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EQUATION FOR THE RADIATION ACCUMULATION OF ELECTRON CENTERS IN ALKALI-HALIDE CRYSTALS

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It has been established experimentally ([2]) that, at room temperature, the accumulation of the concentration of F-centers (n_F) in LiF single crystals under the action of protons proceeds along a curve with a maximum (Fig. 1), while the efficiency of radiation-chemical coagulation of F-centers into M-centers, defined as n_M/n_F^2, increases with dose as a result of certain irreversible processes that increase the probability of close arrangement of electronic centers and their coagulation. With a uniform dose distribution and in the absence of reverse reactions of the type $M \to F$, such an irreversible process is the accumulation of the total concentration of F-centers in the single and associated states

$$n = n_F + 2n_M + 3n_R + \ldots + in_{F_i} + \ldots \tag{1}$$

and the distribution of F-centers among multiple F_i-centers, where $i = 1$ for F-, $i = 2$ for M-, $i = 3$ for R-centers, etc. Let us introduce a measure of the probability of the reaction $F_i + F \to F_{i+1}$, referred to one F_i-center, and call it the coagulation volume of the F_i-center (v_i). Visually, the coagulation volume of an F_i-center may be represented as such a volume of the crystal, surrounding the F_i-center, that the reaction $F_i + F \to F_{i+1}$ will occur only when the center of symmetry of some F-center falls within this volume. With the aid of coagulation volumes, the accumulation of F_i-centers can be described, taking (1) into account, by the system of kinetic equations:

$$dn_F/dn = 1 - 2v_1 n_F - v_2 n_M - v_3 n_R - \ldots - v_i n_{F_i} - \ldots, \tag{2,1}$$

$$dn_M/dn = v_1 n_F - v_2 n_M, \tag{2,2}$$

... ...

$$dn_{F_i}/dn = v_{i-1} n_{F_{i-1}} - v_i n_{F_i}, \tag{2,i}$$

with the initial conditions: at $n = 0$

$$n_F = n_M = ... = n_{F_i} = 0; \qquad dn_F/dn = 1,$$

$$dn_M/dn = dn_R/dn = ... = dn_{F_i}/dn = 0. \tag{3}$$

Let us consider a number of cases.

I. All $v_i = v$ and do not depend on n. The exact solution of system (2) is given by the expressions

$$n_F = ne^{-nv}, \qquad n_M = \frac{n^2 v}{2} e^{-nv}, \dots, \qquad n_{F_i} = \frac{(nv)^i}{i!\, v} e^{-nv}, \tag{4}$$

i.e., the distribution of F-centers among multiple F_i-centers obeys Poisson' s law.

II. All $v_i = v$ and are functions $v(n)$. Using $(2,2) \div (2,i)$, equation $(2,1)$ can be reduced to the form

$$d^2 n_F/dn^2 + (2v - v'/v)\, dn_F/dn + v^2 n_F = -v'/v. \tag{5}$$

The solution of equation (5) is

$$n_F = \exp\left(-\int_0^n v\, dn\right)\left[\frac{1}{v(0)}\int_0^n v\, dn + \int_0^n \frac{v'}{v^2}\left(\int_0^n v\, dn\right)\exp\left(\int_0^n v\, dn\right) dn - \int_0^n v\, dn \cdot \int_0^n \frac{v'}{v^2}\exp\left(\int_0^n v\, d\right.\right. \tag{6}$$

Taking into account that, with increasing n, the coagulation volumes change slowly in comparison with the concentrations of centers, we obtain

$$n_F = \frac{n\bar{v}}{v(0)} e^{-n\bar{v}}, \qquad n_M = \frac{(n\bar{v})^2}{2v(0)} e^{-n\bar{v}}, \dots, \qquad n_{F_i} = \frac{(n\bar{v})^i}{i!\, v(0)} e^{-n\bar{v}}, \tag{7}$$

where $\bar{v} = \frac{1}{n}\int_0^n v\, dn$ is the mean coagulation volume.

III. In the general case, when all v_i are different and depend on n, in order to solve the system (2) a specific form of the functions $v_1(n), v_2(n), \ldots, \ldots, v_i(n)$ is needed. If we assume that the change of v_i with increasing n is caused by a decrease in the concentration of regular anion sites in the lattice, then $v_i(n) = x_i/(N-n)$, where N is the concentration of anion sites in an ideal lattice. At low temperatures the x_i are equal to the coordination numbers of the corresponding centers ($x_F = 12,\ x_M = 18,\ x_R = 24$), $x_4 - x_3 = \ldots = x_3 - x_2$, and from (2) we obtain

$$\frac{d^2 n_F}{dn^2} + \frac{2x_1 + x_2 - x_3 - 1}{N-n}\frac{dn_F}{dn} + \frac{3x_1x_2 - 2x_1x_3}{(N-n)^2} n_F = -\frac{x_3 - x_2 + 1}{N-n}. \quad (8)$$

Putting $u = 9/(N-n)$, we transform equation (8) to the form $d^2n_F/dn^2 + (2u - u'/u)dn_F/dn + {}^8/_9 u^2 n_F = -{}^7/_9 u$, whence

$$n_F = (N/55)(1 - n/N)\left[22(1-n/N)^5 - 15(1-n/N)^{11} - 7\right]. \quad (9)$$

At room temperature, when ionic processes are substantial and the coagulation volumes are large, the first two cases are realized practically, and the distribution of F-centers over F_i-centers may be considered Poissonian (4), (7). In the absence of radiation annealing of anion vacancies, n depends linearly on the irradiation time t, and the form of the formulas obtained does not change when passing to t as the argument. According to (4), (7): 1) the accumulation of F_i-centers proceeds along a curve with a maximum, which agrees with the experimental accumulation curve of F-centers (Fig. 1); 2) the ratio $n_M/n_F = (v/2)n$ is represented by a straight line issuing from the origin, which contradicts experiment (Fig. 2); 3) the efficiency of the reaction $F \to M$ is equal to $n_M/n_F^2 = (v/2)e^{nv}$ and increases exponentially, which contradicts the experimental behavior of n_M/n_F^2 at the beginning of the accumulation process (Fig. 2). Relations (4), (7) were derived under the assumption of a uniform dose distribution and the absence of reverse reactions of the type $M \to F$. Reverse reactions may reduce n_M/n_F and n_M/n_F^2. In the experiment, n_M/n_F and n_M/n_F^2 were larger than follows from ((4), (7), especially at the beginning of the accumulation process of F- and M-centers. It remains to assume that the increase in the efficiency of $F \to M$ is caused by a nonuniform dose distribution over the volume of the crystal.

Earlier we ([2]) considered the process of multiple localization of radiation energy in a solid, which consists in the following. The energy of a single quantum or of a particle that has undergone a collision is distributed in a small volume of localization of the quantum energy, or in the volume of a track ϑ. The phenomenon of multiple localization of radiation energy consists in the spatial overlap of the quantum localization volumes. The number of volumes that

Fig. 1

Figure 1: Fig. 1

coincide at the place of overlap is called the multiplicity of localization r. The distribution

of the irradiated volume by localization multiplicities obeys a binomial law, which passes into Poisson' s law for $r \ll j$, where $j = j_0 t$ is the number of particles that have undergone a collision in a unit volume during time t. The volume of r-fold localization is $\frac{[j\vartheta]^r}{r!} e^{-j\vartheta}$ of the target volume.

The contradictions noted above between formulas (4), (7) and experiment indicate that, owing to multiple localization of the absorbed energy, a uniform dose distribution is impossible not only in principle but also in practice; a LiF crystal irradiated with protons must be regarded as a heterogeneous system. The processes of accumulation of radiation defects in volumes of different localization multiplicity may occur differently, and the equation for the accumulation of electron centers may be represented in the form of a series

$$n_{F_i} = \sum_r \hat{K}_r \left[\frac{\varepsilon r}{\vartheta} \frac{(j\vartheta)^r}{r!} e^{-j\vartheta} \right], \tag{10}$$

each term of which describes the accumulation of centers in a volume of the given multiplicity. In the square brackets is the expression for the absorbed energy in a volume of r-fold localization; ε is the energy absorbed from one particle; $\hat{K}_r$ is the operator of the dependence of the center concentration on the dose in a volume of r-fold localization.

Fig. 1. Dependence of n_F, n_M in LiF single crystals on the time of irradiation with protons of energy 2.7 MeV (the concentration of F-centers was calculated from the absorption coefficient at the maximum of the F-band, corrected according to ([3],[5]): $k_F = k_{F\max} - 0.65 k_M$. Proton-beam intensity $I_2 = 0.7 I_1$

For F-centers the form of this dependence is already known to us from the analysis of the accumulation process under a uniform dose distribution. According to (4), (10), the concentrations of F- and M-centers, in the absence of: 1) reverse reactions of dissociation of complex centers into simple ones; 2) radiation annealing of anion vacancies, are respectively equal to

$$n_F = \eta j_0 \vartheta t \exp\left[-\eta\nu - j_0 \vartheta t \left(1 - e^{-\eta\nu}\right)\right], \tag{11}$$

$$n_M = \frac{1}{2} \eta^2 \nu j_0 \vartheta t \left(1 + j_0 \vartheta t e^{-\eta\nu}\right) \times \exp\left[-\eta\nu - j_0 \vartheta t \left(1 - e^{-\eta\nu}\right)\right], \tag{12}$$

Fig. 2

Figure 2: Fig. 2

where η is the total concentration of F-centers in a volume of single localization; $\eta = \varepsilon/\vartheta\varepsilon_F$, where ε_F is the absorbed radiation energy per one F-center at the linear stage of their accumulation (1). According to (11), (12),

$$n_M/n_F = \eta\nu/2 + j_0\vartheta(\eta\nu/2)e^{-\eta\nu}/t,$$

which agrees well with the form of the experimental dependence n_M/n_F on irradiation time (Fig. 2). The quantities entering equation (13) were determined from experimental–

Fig. 2. Dependence of n_M/n_F, n_M/n_F^2 in LiF single crystals on the time of irradiation with protons of energy 2.7 MeV at two proton-beam intensities $I_2 = 0.7I_1$: a–I_1; b–I_2

···data by the method of least squares. It turned out that for LiF irradiated with protons of energy 2.7 MeV, $\eta v = 0.19$. Determining ϑ from (13), measuring the range of the protons by the thickness of the darkened layer ($R = 65$ μ), and considering the track to be cylindrical, we obtained that the track diameter is 40 Å. According to (11), the maximum concentration of F centers is equal to

$$n_{F\max} = \eta e^{-\eta v}/(1 - e^{-\eta v})e \approx 1/ev$$

and occurs at

$$t_{\max} = 1/j_0\vartheta(1 - e^{-\eta v}) \approx 1/j_0\vartheta\eta v$$

and, for a localization multiplicity,

$$r_{\max} = j_0\vartheta t_{\max} = 1/(1 - e^{-\eta v}).$$

In our experiment $r_{\max} = 5$; the coagulation volume of an F center in LiF at room temperature is $v = 5 \cdot 10^{-20}$ cm^3; the coagulation radius of an F center is

$$r_F = \sqrt[3]{v\left|\frac{4}{3}\right|\pi} = 23 \text{ Å} = 5.7a$$

(a is the lattice parameter). The total concentration of F centers in the track of one proton is $\eta = 4 \cdot 10^{18}$ cm^{-3}.

The physical fact that the dependence of n_M/n_F on t does not pass through the origin is a consequence of the discrete character of the irradiation. Before irradiation, $n_F = n_M = 0$ and $n_M/n_F = 0$. However, in the track of the very first proton this ratio becomes equal to $\eta v/2$ and is the larger, the greater the concentration of centers in the track and their coagulation volumes. Consequently, the effect of a nonuniform dose distribution due to multiple localization of the radiation energy increases with increasing dE/dx of the particles.

Since a crystal irradiated with protons is a heterogeneous system, the efficiency of the reaction $F \to M$ must be determined as

$$\frac{\bar{n}_M}{\overline{n_F^2}} = \frac{v}{2} e^{\eta v} \frac{1 + j_0 \vartheta t e^{-\eta v}}{1 + j_0 \vartheta t e^{-2\eta v}} \exp\left[j_0 \vartheta t (1 - e^{-\eta v}) e^{-\eta v}\right], \tag{14}$$

where $\overline{n_F^2}$ is the mean statistical value of the square of the concentration of F centers. According to (14), the theoretical efficiency of the reaction $F \to M$ begins with the value $(v/2)e^{\eta v}$ and increases with dose approximately according to an exponential law. However, in the experiment $\bar{n}_F$ and $\bar{n}_M$, entering into equations (11), (12), are measured, and the efficiency of the reaction $F \to M$ is determined as

$$\frac{\bar{n}_M}{\bar{n}_F^2} = \frac{v}{2} e^{\eta v} \frac{1 + j_0 \vartheta t e^{-\eta v}}{j_0 \vartheta t} \exp\left[j_0 \vartheta t (1 - e^{-\eta v})\right]. \tag{15}$$

According to (15), $\bar{n}_M/\bar{n}_F^2$ varies with dose along a curve with a minimum, which explains the experimental results (Fig. 2). With increasing dose and the mean localization multiplicity, the maximum of the distribution of the irradiated volume over multiplicities decreases, and the half-width increases [2]; the irradiated crystal becomes increasingly a homogeneous system, and the experimental efficiency of the reaction $F \to M$, determined by formula (15), approaches the theoretical value determined by formula (14).

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Note: Figure translations are in progress. See original paper for figures.

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