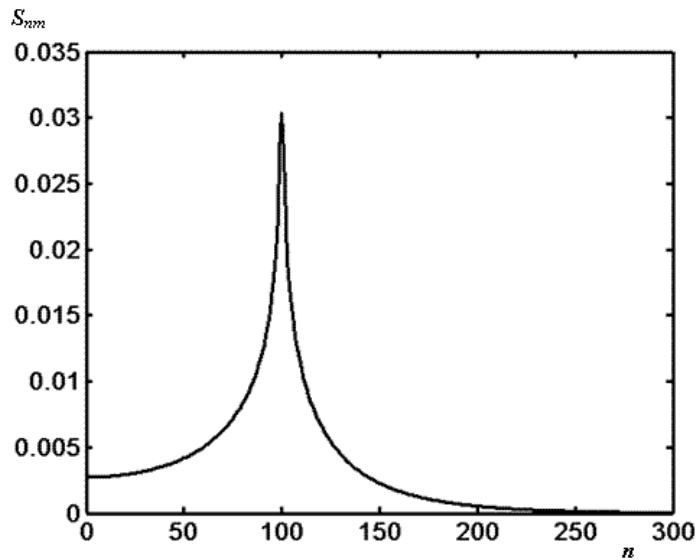

Fig. 3. Probability of the e-h pair generation in cell n because of the reaction in cell $m = 100$

in the area next to the surface (distance between the cell and the surface is smaller than r_o) reflected energy does not absorbed significantly by the layer of the sample, so the energy of the secondary wave is bigger than the same value in case of the cells , which are far from the surface. This is the case of the cells with numbers 1: (n_i-1) or (n_i+1): n. While moving to the centre of the crystal the curve becomes symmetrical. Maximal values among the elements of each line, as it was mentioned above, correspond to the probability of the generation in the same cell where the reaction takes place. The maximal values of the element s_{ii} differ for the different lines (Fig. 3). Dependence of s_{ii} on the number of the cell has several extremes. The maximal value corresponds to the crystal centre, because in that case s_{ii}

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is calculated as a sum of probabilities of generation from all cells of the crystal and at the same time always contains the part, which considering the maximal contribution of the centre cell.

Ordinary differential system describing the process of the reaction with non-local development stage (1-6) was solved using the Runge-Kutta method of 1-5 order with time varied pitch. During the calculation of the kinetics the relative error does not exceed 10^{-12}. Results of the simulation of the processes of the chain reaction initiation and development, initiated by the laser pulse with diameter 600 μm, presented on Fig. 4 and Fig. 5. Constants of the elementary stages, used to simulate the process, were estimated in works [14,15,19]. After the termination of the laser action concentration of reagent A
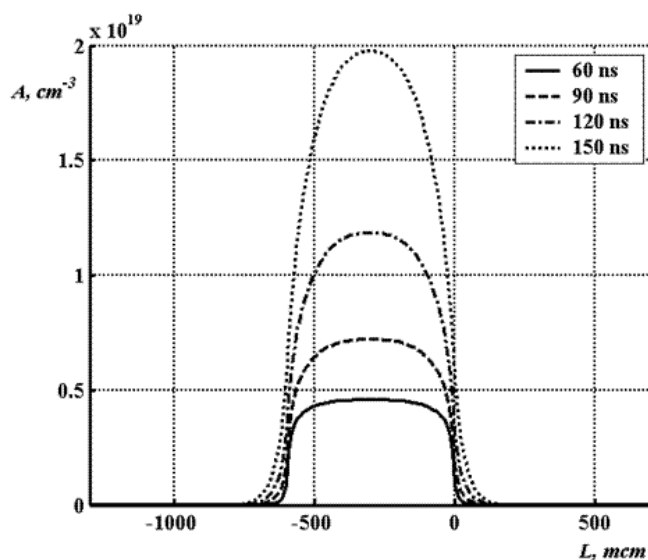
Fig. 4 Calculated distributions of A complexes in the crystal in 60, 90, 120, 150 ns after the impulse termination
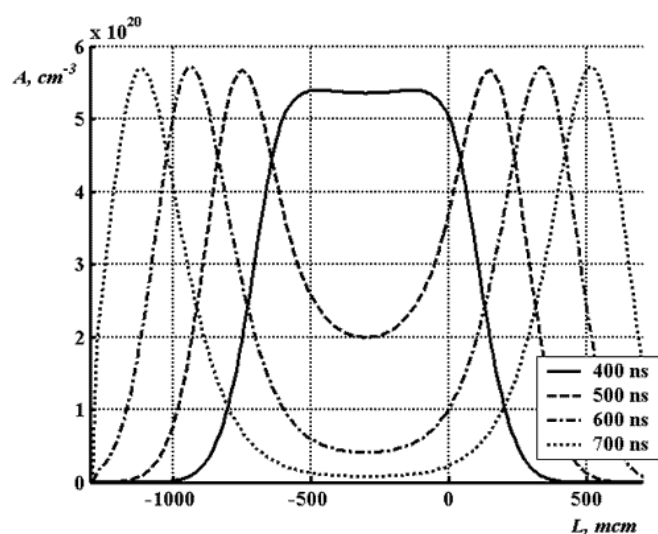
Fig. 5. Calculated distributions of A complexes in the crystal in 400, 500, 600, 700 ns after the impulse termination

(N_6 complex) increases (Fig. 4), while the concentration of the chain carriers decreases (electron-hole pairs) – induction period of the reaction. A similar situation occurs for the homogeneous variant of the chain reaction [20]. Then the reagents' concentrations begin to increase outside the initiated zone at a distance about 100 μm. Estimation of the diffusion shift D·t (D = 0.25 cm²/s diffusion coefficient [21], t – time of calculation) gives the value ~ 1 μm. Hence, the main reason of the reaction initiation outside the irradiated zone is not a diffusion, but generation of the reagents due to the non-local character of the branching stage.

When the induction period is over the concentrations of the holes and complex A begin to grow in step both in the irradiated area and in the area, which was not initially acted by the laser pulse. Development of the chain reaction causes decomposition of the anion sublattice and degeneration of the chain reaction. But by this time concentrations of the reagents outside the radiated zone increase and become more than their critical values, and so two reaction fronts are formed. These fronts move towards the crystal edges (Fig. 5).

3. Resume

Non local behavior of the chain propagation stage causes significant active particles' redistribution. The concentrations of the active particles, generated by means of this way, decrease exponentially outside the reaction area. The active particles are generated symmetrically on all sides outside the reaction area. Optimal area of the crystal for the reaction to develop is the centre of the radiation zone.

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