

## The Kinetics of Radiation-Induced Defect Accumulation in Ionic Solids

E.A. Kotomin<sup>1,2</sup> and V.N. Kuzovkov<sup>1</sup>

<sup>1</sup> Institute of Solid State Physics, 8 Kengaraga str., LV-1063 Riga, Latvia

<sup>2</sup> Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

**Keywords:** Radiation Defects, Ionic Solids, Diffusion, Colloids, Particle Interaction, Many-Particle Effects

**Abstract.** Results of the first-principles study of diffusion-controlled aggregation of Frenkel defects - interstitial atoms and vacancies - under irradiation of solids are presented. Conditions of the efficient radiation-induced aggregation of vacancies and interstitials are studied. A *scenario* of the colloid growth is presented and illustrated for NaCl crystals.

As is well known, the primary radiation defects in ionic solids - the *F* centers (electron trapped by anion vacancy) and the *H* centers (interstitial halide atoms) under intensive irradiation and at high enough temperatures (typically above room temperature) begin to *aggregate* which leads to the formation of alkali metal colloids and gas bubbles (see [1] and references therein); a similar process occurs also in heavily irradiated metals. The intensive experimental studies of the conditions for the defect aggregation and further colloid formation (such as the temperature interval, dose rate, etc) continue nowadays for alkali halides [2,3] and technologically important ceramics [4]. This problem is also interesting from the fundamental point of view, being an example of **pattern formation and defect self-organization** in reaction-diffusion systems far from equilibrium [5].

Recently [6] we presented the first microscopic formalism describing the process of radiation-induced defect aggregation and colloid formation. This theory uses no fitting or uncertain parameters but only several basic defect parameters like the diffusion coefficients and the interaction potentials. However, the continuum approximation used in this study has led to non-physical problems of the cutting off of the interaction potentials at the nearest-neighbour (NN) distance, and large gradients of the correlation functions at these distances. The first point makes results very sensitive to the manner in which the potentials are defined at distances shorter than NN, the second one makes us to use very small coordinate increments in the calculations which strongly restricts the time interval realistically reachable using such an approach. It should be stressed that metal colloid formation is a very slow process which in real experiments often lasts several weeks or longer; another reason why this problem is difficult for the direct computer (Monte Carlo) simulations is that the mobilities of the two kinds of defects involved -interstitials and vacancies- differ typically by 15 orders of magnitude!

In the present paper, we describe briefly results of the microscopic **discrete-lattice theory** of diffusion-controlled aggregation accompanied by the bimolecular annihilation,  $A+B \rightarrow 0$ , under the permanent particle source and theoretically study with its help the cooperative effects in colloid formation observed in ionic solids exposed to irradiation.

The **physical model** includes creation of the interstitials and vacancies (called hereafter just defects A and B), with the (dose) rate  $p$ , AB pairs are not spatially correlated at birth and recombine when during their migration approach each other to within the NN distance. Therefore, their macroscopic concentrations always coincide,  $C=C_A=C_B$ . Isolated (single) defects hop with the activation energy  $E_\lambda$  and are characterized by the diffusion coefficients  $D_\lambda = D_0 \exp(-E_\lambda/k_B T)$ ,  $\lambda = A, B$ . When several defects are closely spaced, the hop rate of a given defect to the nearest empty lattice site is determined by both the local defect configuration and the interaction between defects; this can change its **effective** diffusion coefficient  $D_\lambda^{eff}$  by many orders of magnitude compared to that for a single defect. It affects the effective reaction rate  $K$  of the A and B recombination; for the diluted system in the continuum approximation it is well-known to be  $K_0 = 4\pi r_0(D_A + D_B)$ , where  $r_0$  is the recombination radius.

As follows from previous theoretical studies [6], defect attraction plays a decisive role in the aggregation process, it is incorporated in our model via three types of the NN attractions between the two kinds of NN defects (in the spirit of the Ising model):  $E_{AA}$ ,  $E_{AB}$  and  $E_{BB}$ . Note that only a few theoretical studies have been devoted up to now to the effects of particle interaction (especially, for similar particles) in the kinetics of the bimolecular diffusion-controlled reaction  $A+B \rightarrow 0$ , with the emphasis on fluctuation phenomena, rare exceptions are [7,8]. However, namely particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) under the irradiation.

The mathematical formalism will be described in detail elsewhere [9], it is a generalization of our previous microscopic many-point density approach [6,10,11] for the discrete lattice case which allows us to avoid the mentioned limitations of a continuum model, to increase to computation speed and thus to study the aggregation kinetics in the very wide time interval, up to  $10^5$  s. Theory is based on the Kirkwood superposition approximation for the three-particle densities [10] and thus operates with a set of coupled kinetic equations for the lattice defect densities (concentrations)  $C_\lambda(t)$ ,  $\lambda = 0, A, B$  and the joint correlation functions  $F_{\lambda\nu}(|\mathbf{r}_\lambda - \mathbf{r}_\nu|, t)$  where  $\mathbf{r}_\lambda$  and  $\mathbf{r}_\nu$  are coordinates of two lattice sites and  $t$  is time. Since defect correlations are short-range,  $F_{\lambda\nu}(r, t)$  strives for its asymptotic value of the unity (random particle distribution), as the relative coordinate  $r \rightarrow \infty$ . That is, if some joint density  $F_{\lambda\nu}(r, t)$  considerably exceeds the unity value, it means surplus of the defect pairs  $\lambda\nu$  at a given relative distance compared to the their random (Poisson) distribution, and vice versa. The simultaneous analysis of the joint correlation functions for similar (AA, BB) and dissimilar (AB) pairs, as well as for 0A, 0B pairs (empty site-defect) permit to study the **spatio-temporal evolution** of the strongly non-equilibrium system, in particular, crystals with radiation defects [6,9-12].

It is also convenient to characterize the aggregation process by monitoring the concentrations of *single* defects  $C_\lambda(1)$  (no other defects in NN sites) and *dimer* defects  $C_\lambda(2)$  (two similar defects are NN) which could be calculated from the joint densities in the standard so-called cluster approximation. Lastly, large aggregates could be characterized by the integral values of the number of particles  $N_A$ ,  $N_B$  therein and their sizes (radii)  $R_A$  and  $R_B$ .

**Frenkel defect accumulation in NaCl crystals.** We have applied our theory to the kinetics of defect aggregation in NaCl crystals at 400 K when colloid formation is well pronounced. The first conclusion is that at this temperature starting from the very short

times,  $t \leq 10^{-5}$  s, most interstitials are already aggregated; the concentrations of single and dimer interstitials,  $C_A(1)$  and  $C_A(2)$ , are about 6 orders of magnitude less than the macroscopic (total) concentration  $C = C_A = 10^{-11}$ , i.e. most of interstitials belong to larger aggregates. This is a direct result of high mobility of interstitials A (the activation energy for hops is 0.1 eV only) when even moderate mutual attraction leads to the formation of large aggregates. In contrast, slow mobile vacancies B ( $E_B = 0.9$  eV) exist for a much longer times predominantly as single defects - up to some characteristic time  $t_0$  ( $\approx 1$  s). As  $t > t_0$ , the concentration of single and dimer defects become similar, and at longer times we see growth of more complex aggregates (trimers, etc.).

Our calculations show that below the critical time  $t_0$  a mean number of interstitials in A-aggregate is practically constant,  $N_A \approx 150$ , whereas  $N_B \approx 1$  (single vacancies dominate). However, as soon as  $N_B$  shows a sharp increase at  $t > t_0$ , so does  $N_A$  too. That is, the aggregation of vacancies greatly enhances that of interstitials- we clearly observe the **cooperative process** of the simultaneous aggregation of the two kinds of defects. This conclusion is supported by similar behaviour of the calculated size of these two kinds of aggregates. The physical background of this effect is clear- at  $t > t_0$  most of interstitials are already aggregated and their further growth is restricted by the recombination with slow mobile single vacancies. When the latter begin to aggregate too, they no longer control behaviour (and prevent additional aggregation) of interstitials. As a result, we have a positive back-coupling of the two kinds of aggregation processes. Here it is important to stress the great similarity between two kinds of aggregates in sizes and number of particles reaching 2000-3000 per aggregate. This means that despite the fact that the very mobilities and interaction energies between single interstitials and vacancies greatly differ, their aggregates start to reveal properties common for big conglomerates of any kind of particles.

A very important condition of this cooperative aggregation of interstitials and vacancies could be additionally learnt from our calculations. At  $t < t_0$  the effective diffusion coefficient of vacancies,  $D_B^{eff}$ , practically coincides with that for single vacancies,  $D_B$ , whereas that for the interstitials,  $D_A^{eff}$  dramatically decreases in time by many orders of magnitude due to effective interstitial aggregation. This continues up to the moment  $t_0$  when  $D_A^{eff}$  becomes close in magnitude to the small diffusion coefficient of single vacancies,  $D_B$ . After mobilities of the two kinds of defects become comparable,  $D_A^{eff}$  is stabilized but in its turn,  $D_B^{eff}$  begins to decrease, thus indicating the effective aggregation of vacancies.

The analysis of the time-development of the joint correlation functions of similar defects,  $F_{AA}$ ,  $F_{BB}$ , demonstrates the strong aggregation of **both** interstitials and vacancies. The relative distance of  $r \approx 60 a_0$  where they approach the asymptotic value of unity agrees with our qualitative estimate of the radius of aggregate. Despite very different mobilities and interaction energies of interstitials and vacancies, the cooperative effects in their aggregation lead to the quite similar final aggregates observed at the end of irradiation. The correlation function for the dissimilar defects,  $F_{AB}(r)$ , is anti-correlated to  $F_{AA}$ ,  $F_{BB}$ , i.e. it increases from almost zero at short distances up to unity at  $r \approx 60-70 a_0$ , which gives us an estimate of the average distance between aggregates of dissimilar particles (defects). Lastly, the joint correlation functions "empty site-defect",  $F_{0A}$ ,  $F_{0B}$ , show that these aggregates have small, dense cores (there is almost no empty sites in their centers, but are quite loose on their periphery,  $r \geq 5a_0$ ). It agrees with the fact that at this temperature the colloid growth is indeed well pronounced in NaCl crystals [3]. A study of the effects of dose rate and the

temperature on the defect aggregation efficiency is now in progress. This study is aimed at a detailed comparison of the present microscopic theory and previous mesoscopic formalism [13,14] predicting existence of the critical dose rate, temperature and interaction energy between defects necessary for the efficient colloid growth.

**Conclusion.** We presented results of the first-principles discrete-lattice theory of colloid formation through the aggregation of similar **interacting** particles during the bimolecular reaction  $A+B\rightarrow 0$  (annihilation) with the permanent particle source (prolonged irradiation). We have shown that this process includes several intermediate stages (a dramatic reduction of the mobility of interstitials via their aggregation, then vacancy aggregation) and demonstrates at the latest stage the essentially **cooperative behaviour** in the aggregation of the two kinds of defects leading to their quite similar aggregates.

#### ACKNOWLEDGMENTS

This research has been financially supported by HCM network on the Solid State Atomic Scale Simulations (SSASS) (contract No CHRX-CT93-0134) and Volskswagen Foundation.

#### REFERENCES

- [1] P.W. Levy, *J. Phys. Chem. Solids* **52**, 319 (1991); W.J. Soppe and J. Prij, *Nucl. Technology* **107**, 243 (1994).
- [2] M. Reichling, *Nucl. Instr. Meth.*, **B 101**, 108 (1995).
- [3] E.R. Hodgson, A. Delgado and J.L. Alvarez Rivas, *Phys. Rev. B* **18**, 2911 (1978); J.R.W. Weerkamp, J.C. Groote, J. Seinen and H.W. den Hartog, *Phys. Rev. B* **50**, 9781 (1994).
- [4] S.J. Zinkle, *Nucl. Instr. Meth.*, **B91**, 234 (1994).
- [5] M. Cross and P.C. Holenberg, *Rev. Mod. Phys.* **65**, 3 (1993).
- [6] V.N. Kuzovkov and E.A. Kotomin, *Physica Scripta*, **50**, 720 (1994); *J. Phys: Cond. Matter* **7**, L 481 (1995).
- [7] V.N. Kuzovkov and E.A. Kotomin, *J. Chem. Phys.* **98**, 9107 (1993); *J. Stat. Phys.* **72**, 127 (1993).
- [8] I.M. Sokolov and A. Blumen, *Phys. Rev. E*, **50**, 2335 (1994).
- [9] V.N. Kuzovkov and E.A. Kotomin, to be published
- [10] V.N. Kuzovkov and E.A. Kotomin, *Rept. Progr. Phys.*, **51**, 1479 (1988); **55**, 2079 (1992); *Modern Aspects of Diffusion-Controlled Reactions* (Elsevier: Amsterdam, 1996).
- [11] E.A. Kotomin, V.N. Kuzovkov, W. Frank and A. Seeger, *J. Phys. A: Gen. Math.*, **27**, 1453 (1994).
- [12] V.L. Vinetsky, Yu.K. Kalnin, E.A. Kotomin and A.A. Ovchinnikov, *Sov. Phys.- uspekhi*, **33**, 793 (1990).
- [13] E.A. Kotomin, M. Zaider and W. Soppe, *Phil. Mag.* **A 70**, 313 (1994).
- [14] W. Soppe and E.A. Kotomin, *Nucl. Instr. Meth.*, **B 91**, 87 (1994); E.A. Kotomin, V.N. Kuzovkov, M. Zaider and W. Soppe, *Rad. Eff. and Def. in Solids*, **136**, 209 (1995).

## **Defects in Insulating Materials**

doi:10.4028/www.scientific.net/MSF.239-241

## **The Kinetics of Radiation-Induced Defect Accumulation in Ionic Solids**

doi:10.4028/www.scientific.net/MSF.239-241.387