Chapter 11

VOID SUPERLATTICE FORMATION IN ELECTRON IRRADIATED INSULATING MATERIALS

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Abstract

CaF₂ is widely adopted as deep-UV window material and thin film optical coating. In this study, single crystal CaF₂ were irradiated under 200 keV electron beam at room temperature with in situ TEM observation of the dynamic process of defect aggregate ordering. The void superlattice reached steady state after a critical electron dose with the void radius about 5 nm. Videos recorded during the in-situ observation reveal the dynamic self-organization process of the void superlattice.

These experimental observations are supported by theoretical analysis. First, we suggest a simple scaling estimate of the superlattice parameter as a function of the dose rate and temperature which explains a wide range of experimental data, not only for insulators but also metals. Based on this result, we estimate the lattice parameter for interstitial aggregate (F₂ gas void) lattice in CaF₂ to be ca. 50 a₀ which is in good agreement with experiment. On the other hand, the expected lattice parameter for the possible superlattice of Ca colloids is very small, < 10 a₀, and thus these colloids hardly could be observed.

We performed kinetic Monte Carlo (kMC) simulations of the initial stages of the process when a quasi-random distribution of small Ca colloids and larger interstitial aggeragates (F₂ gas void) is created (short- and intermediate-range order of defects). The kMC model includes interstitial-vacancy pair creation, defect diffusion, similar defect attraction and dissimilar defect recombination. Special attention is paid to the statistical analysis of the defect aggregate distribution functions under different conditions (dose rate, migration and recombination rate). These simulations confirm our

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scaling estimates and demonstrate that under certain conditions the dissimilar aggregate recombination is strongly suppressed which stimulates further void ordering.

1. Introduction

As is well known, irradiation of many metallic and insulating solids with energetic particles, such as heavy ions, neutrons, electrons, can result in a formation of ordered structures including periodic defect walls, bubble lattices, void lattices and periodic compositions in alloys [1, 2, 3]. The particular ordered structures arising in such open dissipative systems far from equilibrium depend on a type, energy, and flux of the energetic particles as well on the temperature. It was noticed [3] that despite the difference in the appearance, a similar underlying mechanism may be invoked to explain the self-organization behavior of these structures. In this paper, we focus on the void superlattice formation in which a long-range ordered superlattice is created with the lattice parameter of the order of 20-50 nm. Such superlattices are relatively well studied experimentally in both metals and insulators [1, 2, 3]. We will focus here on the insulating CaF$_2$.

The very fact that this is a self-organization process poses considerable limitations on the theoretical methods which could be used for its treatment and calls into question many void formation scenarios suggested so far in the literature (see e.g. review article [2]). The reference [3] could be mentioned as an illustration of this point, where the mechanism of a spinodal decomposition in a radiation-induced pattern formation was discussed. However, this approach implies the temporal and spatial evolution of the system towards thermodynamic equilibrium. The more so, the interstitial atoms were neglected and thus the void concentration remains constant (no vacancy recombination with interstitials). However, this has nothing to do with open dissipative systems far from equilibrium under study. It contradicts also to the experimental fact that the voids grow and start ordering under continuous irradiation [3].

A similar criticism could be applied to the attempts to determine the distinctive lattice parameter of the superlattice assuming that this is a space scale characterizing the local minimum in a potential energy curve (quasi-elastic analysis) [4, 5, 6]. As noticed in Ref. [7], “while void-void elastic interaction is strong when voids are closely separated, the short-range of the elastic interaction forces does not explain how voids and bubbles organize themselves over relatively long distances, especially during the early stages of irradiation”. Thus, no surprise that in these theories, however, the energy minima rarely correspond to the observed void lattice parameters or symmetries. The key point here is that the superlattice parameter characterizes the non-equilibrium process. This has also been shown by a recent model, which reveals the dynamic void formation process under the strain field induced by the surface stress at the void/solid interface [3]. A good correlation was established between the nonequilibrium superlattice structures and experimental observations. It was also shown that elastic anisotropy can significantly influence the symmetry of a void superlattice, causing it to replicate that of the host crystal.

The self-organization process leads to the two observations which at the first glance look contradicting. On the one hand, when void lattice is observed, its properties are surprisingly insensitive to the external conditions, such as material, temperature, irradiation type. In particular, it was observed in metals that the lattice parameter of the void lattice is largely
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Insensitive to defect production rates, dose (for high doses) and details of the particle recoil spectrum [1, 7]. The void lattice parameter decreases slightly with increasing damage rate but increases slightly with increasing irradiation temperature over a large range [1, 7]. On the other hand, this is very unstable effect: “The phenomenon was only observed in a very small number of samples within a narrow condition window. Sometimes the results cannot be repeated presumably due to small variations of the experimental conditions that were thought unimportant before” [8]. This can lead to the hasty conclusion that it is indeed very true that the irradiation conditions seem to be in a very narrow window [8]. This contradiction is resolved if we take into account that self-organization phenomena are not deterministic since the reactant density fluctuations play a great role here [9, 10, 11].

This could be well illustrated by recent studies for other self-organized systems, e.g. the spatio-temporal oscillations in catalytic CO oxidation on Pt surface [12]. The nonlinear kinetics of surface reactions therein shows a variety of phenomena such as many kinds of pattern formation, global oscillations, and even chaotic behavior. The ordered structures (reactant patterns) were observed here along with the labyrinth-like structures, which looks similar to radiation-induced well aligned labyrinth-like defect walls [3]. These different-type spatio-temporal structures compete each other. In particular, it was observed in the mentioned CO oxidation study by means of the Monte Carlo modeling that the long-time asymptotics (the structure type) was determined by a random parameter $b$—the difference in a number of spirals with opposite rotation directions which arise in the beginning of a non-linear process. For $b = 0$ the opposite-type spirals annihilate each other, due to which other structures can arise, e.g. well-ordered global synchronization of reactant densities [12]. However, even in this case there is no distinctive time of the structure formation which, in fact, is a random parameter. We believe that these observations are relevant also for self-organization under irradiation. Along with the void superlattice, other above-mentioned ordered structures can arise and compete each other, and the choice between these is a random process. This is why any attempts to detect the parameter window for the void lattice observation hardly could be successful.

In Section 2 the experimental observation is discussed of the void superlattice in the electron irradiated CaF$_2$. We discuss in Section 3 in a more detail several possible stages of such a self-organization process of void lattice formation based on the analysis of existing experimental literature. In Section 4 general scaling estimates for void growth are performed. These estimates are applied for both metals and insulators under electronic irradiation (CaF$_2$) in Section 5. Detailed kinetic Monte Carlo simulations and main results are discussed in Sections 6 and 7. Lastly, the conclusions are summarized in Section 8.

2. Experimental

To remind history, first observation of voids ordering dates back to 1971, it was ion and neutron irradiated Mo [13]. Later, void superlattices have been observed in Ni, Al, and Nb pure metals, after high energy ion or neutron irradiation [1]. Void superlattices were also found in some alloys, for example, in stainless steel. Furthermore, stainless steel is the only metal in which ordered voids can be induced by electron irradiation [14]. Besides void lattices, cluster arrays formed by neutron irradiation in Ni were also observed [15]. After that, experimental observations have become available on periodic defect wall formation
under light ion irradiation in Cu and Ni [16] as well as bubble lattice formation in many metals under inert gas implantation [1, 7]. Observations of gas bubbles ordering have been made on Cu, stainless steel, Ni, Au, V, Mo, Ti and Co, by low energy inert gas irradiation [1, 7].

![Image](image_url)

**Figure 1.** An example of coalescence mode for void growth with increasing dose: two voids grow close to each other and share the same lattice site, they will combine and merge into one big void.

Similar phenomena were also observed in ceramics. When single crystals of CaF$_2$ are irradiated with electron in transmission electron microscope (TEM), ordering of the radiation induced defects occurs which leads to formation of defect superlattices. The lattice was first observed as an indistinct line pattern as early as 1963 by Evans [17], who at that time interpreted the pattern as a Moire effect resulting from formation of free alkali earth metal on the crystal surfaces. Better resolution in the micrographs led Murr [18, 19] to interpret the defect arrays as color center aggregates formed from a planar clustering of the F centers (fluorine vacancies) on the (111) planes. Later, the defect arrays were reinterpreted as being void superlattices having an f.c.c. structure [20].

Using low temperature microscopy, Hobbs showed that the damage initially consists of loop-like defects as was verified later by Chadderton et al [21]. With the increasing electron fluence dislocation tangles develop, superimposed on a background of ordered defect arrays, interpreted as simple cubic superlattices of colloidal alkali earth metal particles, or anion voids [20, 21, 22, 23]. However, the nature of the defects on the superlattice point (i.e., Ca colloids or voids) has not been certain and the ordering mechanism has not been fully understood. In this Section, we mainly discuss the results of our recent in situ TEM observation of the ordering process and its formation mechanism [24]. The importance of the in situ technique is that it allowed the slowly developed process to be analyzed at a fast forward speed. The achieved structure may have an application in the photonic band gap device.

Single crystal plates of a pure CaF$_2$ with either (100) or (111) surfaces planes were
Figure 2. An example of migration mode for void growth with increasing dose: a void grows partially on the superlattice site will migrate and align itself with its neighbors.

studied here. A JOEL 2010F Analytical Electron Microscope (AEM) was adopted for in situ TEM observation and characterization of formation and disordering of the defect superlattice induced by electron irradiation. The TEM has a field emission gun and can be performed in two different modes, Conventional (CTEM) and Scanning Transmission Electron Microscope (STEM). Several techniques are available for such a modern AEM, for example, High Resolution Electron Microscopy (HREM), Electron Diffraction Spectroscopy (EDS), Electron Energy Loss Spectroscopy (EELS) as well as High Angle Annual Dark Field (HAADF) imaging (the so-called Z-contrast imaging). This means we can obtain not only microstructure, morphology, crystallographic information but also compositional data from our samples by using such an AEM. The experiments were performed under 200 keV electron beam at room temperature for the in situ TEM observation of the dynamic process of defect ordering. The dose rate adopted varies from $5 \times 10^{17}$ e/cm$^2$/s to $2 \times 10^{18}$ e/cm$^2$/s. These critical doses of defect superlattice formation and deformation seem to be independent of dose rate. The defect clusters in the defect superlattice have been confirmed by means of advanced electron microscopy to be fluorine gas voids (not Ca colloids or anion voids) [25].

Analysis of the series of TEM images obtained for CaF$_2$ with the current density of $2 \times 10^{18}$ e/cm$^2$/s demonstrates that the defect superlattice is formed at a dose of $6 \times 10^{20}$ e/cm$^2$, it reaches the steady state at a dose of $1 \times 10^{21}$ e/cm$^2$ and the superlattice structure is not destroyed until the accumulated dose is higher than $3 \times 10^{21}$ e/cm$^2$.

We studied also shows three sets of through focus images along the [100], [110] and [111] directions. Voids which are fully enclosed inside the specimen can be imaged by defocusing the image and observing the special form of phase contrast (known also as the Fresnel contrast). All these features appear black dots in the overfocused images and white dots in the underfocused images. This proves that the defects are voids in nature. Sample tilting experiments revealed that the void superlattice has a simple cubic structure with the superlattice oriented parallel to the cubic fluorite matrix. The edge length of the simple
cubic superlattice unit cell lies in the range 15-20 nm, giving the ratio of the superlattice spacing to defect radius (5 nm) about 3. During the in-situ TEM observation of electron induced three dimensional voids formation in CaF\textsubscript{2}, coalescence, migration and preferential growth of small defect clusters are the main three growth processes that have been recorded.

Coalescence occurs when two voids grow near the same superlattice site. They gradually combine and merge into one big void (Fig.1). This phenomenon is often observed at the initial stages of the void lattice formation. Migration occurs when one void grows partially on-site and no other voids are close to it. Then this void will migrate to the lattice site while its on-site part grows and the off-site part shrinks (Fig.2). A column of voids migrate together to line up with other voids are also observed (Fig.3). From another point of view, this can also be regarded as two columns of voids are coalesced into one column (on the left side of the line).

Preferential growth occurs when an on-site void and an off-site void exist close to each other. The on-site void grows at the expense of the shrinkage of the off-site void close to it. It looks like coalescence of two voids without touching each other, or breakdown of the off-site void and migration to the on-site counterpart. It often happens when the superlattice is almost formed (Fig.4).

All these three modes have some similarities, but they usually happen in different situations and various stages during void superlattice formation. The estimate of a percentage of void superlattice that formed by each process shows that coalescence and migration growth modes occur at approximately same probabilities.

![Figure 3](image)

Figure 3. With increasing dose, two lines of voids migrate to align with each other into one line at the right side of the mark. Two lines of voids coalesce into one line at the left side of the mark.

Void superlattices were observed using both 200 keV and 80 keV electrons. By classical binary collision theory, the transferred energy from an 80 keV electron is 9.24 eV to an F atom and 4.04 eV to Ca. Binding energy of Ca-F is 5.47 eV, so the displacement energy for Ca and F, can be estimated to be 43.8 eV and 21.9 eV, respectively [17]. Thus, the
Figure 4. Preferential void growth mode with increasing dose: one of the two closely located voids which is on the void lattice point grows at the expense of shrinkage of the other one.

host atoms cannot be displaced by the electrons with energies we used, the more so, the activation energy for the ionization process is only 0.3 eV [23]. In other words, the defect formation in CaF$_2$ is not induced by the ballistic mechanism typical for metals but rather by a radiolysis mechanism typical for insulators (see Section 5.2).

3. Three Stages of Void Lattice Formation

3.1. General Consideration

The void superlattice formation could be divided into three stages. At the first stage, voids initially are formed randomly in irradiated materials [7]. This is true also for other patterns, e.g. periodic defect cluster walls [1] where the ordered cluster arrangements are formed from an initially random cluster distribution at low doses; as well as gas bubble lattices. In other words, at low doses first of all, disordered structure arises which elements (voids) are large and stable enough to survive coalescence or annihilation with interstitials.

The voids are similar to atoms in disordered system such as glass or liquid. The traditional general statement that voids initially are formed randomly in irradiated materials should be completed with several fundamental void lattice properties [7]:

(i) The random void structure parameter is typically about two orders of magnitude larger than the atomic lattice parameter. (ii) The random void structure parameter decreases slightly with increasing damage rate. (iii) The random void structure parameter increases with increasing the irradiation temperature. Peculiarities of the disordered void structure determine the further stages of the process.

At the second stage, this structure has a trend to “crystallization” through formation, first a short-order and then a long- (global-) order. According to ref. [1, 8], the degree of
ordering improves with increasing the irradiation dose. Migration and preferential growth were dominant at the final stages of the superlattice formation [7].

Two statements could be found in the experimental literature: (a) The void lattice parameter decreases slightly with increasing damage rate [7], and (b) the void ordering is insensitive to the dose rate [3]. The first statement corresponds to the first stage, whereas the second statement could be associated with the second stage of the system ordering because the mean distances between voids in disordered and ordered structures are close. Independence on the dose rate means that a permanent irradiation is the necessary condition for existence of the glass structure but irradiation itself does not order the void structure. The individual voids reveal a continuous growth without coalescence but the superstructure lattice parameter remains constant.

A variation of the void radius leads to the final, third stage of a self-organization process: at a critical dose the superlattice structure is destroyed. These critical doses of void superlattice formation and deformation seem to be independent of dose rate [8]. Similar observation was made for the gas bubble lattices [1]: “At extremely high doses ordering disappears and, instead, a network of bubbles and channels without ordering develops”. Again, the process here, similarly to the stage 2, is not sensitive to the dose rate.

The processes of ordering at the second stage and disordering at the third stage possess different rates. These are diffusion-controlled processes involving migration of individual vacancies and interstitials at the first stage and voids at the second stage. Existence of three stages of self-organization indicates that the void superlattice formation is not a steady-state but an intermediate asymptotics [9, 10, 11] observed in a limited range of the time and the radiation doses. As we show below, the superlattice parameters could be estimated already at the first stage of the process.

3.2. Previous Theoretical Studies

It was Foreman [26] who was first suggested that in metals, under particle bombardment voids are aligned along close-packed directions of the crystal lattice by one-dimensional (1d) self-interstitial-atom (SIA) fluxes oriented in such directions. A void, partially screened by its neighbors, receives at the non-screened parts of its surface an excess of SIAs and, balancing this, at the screened parts an excess of three-dimensionally (3d) diffusing vacancies (this is known as difference in the anisotropy of diffusion [27]). Consequently, this void shrinks at one side and grows at the other such that its center of gravity drifts in the direction of the common center of gravity of its neighbors.

Several relevant kinetic studies were undertaken recently to simulate theoretically the void formation in metals. First of all, these are Monte Carlo studies [28, 29]. Instead of modelling the kinetics of void formation and growth, authors [28] started from a random array of small voids and introduced randomly positioned crowdions and vacancy clusters that interact with the voids. The more so, such an important radiation effect as void nucleation has been omitted. As a result, the radiation-damage problem is transformed into relaxation kinetics of SIA-clusters and vacancy recombination. Since the void concentration decays due to irreversible reaction, the scenario used was to start with a high enough concentration of small voids. The reasonable question was raised in Ref.[29], whether it is reasonable in the face of strong coalescence loss of voids to ask what the effect of continued void nucle-
Figure 5. The jump frequency of vacancies and interstitials (in logarithmic scale) as a function of temperature $T$ for $E_a(i) = 0.1\text{eV}$ and $E_a(v) = 1.0\text{eV}$.

Evans [29] tried to overcome limitations of the modeling [28] through the effects of renucleation and the influence of vacancies. However, this is done in a way very far from real process occurring under irradiation. In fact, in his simulations any void lost due to shrinkage or coalescence was replaced by a new void having the original starting radius. The new void was given random coordinates. As a result, the formation of a perfect superlattice seemed to be elusive. As the author concluded, “there is no indication in the present work that the almost perfect void lattices or bubble lattices that have been produced experimentally could be a result of 1d SIA transport” [29].

Fokker-Planck-type kinetic equations were applied recently [27, 30] in order to study effects of diffusion anisotropy and one-dimensional motion of crowdions in metals.

Another series of more general kinetic studies [3, 7, 9, 10, 11, 31, 32, 33] was based on the standard mesoscopic self-organization approach. This assumes some intermediate steady-state with homogeneously distributed reactants (e.g. considerable steady-state concentration of vacancies and interstitials). In other words, it is assumed that under continues irradiation high concentration of single defects is created but no voids or SIA clusters. Then stability of this state is considered with respect to a small perturbation characterized by the wavenumber $k$. Mathematically this means a bifurcation analysis of the non-linear differential equations. As a result, spatially-inhomogeneous periodic solution could be obtained with the superstructure $L = 2\pi/k_0$. In fact, this contradicts our kinetic Monte Carlo modelling discussed below in Sections 6 and 7 and indicating existence of a similar-defect aggregation (void formation) from the very beginning of the irradiation process. Thus, this mesoscopic approach is unable to predict the kinetics of the radiation damage accumulation and time-development of the void system evolution. The more so, this is a mean-field theory where reactant density fluctuations are, in fact, neglected.

It it is well established that 1d SIA (crowdions) do not exist in many insulating materials, including CaF$_2$. The primary radiation defects – vacancies and interstitials – created therein as the result of the nonradiative decay of self-trapped excitons have no momentum and perform 3d random walks. That is, simple void lattice formation mechanism suggested
for metals is not applicable to most of insulators. This means that another mechanism should exist there. To shed more light on this mechanism, we performed below the kMC modeling of the initial stage of the void formation taking into account radiation defect productions in Frenkel pairs (no cascades), their migration, interaction and recombination. But before discussing the kMC, let us start with some general considerations.

4. Scaling Theory of Void Structure

4.1. Preliminary Estimates

Let us make simple estimates of vacancy (v) and interstitial (i) aggregation driven by their diffusion with the coefficients \( D_v \) and \( D_i \). The standard diffusion coefficient

\[
D = D_0 \exp\left(-\frac{E_a}{k_B T}\right),
\]

where \( E_a \) is the migration energy. Typically \( D_0 \sim 10^{-3} \text{cm}^2/\text{s} \) and the migration energy for vacancies \( E_a(v) \) in both metals and insulators considerably exceeds that for interstitials, \( E_a(i) \) (e.g. 1.3 eV and 0.3 eV for Ni [7] or 1.0 eV and 0.1 eV for NaCl ([33], respectively and references therein). The diffusion coefficient could be written also as

\[
D = \nu a_0^2
\]

where \( \nu \) is the jump frequency, \( a_0 \) the lattice constant (typically \( \sim 4 \text{ Å} \)). The temperature range of interest \( T = 300 - 1000 \text{ K} \).

Simple qualitative estimate of jump frequencies for single mobile vacancies and interstitials shown in Fig.5 demonstrates the orders of magnitude difference in defect mobilities which makes direct 3d Monte Carlo modelling unrealistic: since the time step is defined by very mobile interstitials, it is hardly possible to study vacancy system evolution over reasonable period of time. In such systems the scaling estimates could be the first step.

Typical experimental dose rates \( p \) vary (dependent on irradiation type and material) in the range of \( p = 10^{-6} - 10^{-3} \text{ dpa/s} \). The threshold dose \( G \) for the void lattice formation in b.c.c. metals is a few dpa (e.g. [7], in f.c.c. metals it is larger by an order of magnitude). Thus, for estimates we use the dose \( G = pt = 10 \text{ dpa} \). The superlattice parameter ranges \( L = 20 - 150 \text{ nm} \), whereas the void diameter \( L_0 \) is several times smaller than the \( L \) [1, 2, 7]. There is a clear correlation between \( L \) and \( L_0 \) (Fig.3 in Ref. [6] and Fig.6 in this Chapter): typically \( L_0/L \sim 0.25 \). It is convenient to use hereafter dimensionless lattice parameter \( \lambda \) and void diameter \( \lambda_0 \) defined as

\[
L_0 = \lambda_0 \lambda_0, \quad L = a_0 \lambda_0.
\]

The dimensionless void concentration could be estimated as

\[
C_v = (\lambda_0/\lambda)^3 = 10^{-2},
\]

which is comparable with an estimate of a maximum possible concentration of accumulated immobile defects \( C_v \sim 0.1 \) [9]. For a typical \( G = 10 \text{ dpa} \), 10 defects are created in each unit cell and only 0.1 % of the totally produced defects survive [1] due to a vacancy-interstitial annihilation. If free interstitial atoms were presented in the same concentration, they would definitely destroy a void structure. Indeed, in random walks with diffusion coefficient \( D \) a particle during time \( t_R \) covers the distance \( R \) defined as

\[
t_R = R^2/D
\]

For the typical parameters cited above the interstitials would collide with voids every \( 10^{-6} \text{s} \). This time could be compared with the irradiation time of the order of \( 10^7 - 10^8 \text{s} \), their ratio is astronomically large: \( 10^{10}-10^{13} \). That is, obvious conclusion could be drawn that free and highly mobile interstitials should be bound or trapped somewhere, either in clusters or at dislocations.
Figure 6. Dependence of the observed dimensionless void diameter $\lambda_0$ as a function of the dimensionless void superlattice constant $\lambda$ for a number of metals (based on data from Table 2 [7]). The calculated mean value of the ratio $\lambda_0/\lambda$ is 0.25, std means the standard deviation.

4.2. Scaling Estimates

Let us start with a simple model: single-type particles are created with the dose rate $p$, perform random walks with the diffusion coefficient $D$ (a jump frequency $\nu = Du_0^{-2}$) and form immobile aggregates when encounter each other. At low doses, $G = pt_{\text{max}} << 1$, the aggregate overlap could be neglected. We expect qualitatively that a disordered cluster system with a distinctive spatial parameter $\xi$ is developed. (This is supported by our 2d Monte Carlo modeling [34].) Formation of such a system is a random process, the primary dimer germs are created at arbitrary coordinates where two similar particles meet and become immobile.

In the limiting case of strongly bound aggregates each just created mobile particle has a short lifetime before it finds another particle or aggregate and becomes immobile. This lifetimes is (by an order of magnitude)

$$t_0 = \xi^2 / \nu,$$

(1)

where $\xi$ is an average dimensionless distance between immobile aggregates. At low dose rates concentrations of free particles is low and growth of existing aggregates dominate over formation of new small aggregates. This is true if in the volume $V = \xi^d$ covered by a newly created particle during time $t_0$ only one particle is created,

$$pVt_0 = 1$$

(2)

($d$ is a space dimension). From these two relations, Eqs.(1),(2), the characteristic distance
between voids - the diffusion length \( \xi \) – could be easily obtained (cf [35], p.67)

\[
\xi = \left( \frac{\nu}{p} \right)^{1/(d+2)}.
\]

(3)

Detailed analysis of Eq. (3) is discussed below. The aggregate diameter \( \xi_0 \) at arbitrary time \( t \) could be estimated as a fraction of defect-occupied volume which approximately equals to the dimensionless dose, \( (\xi_0/\xi)^d = pt = G \). The critical dose at which the self-supported system start to disappear due to aggregate overlap is \( G_c \sim 0.1 \).

Let us consider now the case of the two types of particles – vacancies and interstitials – which can annihilate with each other or create the aggregates of dissimilar particles. (This is the case of the electron irradiation of insulators [36]). It is shown in the kinetic MC modeling below that the two subsystems with two relevant spatial parameters for voids (\( v \)) and interstitial (\( i \)) aggregates are formed, their characteristic size could be estimated similarly:

\[
\xi_{v,i} = \left( \frac{\nu_{v,i}}{p} \right)^{1/5}
\]

(4)

A small exponential factor \( 1/5 \) arises here for a real case of \( d = 3 \).

It should be noted that similarly to the one-component system, the preferential growth of both voids and interstitial clusters remains but their annihilation reduces the aggregate growth

\[
(\xi_{0v}/\xi_v)^3 = (\xi_{0i}/\xi_i)^3 = f(pt),
\]

where \( f(pt) \) is a slowly increasing function of time, \( \xi_{0v,i} \) are diameters of the corresponding \( i \) - and \( v \)- aggregates.

An important conclusion arising from Eq. (5) is that

\[
(\xi_{0v}/\xi_{0i}) = (\xi_v/\xi_i),
\]

(6)
i.e. the ratio of the \( i \)- and \( v \)-aggregate radii equals to that of the relevant superstructure parameters. Summing up, the dependence of the diffusion length \( \xi \) for interstitials and vacancies as a function of the dose rate and temperature is predicted by Eq. (4) and illustrated in Fig.7 for the typical metal parameters.

5. Analysis of Experimental Data

5.1. Metals

Our predictions, Eq.(4) and Fig.7, are in a good agreement with three basic experimental observations for vacancy void lattices in metals (e.g. [2, 7] and Fig.8): (i) the diffusion length decreases with increasing the dose rate; (ii) it increases with the temperature; and (iii) the diffusion length is typically about two orders of magnitude larger than the perfect lattice parameter. We explain also a weak dependence on the dose rate \( p \) and jump frequency \( \nu \) by the power factor \( 1/(d + 2) = 1/5 \) in Eq.(4).

Such an excellent agreement of our predicted behaviour for the diffusion length (short-range parameter) \( \xi_v \) and the experimental void lattice (long-range) parameter \( \lambda \) (Fig.8) permits us to suggest their identity \( \xi_v \sim \lambda \). This indicates that at the first stage of above-described self-organized aggregation process voids are created in a disordered system with
Figure 7. The predicted distinctive diffusion lengths $\xi$ (in units of $a_0$) for a self-organization of vacancy clusters (a) and interstitial aggregates (b) as a function of the dose rate $p$ and the temperature $T$ for the typical migration energies: $E_a(i) = 0.1$ eV, $E_a(v) = 1.0$ eV. The diffusion energies typical for metals are given in a legend.
the distinctive mutual distance $\xi_v$. When the ordering occurs, the system “density” (void number per volume) does not change considerably and the superlattice is formed with the lattice constant $\lambda$ close to the $\xi_v$.

As to the interstitials, it is generally believed that in metals their preferential adsorption by dislocations due to a stronger elastic interaction leads to dislocation climb formation and introduces a bias in the defect fluxes to the sinks [1, 37]. This is not the case, however, for insulators (see next Section 5.2.).

5.2. The Electron Irradiation of CaF$_2$

As mentioned above [36], the excitonic mechanism of the radiation damage of MeX insulators qualitatively differs from that in metals: isolated anion Frenkel pairs are produced instead of displacement cascades. At low doses anion atom $X$ moves to the interstitial position thus forming the so-called $H$ center and leaves a vacancy with trapped electron behind (called the $F$ center). Cation sublattice remains practically undamaged. These defects are paramagnetic and well observed by means of ESR. At moderate and high temperatures these two types of defects start to migrate and aggregate. When a cluster of the $F$ centers is created with Me ions inside, a system collapses into a colloid consisting of tens or hundreds of metal atoms. It was indeed well observed that under prolonged irradiation metal colloids and gas bubbles are developed (e.g. in NaCl [38]) which could annihilate in a back reaction.

The void superlattice structure in the electron irradiated CaF$_2$ discussed above differs considerably from the pattern typical for metals: the lattice parameter is very small, $\lambda \approx 50$, whereas void diameter $\lambda_0$ is very large, so that $\lambda_0/\lambda \approx 0.5$.

For this system we can apply Eq.(3), assuming Ca ions remain immobile. There is considerably uncertainty about migration energies for vacancies and interstitials in CaF$_2$. 

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![Figure 8. The temperature dependence of the void superlattice constant for metals (based on data in Table 2 [7]).]
Due to a close packing of the fluorine ions in the (100) direction, the relevant vacancy migration energy is quite low, $\sim 0.33$ eV [39, 40], whereas in other directions it is much higher, $\sim 2$ eV. However, the kinetics of defect recombination, aggregation and finally void formation is controlled by 3d diffusion which is difficult to estimate from such theoretical data. This is why we used here the experimental estimates based on the kinetics of $F - H$ center recombination [41] $E_a(i) = 0.4$ eV, $E_a(v) = 0.7$ eV. These parameters were used by us earlier in the successful modeling of the metal colloid formation in CaF$_2$ irradiated by low-energy electrons [42]. Typical dose rates of the electron irradiation correspond to the range of $p = 10^{-4} - 10^{-1}$ dpa/s.

The expected superlattice parameters for vacancies and interstitials are plotted in Fig.9. If we accept $\log p = -3... - 2$ and $T = 300$ K [8], the expected interstitial superlattice parameter is 30-60 $a_0$, in good agreement with the experimental value of 50 $a_0$ (Section 2). On the other hand, the expected lattice parameter for vacancies (metallic colloids) is very small, less than 10 $a_0$. In other words, small (and probably, hardly observable) metallic colloids are supposed to adjust to the superlattice of larger halogen bubbles.

6. Kinetic Monte Carlo Simulations

One of the main goals of our kMC modeling is to demonstrate an appearance of stable large vacancy and interstitial clusters whose growth dominates over formation of small dimers and other new aggregation germs. This needs reliable statistics for the cluster size (number of defects) distribution. This statistics should be accompanied with the calculation of the distinctive spatial scale $\xi$. The kMC modeling is supposed to show that in a wide time interval $\xi$ remains practically constant (until big clusters start to coalesce - see Section 2 with experimental examples). This could be observed only when the average cluster size is large enough, $\xi_0 \gg 1$ (in units of the lattice constants $a_0$). In other words, we are interested neither in short times, when $\xi_0 \sim 1$, nor in long times, when the clusters start to overlap and $\xi_0 \sim \xi$, but focus here on the transient fluctuation-controlled asymptotics [9, 10, 11] when Eq.(3) is valid.

As a rough estimate, let us assume that $\xi_0 = 5$ and $\xi/\xi_0 = 5$ (no cluster overlap). This leads to the minimum cluster spatial scale of $\xi = 25$. Next, our modeling has to be performed on d-spatial lattice structure with the linear size L (volume is $V = L^d$). To observe the structure with the distinctive size $\xi$, the linear size of the whole system should be much larger: if we assume as a minimum $L = 10\xi$, a large system with $L > 250$ is needed. In this system a number of clusters is of the order of $(L/\xi)^d = 10^d$. This is not too much; say, for d=2 we expect only $10^2$ clusters. This is not sufficient for a reliable statistics which thus needs performing a series of additional tests with different realizations. In 1d case the situation gets even worse: if $L = 10\xi$ one expects only 10 clusters! Thus, we do not consider here 1d systems, also because these differ topologically from higher-dimensional systems, d> 1. Our estimates show that for 2d case and $L = 250$ each concentration increment $\Delta C = 0.01$ requires about 20 minutes of real computational time. This is acceptable and permits also calculations of several independent runs, in order to obtain reliable statistics. Thus, the results reported in this paper are obtained as an average over at least 15 (mostly, 50) independent kMC realizations. In the 3d case computer demands dramatically increase; the time necessary for the same concentration increment increases by almost four orders of
Figure 9. The predicted superlattice constants (in units $a_0$) for vacancy clusters (metal colloids) (a) and interstitial aggregates (halogen gas bubbles) (b) in electron irradiated CaF$_2$ as a function of the dose rate $p$ and the temperature $T$.

magnitude. For instance, a smallest concentration increase, e.g., $\Delta C = 0.001$ would take $\sim 10$ hours of a real computational time which is beyond our computer facilities. Based on these arguments, we restrict ourselves in further modeling to the case of $d=2$.

In calculations we used a discrete square lattice $L \times L$ of size $L$ in the units of lattice constant $a$ (typically, $L = 2^8 = 256$). The kinetic model for two kind of particles, $i$ and $v$, consists of the following processes:

(i) Creation of an uncorrelated defect pair $i$ and $v$ in empty lattice sites with dose rate $p$. 
Figure 10. Snapshots of $L \times L = 256 \times 256$ lattice fragments. Concentrations $C = 0.05, 0.10, 0.15$ correspond to first, second and third column, respectively. a-c) normal: $\nu_i = r = \nu_v$; d-f) fast diffusion and reaction: $\nu_i = r = 8\nu_v$; g-i) fast reaction: $r = 8\nu_v, \nu_i = \nu_v$; j-l) fast diffusion: $\nu_i = 8\nu_v, r = \nu_v$. Several cluster coalescence events are shown in circles. Red (grey) and blue (black) colors correspond to interstitials and vacancies, respectively.

(ii) Thermally activated jumps into nearest neighbor (NN) empty site with the rate [43, 44]

$$\bar{\nu}_{i,v} = \frac{2\nu_{i,v}}{1 + \exp(E_F - E_I)},$$  (7)
where

\[ E_{F,I} = -\varepsilon_{XX} N_{F,I}^{XX}. \] (8)

The NN interaction is accounted for the initial \((E_I)\) and final \((E_F)\) states of a defect jump by calculating the number of occupied nearest neighboring sites \(N_{F,I}^{XX}\) (where \(XX\) is \(ii\) or \(vv\)).

(iii) Lastly, we take into account also the annihilation reaction with the rate \(r\) between \(i\) and \(v\) \((i + v = 0)\) which are NN.

All energies here are given in the units of \(k_B T\). An interaction between defects modifies the jumping rate \([43, 44]\), Eq.(7). As a basic model, one can consider the irreversible defect clustering when new defect sticks to the existing cluster as soon as approaches to within a NN distance to its boundary. However, we considered here a more general model of a strong but reversible binding with the finite attraction energies \(\varepsilon_{ii} = \varepsilon_{vv} = 7.8\) (0.2 eV at room temperature). We neglect interactions between dissimilar defects, \(\varepsilon_{iv} = 0\).

Thus our model has four parameters: hopping rates of interstitials, \(\nu_i\), and vacancies, \(\nu_v\), defect creation rate \(p\) (in displacements per atom per second, dpa), and the recombination rate \(r\), respectively. It is convenient to use time units such that \(p = 1 s^{-1}\) and to fix a vacancy hopping frequency, which we have chosen \(\nu_v = 0.25 \times 10^{06} s^{-1}\). Computer simulations were performed on the BalticGrid computers \([45]\), where a number of independent jobs were run simultaneously in order to acquire good statistics of the results.

We have simulated four different cases:

- a symmetrical (normal) diffusion \((\nu_i = \nu_v = r)\);
- a fast interstitial diffusion and reaction \((\nu_i = r = 8\nu_v)\);
- a fast reaction \((r = 8\nu_v, \nu_i = \nu_v)\);
- and lastly, a fast interstitial diffusion \((\nu_i = 8\nu_v, r = \nu_v)\).

We analyze below how a choice of these parameters affects the cluster growth and size distribution.

It should be stressed here that in present kMC modeling we neglect long-range (e.g. elastic) defect interactions which are likely responsible for the void ordering and final superlattice formation. Instead, we focus on the detailed study of the first stage of the stable disordered void formation.

7. Main Results

7.1. Snapshots

The spatial developments of clusters of interstitials and vacancies in four above-discussed cases as a function of radiation dose (defect concentration) are presented in snapshots in Fig.10. Visually inspecting snapshots one can find a coalescence of growing nearest clusters (marked by circles) practically in all considered limits with an increase of defect concentration. The mean distances between clusters and the size distributions are discussed
below, in Section 7.2 and 7.3. It is shown that growing nearest clusters periodically coalesce (marked by circles). In the symmetrical case (Fig.10.a-c) both types of defects produce clusters of similar size. While created, the cluster center of mass does not move but a cluster grows in size due to flux of newly created defects. That is, the number of stable large clusters remains nearly constant as the dose reaches $\sim 1.4$ dpa.

In the case of a fast interstitial diffusion and fast reaction (Fig.10.d-f) the sizes of interstitials become larger than those of vacancies (in agreement with Eq.(3)) and some clusters disappear due to recombination with newly created mobile single defects. Thus, clusters are more flexible and thus the defect concentration of $C = 0.1$ is reached only at the dose of 11.3 dpa, which by one order of magnitude exceeds that in the symmetrical case discussed above. The small vacancy clusters form a kind of a background for large interstitial clusters. This is in line with Eq. (6) suggesting that the ratio of interstitial and vacancy cluster sizes is equal to that of the average distances between interstitial and vacancy clusters (characteristic lengths) (to be discussed below). In the case of fast reaction (Fig.10. g-i) both types of clusters reveal similar sizes as in Fig.10.a-c, but now with a broad distribution from very small to large clusters. This is result of cluster recombination at some areas and new cluster formation in other areas. The necessary radiation dose is similar to the case of fast diffusion and reaction (11.4 dpa). Lastly, for a fast interstitial diffusion (Fig.10.j-l) one observes very fast accumulation of large interstitial clusters (at dose only 0.2 dpa) with background of very small vacancy clusters.

7.2. Superstructure Size

To quantify the spatial distribution of defects, we estimated the average distances between similar type clusters (the characteristic length $\xi$). Assuming that the centers of mass
for all clusters larger than dimer are equally spaced in the lattice, one gets $\xi^2 M = L^2$, where $M$ is number of clusters on a square lattice with sizes $L \times L$, which leads to $\xi = L/M^{0.5}$. (Other definition of the characteristic length are possible, however they have no effect on qualitative conclusions drawn from simulations).

Let us consider now the results for these calculations starting with the symmetrical case, Fig.11.b. (Since we assume equal jumping rates for both interstitials and vacancies in all three cases in Fig.11, the cluster sizes and average distances between them are the same for both kinds of defects.) As one can see, the characteristic length in Fig.11.b weakly depends on a dose. This means that despite the existing clusters grow in size but their amount is stabilized at dimensionless concentration $C > 0.02$. In contrast, in the fast reaction case, Fig.11.a, the average-size clusters become unstable and can disappear easily due to efficient recombination which results in a well observed increase of the average distance between clusters. This means also that effectively the clusters can diffuse due to a complete recombination at some area with the following creation of new clusters at another area. Nevertheless, at $C \sim 0.1$ large stable clusters are formed, Fig.10.i.

Let us consider an opposite case of a slow reaction, $r = \nu v/10$, when defect diffusion becomes the limiting process, Fig.11.c. The characteristic feature of such a slow reaction is that most of created defects survive and join the clusters. The cluster centers of mass are immobile and the distance between clusters remain constant at concentrations $C > 0.02$.

The results for normal and slow reaction rates in the concentration range $0.05 < C < 0.20$ differ only by several percent from our qualitative estimate of $\xi \approx 22$ suggested in Section 6 for a given jump frequency $\nu$. As is seen in Fig.11, transient process of the characteristic length $\xi$ formation is observed at small $C < 0.05$. New small clusters are still created in this region, which is confirmed by the variation of the parameter $\xi$. In fact, large clusters had not enough time to be created. Using the relation $C = (\xi_0/\xi)^2$, the cluster

Figure 12. Dependence of the dimensionless characteristic length $\xi$ for interstitial clusters on defect concentration. Parameters $\nu v = 0.25 \times 10^6$ and $L = 256$. Reaction rate $r$ coincides with the interstitial hopping rate ($r = v_1$, normal reaction condition) and equals to: a) $v_1$, b) $2v_1$, c) $4v_1$, d) $8v_1$. 

size of $\xi_0 \approx 5$ is expected for $C = 0.05$, this estimate could be used as the criterium for statistically reliable results. In other words, the concentration range below $C < 0.05$ should be neglected in the cluster statistical analysis. For $C = 0.20$ when coalescence begins (the limiting value in Fig.11), similar estimates give $\xi_0 \approx 10$, which is only twice smaller than the characteristic length itself, $\xi \approx 22$.

The total radiation dose $G$ necessary to obtain the given defect concentration $C$ depends almost linearly on the reaction rate. For example shown in Fig.11, to reach $C = 0.1$ one needs 11.4, 7.4, and 0.21 dpa for a fast ($r = 10\nu_i$), normal ($r = \nu_i$), and slow ($r = \nu_i/10$) reaction rates, respectively. It should be reminded that the quasi-steady average distances between defect clusters correspond to a prolonged intensive irradiation when a number of defects survived in clusters is only a small fraction of those created and recombined (a total dose). Thus, for a normal reaction rate the ratio of created vs survived defects at $C = 0.1$ is $G/C \sim 1.4/0.1 \sim 14$, i.e. more than an order of magnitude. For a fast reaction this is already two orders of magnitude. Despite the fact that under irradiation new small defect clusters are created, coalesce, or are destroyed by mobile dissimilar defects ($v-i$), it is clear from Fig.11.b that the characteristic length $\xi$ for both the normal and slow reaction rates remains nearly constant (within percent accuracy) which is a counter-intuitive result. In other words, large clusters of both vacancies and interstitials reveal nontrivial high stability with respect to recombination with a continuous flux of newly created mobile dissimilar defects.

Fig.12 is complementary to Fig.11 and shows that the characteristic length of interstitial clusters strongly depends on defect mobility. On the other hand, the characteristic length for vacancies remains the same, in a complete agreement with Eq.(3).

### 7.3. Cluster Distribution

The cluster density function $P(s, C)$ containing $s$ atoms in a general case depends on accumulated total defect concentration $C$ as well as such system parameters as diffusion and reaction rates.

The standard method to analyze the dynamics of cluster distribution is based on the dynamic scaling assumptions ([46] and references therein) using a few universal parameters. When the scaling assumption holds, the universal scaling function $F$ exists such that the density function could be presented as

$$F(s/S) = P(s, C)S^2/C$$

where $S$ is the average island (2d aggregate) size, $s$ is the area of an aggregate, $C$ defect concentration. Here we calculated scaling functions $F$ and for the better statistics averaged them over a series of kMC simulations with identical parameter sets.

We distinguish the distribution functions for interstitials and vacancies, which are shown by red and blue bars in Figs.13-14, respectively. The smoothness of the distribution characterizes the statistics of independent simulation runs.

Fig.13 demonstrates clearly the time evolution of the cluster size distribution. The role of defect diffusion could be well understood from the first two rows; both types of defects are mobile in the first row (the symmetrical case) whereas only interstitials remain mobile in the second row, $\xi_v = 0$ (this corresponds in fact to the case of fast interstitial diffusion).
As it was mentioned above, in the first case, the defect concentration $C = 0.05$ under given conditions of the kMC modeling corresponds to the critical low-bound value when one can start analyzing the characteristic length. As the concentration reaches $C = 0.15$, the cluster size distribution is stabilized and its maximum corresponds to small clusters ($\xi_0 \sim 10$ for the symmetrical case). The defect distributions are clearly diffusion-controlled which follows from a comparison of the first and second row in Fig.13: immobile vacancies do not cluster and thus remain predominantly single defects, there is no relevant characteristic length in this case.

The first row in Fig.14 shows the results for the fast interstitial diffusion and fast reaction. As one can see large different in mobilities of interstitials and vacancies leads to the suppression of the vacancy cluster formation, their distribution has no clear maximum, single defects and dimers dominate. This is similar to the fast diffusion case, Fig.13, second row, but the average interstitial cluster size is larger in the former case due to more efficient aggregation. Lastly, Fig.14, second row, demonstrates the pure effect of the reactant recombination rate which was varied from fast through normal and then the slow limits (from left to the right). The important conclusion is that the fast reaction prevents formation of well developed defect clusters with a dominant size; small clusters dominate here, whereas such clusters are formed in the symmetrical case (middle window) and then become smaller at slow reaction.

A special attention in dynamic scaling theory is paid to a regime, when the total cluster density $M/L^2$ remains nearly constant over a wide concentration $C$ range. It is expected that within this region the scaled cluster distribution functions $P$ should converge to a single universal scaling function. As an example, we compare the cluster distribution functions in Fig.15 for three concentrations: 0.08, 0.09 and 0.10 for the case of fast diffusion and
Figure 14. Cluster scaling function dependence on hoping and reaction rates at fixed concentration, $C = 0.15$. First row, parameters $v_v = 0.25 \, 10^6$, $L = 256$. Hopping frequencies $v_j = r$ are equal to: a) $2v_v$, b) $4v_v$, c) $8v_v$. Second row corresponds to the reaction rates $r = 10v_i$, $r = v_i$, and $r = 0.1v_i$, respectively.

Figure 15. Scaling of cluster distribution functions. Parameters: $v_v = 0.25 \, 10^6$, $r = v_i$ and equal to: a) $16v_v$, b) $32v_v$. Defect concentrations $C$ are given in legend.

reaction. One can see the formation of scaling function irrespective of the defect diffusion and reaction rate (cases a and b).

In fact, the total cluster density $M/L^2$ decreases that is seen also from the slight but monotonic characteristic length growth in Fig.12. According to Eq.(9), this decrease is compensated by an increase of $S^2/C$ ratio in order to keep $F$ constant.

8. Conclusion

In this Chapter we discussed experimental and theoretical results for the void superlattice formation in insulating CaF$_2$ which is widely used in deep-UV windows and thin film optical coating. Electron beam induced radiation defects in this type of materials strongly differ from those in metals. First of all, the defects are created complementary, in Frenkel
pairs, rather in cascades, second, they possess 3d random walks rather 1d crowdion motion. Thus a scenario of the void formation and ordering in CaF$_2$ could differ considerably from that in metals.

In the kMC simulations of the radiation defect clustering we focused on the initial stage of what is generally believed is a random distribution of small voids (and interstitial clusters). As we demonstrated, this point of view is not quite correct since the distribution of voids and interstitial clusters is not a random process. In fact, the defect cluster structure is characterized by the short- and intermediate order (similar to disordered solids) while long-range order (super-lattice) arises at the next step. We paid a considerable attention to the size and space distribution functions of the defect clusters. We have demonstrated here also that a non-trivial effect of the retaining a nearly constant number of the voids and interstitial clusters under intensive irradiation and suppressed cluster coalescence occurs only under certain combination of defect migration and recombination rates. In particular, too fast recombination rate of vacancies and interstitials prevents formation of large stable clusters whereas the combination of fast reaction with fast interstitial diffusion supports this process. The latter regime demonstrates the growth of large uniform-size mobile clusters which is a necessary precondition for the further void superlattice formation.

Simple scaling estimates and the kMC modeling confirm that the void superlattice observed in CaF$_2$ (Section 2 and Ref.[25]) is created by F$_2$ gas, not Ca colloids which are expected to be much smaller in size ($< 10a_0$). It should be stressed here that in present kMC modeling we neglected long-range (e.g. elastic) defect interactions which could be responsible for the void ordering and final superlattice formation. This is subject of the current study.

**Acknowledgments**

This research was partly supported by US DOE Basic Energy Sciences with grant DE-FG02-02ER46005 and ESF grant 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.

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