

Kinetics of lattice defects induced in lithium fluoride crystals during irradiation with swift ions at room temperature

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ABSTRACT

Rate equations are employed to the kinetic description of lattice defects, created in lithium fluoride by ion irradiation. The F centers are assumed to be created in a mobile state (anion vacancies or excited F^* centers), having a certain relaxation time to become stable at room temperature. Concentrations of the F centers and their aggregates are analyzed depending on the irradiation conditions and model parameters. Comparison of the swift ion and electron/gamma irradiations using the suggested model captures the prominent experimental results of a higher complex defect fraction, which created under irradiation with the heavier projectiles.

1. Introduction

Similarly to other alkali halide crystals, having the exciton mechanism of defect formation, lithium fluoride is very sensitive to irradiation with ions, passing in the electronic stopping regime [1]. Such swift ions produce Frenkel pairs in the anion sublattice around their trajectories as a result of recombinations of electron-hole pairs [2]:



or decays of self-trapped excitons:



At room temperature, the anion vacancies tend to capture electrons, forming F centers with absorption maximum at 248 nm. The F centers, having migration barrier above 1 eV, are not mobile unless heating up to ~600 K (annealing) [3,4] or optical excitation (bleaching). However, formation of F_2 and more complex centers during irradiation at room temperature indicates that the anion vacancies have certain time before binding with electrons in the ground state, and the lifetime of the ionized or excited state of F centers should be enough at least for several tens of diffusion jumps [5–7]. Complementary H centers with the migration energy ~0.1 eV remain mobile at room temperature until

recombine with F centers, either interact with bulk defects, or aggregate.

The aggregates of both kinds can grow due to the concordant defect attachment or shrink, capturing the opposing ones, until the mobile defects are available. These processes can be described with rate equations, which take into account de-excitation of F centers. The suggested model can be employed for kinetics analysis of radiation-induced defects with different parameters of irradiation and subsequent treatment. It considers the factor of time, which was not taken into account in the models of the absorbed energy accumulation [7,8–10].

2. Model description

We assume spatially uniform distribution of the primary defects, when components of genetic Frenkel pairs recombined or became well-separated, and concentration of the defects changes mainly due to their interactions rather than diffusion through the crystal. Thus the defect ensemble can be described by the time-dependent distribution functions f_* , f_n , and h_n . The first one f_* corresponds to the atomic concentration of anion vacancies before binding with electrons in the ground state. The lifetime τ_* of the ionized (v_n^+) or excited (F^*) state of F centers should be enough at least for several tens of diffusion jumps before the reactions

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Unless specified we will use F^* for both kinds of the F -center mobile precursors. Distributions f_n describes concentrations of F ($n = 1$) and F_n centers. Their evolution is governed by aggregation



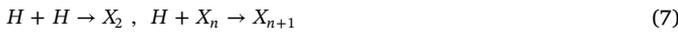
and shrinking due to capturing the interstitials



In the particular case of two excited F centers we also assume their merger: $F^* + F^* \rightarrow F_2$. The annihilation reactions $H + F$ and $H + F^*$ simply restore the lattice. Reaction $H + v_a^+$ leaves either valence hole e^+ or V_K center, those we do not count as lattice defects. The processes (3)-(5) are taken into account in the following rate equations:

$$\begin{aligned} \frac{df_1}{dt} &= \frac{1}{\tau_*} f_* - D_F f_* r_F (1) f_1 + D_H h_1 (r_F (2) f_2 - r_F (1) f_1) \\ \frac{df_2}{dt} &= D_F f_* (r_F (1) f_1 + 2 r_F (1) f_* - r_F (2) f_2) + D_H h_1 (r_F (3) f_3 - r_F (2) f_2) \\ \frac{df_n}{dt} &= D_F f_* (r_F (n-1) f_{n-1} - r_F (n) f_n) + D_H h_1 (r_F (n+1) f_{n+1} - r_F (n) f_n), \quad n \geq 3 \\ \frac{df_*}{dt} &= -f_* \left(\frac{1}{\tau_*} + D_F (4 r_F (1) f_* + \sum_{n=1}^{\infty} r_F (n) f_n + \sum_{n=1}^{\infty} r_H (n) h_n) + D_H h_1 r_F (1) \right) \end{aligned} \quad (6)$$

where h_1 is the atomic concentration of single H centers, and those aggregation results in formation of the corresponding complex defects, described with h_n .



Aggregation of the vacancy centers is extensively studied experimentally, since the F centers have a prominent optical absorption peak with maximum at 248 nm, and the F_2 - F_4 centers absorb light in the region of 300–700 nm [3,4]. Further aggregation of the F centers results in the local depletion of the anion atoms and formation of lithium colloids with absorption band around ~445 nm. Their growth at high-dose irradiation can be studied with different techniques, including optical microscopy of the cleaved crystal [11,12]. At the same time the H centers does not present in the absorption spectra at room temperature due to their high mobility, and we can only guess about their aggregation mechanism at the early stage [13,14]. However, the high-dose irradiations reveal formation of the fluorine gas bubbles, so the reactions (7) can be reasonable assumed.

Note, that charged complex vacancy centers can be stable at room temperature, if the total charge is balanced by impurities or other defects. For example, F_3^+ centers, having peak at 448 nm, strongly overlaps with F_2 in the absorption spectra, but can be distinguished by means of luminescence spectrometry [15–21]. We assume all aggregates as stable regardless their charge.

Similar to the reactions (4), capturing the mobile vacancies leads to shrinking of the interstitial aggregates



Thus kinetics of the interstitial defects can be described with the following equations in addition to the Eqs. (6)

$$\begin{aligned} \frac{dh_2}{dt} &= D_H h_1 (2 r_H (1) h_1 - r_H (2) h_2) + D_F f_* (r_H (3) h_3 - r_H (2) h_2) \\ \frac{dh_n}{dt} &= D_H h_1 (r_H (n-1) h_{n-1} - r_H (n) h_n) + D_F f_* (r_H (n+1) h_{n+1} - r_H (n) h_n), \quad n \geq 3 \\ \frac{dh_1}{dt} &= -D_H h_1 (3 r_H (1) h_1 + \sum_{n=1}^{\infty} r_H (n) h_n + \sum_{n=1}^{\infty} r_F (n) f_n) \\ &\quad - (D_H r_F (1) + D_F r_H (1)) h_1 f_* + D_F f_* r_H (2) h_2 \end{aligned} \quad (9)$$

Here D_F and D_H are the diffusion coefficient of F^* and H centers correspondingly; r_F and r_H are the reaction factors, which describe reaction rates of the corresponding aggregates with mobile defects. For simplicity we assume no elastic or electrostatic interaction between defects and therefore no bias of the aggregates toward interstitials or vacancies. Moreover, as the aggregates are rather small, they do not disturb the point defect concentration in their vicinities, and the

reaction factors are proportional to their surfaces, that is

$$r_F(n) = n^2, \quad r_H(n) = n^2 \quad (10)$$

Although the concentrations of color centers remain far from equilibrium, at room temperature they can be stored for very long. Thus, we assume all defect interactions are irreversible, including de-excitation of the F^* centers. Since thermal generation of defects can be neglected in comparison with the irradiation-induced one, our Eqs. (6) and (9) do not provide a detailed balance distribution. That should be adjusted for modelling of annealing processes and the Ostwald ripening of defect aggregates. Note also, that under irradiation an F center can capture a valence hole or V_K center and restore its mobility [4]



This process should be taken into account for prolonged irradiations. The similar effect might be provided by optical bleaching, when the F centers are excited by UV light ($F \rightarrow F^*$) [22,23].

3. Results and outcomes

The rate equations (6) and (9) include three characteristic times: the relaxation time of F^* centers τ_* , their diffusion time $\tau_F \sim \lambda^2/D_F$, and diffusion time of H centers $\tau_H \sim \lambda^2/D_H$; where λ is the diffusion jump lengths. We assume that at room temperature τ_F is much larger than τ_H [5]. It could be expected, that relatively short relaxation time τ_* will be favorable to the predomination of the single F centers. However, generally the equations should be solved numerically.

Assuming almost simultaneous formation of the primary defects in the projectile vicinity, one can start from their initial concentrations. Although a certain fraction of the F centers can be formed in the ground state, we will not include this in the present calculations:

$$\begin{aligned} f_*(0) &= h_1(0) = f_0 \\ f_n(0) &= 0, \quad \forall n \\ h_n(0) &= 0, \quad n \geq 2 \end{aligned} \quad (12)$$

Temporal dependences of point and complex defect concentrations, which calculated according to the rate equations, are presented in the Fig. 1.

We evaluated the number of primary defects in their aggregates as

$$A_n = \sum_{n=2}^{\infty} n f_n, \quad B = \sum_{n=2}^{\infty} n h_n \quad (13)$$

Unless we include some other defect sinks like impurities or crystalline defects, the conservation law $f_* + f_1 + A_n = h_1 + B$ should hold. When sufficient time after termination of the irradiation has passed, only stable defects survived, and $f_1 + A_n = B$. It is the remaining concentrations of single F and complex F_n centers that can be compared with the results of optical spectrometry, EPR, NMR and other experimental measurements [24–28]. It is also important, when complex defects are considered for dosimetry purpose [15–17].

Since the F^* centers are participating both in the first and the second order reactions, their initial concentration at given τ_* determines probabilities of their encounters and interaction with other defects. Thus in a dilute ensemble of primary defect the single F centers will predominate at $t \gg \tau_*$, while high concentration will stimulate their active aggregation. Concentrations of the stable vacancy defects depending on the initial concentration of the mobile centers (f_0) are plotted in the Fig. 2. for different values of the relaxation time τ_* .

This effect of the initial concentration can shed light on the difference between LiF crystals, irradiated with similar dose of heavy ions and electrons or γ rays. Initial conditions (12) can simulate the ion irradiation. For γ one can add in the r.h.s. of the rate equations for f_* and h_1 in (6) and (9) defect generation rate g and assume $f_*(0) = h_1(0) = 0$. For comparison we chose the same total Frenkel pair generation

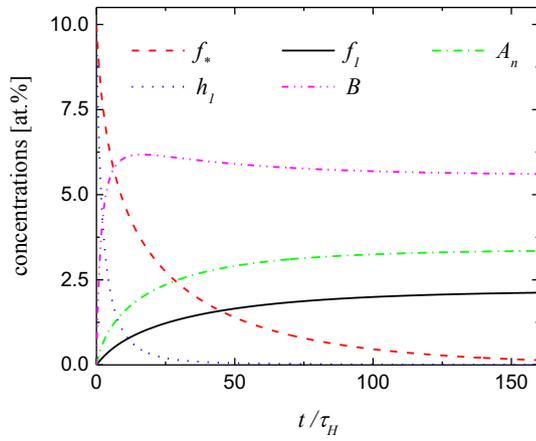


Fig. 1. Temporal dependence of defect concentrations. $\tau_F=10\tau_H$, $\tau_*=10^2\tau_H$.

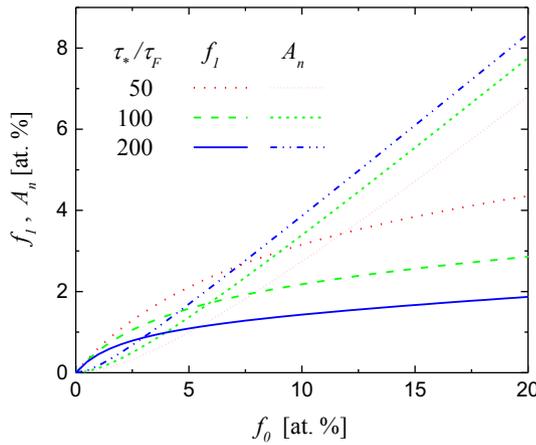


Fig. 2. Concentrations of vacancy defects depending on the initial number of Frenkel pairs and the F -center relaxation time τ_* .

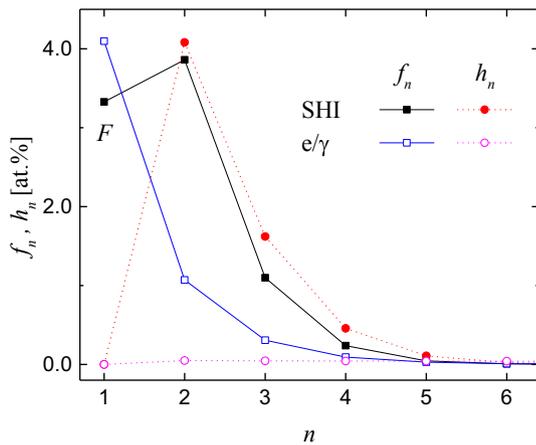


Fig. 3. Distributions of stable defects after the same number of Frenkel pairs, generated in a swift ion vicinity and during a gradual accumulation (electron or γ -irradiation).

density:

$$\int_0^{t_i} g(t) dt = f_0 \quad (14)$$

where $t_i \gg \tau_*$ is the irradiation time for electrons/ γ .

The difference for the same absorbed dose can be seen on the Fig. 3. Whereas the concentrations of single F centers are comparable, their aggregates are formed much more effectively under ion irradiation.

This result is in the concordance with the experimental data and Monte-Carlo simulations [5]. More detailed evaluation of the defect kinetics in the ion track should take into account the local transient heating of the target material. This effect of swift ions is very important at cryogenic temperatures, when diffusional separation of the Frenkel pair components, which is crucial for their stability, would be suppressed otherwise [29]. This heating can also play a certain role for further processes of recombination and aggregation [30,31]. In our case the diffusion coefficients D_F and D_H increase, and moreover, even the stable F centers in the ground state temporary gain mobility. These effects can be included in the model, but more detailed information on the spatial distributions of primary defects and the lattice temperature in vicinities of the ion trajectories is required. This could be a step towards growing sensitivity and spatial resolution of the experimental techniques in the study of color centers.

This work has been carried out using computational resources of MCC NRC «Kurchatov Institute», <http://computing.nrcki.ru/>.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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