The microscopic theory of diffusion-controlled defect aggregation

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Abstract

The kinetics of diffusion-controlled aggregation of primary Frenkel defects (F and H centers) in irradiated CaF_2 crystals is theoretically studied. Microscopic theory is based on the discrete-lattice formalism for the single defect densities (concentrations) and the coupled joint densities of similar and dissimilar defects treated in terms of the Kirkwood superposition approximation. Conditions and dynamics of the efficient F center aggregation during crystal heating after irradiation are analyzed. Copyright © 1998 Elsevier Science B.V.

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1. Introduction

The primary radiation defects in ionic solids – the F centers (electron trapped by anion vacancy) and the H centers (interstitial halide atoms) – under intensive irradiation and at high enough temperatures are known to reveal *aggregation* which leads to the formation of alkali metal *colloids* and gas bubbles (see [1] and references therein). The intensive experimental studies of the conditions and efficiency of the metal colloid formation (such as the temperature interval, dose rate, etc.) continue nowadays for many alkali halides [2,3] and technologically important ceramics [4]. This problem is also interesting from the fundamental point of view, being an example of *pattern formation* and *self-*

organization in reaction–diffusion systems far from equilibrium [5]. In our case the process includes A, B particle random walks on a lattice (diffusion), particle interaction and bimolecular annihilation of dissimilar particles, $A + B \rightarrow 0$. Irradiation is modeled by a permanent particle source with a given dose rate (intensity).

Colloid growth study by means of the direct computer (Monte Carlo) simulations is a very difficult problem since the mobilities of the two kinds of defects involved – H and F centers – differ typically by 15 orders of magnitude and for monitoring slow F center aggregation, the time increment is dictated by mobility of fast H centers.

Existing analytical theories of the radiation-induced defect aggregation and colloid formation could be classified into three categories: macroscopic, mesoscopic, and microscopic [6,7]. We refer to as *microscopic* the first-principle theory which treats

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elementary processes at atomic scale and using no fitting or uncertain parameters but only several basic defect parameters like the diffusion energies and interaction energies. A simplified continuum approximation has been used up to now. More realistic, discrete-lattice microscopic theory was developed very recently [7] and applied to the F center aggregation in NaCl exposed to irradiation [8].

In this paper, we present briefly results obtained for microscopic simulations of the F center aggregation in CaF_2 crystals used as optical windows and potentially, in lithographic applications. We focus on the aggregation process *after* irradiation when a crystal is heated a given rate.

2. A model

Our physical model includes creation of the H and F centers (called hereafter defects A and B), with the dose rate p, AB pairs are not spatially correlated at birth and recombine when during their migration approach each other to within the nearest-neighbor (NN) distance. Therefore, their macroscopic concentrations always coincide, $n = n_A = n_B$. Isolated (single) defects hop with the activation energy E_λ is characterized by the diffusion coefficient $D_\lambda = D_0 \exp(-E_\lambda/k_B T)$, $\lambda = A, B$. When several defects are closely spaced, the hop rate of a given defect to the nearest empty lattice site is determined by both the local defect configuration and the interaction between defects; this can change its *effective* diffusion coefficient D_λ^{eff} by many orders of magnitude compared to that for a single defect. It affects the effective reaction rate K of the A and B recombination; for the dilute particle system in the continuum approximation it is well known to be $K_0 = 4\pi r_0(D_A + D_B)$, where r_0 is the recombination radius. Defect interaction is incorporated in the model via three types of the NN attraction energies for the two kinds of NN defects (in the spirit of the Ising model): E_{AA}, E_{AB} and E_{BB}. Namely, particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) phenomena under the irradiation.

The experimental estimates of the activation energies for H and F centers in CaF_2 are 0.46 and 0.7 eV [9]. The attraction energies determining the H and F center attachment/detachment to/from similar-particle aggregates are less known. Calculations of the elastic interaction between F centers in KBr give the attraction energy about 0.02 eV [10]. This value will also be used in our calculations; for simplicity we assume that $E_{AA} = E_{BB}$ and $E_{AB} = 0$. In our calculations we simulated the experimental conditions of the low-energy electron irradiation [3] characterized by the dose rate about $p = 10^{17} cm^{-3} s^{-1}$, which lasts for 30 min, with a subsequent heating at the rate of 1.3 K/min.

The *mathematical formalism* and the relevant computer code *Kinetica* will be described in detail elsewhere [11], it is a generalization of our previous microscopic many-point density approach [7] for the discrete-lattice case. This allows us to avoid the limitations of a continuum model, to increase the computation speed and thus to study the aggregation kinetics in a very wide time interval, exceeding many orders of magnitude. Theory is based on the Kirkwood superposition approximation for the three-particle densities. This formalism operates with a set of coupled kinetic equations for the lattice defect densities (total concentrations) $n_\lambda(t)$, $\lambda = 0, A, B$ and the joint correlation functions $F_{\lambda\nu}(|r_\lambda - r_\nu|, t)$ where r_λ and r_ν are coordinates of two lattice sites and t the time. Since defect correlations are short-range, $F_{\lambda\nu}(r, t)$ strives for its asymptotic value of the unity (random particle distrubution), as the relative coordinate increases, $r \to \infty$. That is, if some joint density $F_{\lambda\nu}(r, t)$ considerably exceeds the unity value, it means surplus of the defect pairs $\lambda\nu$ at a given relative distance compared to their random (Poisson) distribution, and vice versa. The simultaneous analysis of the joint correlation functions for similar (AA, BB) and dissimilar (AB) pairs, as well as for 0A, 0B pairs (empty site-defect) permit to study the *spatio-temporal* evolution of the strongly non-equilibrium system, in particular, crystals with radiation defects [7,11].

It is also convenient to characterize the aggregation process by monitoring the concentrations of *single* defects $n_\lambda^{(1)}$ (no other defects in NN sites) and *dimer*

defects $n_\lambda^{(2)}$ (two similar defects are NN), which could be calculated from the joint densities in the standard *cluster approximation* [12]. Lastly, large defect aggregates could be characterized by the integral values of the mean number of particles N_A, N_B therein and their radii R_A and R_B.

3. Main results

Let us study the kinetics of defect concentration growth under CaF_2 irradiation at low temperatures when the F centers are definitely immobile but the H centers are moving either slowly (150 K) or already quite mobile (193 K). The first conclusion from the upper curve in Fig. 1 plotting a total concentration of H- (and F) defects is that at the end of irradiation (shown by an arrow) we are still in almost a linear regime of the defect accumulation. Under such a dose rate the concentration saturation could be expected only after 2–3 h of irradiation. Additional calculations show that neglect of the defect interaction would lead to one-to-two orders of magnitude reduction in defect concentrations at the end of irradiation (where a real saturation takes place), $n \approx 10^{18} \, cm^{-3} \, s^{-1}$, accompa-
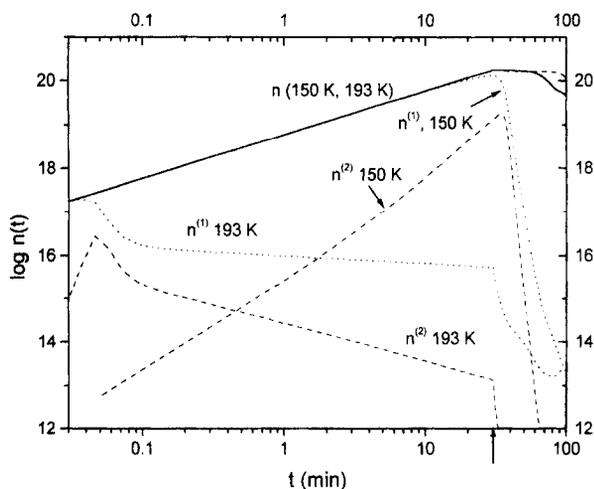
nied by a very fast recombination when irradiation is switched off.

Fig. 1 shows that total concentrations of H centers almost coincide at the two temperatures, H concentration at 150 K irradiation exceeds that at 193 K irradiation only at $t > 70 \, min$ when irradiation is switched off and sample is heated up by $\approx 30 \, K$. It is well seen that at a certain time t_0 concentration of single H centers, $n^{(1)}$, sharply descreases due to growth of dimer concentration, $n^{(2)}$, and the latter drops also due to growth of larger aggregates. The time t_0 decreses by three orders of magnitude when the irradiation temperature increases from 150 up to 193 K.

It should be reminded that F centers are complementary to the H centers and thus their total concentrations always coincide. At temperatures shown in Fig. 1 the F centers are immobile and their aggregation occurs only during sample heating *after* an irradiation. Let us consider this process.

Curves 1 in Fig. 2 show that the aggregate's size for the F centers and a mean number of defects therein begin to grow only at 250 K when the F centers become mobile. This temperature is in qualitative agreement with the experimental data on colloid growth in CaF_2 [3] as well as growth of M_A center concentration under pulsed electron irradiation of crystals doped with Na [13].

However, the electron irradiation experiments reveal small (1–2 nm in radius) aggregates of the F centers, whose size remains constant until heating up to 250 K. The fact that aggregate's size is independent of the irradiation temperature indicates for a process which takes place during irradiation and is characterized by a low activation energy (condsiderably less than that for the F center diffusion). To our mind, there are two candidates for this radiation-induced process. (i) Radiation-enhanced F center migration when the F center traps a hole, converts into an anion vacancy whose diffusion energy is about 0.4 eV, makes several hops and transforms (sooner or later) again into the F center after trapping an electron. (ii) Self-trapped excitons, making a diffusion motion with the activation energy not exceeding 0.4 eV, decay into pairs of the F, H centers not in regular lattice sites but preferentially nearby pre-existing F centers (e.g., due to drift
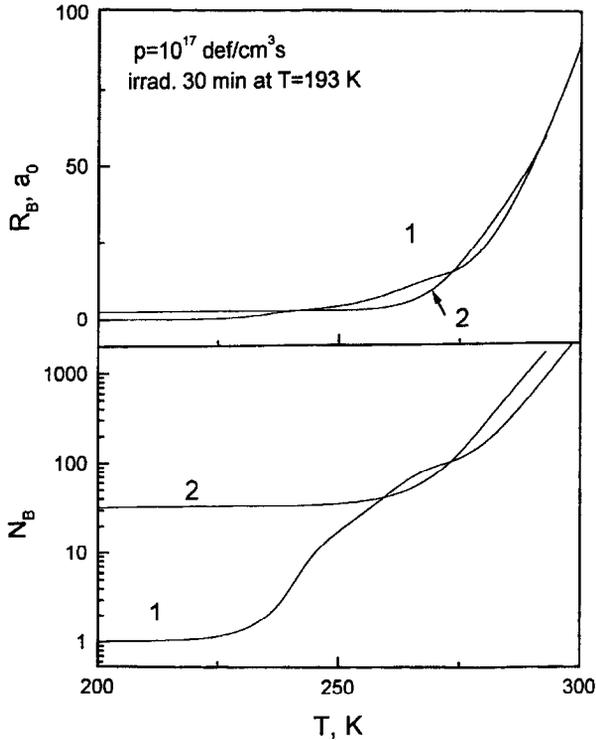

Fig. 1. Dynamics of the H center aggregation with the dose rate $p = 10^{17} \, cm^{-3} \, s^{-1}$ for irradiation at 193 and 150 K. The quantities n, $n^{(1)}$ and $n^{(2)}$ are total concentration, concentration of single and dimer centers, respectively. The end of irradiation is marked by an arrow.

Fig. 2. Heating-induced growth of the mean radius of F aggregates, R_B (in units of the F–F distance, $a_0 = 2.73\,\text{Å}$), and a mean number of particles inside each aggregate, N_B. Curves 1 are for standard parameters described in the text, in curves 2 the activation energy for the radiation-enhanced F center diffusion is 0.4 eV.

in a lattice stress caused by defects). High mobility of the self-trapped excitons in CaF_2 is known from an efficient exciton energy transfer from host lattice to impurities [14]. In fact, in the second case F center aggregation induced by irradiation is again analogous to the radiation-enhanced F center diffusion with a reduced activation energy.

To simulate the radiation-enhanced process under question, we performed calculations with the F center activation energy of 0.4 eV under irradiation and 0.7 eV after irradiation. Curves 2 in Fig. 2 show remarkable agreement with the experiment – formation of small F aggregates with a radius of several nm which transform into larger aggregates at the temperatures when F centers are mobile. Evidently, it occurs via a slow motion of these small aggregates, as well as emission of F centers from small aggregates and

their attachment to larger aggregates. This is nothing but the so-called Ostwald ripening. Unfortunately, due to computational difficulties we cannot study the latest stage of the large aggregate growth, but its typical size of $100a_0 = 27\,\text{nm}$ is close to the experimental value (25 nm).

The analysis of the kinetics of the total F center concentration, as well as that for single F centers and F_2 dimers, plotted as a function of the temperature shows that at 200 K practically only single F center exists in the concentration close to $10^{21}\,\text{cm}^{-3}\,\text{s}^{-1}$ whereas concentration of dimers is smaller by three orders of magnitude. As the temperature reaches that of the F center mobility, 250 K, both concentrations drop by many orders of magnitude. However, the total F concentration decreases insignificantly thus indicating that most of the F centers are gathered now into large aggregates (colloids). This is another confirmation to what we concluded from Fig. 2.

Simulations of the radiation-enhanced F center mobility show that due to formation of small aggregates at low temperature, concentrations of F and F_2 centers are additionally reduced by 6 and 10 orders of magnitude, respectively. They decrease at 250 K, as in the previous case, when the F centers perform diffusion walks and thus could encount each other and aggregate.

Calculations of the *effective diffusion coefficient*, D_A^{eff}, show that the H centers (which are mobile under the irradiation temperature) are aggregated very quickly, in fractions of a minute. This reduces H average diffusion coefficient by two orders of magnitude as compared with the diffusion of free H centers in a regular lattice. In fact, at this stage the main contribution to the mobility comes from newly created H centers before they join aggregates. After the irradiation is finished, the mobility drops down additionally because no free H centers are created any longer. Upon heating, the effective diffusion coefficient begins to increase because of the separation of some of H centers from their aggregates and their recombination with the F centers. This recombination is an important factor for a considerable growth of the H center aggregates which takes place simultaneously with the aggregation of the F centers, at $T > 250$ K. Recombination

results in disappearance in the region around small H aggregates of dispersed F centers. This creates an additional free space necessary for a further considerable growth of the H aggregates.

Unlike the H centers, the F centers remain immobile up to the time $t_0 = 60$ min when the temperature approaches F center mobility edge. However, if the radiation-enhanced F center diffusion takes place, mobility of the F centers during irradiation is close to that for the H centers and the F centers begin to aggregate already at low temperatures (see curves 2 in Fig. 2). However, growth of large F aggregates begins at any rate much later, at $T > 250$ K.

It is interesting to compare the above-said with the irradiation at high temperatures when *both* H and F centers are very mobile. To this end we performed calculations for the irradiation at room temperature, 300 K. In agreement with experiments, a concentration of electron centers (metal area) at the end of irradiation is nearly the same as at low-temperature irradiation. Unlike $T = 193$ K, now we observe growth of the F aggregates *during* the irradiation. However, the mean size of this aggregate remains small ($R_B < 10a_0$ after 30 min) due to the efficient F–H recombination. This is again in agreement with experiments. When the irradiation is switched off, the F aggregates begin to grow. This process could be well illustrated by the analysis of the joint correlation functions characterizing the relative *spatial distribution of defects* (Fig. 3).

Large magnitudes of the joint correlation functions of similar defects, F_{AA}, F_{BB}, at short relative distances clearly demonstrate the strong aggregation of *both* H and F centers. At the end of irradiation (Fig. 3(a)) the relative distance of $r \approx 10a_0$, where F_{BB} (curve 2) approaches the asymptotic value of unity, agrees with the above-mentioned calculation of the effective radius R_B. The effective radius of the H aggregates is larger, about $30a_0$. After 25 min of heating up to 330 K (Fig. 3(b)) these radii increase significantly, up to $R_B \approx 30a_0$ and $R_A \approx 70a_0$, respectively.

The correlation function for the dissimilar defects, $F_{AB}(r)$ (curve 4), is anti-correlated to F_{AA}, F_{BB}. At the end of irradiation it increases from zero at $r \leq a_0$ up to unity at $r \approx 30a_0$, which gives us an estimate of the average distance *between* H- and F aggregates.
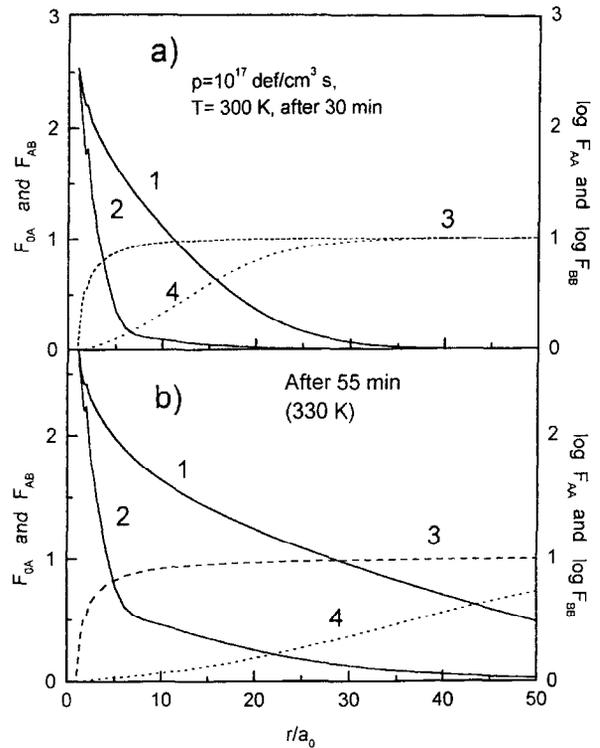

Fig. 3. The joint correlation functions vs. the dimensionless relative distance r between defects for irradiation at 300 K; (a) corresponds to the end of irradiation, whereas (b) after subsequent 25 min heating (up to 330 K). Curves 1 and 2 demonstrate the H–H and F–F correlations, curve 3 the "empty site-F center" correlation, and curve 4 the correlation of dissimilar defects (F–H). Note that F_{AA} and F_{BB} are plotted in the semi-logarithmic scale.

Lastly, the joint correlation function "empty site-F center", F_{0A}, curve 3, shows that these aggregates have small, dense cores (there is almost no empty sites in their centers) but they are quite loose on their periphery, $r \geq 10a_0$.

4. Conclusion

The presented microscopic theory of diffusion-controlled radiation defect aggregation reproduces main experimental results on the electron-irradiated CaF_2 and permits to understand the mechanism and kinetics of this process. First conclusion is that small metal colloids observed under irradiation at low temperatures ($T \approx 200$ K) can arise only due to

radiation-enhanced F center diffusion. Study of its mechanism is of great interest. Another conclusion is that metal colloids have a dense core but could be rather loose at their periphery. Growth of the F aggregate occurs simultaneously with that for the H centers. Theory shows that the critical temperature at which begins an intensive F center aggregation is defined not only by the activation energy of the F center diffusion but significantly affected by the interaction energy between F centers and their aggregates; this determines the rate of a single F center attachment/detachment to the aggregate necessary for the transformation of small metal colloids into larger colloids (Ostwald ripening).

Acknowledgements

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