Microscopic theory of colloid formation in solids under irradiation

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Abstract

Results of the first-principles study of diffusion-controlled aggregation of Frenkel defects—interstitial atoms—under irradiation of solids are presented. Conditions of the efficient radiation-induced aggregation of vacancies and interstitials are studied and the scenario of this process is presented.

Keywords: Frenkel defects; Alkalihalides; Clusters; Defect formation; Diffusion; Nucleation

As is well known, the primary radiation defects in ionic solids, the \textit{F} centers (electron trapped by anion vacancy) and the \textit{H} centers (interstitial halide atoms), under intensive irradiation and at high enough temperatures (typically around 100 °C) begin to aggregate which leads to the formation of alkali metal colloids and gas bubbles (see [1,2] and references therein). A similar process occurs also in heavily irradiated metals. Intensive experimental studies of the conditions for defect aggregation and further colloid formation (such as the temperature interval, dose rate, etc.) continue with respect to alkali halides [3] and technologically important ceramics [4]. This problem is also interesting from the fundamental point of view, being an example of pattern formation and 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 such as the diffusion constants and interaction potentials. However, the continuum approximation used in this study has led to non-physical problems of the cutting off of 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, and the second requires the use of very small coordinate increments in the calculations which strongly restricts the time interval reachable realistically 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 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 results of the microscopic discrete-lattice theory of diffusion-controlled aggregation during the bimolecular annihilation, \textit{A + B → 0}, under the permanent particle source and with its help we study theoretically the cooperative effects in colloid formation under irradiation.

The physical model includes creation of the interstitials and vacancies (called hereafter defects A and B), with the (dose) rate \( p \); AB pairs are not spatially correlated at birth and recombine when during their migration they 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 \( D_\lambda = D_0 \exp(-E_\lambda/k_B T) \), \( \lambda \equiv A, B \). 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 coefficients $D_{\text{eff}}$ by many orders of magnitude compared with 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 that $K_0 = 4\pi r_0(D_A + D_B)$, 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 NN attraction between the two kinds of NN defect (in the spirit of the Ising model): $E_{\text{AA}}, E_{\text{AB}}$ and $E_{\text{BB}}$. 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 $A + B \rightarrow 0$, with the emphasis on fluctuation phenomena; rare exceptions are [7,8]. However, particle interactions make the kinetic equations essentially non-linear and thus able to manifest the self-organization (pattern formation) under 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 the computation speed and thus to study the aggregation kinetics in a very wide time interval, up to $10^5$ s. The 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) $C_i(t)$, $i = 0$, A, B and the joint correlation functions $F_{ij}(r_i, r_j, t)$ where $r_i$ and $r_j$ are coordinates of two lattice sites and $t$ is time. Since defect correlations are short range, $F_{ij}(r, t)$ strives for its asymptotic value of unity (random particle distribution), as the relative coordinate $r \rightarrow \infty$. That is, if some joint density $F_{ij}(r, t)$ exceeds considerably the value of unity, there is a surplus of the defect pairs $ij$ at a given relative distance compared with their random (Poisson) distribution, and vice versa. The simultaneous analysis of the joint correlation functions for similar (AA, BB) and disimilar (AB) pairs, as well as for 0A, 0B pairs (empty site-defect) allow study of the spatiotemporal 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 $C_i(1)$ (no other defects in NN sites) and dimer defects $C_i(2)$ (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 $R_B$.

Let us now apply our theory to the set of parameters typical for NaCl crystals at 400 K when colloid formation is well pronounced. (The parameters used are given in the caption to Fig. 1.) The first conclusion from this figure is that at 150 °C starting from very short times, $t \leq 10^{-2}$ 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 the interstitials belong to larger aggregates. This is a direct result of the 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 much longer times predominantly as single defects, up to some characteristic time $t_0$ ($t_0 \approx 1$ s). As $t > t_0$, the concentrations of single and dimer defects become similar, and at longer times we see the growth of more complex aggregates (trimers, etc.).

Our calculations show that below the critical time $t_0$ the mean number of interstitials in an 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 $N_A$. That is, the aggregation of vacancies greatly enhances that of interstitials, we observe the cooperative process of the simultaneous aggregation of the two kinds of defect. This conclusion is supported by similar behavior of the calculated size of these two kinds of aggregate. The physical background of this effect is clear; at $t > t_0$ most of the 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 the behavior (and prevent additional aggregation) of interstitials. As a result, we have a positive back-coupling of the two kinds of aggregation process, which we called the cooperative effect. Here it is important to stress the great similarity between the two kinds of aggregate in sizes and number of particles reaching 2000–3000 per aggregate. This means that despite the fact that the mobilities and interaction energies between single interstitials and vacancies differ greatly, their aggregates start to reveal properties common for large conglomerates of any kinds of particle.

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

The relative spatial distribution of defects at the late aggregation state (\( t = 10^5 \) s) is seen in Fig. 2. The joint correlation functions of similar defects, \( F_{AA} \), \( F_{BB} \), demonstrate the strong aggregation of both interstitials and vacancies. The relative distance \( r \approx 60a_0 \) where they approach the asymptotic value of unity agrees with our qualitative estimate of the radius of the aggregate. Another important conclusion is suggested from this figure. Despite the very different mobilities and interaction energies of interstitials and vacancies, the cooperative effects in their aggregation lead to quite similar final aggregates observed at the end of irradiation. The correlation function for the dissimilar defects, \( F_{AN}(r) \), is anti-correlated to \( F_{AA}, F_{BB} \), i.e. it increases from almost zero at short distances up to unity for \( r \) approximately \( 60a_0 – 70a_0 \), which gives us an estimate of the average distance between aggregates of dissimilar particles (defects). Lastly, the joint correlation functions "empty site-defect", \( F_{DA}, F_{DB} \), show that these aggregates have small dense cores (there are almost no empty sites in their centers, but they are quite loose at their periphery, \( r \geq 50a_0 \)). This agrees with the fact that at this temperature colloid growth is indeed well pronounced in NaCl crystals [3]. A study of the effects of the dose rate and the temperature on the aggregation kinetics is now in progress.

In conclusion, we have 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 a permanent particle source (permanent irradiation). We have shown that this process includes several intermediate stages (a reduction in the mobility of interstitials via their aggregation, then vacancy aggregation) and demonstrate at the latest stage the essentially cooperative behavior in the aggregation of the two kinds of particle/defect leading to quite similar aggregates.

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References