Effect of radiation-induced emission of Schottky defects on the formation of colloids in alkali halides
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Formation of vacancy clusters in irradiated crystals is considered taking into account radiation-induced Schottky defect emission (RSDE) from extended defects. RSDE acts in the opposite direction compared with Frenkel pair production, and it results in the radiation-induced recovery processes. In the case of alkali halides, Schottky defects can be produced as a result of the interaction of extended defects with excitons, as has been suggested by Seitz in 1954. We consider a model that takes into account excitonic mechanisms for the creation of both Frenkel and Schottky defects, and which shows that although the contribution of the latter mechanism to the production of primary defects may be small, its role in the radiation-induced evolution of microstructure can be very significant. The model is applied to describe the evolution of sodium colloids and the formation of voids in NaCl, which is followed by a sudden fracture of the material, presenting a potential problem in rock salt-based nuclear waste repositories. The temperature, dose rate and dose dependence of colloid growth in NaCl doped with different types of impurities is analyzed. We have found that colloid growth may become negative below a threshold temperature (or above a threshold dose rate), or below a certain impurity concentration, which is determined by the RSDE, that depends strongly on the type and concentration of the impurities. The results obtained with the model are compared with experimental observations.
sub-lattice is not damaged in the primary displacement process. The H center is an interstitial halide ion with a trapped hole, and an F center is a vacancy in the halide sub-lattice with a trapped electron. We have proposed that \( V_F \) centers (a cation vacancy with a trapped hole) can be created as secondary reaction products as a result of interactions between H centers and dislocations [7–9] and we have developed a model for the evolution of sodium colloids and chlorine bubbles in NaCl resulting in the formation of voids followed by sudden fracture of the material, which is in qualitative agreement with experimental data [4–6]. An important experimental observation that still needs to be clarified is that a majority of impurities strongly facilitate the colloid growth as compared to the nominally “pure” crystals (containing about 100 appm (atomic parts per million) of unintentional contaminations). In order to explain this observation it was necessary to assume that the dislocation density varies by two orders of magnitude as a function of the dopant (Fig. 1), which is rather unlikely and it has so far not been supported by experimental data either.

In our model we have assumed (as it is commonly believed) that (i) the primary radiation-induced defects are exclusively Frenkel pairs consisting of H and F centers and (ii) that they are produced in the bulk crystal. However, as has been suggested recently in [10], the surfaces of the EDs can act as a source for the production of radiation-induced Schottky defects that do not exist in the bulk. A Schottky defect is (1) a single vacancy or (2) a self-interstitial atom (SIA), or (3) a small defect aggregate, which can be ejected from the ED surface and in that case it does not require a counterpart of the opposite sign in contrast to the bulk production of Frenkel defects, in which the total numbers of vacancies and SIAs must be equal. By

![FIGURE 1 Comparison of the experimental data obtained for the dose dependence of the colloid volume fraction (which is proportional to the latent heat of melting (LHM) of Na) in crystals doped with different impurities and irradiated at 100 °C, at a dose rate of 240 Mrad/h with theoretical results obtained for different dislocation densities [9].](image-url)
In the present work, radiation-induced emission of Schottky defects from EDs in alkali halides is considered. This mechanism is based on the interaction of EDs with excitons produced by ionizing irradiation, as has been first suggested by Seitz in 1954 [11]. The mechanism is applied to modeling of the evolution of sodium colloids in irradiated NaCl. The temperature, dose rate and the dose dependence of colloid growth in NaCl crystals is considered as a function of the dopant type and concentration. It is shown that the colloid growth may become negative below a threshold value for the temperature (or above a threshold value for the dose rate), or below a certain value of the impurity concentration, which depends on the mechanism of radiation-induced Schottky defect emission that depends strongly on the type and content of impurities.

2 EXCITONIC PRODUCTION OF FRENKEL AND SCHOTTKY DEFECTS

In a large number of inorganic insulators (halides, hydrides, azides, many silicates, ice, carbonates, chlorates, bromates) permanent atom displacement occurs as a consequence of electronic excitations generated by the interaction of matter with ionizing radiation [12]. This phenomenon is called radiolysis. In alkali halides the deposition of energy by ionizing radiation is much more efficient than the knock-on displacement processes in metals. The electronic losses along fast charged particle (and primary knocked on atom) trajectories by far outweigh the energy transference by mechanical collisions, so most of the particle or quantum energy is available to generate radiolytically induced displacements.

The primary products of ionising radiation are the electrons, holes and excitons, the wave functions of which spread to reveal a certain spatial distribution [13]. In order to cause atomic displacements the energy of the electronic excitations should be dissipated locally. Two types of localization of the electron and hole orbitals are feasible in solids: trapping by defects and self-trapping. Seitz [11] proposed in 1954 that an electron–hole pair or an exciton, which is localized near dislocation jogs, might cause movement of dislocation jogs, and as a consequence the creation of Schottky defects (i.e., equal numbers of anion ($V_a^-$) and cation ($V_c^-$) vacancies or F and V$_F$ centers). Owing to the heat generated locally during the exciton annihilation, the jog is assumed to be displaced while a divacancy arises in the lattice. The main argument against this mechanism was that it would not cause the production of interstitial ions, which were observed abundantly. In 1965 Pooley [14] and Hersh [15] suggested independently that an F–H pair is generated from a self-trapped exciton (STE) in the bulk. This is called the Pooley–Hersh mechanism or excitonic mechanism of Frenkel pair production. A similar mechanism has been advanced by Lushchik et al. followed by a large number of experiments on the creation of Frenkel defects by excitons (see Ref. [16]). Attempts to find a correlation between the efficiency of defect creation and the number of dislocations have failed. Therefore, Seitz’s mechanism has been ruled out, and at present it is commonly believed that the main mechanism of primary defect production in alkali halides is the excitonic (or electron–hole) mechanism of Frenkel pair creation [16].

We will now consider a simple model that takes into account excitonic mechanisms for both Frenkel and Schottky defect creation, which will demonstrate that although the contribution of the latter mechanism to the primary defect production may be small, its role in the radiation-induced evolution of microstructure can be very significant.
The relevant material/model parameters used in this paper have been defined and their values have been given in Table 1.

We assume that initially ionizing radiation produces free excitons, which can move with the same velocity as a thermal electron, i.e. $10^7 \text{ cm/sec}$. The excitons are presumably scattered strongly as a result of interactions with vibrational lattice modes of the crystal and therefore show a stochastic diffusion like motion. According to Seitz [11], the mean free path associated with this type of scattering is of the order of atomic dimensions, say $10^{-7} \text{ cm}$, which yields an exciton diffusion coefficient $D_{\text{ex}}^\text{free} \approx 1 \text{ cm}^2/\text{sec}$. These freely migrating excitons can become either self-trapped excitons (STE) in the bulk or be trapped at EDs or impurity ions. At low temperatures, the STE is immobile and it decays creating a Frenkel pair in the bulk [14, 15] with some probability, $P_{\text{FP}}$. At elevated temperatures, the STE can perform thermally activated jumps [17, 18] and migrate in the crystal and it can be trapped at an ED or at an impurity ion. Trapping at EDs may result in the creation of Schottky defects [11] while trapping at an impurity ion may or may not result in Frenkel pair creation, depending on the type of impurity. We consider two types of impurities with respective sink strengths for excitons $k_{\text{IFP}}^2 = \beta_{\text{ex}} c_{\text{IFP}}$ and $k_0^2 = \beta_{\text{ex}} c_{\text{IFP}}$, where $\beta_{\text{ex}}$ is the exciton-impurity recombination constant, and $c_{\text{IFP}}$ is the concentration of the impurities, at which exciton trapping results in Frenkel pair creation while $c_{\text{IFP}}$ is the concentration of the impurities that trap excitons without producing an FP. Accordingly, the rate equation for the mean exciton concentration, $c_{\text{ex}}$, can be written in a form similar to that of the rate equations for PD concentrations during exposure to ionizing radiation [8]:

$$\frac{dc_{\text{ex}}}{dt} = K_{\text{ex}} - \frac{c_{\text{ex}}}{\tau_{\text{ex}}} - D_{\text{ex}} c_{\text{ex}}(k_{\text{ED}}^2 + k_{\text{f}}^2), \quad k_{\text{f}}^2 = k_{\text{IFP}}^2 = k_0^2, \quad k_{\text{ED}}^2 = \sum_S k_S^2, \quad S = \text{C, D, G},$$

where $K_{\text{ex}} = K/E_{\text{ex}}$ is the production rate of excitons, $K$ is the energy absorption rate, $E_{\text{ex}}$ is the exciton creation energy, $\tau_{\text{ex}}$ is the exciton lifetime in a perfect crystal before it decays and transfers its energy to the lattice, $k_{\text{f}}^2$ is the sink strength of the EDs of type S for excitons, and the subscript $S = \text{C, D, G}$ corresponds to colloids (three-dimensional sinks), dislocations (linear sinks) and grain boundaries (planar sinks), respectively.

The FP production rate in the bulk crystal, $K_{\text{FP}}^0$, is given by the product of the probability of FP creation from the exciton decay in the bulk, $P_{\text{FP}}$, and the exciton decay rate, which corresponds to the second term at the right-hand side of Eq. (1). Under steady-state conditions one has

$$K_{\text{FP}}^0 = \frac{c_{\text{ex}} P_{\text{FP}}}{\tau_{\text{ex}}} \frac{dc_{\text{ex}}/dt \to 0}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} = \frac{K_{\text{ex}} P_{\text{FP}}}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)},$$

where $l_{\text{ex}} = (\tau_{\text{ex}} D_{\text{ex}})^{1/2}$ is the mean free diffusion path of the exciton i.e. the average displacement of the exciton before it decays, which in fact determines the relative efficiency of the FP or the SD production process. $l_{\text{ex}}$ is determined by the diffusion of the free exciton at low temperatures and by STE jump diffusion at elevated temperatures and it may vary from several to several hundred lattice constants for the different alkali halides [17]. In NaCl the onset of the jump diffusion of the STE is located at $T > 180 K$, and according to experimental data [18] $l_{\text{ex}}$ reaches several dozens of atomic spacings at $T = 350 K$.

The total FP production rate (in the bulk and at impurity traps) is given by

$$K_{\text{FP}}^0 = \left( \frac{c_{\text{ex}}}{\tau_{\text{ex}}} D_{\text{ex}} c_{\text{ex}} k_{\text{IFP}}^2 \right) P_{\text{FP}} \frac{dc_{\text{ex}}/dt \to 0}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} = K_{\text{ex}} P_{\text{FP}} \frac{1 + \tau_{\text{ex}} D_{\text{ex}} k_{\text{IFP}}^2}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)},$$

and the production rate of SDs at EDs of type S is given by

$$K_{\text{SS}} = D_{\text{ex}} c_{\text{ex}} k_S^2 P_{\text{SS}} \frac{dc_{\text{ex}}/dt \to 0}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} = K_{\text{FP}}^0 P_{\text{FP}} \frac{1}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} \frac{k_S^2}{k_{\text{IFP}}^2},$$

and the production rate of SDs at EDs of type S is given by

$$K_{\text{SS}} = D_{\text{ex}} c_{\text{ex}} k_S^2 P_{\text{SS}} \frac{dc_{\text{ex}}/dt \to 0}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} = K_{\text{FP}}^0 P_{\text{FP}} \frac{1}{1 + \tau_{\text{ex}} D_{\text{ex}} (k_{\text{ED}}^2 + k_{\text{f}}^2)} \frac{k_S^2}{k_{\text{IFP}}^2},$$
where $P_{SS}$ is the probability of SD creation at EDs of type $S$ by a trapped exciton. We will assume that $P_{SS} = 1$ and that the probability of FP creation from an STE $P_{FP} \approx 0.1$, which is based on experimental data indicating that the efficiency of the stable pair production in NaCl never exceeds the value 10% [19].

In a pure crystal (i.e. $k^2 = 0$) the loss of excitons at ED has a negligible effect on the FP production, and the total production rate of SDs is small compared to the FP production rate.

**FIGURE 2** Frenkel vs. Schottky production rate as a function of the dislocation density and the concentration of impurity ions, $C_{IFP}$, which can trap excitons and produce Frenkel pairs. The concentrations of the impurity ions, which can trap excitons without producing Frenkel Pairs, $C_{I0}$ are indicated.
if $l_{ex}^2 k_{ED}^2 \ll 1$. For a typical value of the ED sink strength, $k_{ED}^2 \approx (10^{10} - 10^{11}) \text{ cm}^{-2}$, this condition is realized for $l_{ex} < 50 b$, where $b$ is the atomic spacing. Figure 2 shows the Frenkel vs. Schottky defect production rate at dislocations in NaCl for $l_{ex} = 20 b$ as a function of the dislocation density and the concentration of the impurity ions. Increasing the concentration of the impurities, which can trap excitons and produce FPs, has a negligible effect on the total FP production rate (Fig. 2c), and it increases the threshold dislocation density below which the SD production rate is small compared to the total FP production rate (in the bulk and at impurities) up to $10^{11} \text{ cm}^{-2}$ (Fig. 2b).

This result is consistent with a present day view based on the experimental results showing very little or no correlation between the efficiency of primary defect creation at low temperatures and the number of dislocations or concentration of impurities [16]. At high temperatures ($> 200 \text{ K}$), however, this correlation may be quite significant [17]. Figure 2d shows that increasing the concentration of the impurities, which could suppress FP production, would make the Frenkel pair production sensitive to the impurity level. In the next section we will show that because SDs are produced in highly localized regions in close proximity of the surface of EDs, the main consequence of this is a drastic change of the local equilibrium concentrations of the point defects in the vicinity of the EDs, which in turn determine the growth or shrinkage rate of the EDs.

### 3 COLLOID GROWTH RATE

The colloid growth (or shrinkage) rate is controlled by the difference of F and H center influxes:

$$\frac{dR_c}{dt} = \frac{1}{R_c} [Z_F^C D_F (\bar{c}_F - c_{eq}^F) - Z_H^C D_H \bar{c}_H].$$

where $Z_F^C$ and $Z_H^C$ are the colloid capture efficiencies for F and H centers, respectively, $c_{eq}^F$ is the local equilibrium concentration of F-centers at the colloid surface and $\bar{c}_F, \bar{c}_H$ are the mean concentrations of PDs in the bulk, which are determined by the rate equations [7]

$$\frac{d\bar{c}_{F,H}}{dt} = K_{FP}^{\text{tot}} - k_{F,H}^2 D_{F,H} (\bar{c}_F - c_{eq}^F) - \beta_r (D_F + D_H) \bar{c}_F \bar{c}_H;$$

$$k_{F,H}^2 = Z_{F,H}^D \rho_d + Z_{F,H}^C 4\pi N_C R_c,$$

where $K_{FP}^{\text{tot}}$ is the generation rate of the F and H pairs, $k_{F,H}^2$ are the sink strengths of the EDs, $\beta_r$ is the constant of the bulk recombination of PDs, $N_C$ is the number density of the colloids, $R_c$ is the mean radius of the colloids, $\rho_d$ is the dislocation density and $Z_{F,H}^D$ are the dislocation capture efficiencies for F and H centers, respectively, the difference of which is the driving force for dislocation climb and colloid growth [7], $c_{eq}^F$ is the statistical average of the local equilibrium concentrations at all EDs, which are controlled by the rate of emission of SDs from the EDs.

#### 3.1 Local Equilibrium Concentrations in the Vicinity of EDs

In conventional theory of rate equations, the local concentrations at the ED surfaces are usually assumed to be determined by thermodynamic equilibrium conditions in the diffusion-
limited case when there are no special barriers hampering the transfer of point defects to sinks [20, 21]. We will show that even in the diffusion-limited case, this assumption is not valid in the important ranges of irradiation temperatures and dose rates.

The flux of PDs to a sink is obtained by solving the diffusion equations for the "sinks" embedded in an effective medium with boundary conditions of the general type at the interior surface, which are determined by the type of ED:

\[ j_{ss} = \frac{v_s}{\omega} [c_s(S) - c_{ss}^{eq}], \]  

(8)

where \( j_{ss} \) is the component of the flux of the point defects along the normal at the ED–matrix interface, directed towards the ED, \( \omega \) is the atomic volume, \( v_s = D_s/b \) is the transfer velocity from the matrix to the ED or vice versa, where \( D_s \) is the local PD concentration near the ED surface, and \( c_{ss}^{eq} \) is the local equilibrium concentration, implying that the flux is zero when \( c_s(S) = c_{ss}^{eq} \). It is useful to define a local emission rate, \( K_{ss}^{loc} \) as the rate of SD emission per one surface atom of the ED:

\[ K_{ss}^{loc} = \frac{v_s}{b} c_{ss}^{eq} = \frac{D_s}{b^2} c_{ss}^{eq}. \]  

(9)

In the absence of the radiation field, one has \( c_{ss}^{eq} = c_{ss}^{eq} \), which can be obtained from thermodynamics by minimizing the free energy of the system containing identical EDs. Under irradiation, \( c_{ss}^{eq} \) is generally given by the sum of \( c_{ss}^{eq} \) and \( c_{ss}^{irr} \) due to the radiation-induced emission of SDs. Here, \( c_{ss}^{irr} \) has a purely kinetic origin and cannot be obtained from thermodynamic considerations. However, one can evaluate \( c_{ss}^{irr} \) from the radiation-induced local emission rate, \( K_{ss}^{irr} = D_s c_{ss}^{eq} / b^2 \), which is given by the ratio of the emission rate from all EDs of type \( S \), \( K_S \) (Eq. (4)), and the number of ED surface atoms per unit
volume. In the case of dislocations (1D), grain boundaries (2D) and colloids (3D) one has, respectively

\[
K_{Sd}^{\text{ir}} = \frac{K_{Sd}}{2\pi r_d \rho_D b} = |k_{D}^{2} = Z_{ex}^{D} \rho_D| = \frac{K_{FP}^{2} Z_{ex}^{D} l_{ex}^{2}}{P_{FP} 2\pi r_D b}, \quad Z_{ex}^{D} = \frac{2\pi}{\ln (\pi/k_{D} r_D)},
\]

\[
K_{Sg}^{\text{ir}} = \frac{K_{Sg}}{3b/l_{G}} = \frac{K_{FP}^{0} Z_{ex}^{D} l_{ex}^{2} l_{G}^{2}}{P_{FP} 3b}, \quad k_{G}^{2} = k_{tot}^{2} l_{G} \left( \coth [k_{ex} l_{G}] - \frac{1}{k_{tot} l_{G}} \right)^{-1},
\]

\[
K_{Sc}^{\text{ir}} = \frac{K_{Sc}}{4\pi N_{C} R_{C}^{2} b} = |k_{C}^{2} = 4\pi N_{C} R_{C} | = \frac{K_{FP}^{0} l_{ex}^{2}}{P_{FP} b R_{C}},
\]

\[
c_{Ss}^{\text{ir}} = K_{Ss}^{\text{ir}} \times \frac{b^{2}}{D_s}, \quad D_s = D_s(T) + \frac{K_{FP}^{0} l_{ex}^{2} b^{2}}{P_{FP} b R_{C}}, \quad c_{Ss}^{eq} = c_{Ss}^{th}(T) + c_{Ss}^{ir}
\]

where \(Z_{ex}^{D}\) and \(r_{D}\) are the dislocation capture efficiency and capture radius for excitons, respectively, and \(l_{G}\) is the grain size. Note that radiation-induced PD diffusion is also taken into account in Eq. (13) by assuming that a PD can jump to an adjacent site upon receiving the exciton energy. As a result, both diffusion and emission of PD from ED are determined generally by the sum of the thermal and radiation-induced contributions.

Note that thermal equilibrium can be realized only in a system with identical “sinks” in the absence of the radiation field. Similarly, if thermal emission and bulk production of FPs were forbidden \((c_{Sd}^{th} \rightarrow 0, l_{ex} \rightarrow \infty)\), the mean PD concentrations in a crystal with identical EDs under irradiation would coincide with \(c_{Ss}^{ir}\), and hence there would be no flux across their surfaces, which means that \(c_{Ss}^{ir}\) is an exact kinetic analogue of the thermodynamic equilibrium concentration, which operates in the open, i.e. “non-equilibrium” radiation environment. Accordingly, it depends on the irradiation dose rate and microstructural parameters, which determine the rate of the exciton annihilation with EDs.

The type of SDs produced owing to the heat generated during the exciton annihilation with EDs is different for different EDs. Dislocations and grain boundaries have to emit equal numbers of anion \((v_{-}^{a})\) and cation \((v_{-}^{c})\) vacancies or F and \(V_{F}\) centers. On the other hand, colloids can only emit F-centers, which causes shrinkage as some of the emitted F-centers will diffuse away and are absorbed by other EDs. Colloids can also absorb F-centers emitted by particular EDs, and the net growth or shrinkage rate of each one is determined by the difference between its local equilibrium concentration and the statistical average of the local equilibrium concentrations for all EDs in the system, \(c_{Ss}^{ir}\). This difference is nonzero if at least two types of EDs are present, since \(c_{Ss}^{th}\) depends on the ED type as follows from Eqs. (10) to (13). Figure 3a shows that \(c_{Ss}^{ir}\) depends on the colloid radius and is larger than \(c_{Sd}^{ir}\) for small colloids making them shrink in the presence of dislocations. This radiation-induced “annealing” is very similar to thermal annealing but its rate depends on the irradiation dose rate and the microstructure.

A comparison of the thermal and radiation-induced equilibrium F-center concentrations at colloids for a typical laboratory dose rate (Fig. 3b) shows that the latter dominates completely at temperatures below 100°C. In the following section, the radiation-induced emission of SDs will be taken into account in the net growth rate of colloids together with the absorption of FPs produced in the bulk.
FIGURE 3. The equilibrium concentration of F centers close to the colloids, $c_{\text{eq}}(c_F)$, and dislocations, $c_{\text{eq}}(c_D)$, in NaCl for $\lambda = 240$ Mrad. (a) $c_{\text{eq}}(c_F)$ vs. $c_{\text{eq}}(c_D)$ in the low-temperature region ($T \leq 300^\circ$C), where they do not depend on temperature. (b) Temperature dependence of $c_{\text{eq}}(c_D)$ at $R_c = 1$ nm.
3.2 The Effects Associated with Radiation-induced Schottky Defect Emission

An edge dislocation is biased towards absorption of H-centers due to stronger elastic interaction with these centers as compared to F-centers. The dislocation bias is determined by the ratio of the relaxation volumes associated with H and F-centers, \( \Omega_H / \Omega_F \), and it is given by the following expression [7, 8]

\[
\delta_d = \frac{Z_H^D - Z_F^D}{Z_F^D} = \frac{\ln (\Omega_H / |\Omega_F|)}{\ln (2/L_kHk_B)} \cdot \frac{\mu b (1 + \nu)}{3\pi k_B T (1 - \nu)} \Omega_H
\]  

(14)

where \( \mu \) is the shear modulus of the matrix, \( \nu \) is the Poisson ratio, \( k_H \) is the square root of the total sink strength of all extended defects for H-centers, and \( k_B \) is the Boltzmann factor. Due to the dislocation bias for H-centers, the excess F-centers, which are left in the matrix, might agglomerate.

Agglomeration of F-centers gives rise to the formation of colloidal Na-metal with a crystal lattice, which is expected to be coherent with the host matrix as long as the colloids are sufficiently small. In this coherent state, there exists a misfit, \( \varepsilon \), which is equal to the difference between the lattice constants of the colloid and that of the host lattice. A positive (or negative) misfit means that the colloid is under compressive (or tensile) stress with a radial component \( \sigma_\varepsilon \). In NaCl, coherent sodium colloids have a negative misfit of about 6%, which increases the thermal equilibrium concentration at the colloid surface:

\[
c_{FC}^th = c_F^{(e)} \exp \left( \frac{2\gamma / k_BT_C + \sigma_\varepsilon \omega}{k_BT} \right), \quad c_F^{(e)} = \exp \left( - \frac{E_F^F}{k_BT} \right), \quad \sigma_\varepsilon = - \frac{3K_C \varepsilon}{1 + 3K_C / 4\mu},
\]  

(15)

where \( K_C \) is the colloid bulk modulus, \( \gamma \) is the colloid surface energy, \( E_F^F \) is the formation energy of the F-center at a flat colloid–matrix interface.

The growth rate of the colloid volume fraction calculated using Eq. (5) taking into account both thermal (Eq. (15)) and radiation-induced (Eq. (13)) dissolution is presented in Figure 4 as a function of irradiation temperature and impurity concentration.

It can be seen that exciton-induced emission of Schottky defects suppresses colloid growth and can make the growth rate negative for sufficiently “pure” crystals (\( C_{IFP} < 100 \) ppm) at any irradiation temperature (Fig. 4a). Impurity ions, which are capable to trap excitons and produce Frenkel pairs enhance the colloid growth drastically, since they screen EDs from excitons. By increasing \( C_{IFP} \) to about \( 10^4 \) ppm, the SD emission is suppressed and the colloid growth rate saturates at its maximum value corresponding to the “classical” limit of FP production in the bulk (\( l_{ex} = 0 \)), in which the rate of colloid growth does not depend on the impurity concentration (Fig. 4b).

On the other hand, impurity ions, which can trap excitons without producing Frenkel pairs, act in the opposite direction and reduce colloid growth rate, since they suppress both the production of FPs in the bulk and emission of SDs from EDs. Unintentional contamination of nominally “pure” crystals up to \( 100 \) ppm of impurities of both types results in a substantial enhancement of colloid growth, which can be further increased by addition of FP producing impurities (Fig. 5a) or decreased by addition of impurities suppressing FP production (Fig. 5b).

These trends shed some light on our recent experimental results on electron irradiation of natural and differently doped synthetic NaCl crystals to super high doses (Fig. 5b). Nominal pure samples produced very different amounts of colloidal sodium ranging from 3% to 22% after 1000 Grad, which is consistent with the theoretical prediction of the instability of colloid growth for low impurity levels. All samples containing 400 ppm of
FIGURE 4 Dependence of the growth of the colloid volume fraction rate as a function of the temperature and the concentration of the impurities producing FPs, $C_{FP}$, at the following microstructural and irradiation parameters: $R_C = 5$ nm and $N_C = 2 \times 10^{16}$ cm$^{-3}$, $\rho_0 = 5 \times 10^5$ cm$^{-2}$, $K = 240$ Mrad/h. In (b) irradiation temperature is 100°C.
FIGURE 5 Dose dependence of the colloid volume fraction in NaCl for $K=1$ Grad/h, $T=100^\circ$C calculated assuming $N_C=2 \times 10^9$ cm$^{-3}$, $\rho_D=5 \times 10^{10}$ cm$^{-2}$. The calculations have been carried out for samples with different impurity concentrations. The concentration of impurity ions, which can trap excitons and produce Frenkel pairs, $C_{IFP}$ is indicated in the figures. The concentrations of impurity ions, which can trap excitons without producing Frenkel pairs are, $C_K=100$ appm (a); or $C_K=1000$ appm (b). The symbols represent the experimental results of irradiated natural (results published by Donker and Garcia Celma [22]) and our own results for synthetic samples doped with NaBr (400 appm), NaF (1000 appm) and KBF$_4$ (300 appm).
FIGURE 6 Dependence of the growth rate of the colloid volume fraction during irradiation as a function of the temperature and the dose rate for nominally pure NaCl.

$C_{IFP} = C_{I0} = 100$ ppm for fixed material parameters $R_e = 5$ nm, $N_c = 2 \times 10^{10}$ cm$^{-3}$, $p_D = 5 \times 10^6$ cm$^{-3}$, $N_w = 2 \times 10^5$. 

$0.4 \leq \text{DOSE RATE} \leq 1$ Mrad/h, $100 \leq \text{DOSE RATE} \leq 10^3$ Mrad/h, $10 \leq \text{DOSE RATE} \leq 10^4$ Mrad/h.

$0^\circ C \leq \text{TEMPERATURE} \leq 100^\circ C$.

$0 \leq \text{VOLUME PR GROWTH RATE/\% C/\% Grad} \leq 200$.

$0.02 \leq \text{VOLUME PR GROWTH RATE/\% C/\% Grad} \leq 0.4$.

$0 \leq \text{TEMPERATURE} \leq 240$ Mrad/h.

$0.2 \leq \text{Dose Rate} \leq 1$ Mrad/h.
Br produced at most about 3% of colloidal sodium, while other dopants enhanced the colloid production, which suggests that Br doping may suppress FP creation in the bulk and other dopants do not.

It should be noted that in the "classical" limit of FP production in the bulk ($l_{ex} = 0$), the rate of colloid growth does not depend on the impurity concentration.

4 DISCUSSION AND CONCLUSIONS

In the present paper, a model has been proposed that takes into account excitonic formation of Frenkel and Schottky defects, which shows that although the contribution of Schottky defect formation to the primary defect production may be small, its role in the radiation-induced evolution of microstructure can be very significant. These observations might have serious consequences for predictions of the behavior of the materials in nuclear reactors or in a nuclear waste repository. The predictions can be made on the basis of the results of laboratory irradiation (which is several orders of magnitude more intense than the real one) in combination with an adequate model describing the temperature and dose rate dependence of the formation of radiation damage. Figure 6 shows the temperature and dose rate dependence of the growth of the volume fraction of Na-colloids in nominally pure NaCl under laboratory irradiation (for 240 Mrad/h to 1 Mrad/h) and in a repository (which can be 0.2 Mrad/h and lower). A significant new result is the predicted radiation-induced dissolution of colloids in the region of sufficiently low temperatures (or high dose rates), which should be verified experimentally in the future. Another important application of the results presented in this paper is connected with the impurity effect. In real crystals, there are always impurities with some concentration. These impurities might, depending on the type, either increase or decrease the ratio of Frenkel to Schottky defect production. A combination of these opposite trends might be responsible for the large differences observed for the response to irradiation among the NaCl samples doped with different impurities.

We need to collect more information about the material parameters controlling the ratio of Frenkel to Schottky defect production, such as $l_{ex}$, in order to make definite conclusions, and further experiments are needed to verify those predictions of the model, which are relevant for technological applications.

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References