

THE KINETICS OF DEFECT AGGREGATION AND METAL COLLOID FORMATION IN IONIC SOLIDS UNDER IRRADIATION

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Results of a microscopic theory describing diffusion-controlled aggregation of radiation Frenkel defects — F and H centers — are discussed. We suggest interpretation of experimental data on metal colloid formation in the two ionic solids with different crystalline structures — LiF and CaF₂ — observed under electron irradiation with subsequent heating. Theory successfully reproduces the main experimental observations including Ostwald ripening of small colloids into large colloids in the narrow temperature interval and suggests that radiation-enhanced F center diffusion occurs in CaF₂ with as low activation energy as 0.4 eV. In contrast, the activation energy for a single F center diffusion in LiF is found to be as high as 1.5 eV. The key role of mutual defect elastic attraction in their aggregation is demonstrated.

Keywords: Radiation defects; F , H centers; Defect aggregation; Metal colloids; Diffusion-controlled reaction; Defect interaction; Precipitation and ripening; Ionic solids; LiF; CaF₂

1. INTRODUCTION

It is well known that the primary radiation defects in binary ionic solids — the F center (electron trapped by an anion vacancy) and the H center (interstitial halide atoms) — aggregate under intensive irradiation at temperatures high enough to allow defect diffusion. This leads to the formation of *alkali*

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metal colloids (see [1] and references therein), and this process is generally believed to occur via diffusion-controlled aggregation of single F centers. Their smallest aggregate centers ($F_2(M)$, $F_3(R)$, *i.e.* two and three anion vacancies with trapped electrons) can be identified by characteristic optical absorption bands, whereas large aggregates transform into metal colloids with a broad optical extinction band. Intensive optical studies of the small F -center aggregates and metal colloids have been undertaken for many alkali and alkaline-earth halides [1].

Irradiated LiF crystals are of special interest since they provide excellent thermal stability for complex colour centers, and are used, *e.g.*, for dosimetry [1] and laser applications [2, 3]. Despite numerous experimental studies of the F center aggregates produced in LiF under different kinds of irradiation [2–7], the *kinetics* of the F center aggregation leading to the metal colloid formation is not well understood. In particular, there is uncertainty in the experimental (indirect) estimates of the activation energies for the single F center activation energy for diffusion hops. There exist several indirect estimates of the diffusion energy published in the literature, *e.g.*, 0.66 eV [8] and 0.85 eV [3]. Recently, F center aggregation kinetics in LiF upon irradiation with low energy electrons at 300 K with focus on Li colloid growth during annealing after irradiation was studied in Ref. [9].

A study [9] of a series of absorption spectra for low temperatures, where, F and M centers are predominant, has clearly demonstrated that during heating the F centers and dimer-, trimer-centers transform into a broad band at 2.9 eV associated with Li metal colloids [4]. The F -type center aggregation is accelerated above 360 K and is completed at 490 K. The observed shape of the 2.9 eV band is typical for the extinction due to spherical metal colloids, which can be calculated from the Mie theory [10, 11]. This theory has been successfully applied to the analysis of colloid extinction bands in many alkali halides and alkaline earth fluorites [1]. However, for the LiF data [9] the optical absorption bands cannot be well fitted using simple Mie theory. Most probably, this is caused by a non-spherical shape of Li metal colloids, which is in agreement with earlier conclusions that these colloids have a *platelet* morphology [4, 12]. The great difference between LiF and say, CaF_2 crystals is that in the latter the free Ca metal lattice almost perfectly matches its sublattice in CaF_2 , whereas in LiF the Li sublattice constant is much smaller than for a free Li metal (the

difference in a volume of the unit cell is as big as 25%) and also the crystal-line structure is different. The initial F center concentration can be estimated as the ratio of the area density to the electron penetration depth (about 10^3 Å for 2.5 eV electrons [13]) which gives $n_0 = 6 \cdot 10^{20} \text{ cm}^{-3}$.

A similar study has been also performed for CaF_2 crystals [14] which is an important material for optical components and nano-lithography. In this study no single F centers have been detected, even under irradiation at temperatures as low as 200 K, only a broad absorption peak was observed and attributed to colloids. Upon subsequent heating this peak undergoes a transformation in position and shape until it is stabilized at a certain temperature. It was found that Mie theory describes this peak well. The extracted colloid radius rapidly grows up to 20–25 nm within a narrow temperature interval around 250 K where the F centers become mobile. The beginning of the F center mobility around 250 K is supported by several independent experiments. However, it is unclear why no single F centers are observed in above mentioned experiments at 200 K. Another question is why colloid growth due to diffusion-controlled F aggregation is not accompanied by significant decrease of the metal area density as a result of F – H center recombination. It should be noted that metal colloid formation was also intensively studied in detail in NaCl using an irradiation at various but constant temperatures [15]. In this paper we suggest an interpretation to above-mentioned results for irradiated and heated LiF and CaF_2 .

2. THEORY

Existing theories of radiation-induced defect aggregation and colloid formation can be classified, in terms of the mathematical formalisms used, into three categories: macroscopic, mesoscopic and microscopic [16]. The *first, macroscopic* approach is based on rate equations and contains many parameters like reaction rates which should be found from independent experiments or calculations. Any spatial inhomogeneities in reactant distribution and their interactions are neglected here [17]. The latter two effects are taken into account in the *mesoscopic* theory [18] which is suited to study conditions (dose rate, defect mobilities and defect interactions) under which spatial local fluctuations in defect densities are no longer damped but increase in amplitude. This results in breaking of the

translational symmetry of the homogeneous defect distribution via the *spatial modulation* of the average defect concentrations. However, this formalism is unable to predict the time development (*kinetics*) of defect accumulation under irradiation, which is experimentally measured.

Lastly, the most refined and accurate microscopic formalism, used in this paper, treats basic processes on the atomic level and uses no *a priori* parameters except diffusion coefficients of defects and their interaction energies which can be calculated quantum mechanically. Mathematically, the relevant formalism of many-particle densities is based on the coupled kinetic equations for *joint densities* of similar and dissimilar defects (vacancies and interstitials) treated in terms of a modified Kirkwood superposition approximation [19]. Combination of all three approaches is important for understanding the entire process of colloid formation. Critical comparison of mesoscopic and microscopic formalisms was presented in Ref. [20].

A qualitatively new feature of our microscopic (atomistic) theory compared to several previous (macroscopic or mesoscopic) approaches is the direct incorporation of the effects of relative spatial distribution of similar (F - F , H - H) and dissimilar (F - H) defects. This is done in terms of three kinds of the *joint correlation functions*, $F_{ij}(r, t)$, $i, j = F, H$. The spatial correlations of the F and H centers turn out to be closely related and strongly affect the reaction kinetics. For instance, the aggregation of F centers results in decrease of the concentration of close F, H pairs and thus increases their average distance, as compared to the random defect distribution. In its turn, this strongly reduces the rate of the F, H recombination. Another new feature of theory is incorporation of *similar defect interactions* into diffusion-controlled kinetics, which qualitatively changes the defect average mobility due to similar defect aggregation and thus the reaction kinetics under study. As a result, our kinetic equations, unlike previous simple theories, turn out to be strongly non-linear. In fact, we solve a set of 35 coupled equations for the macroscopic defect concentrations, joint correlation functions, effective interaction potentials, etc.

In our calculations dealing with the initial stages of colloid formation, we consider the creation of F and H centers with a given dose rate and their recombination when, during their random walks in a lattice with the diffusion coefficients D_F and D_H , defects approach each other to within the nearest neighbour (NN) distance. Defect interaction is incorporated in our model via NN attraction energies between similar defects, E_{FF} and E_{HH} .

Thus, the input parameters for colloid growth simulations are activation energies for diffusion, E_F and E_H , and attraction energies between defects, as well as the temperature and dose rate p (which in present experiments is estimated as $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$). The activation energy for H center diffusion in LiF is 0.15 eV [21] whereas for the F centers the relevant energy is uncertain. This is why we have modelled the F aggregation kinetics varying the F center activation energy from 1 to 1.5 eV. In CaF_2 we use the diffusion energies for the H and F centers to be 0.46 eV and 0.7 eV [22]. The attraction energies determining F and H center attachment/detachment to/from similar-particle aggregates are even less well known. Calculations of the elastic interaction between two nearest F or H centers in KBr yield an attraction energy of about 0.04 eV [23]. This value we also used in our calculations as an initial guess. For simplicity we assume that similar particle interactions are equal for different defects, *i.e.* $E_{\text{int}} = E_{FF} = E_{HH}$.

We calculate the time development of both, electron and hole defect *total* concentrations (which are densities of all defective lattice sites, *i.e.* the total concentration of F -type centers is nothing but a combination of single, dimer, trimer and higher aggregate concentrations), $n_F(t) = n_H(t)$, as well as concentrations of single (isolated) defects (no other defects in NN lattice sites) and *dimer* defects (two similar defects are NN). Larger aggregates are characterized by the integral values of the number of particles N_F , N_H therein and their radii R_F and R_H . Large aggregates of F centers transform into metal colloids.

3. MAIN RESULTS

3.1. LiF

During irradiation at 300 K the H centers are quite mobile. The temporal evolutions of the total H -type center concentration, as well as single H and dimer H_2 centers are plotted in Figure 1. It is seen that due to fast aggregation of the H centers at the very early stages of irradiation the concentration of H_2 centers rapidly increases and approaches that of single H centers. This is why after a short time t_0 the single H center concentration begins to decrease. Intensive H -aggregation leads to an almost simultaneous decrease of the density of H_2 centers due to a growth of larger H

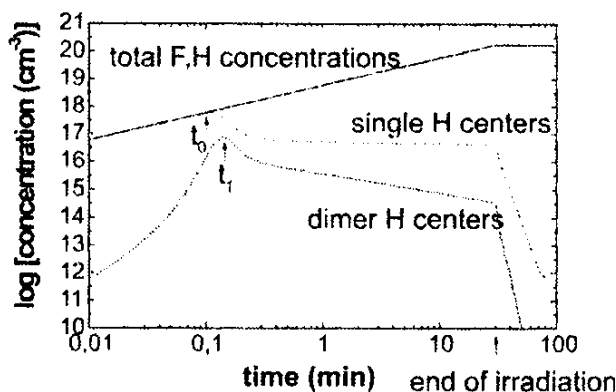


FIGURE 1 Prediction of the F , H center and H_2 aggregate center concentrations growth in LiF for a defect production rate of $10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ [9].

aggregates at time t_1 . This process is greatly enhanced by sample heating after irradiation.

In its turn, up to 100 min all F centers are immobile and thus remain single. Their concentration grows linearly with irradiation time (Fig. 1) exceeding $3 \times 10^{20} \text{ cm}^{-3}$, *i.e.* several percent of the fluorine lattice sites are occupied by F centers. This is in agreement with experimental data [9]. F center aggregation begins only after sample heating up to 350 K. We calculated the decay kinetics of the total F -type defect concentration and concentration of the single F centers for three activation energies of diffusion, varying it from 1 eV to 1.5 eV and assuming a defect interaction energy of 0.04 eV. Calculations for 1 eV diffusion energy yield a very sharp F center decay clearly contradicting the experimental data whereas for the 1.2 eV and 1.5 eV diffusion energies the F center concentration decays much smoother and the temperature range agrees well with experimental data [9].

The relevant calculations of the aggregate radius and of the number of F centers inside aggregates show that for a diffusion energy of 1.5 eV both quantities grow considerably above 350 K reaching a radius of 22 nm containing more than 10^5 defects at 425 K. Calculations for the F center activation energies of 1.2 eV and 1.5 eV predict a considerable decay of the total F center concentration due to a recombination of a considerable fraction of the isolated F centers with aggregates of the H centers, which happens when mobile F centers start random walks instead of joining other F centers or their aggregates. The experiments show much smaller decay of concentrations and do not yield information on H aggregates whose optical absorption lie in the UV. Probably, in reality most of the H centers are

not accumulated in loose aggregates in the bulk, as is assumed in our model, but disappear in dislocation loops and probably a large portion of them is desorbed from the surface.

The interaction between the defects strongly affects the F center aggregation kinetics; an interaction energy increase by 25 to 30% (0.03–0.04 – 0.05 eV) shifts the F center decay temperature up by 50 K. Obviously, this is a result of the F center recombination with mobile H centers escaped from their aggregates: the higher an attraction energy between defects inside the aggregate, the stronger H defects are bound to each other and respectively, the higher the temperature at which a fraction of them can be released from the aggregates and recombine with the F centers.

CaF₂

We calculated the kinetics of defect concentration growth under CaF₂ irradiation at low temperatures when the F centers are definitely immobile but the H centers are moving either slowly (150 K) or are already quite mobile (193 K). With the dose rate of $p = 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$ corresponding to the experimental conditions [14], until the end of 30 min irradiation the defect concentration grows still almost linearly with time; the concentration saturation is expected after 2 h of irradiation only. The magnitude of the defect concentration achieved (10^{20} cm^{-3}) agrees well with the experimental value. The simulation of a very intensive irradiation exceeding that used in the experiments by three order of magnitude [14], gives a theoretical prediction of the saturation concentration of $10^{22} \text{ cm}^{-3} \text{ s}^{-1}$. Calculations clearly demonstrate that neglect of defect interaction leads to up to two orders of magnitude reduction in defect concentrations under their saturation and a very fast recombination when irradiation is switched off.

The analysis of the time development of a total H -aggregate concentration, single and dimer centers shows that total concentrations of H centers monotonously grow and almost coincide at the two temperatures as $t_0 < 70$ min when irradiation is switched off and the sample is heated up by about 50 K. In contrast, as for LiF (Fig. 1), the concentration of single H centers starts to decrease rapidly due to the increase of dimer concentration, and the latter drops also at a certain time t_0 due to growth of larger aggregates. The time t_0 decreases by three orders of magnitude when the irradiation temperature increases just by 43 K, from 150 K up to 193 K. The F centers

at these temperatures are still immobile and their aggregation occurs only under sample heating after irradiation. For the defect interaction energy $E_{\text{int}} = 0.02$ eV the size of F center aggregate (curve 1 in Fig. 2a) and the mean number of defects therein (curve 2 in Fig. 2b) start to grow at 250 K, just when the F centers become mobile. This temperature is in good agreement with the experimental data discussed above as well as with the temperature characterising the rapid growth of M_A center concentration in Na-doped crystals under pulsed electron irradiation, which also occurs through F center diffusion [24]. Small increase of the interaction energy even by 0.01 eV considerably shifts the colloid growth process to higher temperatures (curve 2 in Fig. 2a).

For the F center diffusion energy of 0.7 eV no F center aggregation can take place below 250 K. However, the electron irradiation experiments reveal small (1–2 nm in radius) aggregates of F centers, which size remains constant until heating up to 250 K. This indicates a process which takes place during irradiation and is characterized by a low activation energy (considerably less than that for the F center normal diffusion). These are two speculative *scenarios* for such radiation-induced processes.

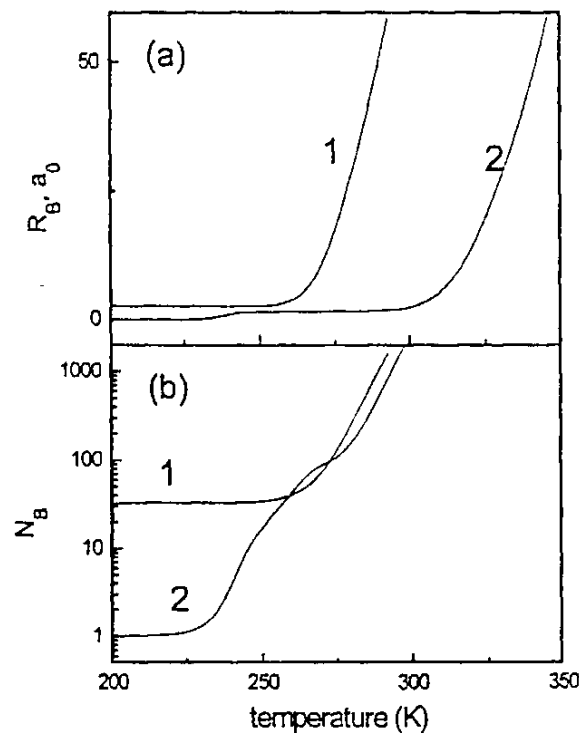


FIGURE 2 (a) Heating-induced growth of the mean radius R of F aggregates in CaF_2 (in unit of the F - F distance, 2.73 Å). (b) Mean number of defects in each aggregate, N . Curves 1 and 2 in (a) are for defect attraction energies of 0.02 and 0.03 eV, respectively. In (b) curve 1 shows the effect of the radiation-enhanced F center diffusion whereas in curve 2 it is neglected [14].

(i) Radiation-enhanced F center migration when the F center traps an unrelaxed hole, which are present in large concentrations under irradiation, converts into an anion vacancy, with diffusion energy of about 0.4 eV, makes several hops and transforms sooner or later again into the F center by trapping an electron. (A similar mechanism was presented in the mid-60's in semiconductors by J. Corbett). (ii) Self-trapped excitons possessing diffusive motion above 160 K, could decay into a pair of the F , H centers not in a regular lattice sites but preferentially nearby pre-existing F centers (e.g., due to drift in a lattice stress caused by F centers). High mobility of the self-trapped excitons in CaF_2 is known from an efficient exciton energy transfer from host lattice to impurities in $\text{CaF}_2:\text{Eu}$ [25]. At room temperature its lifetime is estimated to be as long as 10^{-5} s [26]. Decay of excitons in the vicinity of pre-existing defects was indeed demonstrated for doped KCl crystals [27]. In fact, in the second mechanism F center aggregation induced by irradiation is again analogous to the F center diffusion but with a reduced activation energy.

To simulate such a radiation-enhanced process, we performed calculations for the F center effective activation energy of 0.4 eV under irradiation and with usual energy of 0.7 eV after irradiation. Curve 1 in Figure 2b demonstrates formation of stable small F aggregates with a radius of several nm. These small aggregates transform into larger aggregates *only* at temperatures above the F center mobility edge (remember that the critical temperature depends also on the interaction energy). Unfortunately, due to computational difficulties we cannot follow the latest stage of the large aggregate growth but the typical size reached by the aggregate, $R = 100 a_0 = 28$ nm, agrees qualitatively with the experimental value (25 nm).

Analysis of the the calculated dynamics of the total F center concentration as a function of the temperature shows that it decreases insignificantly during heating up to 350 K, in agreement with experiment and thus indicating that most of F centers have transformed now to large aggregates.

Important information about F center aggregation comes from calculations of the effective diffusion coefficient [19]. This decreases by three orders of magnitude at $t = 80\text{--}90$ min which corresponds to the beginning of the F mobility at $T = 250$ K. Stabilization of D^{eff} means formation of stable aggregates where defects are bound by mutual attraction. This is in a dynamical equilibrium with the single F centers leaving and joining the aggregates. At high enough temperatures the aggregates must disappear

since attraction energy becomes small compared to the thermal energy kT . The stronger attraction between defects, the lower is the effective F center mobility.

Defect aggregation is accompanied by a great decrease in the F and H recombination rate K [19b]. First, K drops rapidly in the very beginning of irradiation — by three orders of magnitude in about a minute. Its stabilized value does not depend on the attraction energy between defects. This is caused by the fast H center aggregation discussed above. As a result, such H aggregates are quite immobile which prevents H and F recombination. The main contribution to the recombination comes from newly created

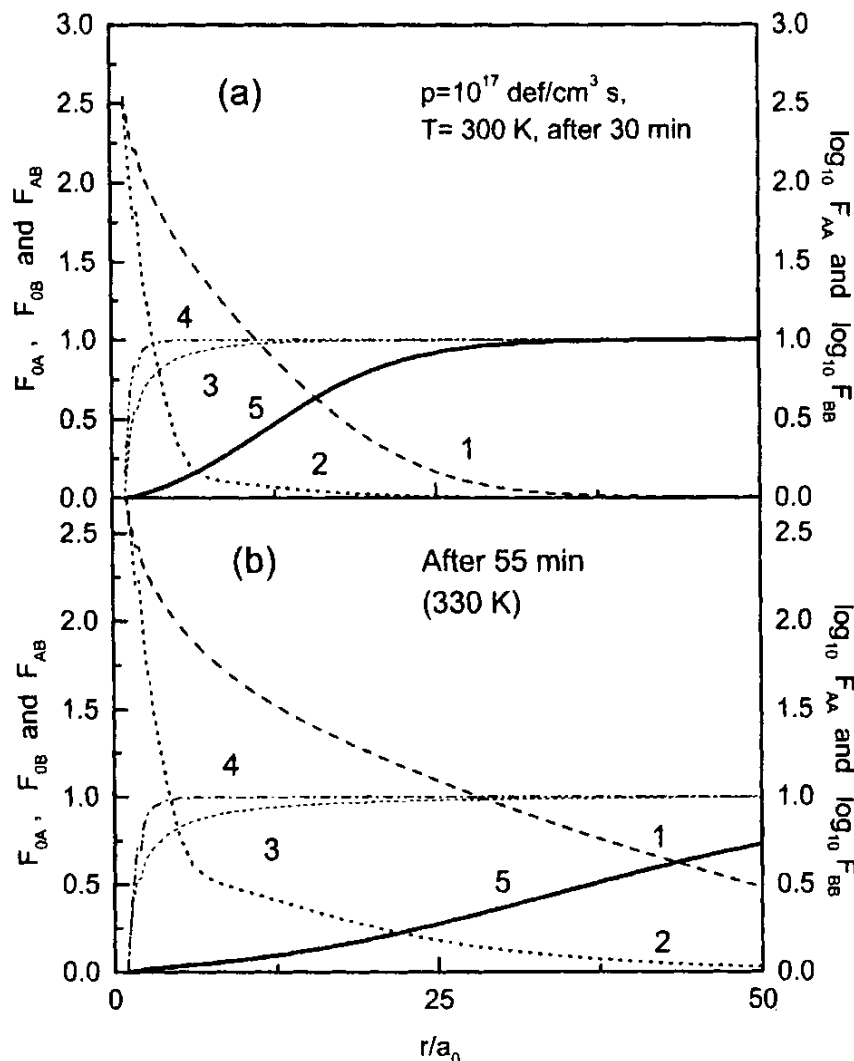


FIGURE 3 The joint correlation functions $F_{ij}(r)$, $i, j = 0$ (empty site), A-defect (H center), or B-defect (F center) vs the relative distance r between defects in CaF_2 (in units of F - F distance). (a) corresponds to the end of irradiation whereas (b) shows relative defect distribution after subsequent 25 min heating. Curves 1 and 2 demonstrate the H - H and F - F center spatial correlations, curves 3 and 4 empty site— F center, and empty site— H center correlations, curve 5 correlations of dissimilar (F - H) defects. Note semilogarithmic scale for F_{HH} and F_{FF} [14].

centers whose concentration is proportional to the dose rate p . This is why, when irradiation is switched off, the reaction rate reduces additionally, by an one-two orders of magnitudes.

Lastly, the spatial correlations of similar and dissimilar defects could be easily seen in the joint correlation functions shown in Figure 3. Large values of the correlation functions of similar defects F_{AA} , F_{BB} ($A = H$ center, $B = F$ center, note there logarithmic scale) at short relative distances r clearly demonstrate a strong aggregation of both H and F centers. At the end of irradiation shown in (a) a relative distance where F_{BB} (curve 2) approaches the unity is $r = 10 a_0$. This gives an estimate of the aggregate radius. The effective radius of the H aggregates is larger, $30 a_0$. After 25 min of heating shown in (b) the radii of the F and H aggregates increase to $30 a_0$ and $70 a_0$, respectively. The correlation function of dissimilar defects F_{AB} (curve 5) is anticorrelated to F_{AA} and F_{BB} . At the end of irradiation, it increases from zero at $r < a_0$ up to unity at $r = 30 a_0$ which gives us an estimate of the average distance between H and F aggregates. The analysis of the correlation functions of empty site with the H or F center (curves 3 and 4) shows that these aggregates have small, dense core (there are almost no empty sites in their centers) but they are quite loose on their periphery, $r > 10 a_0$.

4. CONCLUSIONS

Initial stages of the F center aggregation kinetics and the relevant metal colloid formation depend on *both* the F center mobility (controlled by the activation energy for diffusion) and the defect attraction energies inside aggregates of F and H centers (E_{FF} and E_{HH} , respectively). Similar defect aggregation and colloid formation strongly reduce the F - H recombination rate and thus permit the accumulation of much larger total defect concentrations as compared to the kinetics for non-interacting defects. Based on our computer modelling, the F center diffusion energy in LiF is about 1.5 eV, considerably larger than estimated previously. In contrast, small metal colloids observed in CaF_2 under irradiation at low temperatures ($T \approx 200$ K) arise most likely from radiation-enhanced F center diffusion or preferential exciton decay characterised by the activation energy of 0.4 eV.

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