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New mechanism for radiation defect production and aggregation in crystalline ceramics

V.I. Dubinko^{a,b,*}, A.A. Turkin^{a,b}, D.I. Vainshtein^b, H.W. den Hartog^b^a *Kharkov Institute of Physics and Technology, 310108 Kharkov, Ukraine*^b *Solid State Physics Laboratory, University of Groningen, 4 Nijenborgh, NL-9747 AG Groningen, The Netherlands*

Abstract

In many ceramic solids, the number of primary displaced ions is different for different sublattice components, either because the ion masses and displacement energies differ in simple binary collisions (like in alumina) or because radiolytic displacements occur on a single sublattice (like in halides). However, irradiation produces not only metal colloids or gas precipitates, but stoichiometric dislocation loops, and voids as well. We propose a secondary displacement mechanism of vacancy production at a dislocation as a result of its interaction with a primary interstitial ion in another sublattice which explains the observed phenomena. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ceramic materials have found widespread application in many segments of nuclear industry [1]. Important geological applications are related with nuclear waste management, e.g. synthetic ceramic processing of high-level waste (HLW) in ceramic waste forms and the planned storage of HLW in stable geological formations [1,2]. In Europe these formations are rock salt (NaCl), clay and granite.

This paper focuses on physical and chemical processes leading to the formation and evolution of voids and other extended defects in ionic systems under high-dose irradiation. By voids we mean cavities, either empty or filled with gas below the equilibrium pressure. The growth of such voids is driven by agglomeration of stoichiometric vacancies rather than by agglomeration of gas atoms. Consequently, the mechanisms of void formation are much more complex and unclear than those of formation of non-stoichiometric defect aggregates

such as metal or gas precipitates. We need to understand these mechanisms because of drastic effects that the void formation has on mechanical properties of materials.

Among materials under investigation is, first of all, NaCl, which is one of the candidate host rock materials for HLW storage. It is also a model material, which has been studied systematically [2–8], and its fundamental properties can be used to understand the radiation stability of many other ionic systems. Aluminum oxide, α -Al₂O₃, is another important ionic material [1,9,10], which will be considered in some detail in order to obtain a more general understanding of the void formation mechanisms in ionic materials.

Void formation and evolution is rather well studied in metals under irradiation [11,12]. However, the processes of formation of radiation damage in metals are quite different from those in ionic compounds. It is known that the numbers of displaced ions are generally different for different sublattice components, either because radiolytic displacements occur on a single sublattice (like in alkali halides or in fluorite) or because the target ion masses and displacement energies differ in simple binary collisions (like in α -Al₂O₃). The diffusion rates of the resulting defect species also differ on each sublattice, which implies that formation of commonly observed stoichiometric defect aggregates (e.g. perfect

* Corresponding author. Tel: +31-503 634 178; fax: 31-503 634 879.

E-mail addresses: dubinko@phys.rug.nl (V.I. Dubinko); h.w.den.hartog@phys.rug.nl (H.W. den Hartog).

dislocation loops and voids) requires *secondary mechanisms* to form the components needed to preserve local stoichiometry. Non-stoichiometric defect aggregation is also a common phenomenon in ionic crystals, an extreme example of which is formation of metal and gas precipitates [4–10].

Until recently, the only well-known secondary mechanism was that proposed by Hobbs et al. [3] for halides to explain *perfect dislocation loop formation and climb* in the absence of displacements in the cation sublattice.¹ The mechanism requires two *H* centers (interstitial anions) meeting at the dislocation core, which results in addition of one stoichiometric interstitial pair to the dislocation and leaves behind an immobile molecular center, i.e. halogen molecule trapped in a *stoichiometric vacancy pair* (a stoichiometric vacancy pair consists of two adjacent vacancies, one in the cation and one in the anion sublattice). This mechanism of dislocation climb cannot explain the simultaneous void formation observed in many ionic systems [5–10,13–15] at elevated temperatures, especially under such irradiation conditions that displacements occur predominantly on a single sublattice. To do so, one needs a source of stoichiometric vacancy pairs required for the void growth. The vacancy pairs formed by the conventional mechanism [3] cannot be such a source since they are occupied by halogen molecules and are essentially immobile. So to explain the void formation in alkali halides we have proposed recently an *alternative mechanism of dislocation climb* [6–8].

By this mechanism, a *H* center (a halide interstitial ion with a trapped hole) that approaches a dislocation can displace a lattice cation and form with this ion a stoichiometric interstitial pair (needed for the dislocation climb) leaving behind a hole trapped next to a *cation vacancy* (see Fig. 1). The latter is known as the V_F -center, which is a mobile ‘antimorph’ of the *F* center (electron trapped in an *anion vacancy*) so that their recombination results in the formation of *stoichiometric vacancy pair*. This reaction is more straightforward than the one proposed by Hobbs et al. [3], and which is used in the Jain–Lidiard model [4] describing the growth of metallic colloids in alkali halides. The new reaction requires only one *H* center and, which is most important, provides a stoichiometric number of cation and anion vacancies needed for void formation and growth. This approach will be extended further in the present paper to describe other ionic crystals.

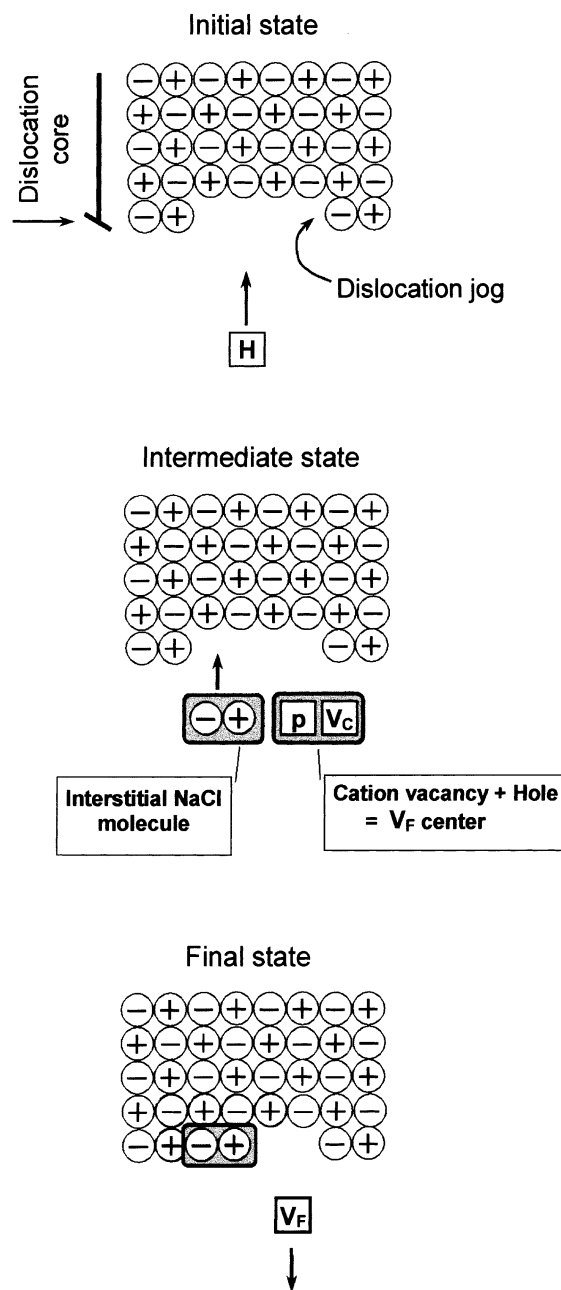


Fig. 1. Production of the V_F center as a result of absorption of an H centers by an edge dislocation. When an H center approaches the dislocation, it displaces a lattice cation and forms with it a interstitial molecule. A cation vacancy, V_C , and a hole, p , are produced in the same reaction. The interstitial molecule joins a dislocation jog leaving behind the hole trapped at the cation vacancy, that is a V_F center. A recombination of the V_F center with an *F* center produces a vacancy pair that restores the previous state of the dislocation. So, the production of V_F centers requires a bias of dislocations for H centers.

¹ Stathopolous and Pells [13] proposed a complementary mechanism of loop formation in Al_2O_3 , according to which Al interstitials aggregate to produce dislocation loops, while a stoichiometric number of Al and O vacancies remain in the lattice (see Section 5).

The paper is organized as follows. In Section 2, we summarize the biases of extended defects for absorption of point defects, which is a driving force of microstructural evolution under irradiation. In Section 3, we discuss a new mechanism of formation of voids in NaCl as a result of collisions between sodium and chlorine colloids. In Section 4, we consider simultaneous evolution of voids, sodium and chlorine colloids in NaCl, leading to the formation of cracks as a result of collisions between voids and sodium colloids. In Section 5, we discuss a mechanism of void and aluminum colloid formation in α -Al₂O₃, based on the extended model of anion vacancy production at dislocations. The results are summarized in Section 6.

2. Biases of extended defects for absorption of point defects

An important implication of the present model [6–8] is that the production of V_F centers by dislocations requires excess of incoming H centers over F centers, since the latter induce a back reaction (Fig. 1). Similarly, the production of stoichiometric vacancy pairs at the void surface as a result of recombination between F and V_F centers requires an excess of incoming F centers over H centers. This means that all reactions involved in the production and absorption of V_F centers at extended defects (ED) are controlled by the biases for absorption of primary defects, i.e. H centers or F centers.

An edge dislocation is biased towards absorption of H centers due to a stronger elastic interaction with them

as compared to F centers. The dislocation bias is determined by the ratio of relaxation volumes associated with H and F centers, Ω_H/Ω_F , and is given by [8]

$$\delta_d = \ln \left(\frac{\Omega_H}{|\Omega_F|} \right) / \ln \left(\frac{2}{L_H k_H} \right), \quad (1)$$

$$L_H = \frac{\mu b(1+\nu)}{3\pi kT(1-\nu)} \Omega_H,$$

where b is the host lattice spacing, μ the shear modulus of the matrix, ν the Poisson ratio, k_H is the square root of the total sink strength of all ED for H centers, and kT has its usual meaning. So the dislocation bias is a potential source of extra F centers and V_F centers under irradiation. But this potential can be realized only provided that there are other extended defects with lower (or negative) bias for H centers that could be the sinks for the extra F centers, such as colloids and voids. The biases of other ED, modeled as spherical inclusions in an elastic medium, have been derived in our previous paper [8] and will be discussed shortly.

The bias of a spherical inclusion of a radius R for H centers, δ_s , is given by

$$\delta_s(R, \sigma_{rr}) \approx \alpha^{im}(b/R) + \alpha^d(\sigma_{rr}/\mu) + \alpha^{\mu, \xi}(\sigma_{rr}/\mu)^2, \quad (2)$$

where the dimensionless bias constants, α , represent different modes of elastic interaction between inclusion and point defects. They are defined to be positive as shown in Table 1. It can be seen that δ_s depends on the inclusion radius and the normal stress at the inclusion boundary, σ_{rr} which are different for colloids, gas bubbles and voids.

Table 1
Material parameters of NaCl and Na colloids used in calculations

Parameter	Value
Irradiation temperature, T (K)	373
Dose rate (K), displacement per atom per second (dpa/s)	3×10^{-5}
Dislocation density, ρ (m ⁻²)	10^{14}
Diffusion coefficient of H-centers, D_H (m ² s ⁻¹)	$10^{-6} \exp(-0.1 \text{ eV}/kT)$
Diffusion coefficient of F-centers, D_F (m ² s ⁻¹)	$10^{-6} \exp(-0.8 \text{ eV}/kT)$
Diffusion coefficient of V_F centers, D_V (m ² s ⁻¹)	$10^{-6} \exp(-0.69 \text{ eV}/kT)$
Formation energy of F centers, E_F^f (eV)	0.9
F–H recombination rate constant, β_r (m ⁻²)	10^{20}
Matrix shear modulus, μ (GPa)	15
Coherent colloid shear modulus, μ_C (GPa)	10
Surface energy of NaCl, γ (J/m ²)	0.82
Atomic volume of the host lattice, ω (m ⁻³)	4.4×10^{-29}
Ratio of relaxation volumes of H and F centers, $\Omega_H/ \Omega_F $	1.8
Dislocation bias, δ_d	0.26
Colloid misfit, ε	0.068
Misfit bias, δ_ε	0.13
Image interaction constant α^{im}	1
Elastic-diffusion anisotropy interaction constant, α^d	1
Modulus minus elastic anisotropy interaction constant, $\alpha^{\mu, \xi}$	10
The standard heat of formation of one NaCl molecule, q_{NaCl} (eV)	4.26

Since the colloids are formed by F centers they are expected to be coherent with the host matrix as long as they are small. In this, coherent, state, there exists a misfit, ε , which is equal to the difference between the lattice constants of the colloid and that of the host lattice. Positive (or negative) misfit means that colloid is under compressive (or tensile) stress given by $\sigma_{rr} = \sigma_\varepsilon$

$$\sigma_\varepsilon = -\frac{3K_C\varepsilon}{1 + 3K_C/4\mu}, \quad (3)$$

where K_C is the colloid bulk modulus. In NaCl, coherent sodium colloids have a negative misfit of about 7% and, hence, a positive misfit bias, δ_ε , which means that they can grow only if the dislocation bias is larger than δ_ε

$$\delta_\varepsilon = \alpha^d(\sigma_\varepsilon/\mu) + \alpha^{\mu,\varepsilon}(\sigma_\varepsilon/\mu)^2, \quad (4)$$

The normal stress at the bubble surface is given by the difference between its surface tension and the gas pressure, P : $\sigma_{rr} = 2\gamma/R_B - P$, where γ is the surface free energy of a bubble. Accordingly, its bias has both positive and negative constituents that depend on the gas pressure

$$\delta_B(R_B, P) \approx \alpha^{im} \frac{b}{R_B} + \frac{\alpha^d}{\mu} \left(\frac{2\gamma}{R_B} - P \right) + \frac{\alpha^{\mu,\varepsilon}}{\mu^2} \left(\frac{2\gamma}{R_B} - P \right)^2. \quad (5)$$

For voids we have $P \ll 2\gamma/R$, and so their bias decreases steadily with increasing size as

$$\delta_V(R_V) \approx \left(\alpha^{im} + \frac{\alpha^d 2\gamma}{\mu b} \right) \frac{b}{R_V} + \frac{\alpha^{\mu,\varepsilon}}{\mu^2} \left(\frac{2\gamma}{R_V} \right)^2. \quad (6)$$

Accordingly, voids can grow if their size exceeds a critical one determined by the mean bias and the void bias constants. Below this size, voids would capture more H centers than F centers, which would fill them with gas. In the following section, we consider a mechanism of overcritical void formation.

3. Void formation in NaCl due to a back reaction between sodium and chlorine colloids

When several H centers come together they combine to form a halogen bubble that ‘digs its own hole in the lattice by displacing a lattice cation and a neighboring lattice anion on to the edge of the dislocation loop’ [16]. This process is analogous to the loop punching by growing gas bubbles in metals [17–19]. The threshold pressure for the loop punching is inversely proportional to the bubble radius [19]

$$P^{th} \approx (\mu b + 2\gamma)/R_B. \quad (7)$$

At such a high pressure, a small halogen bubble, $R < R^{th}$, has a higher bias for H centers than the dislo-

cation or colloid bias, and so it can absorb extra H centers and grow via SIA-loop punching. With increasing bubble radius beyond some threshold value, R^{th} , its bias decreases very rapidly to the mean bias of the system (determined by the biases of dislocations and sodium colloids) resulting in the formation of a stable bubble, as shown in Fig. 2. Stable bubbles can no longer absorb extra H centers and grow, nor can they absorb extra F centers required for the bubble–void transition via the recombination with V_F centers, as has been

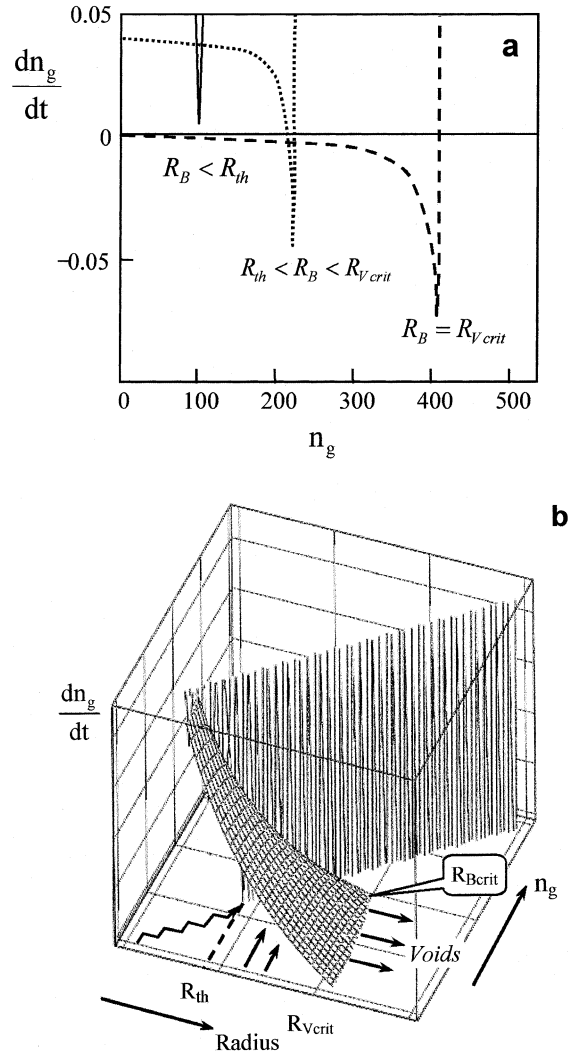


Fig. 2. The rate of accumulation of halogen molecules, dn_g/dt , in a bubble as a function of n_g at fixed bubble radii, R_B (a); as a function of n_g and R_B (b). At $R_B < R_{th}$, dn_g/dt for any n_g , and a bubble grows in size by pressure-driven plastic process; At $R_B > R_{th}$, a stable size appears, $dn_g/dt = 0$, which becomes unstable at $R_B > R_{Bcrit}$ and disappears at $R_B > R_{Vcrit}$. Above these points, voids may grow via agglomeration of incoming V_F centers and extra F centers.

suggested in the previous works [7,8]. To do so, the bubble radius must become larger than a critical value, R_{Berit} , shown in Fig. 2(b), but the stable radius is always smaller than the critical one. Their exact values depend on the equation of gas state (such as the Van der Waals gas law used in [8]) but the stable bubble radius can be only slightly larger and is practically determined by R^{th} , which depends only on the bias parameters as follows:

$$R^{\text{th}} = \frac{4b\alpha^{\text{im}}\alpha^{\mu,\xi}}{4\alpha^{\mu,\xi}\bar{\delta} + (\alpha^{\text{d}})^2}, \quad (8)$$

where $\bar{\delta}$ is the mean bias of the system. It can be seen from Eq. (8) that the positive quadratic dependence of the bubble bias on pressure (at $\alpha^{\mu,\xi} > 0$) is a *primary driving force* for the separation of the H and F centers into bubbles and metal colloids. Without it (at $\alpha^{\mu,\xi} \leq 0$) small molecular centers would be stable and would not grow to become bubbles. At $\alpha^{\mu,\xi} > 0$, bubbles are forced

to grow up to a stable size Eq. (8), which is however not large enough to enable them to capture extra F centers required for the bubble–void transition.

If we calculate the mean radii and number densities of bubbles and colloids at a constant dislocation density (which we can do now since we have the bubble mean radius Eq. (8), and their volume fraction is determined by mean parameters of sodium colloids, which are calculated in the same way as in [8]) it appears (see Fig. 3(a)) that colloids can grow early enough to sizes exceeding the mean distance between the bubbles resulting in the direct collisions between them. That would initiate an explosive back reaction between the radiolytic sodium and chlorine.

The amount of released energy in the back reaction is proportional to the energy released due to the formation of one NaCl molecule, q_{NaCl} , and to the number of molecules formed as a result of the collision. The latter is limited by the mean number of chlorine atoms in a

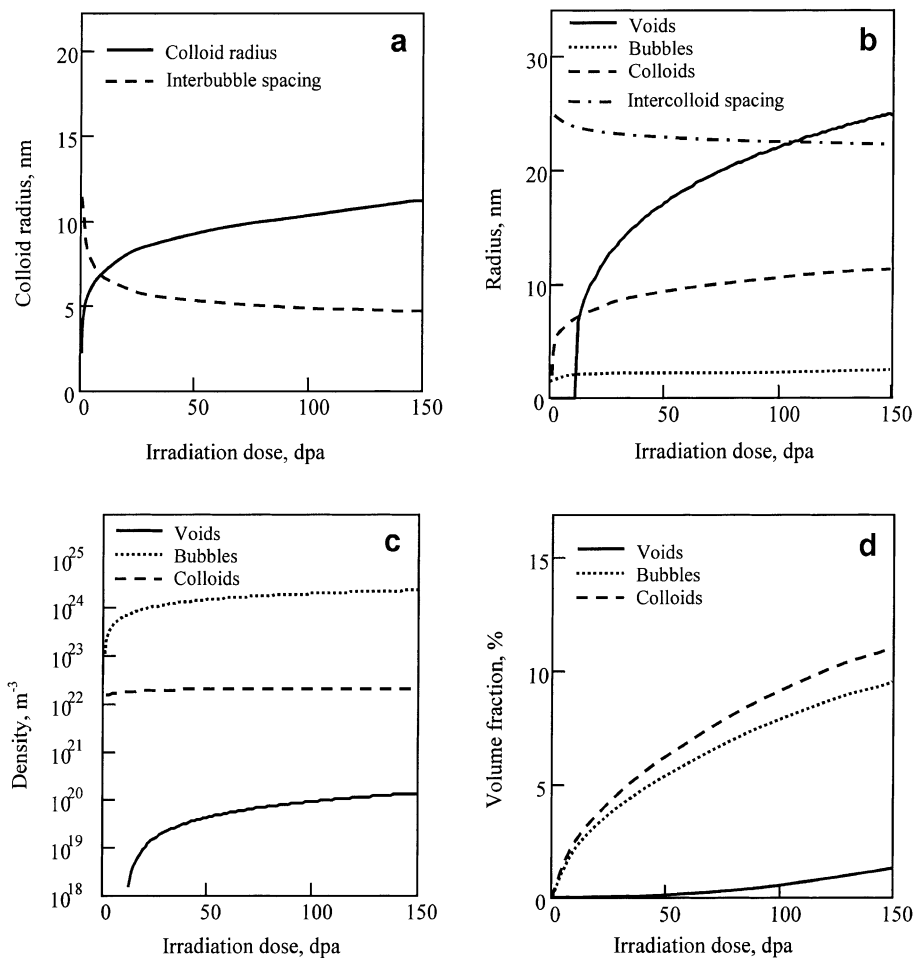


Fig. 3. Evolution of bubbles, colloids and voids with increasing irradiation dose (in displacements per atom, dpa) at a constant dislocation density 10^{14} m^{-2} and a probability of void formation $P_{\text{void}} = 10^{-3}$.

bubble, which is two orders of magnitude smaller than the number of sodium atoms accumulated in a colloid by the time of collision (Fig. 4). The released energy heats up the reaction products resulting in an instantaneous temperature and pressure increase, which can be estimated as it has been done in [20] for the void–colloid collision (see also the next section)

$$\Delta T \approx \frac{2}{5} \frac{q_{\text{NaCl}}}{k} \approx 10^4 \text{ K}, \quad \Delta P \approx \frac{2}{5} \frac{q_{\text{NaCl}}}{\omega} \approx \mu, \quad (9)$$

where k is the Boltzmann constant. The pressure increase given by Eq. (9) is higher than the threshold pressure given by Eq. (7), and although it is extremely short (in the picosecond range) it can induce some plastic growth of the cavity filled with reaction products before it cools down. As a result, one would expect the formation of an empty cavity in the vicinity of the colloid with a radius somewhat exceeding the bubble radius before the collision. It means that there is a probability of explosive formation of cavities having a radius larger than the critical one, R_{Vcrit} , given by

$$R_{\text{Vcrit}} = b \left(\frac{1}{2} \frac{\alpha_{\text{iv}}}{\delta} + \sqrt{\frac{1}{4} \left(\frac{\alpha_{\text{iv}}}{\delta} \right)^2 + \frac{4\gamma^2 \alpha^{\mu, \xi}}{\delta (\mu b)^2}} \right), \quad (10)$$

$$\alpha_{\text{iv}} \equiv \alpha^{\text{im}} + \alpha^{\text{d}} \frac{2\gamma}{\mu b}.$$

Both R^{th} and R_{Vcrit} are estimated to be $\sim 1\text{--}2$ nm, which is much smaller than the colloid mean radius ($\sim 5\text{--}10$ nm).

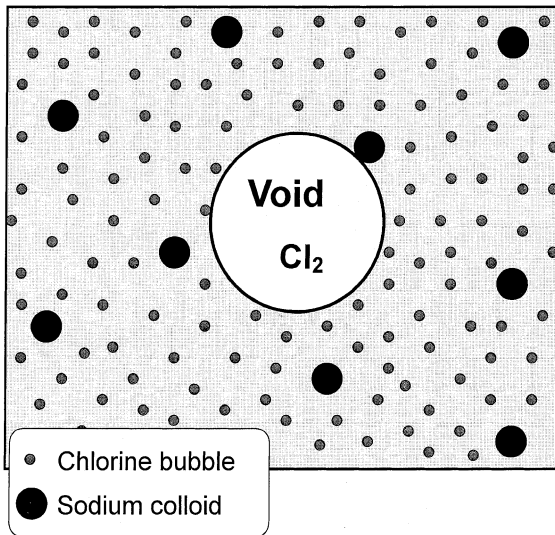


Fig. 4. Illustration of the distribution of chlorine bubbles, sodium colloids and voids in irradiated NaCl crystals. The bubble size is $\sim 1\text{--}2$ nm; the colloid size \sim interbubble spacing $\sim 5\text{--}10$ nm; the void size is about intercolloid spacing $\sim 20\text{--}30$ nm, when their collisions with colloids start.

So the colloid growth is only slightly affected by the collisions, resulting in a negative correction to the colloid growth rate proportional to the colloid volume fraction, which is less than 10% in most cases. But the possibility of formation of overcritical voids is very important for a subsequent growth of large voids and their impact on the material stability observed experimentally [5–8,20]. Overcritical voids have been shown [8] to grow very fast as compared to the bias driven growth of colloids, since voids have no misfit bias, and their growth is practically limited by absorption of V_F centers. An important parameter is, of course, the number density of voids, which have been measured to range from 10^{19} to 10^{20} m^{-3} in most of our experiments, which is two and four orders of magnitude lower than the calculated number density of colloids and bubbles, respectively (see Fig. 3 and [8]). The void nucleation rate is given by the product of the number of collision between colloids and bubbles per unit time and the probability of formation of an overcritical void in one collision, P_{void} .

$$\frac{dN_{\text{v}}}{dt} = \frac{dV_{\text{C}}}{dt} \times N_{\text{B}} \times P_{\text{void}}, \quad (11)$$

where V_{C} is the colloid volume fraction and N_{B} the bubble number density. If we assume $P_{\text{void}} = 10^{-3}$ we will obtain the void formation rate observed experimentally, as will be shown in the following section:

4. Evolution of bubbles, colloids and voids in NaCl under electron irradiation

The bias driven evolution of the system in the case of the bubble–void transition induced by the bubble–colloid collisions is shown in Fig. 3. As in [8], we have assumed a constant dislocation density of 10^{14} m^{-2} , but we did not have to assume the bubble number density. The latter has been calculated using the equation for the bubble radius Eq. (8) and the balance between the bubble and colloid volume fractions. The void influence on the mean system bias is weak due to their low number density (Fig. 3(c)) while their radius grows much faster than that of colloids and bubbles. (Fig. 3(b)).

According to the present model, chlorine bubbles are the most finely dispersed ED in the system (the interbubble spacing is typically about 5 nm) so that they start to collide with growing voids first, filling them with chlorine gas (Fig. 4). The chlorine molecules within the ‘bubbles’ are in a solid or liquid state due to a super high pressure (in the GPa range), but after collision with a void it becomes a gas. One can estimate the number of chlorine atoms, n_{Cl} , captured by a void of radius R_{V} as a product of the void volume and the bubble volume fraction, V_{B} , divided by the chlorine atomic volume, ω_{Cl}

$$n_{\text{Cl}} = \frac{4\pi}{3} R_V^3 \frac{V_B}{\omega_{\text{Cl}}} \quad (12)$$

The bubble volume fraction grows with irradiation dose at the same rate as the colloid volume fraction, $V_C = \frac{\omega}{\omega_{\text{Cl}}} V_B$, due to the balance between sodium and chlorine atoms stored in the unit volume of the matrix, where ω is the atomic volume of NaCl. Accordingly, the gas pressure in the voids (where it is in molecular form) is also determined by the colloid volume fraction

$$P = \frac{(n_{\text{Cl}}/2)kT}{(4\pi/3)R_V^3} = \frac{kT}{2\omega_{\text{Cl}}} V_B = \frac{kT}{2\omega} V_C, \quad (13)$$

where we have used the equation of state of an ideal gas, which is valid in this pressure region. An estimate done for 100°C shows that even at maximum values of $V_C \approx 10\%$, the pressure is 5×10^{-3} Gpa (50 atm), which is still lower than the surface tension of a void as large as 200 nm. So this pressure only slightly decreases the void bias, which may increase the void diffusion growth rate. However, the chlorine accumulation in voids provides a very important possibility for the explosive back reaction with metallic sodium when a growing void hits the first colloid, which is much more powerful than that induced by direct colloid–bubble collisions.

The amount of released energy in this reaction is also proportional to the energy released due to formation of

one NaCl molecule, q_{NaCl} , and to the number of molecules formed as a result of collision, n_{NaCl} . The latter is equal now to the mean number of sodium atoms in a colloid, which is close to the number of chlorine atoms accumulated in the void at the time of the collision, and which is two orders of magnitude larger than that in one bubble (Fig. 4). Accordingly the temperature and pressure increase can be estimated as

$$\Delta T = \frac{q_{\text{NaCl}} n_{\text{NaCl}}}{C_p n_{\text{NaCl}}} \Big|_{C_p = \frac{5}{2}k} = \frac{2}{5} \frac{q_{\text{NaCl}}}{k} \approx 10^4 \text{ K}, \quad (14)$$

$$\Delta P = \frac{n_{\text{NaCl}} k \Delta T}{(4\pi/3)R_V^3} \Big|_{n_{\text{NaCl}} = \frac{4\pi}{3} R_V^3 \frac{V_C}{\omega}} \approx \frac{2}{5} \frac{q_{\text{NaCl}}}{\omega} V_C \approx \mu V_C, \quad (15)$$

where C_p is the specific heat capacity of NaCl per molecule. The pressure increase due to the colloid–void reaction is proportional to the colloid volume fraction, and is lower than the ultimate pressure increase given by Eq. (9) for the colloid–bubble collision. However, the reaction volume in the present case is much larger, and such an increase of pressure (in the GPa range) may initiate a crack propagation from the void along the matrix cleavage plane (100) if it is bigger than some threshold value [20]: $P_f = \sigma_f/2$, where σ_f is the fracture stress corresponding to the Griffith crack of the length equal to the void diameter. Fig. 5 shows the void–crack evolution with increasing irradiation dose and the

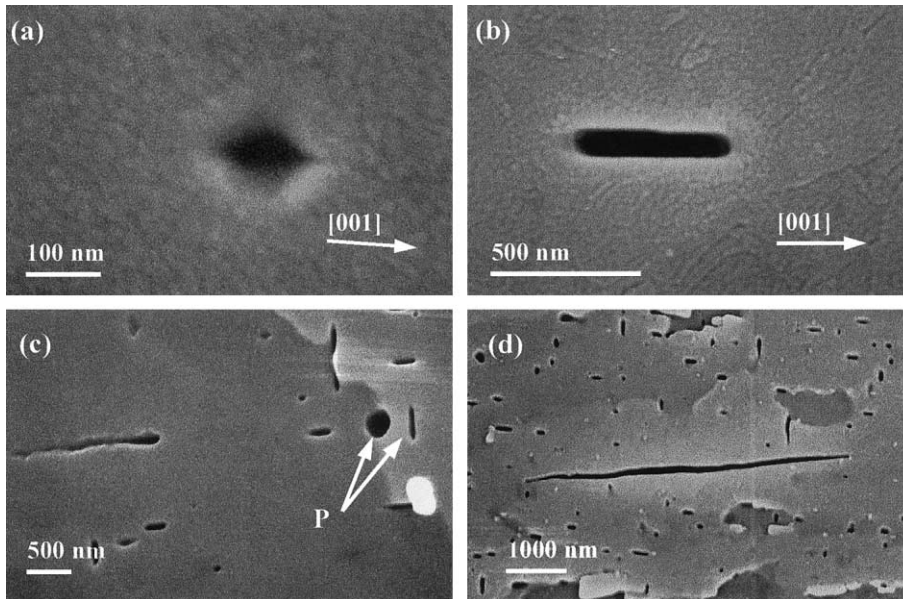


Fig. 5. SEM micrographs showing vacancy voids and cracks in natural rock salt crystals irradiated with 0.5 MeV electrons. (a) Equiaxial void at high resolution after irradiation to 30 dpa; latent heat of melting (LHM) of metallic Na is 0.45 J/g. (b) ‘Penny-shaped’ crack formed after irradiation to 130 dpa, LHM of metallic Na is 0.8 J/g. (c) ‘Penny-shaped’ cracks in natural rock salt irradiated up to 130 dpa Grad; LHM of metallic Na is 1.2 J/g. The letter ‘P’ with the arrows shows two adjacent voids with different orientations. (d) Large crack formed after irradiation to 130 dpa, LHM of metallic Na is 2.5 J/g.

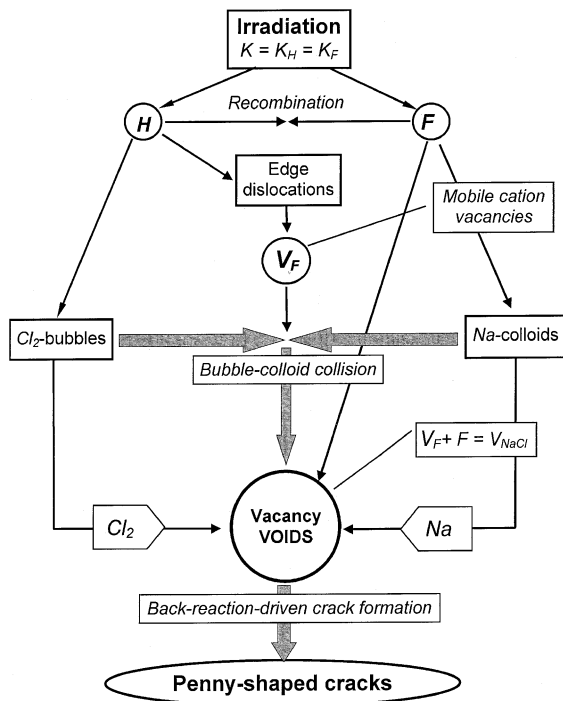


Fig. 6. Radiation-induced reactions between point defects (H- and F-centers, and cation vacancies) and extended defects (bubbles, dislocations and colloids) resulting in the void formation. Release of stored energy due to collisions with chlorine bubbles and sodium colloids induces the void-crack transition and a subsequent fracture of crystal.

amount of stored energy in natural rock salt crystals.² It is seen that the crack length increases gradually, which can be explained by a combined mechanism of diffusion accumulation and explosive release of energy in voids [21], by which the final crack length is determined by the rates of two competing processes, namely, the production and dissipation of heat. In some cases, the former process dominates resulting in a sudden fracture of the material [20,21].

Fig. 6 summarizes the radiation-induced reactions between point defects (PD) and extended defects (ED) based on the present model. Primary radiation-induced PD, namely, H and F centers, separate ultimately into bubbles, dislocations and metal colloids, which results in the production of secondary PD (V_F centers) and ED (voids). The voids absorb fine chlorine bubbles during their growth and accumulate a large number of chlorine molecules before the collision with colloids starts, which changes the scale of the back reaction from the atomic to

the macroscopic one. Thus, the structural stability of NaCl under irradiation is determined both by the amount of stored energy (measured via colloid volume fraction) and by the void size distribution.

5. Void and aluminum colloid formation in electron irradiated α -Al₂O₃

In ceramic materials the displacement may occur either radiolytically by conversion of radiation-induced electronic excitations into atom (ion) motion (as in the case of NaCl analyzed above), or ballistically, by transfer of kinetic energy from an incident projectile (electron, proton, neutron, ion). In compounds, the displacements may not always occur stoichiometrically, which suggests that it is worthwhile to transpose the mechanisms of void formation studied in the model material NaCl to a much wider group of ionic compounds. A characteristic example is alumina (α -Al₂O₃), where the displacement threshold energies of aluminum and oxygen have been reported to be 18–20 and 50–76 eV, respectively [13–15,22,23]. Due to such a large difference, the aluminum/oxygen displacement ratio is about 3–4 for irradiation with fission spectrum neutrons; this ratio is increased to ~14 for irradiation with 1 MeV electrons, and finally, only aluminum ions are displaced under irradiation with electron energy less than 390 keV. However, even irradiation with a sub-threshold electron energy of 300 keV has been shown to produce stoichiometric dislocation loops at temperatures >800 K [13], and both aluminum colloids and voids have been formed under irradiation with 1 MeV electrons in the range 880–1130 K [14,15]. Voids are readily formed under neutron irradiation as well between 925 and 1100 K [1], but there are no reports of aluminum colloids being observed in neutron-irradiated alumina to our knowledge.

These phenomena can be understood in the framework of a model similar to that for NaCl, but in which anion (O) vacancies (or rather F centers required for both the colloid and void formation) are produced at dislocations as a result of their reaction with cation (Al) interstitials. The basic secondary mechanism of anion vacancy production in this model is close to that proposed by Stathopoulos and Pells [13], according to which Al interstitials aggregate to produce a stoichiometric (although faulted) dislocation loop, while a stoichiometric number of Al and O vacancies remain in the lattice.

Consider the implications of this model first in the case when only aluminum ions are displaced in the primary damage process. Then climbing dislocations can be a source of anion vacancies, agglomeration of which would result in the formation of aluminum colloids, which is not restricted by anion interstitials since the latter are not produced. Accordingly, the colloid growth

² The amount of stored energy is measured in terms of latent heat of melting (LHM) of metallic Na, indicated in Fig. 5, which is proportional to the colloid volume fraction.

is not prevented by their large misfit bias for the interstitials (Al colloids have a negative misfit of ~7%), which however, prevents their conversion to voids, since the latter would require a bias for vacancies in order to form stoichiometric vacancy pairs. Voids can arise, however, as a result of formation of stoichiometric vacancy pairs at the surface of oxygen bubbles, since bubbles in alumina may grow by absorbing aluminum vacancies and become unstable with respect to the transition to voids after a critical number of oxygen molecules is reached (Figs. 7 and 8). In contrast to the NaCl case (Fig. 3), the transition point may be reached via a step-by-step absorption of cation and anion vacancies, which may explain much higher void densities observed in α -Al₂O₃ [15]. The reaction scheme of microstructural evolution in this limiting case is shown in Fig. 7.

In a more general case, when both aluminum and oxygen ions are displaced in the primary damage process, the colloid growth may be prevented by absorption of anion interstitials. To allow colloid growth, their anion bias, $\delta_{\text{anion}}^{\text{C}}$ must be smaller than a critical value given by

$$\delta_{\text{C}}^{\text{anion}} < \delta_{\text{d}}^{\text{anion}} + \delta_{\text{d}}^{\text{cation}} \frac{K_{\text{cation}}}{K_{\text{anion}}}, \quad (16)$$

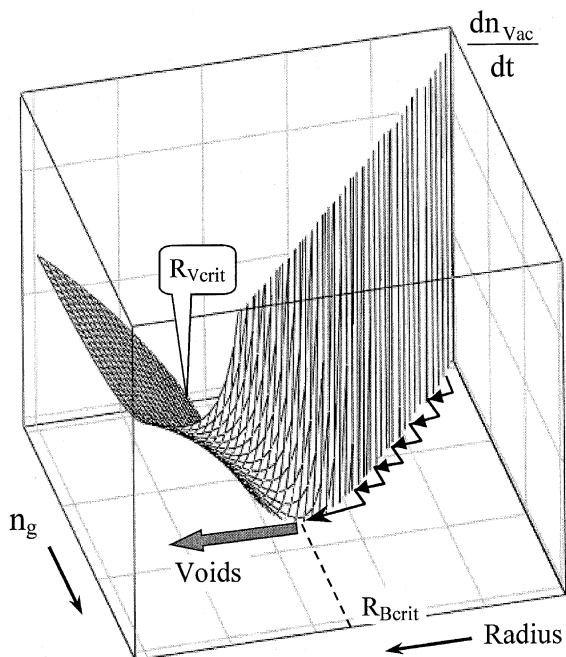


Fig. 7. The rate of accumulation of aluminum and oxygen vacancies, dn_{vac}/dt , in a bubble in Al₂O₃ as a function of bubble radius and number of oxygen molecules, n_g . Stoichiometric accumulation (increase of the radius at a constant n_g) becomes possible only above R_{Bcrit} resulting in the bubble-void transition.

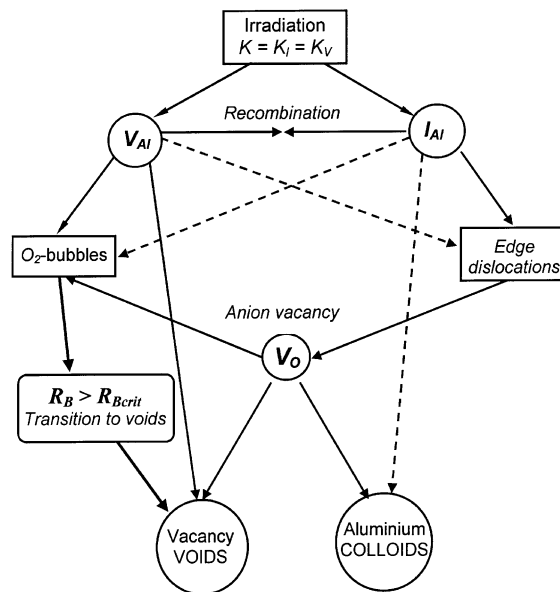


Fig. 8. Diagram of radiation-induced reactions between point defects and extended defects, which may explain the void and aluminum colloid formation observed in α -Al₂O₃ under sub-threshold electron irradiation, which displaces only aluminium ions. Anion vacancies (V_{O}), which are required for the void and aluminum colloid formation, are produced at dislocations as a result of their reaction with cation interstitials (I_{Al}).

where $\delta_{\text{d}}^{\text{anion}}$ and $\delta_{\text{d}}^{\text{cation}}$ are the dislocation biases in the respective sublattices that provide extra anion vacancies required for colloid growth, and $K_{\text{cation}}/K_{\text{anion}}$ is the aluminum/oxygen displacement ratio. The dislocation cation bias is expected to be small in alumina as compared to the anion biases, since the structure of α -Al₂O₃ is dominated by the anion sublattice of the larger oxygen ions [9]. So the criterion (16) may be satisfied at sufficiently high aluminum/oxygen displacement ratio, such as that realized under irradiation with 1 MeV electrons, when both colloids and voids are formed [14,15]. Under neutron irradiation, aluminum/oxygen displacement ratio decreases from 14 to 4, which may be the cause of suppression of colloid formation.

This simple picture does not provide yet a quantitative description of the microstructural evolution in α -Al₂O₃. However it may give a better understanding of the underlying mechanisms of formation of extended defects in non-metallic compounds under irradiation.

6. Summary

1. A new secondary displacement mechanism of vacancy production at a dislocation as a result of its interaction with a primary interstitial ion in another sublattice has been proposed.

2. Two limiting cases have been considered, namely, NaCl and α -Al₂O₃, in which only anion or cation sublattice is primarily damaged, and the secondary point defects are V_F centers or F centers, respectively.
3. In NaCl chlorine bubbles grow to a stable size, and voids may arise as a result of their collisions with growing sodium colloids.
4. Voids in NaCl can grow fast via agglomeration of F and V_F centers to the dimensions exceeding the mean distance between bubbles and colloids, eventually absorbing them, and, hence, bringing the halogen gas and metal to a powerful back reaction.
5. Sudden release of stored energy due to a back reaction inside voids results in a drastic rise of the temperature and gas pressure within voids, which may cause cracks in the matrix resulting in the material destruction.
6. In α -Al₂O₃ diffusion-driven transition from oxygen bubbles to voids is possible, which may be the cause of high number densities of voids observed under electron or neutron irradiation.
7. Aluminum colloids in α -Al₂O₃ may grow if the aluminum/oxygen displacement ratio is high, which is in qualitative agreement with experimental observations.
8. The proposed concept of bias-driven evolution of extended defects may be a prototype of an adequate description of the long-term behavior of the important insulating materials in intense radiation fields, which can be employed for an evaluation of the critical effects expected under storage conditions and development of radiation resistant materials.

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