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Kinetics of nanocavity formation based on *F*-center aggregation in thermochemically reduced MgO single crystals

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The dynamics of interacting *F* centers resulting in *F* aggregates and nanocavities is modeled in thermochemically reduced MgO single crystals. We have recently shown that thermal annealing of thermochemically reduced MgO with an exceptionally high *F*-center concentration ($6\times10^{18}\,\mathrm{cm}^{-3}$) induces a brown coloration in the crystals, which was attributed to scattering from nanosize cavities with their walls plated with magnesium metal [Phys. Rev. B **62**, 9299 (2000)]. In the present paper, a theory of the nanocavity formation process is developed based on diffusion-controlled aggregation of elastically interacting *F* centers and their annihilation at traps. We show that in contrast to the generally accepted viewpoint, the *F* centers in the bulk are not annealed out at the external sample surface but at internal defects, such as dislocations, subgrain boundaries, and impurities. The mutual attraction of the *F* centers is a key factor controlling the aggregation process.

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I. INTRODUCTION

It is well known that thermal annealing of *F* centers in additively colored, also known as thermochemically reduced, alkali halides gives rise to optical extinction bands due to intrinsic metallic colloids.[1] These bands have a bell-shaped dependence on the temperature and are usually analyzed using Mie theory. We have recently reported an observation of this process in MgO single crystals subjected to a very severe thermochemical reduction (TCR) process.[2] Unlike irradiation with particles, such as neutrons and ions, TCR results in stoichiometric excess of substitutional Mg ions, without the presence of oxygen interstitials. The resulting concentration of *F* centers was extraordinarily large, $\approx 6\times10^{18}\,\mathrm{cm}^{-3}$. The formation of an extinction band centered at ≈3.6 eV, which produces a brown coloration in the crystals, occurs after subsequent annealing in a reducing atmosphere in the temperature range of 1373–1673 K, and has a typical bell-shaped dependence on the temperature (Fig. 1). This extinction band was associated with nanocavities with their walls plated with magnesium with an average size of 3 nm as imaged by transmission electron microscopy.

The analysis of the *F*-center annealing kinetics in thermochemically reduced MgO crystals has demonstrated that the annealing rate strongly depends on the initial *F*-center concentration: the higher the concentration, the lower the rate.[3] We have proposed that for MgO crystals with low and intermediate *F*-center concentrations ($<10^{17}\,\mathrm{cm}^{-3}$) their thermal destruction is due to the more mobile defects such as Mg vacancies or impurities. Only in samples with an extremely high *F*-center concentration ($>10^{18}\,\mathrm{cm}^{-3}$), do the *F*-center *intrinsic* diffusion and aggregation result in unusual extended defects: magnesium-plated nanocavities. The experimentally estimated activation energy for the latter process is 3.4 eV,[3] close to the theoretically predicted value of 3.1 eV,[4] and much larger than generally believed. The present paper describes a model and simulations of the nanocavity formation process.

II. MODEL

In order to develop a model of metal colloid formation, we will first analyze the experimental data. Figure 1 clearly shows that the *F*-concentration decay and the growth of the Mg-colloid band start simultaneously at the temperature $T_1\approx 1500\,\mathrm{K}$, whereas complete destruction of both single *F* centers and colloids takes place at $T_2\approx 1800\,\mathrm{K}$. We assume that at temperature T_1 single *F* centers become mobile, make random walks in the lattice, and aggregate upon meeting each other in the nearest-neighbor (NN) lattice sites, giving rise to *F* aggregates (F_2, F_3, etc.), leading finally to metallic colloids. In the initial stage of the diffusion-controlled aggregation kinetics, the mean distance, l_0, between single *F* centers is $l_0=(n_0)^{-1/3}$, where n_0 is the initial *F*-center concentration. To form an F_2 dimer center, two single *F* centers during their random walking for τ sec have to diffuse the distance $l_0=\sqrt{D(T)\tau}$; here $D=D_0\exp(-E_a/kT)$ is the diffusion coefficient, E_a the activation energy, and D_0 the pre-

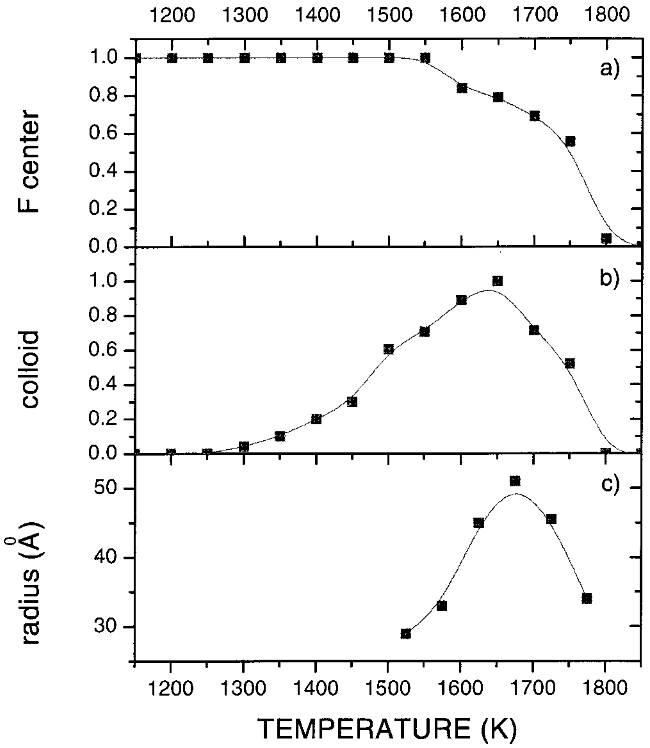

FIG. 1. Experimental kinetics of single F-center concentration decay and Mg colloid growth (Ref. 2). Colloid radius estimate is based on Mie theory, $n_0 = 6 \times 10^{18}\,\mathrm{cm}^{-3}$.

exponential factor. Using the above-mentioned E_a estimate of 3.5 eV, a typical value of $D_0 = 10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, and $n_0 = 10^{18}\,\mathrm{cm}^{-3}$, we obtain $\tau = 10\,\mathrm{min}$, in good agreement with the experimental data. It is generally believed that at temperature T_2 the F centers disappear at the external sample surfaces. However, under this assumption, defects have to move over a distance $d \approx 0.1\,\mathrm{cm}$ (sample thickness), which implies a diffusion time eight orders of magnitude longer than for aggregation. Indeed, increasing the temperature from T_1 to T_2 enhances the diffusion coefficient by only two orders of magnitude and the corresponding walking distance by one order of magnitude, whereas $l_0 = 10^{-6}\,\mathrm{cm}$ and $d = 0.1\,\mathrm{cm}$ differ by 5 orders of magnitude. Thus, at these temperatures (1500–1800 K) mobile F centers do not have a chance to reach the external sample surfaces in the minute time scale and can only annihilate at internal sinks.

An additional strong argument in favor of the key role played by the internal sinks in the annihilation of oxygen vacancy defects is the experimental fact that in TCR crystals where the initial F-center concentration is only one order of magnitude smaller, the colloid band is not produced when the crystal is subsequently reduced, even though the F annihilation kinetics remain similar.[3] This means that there are *two* space scales in the F center kinetics: the aggregation scale l_0 and the sink scale l. If $l_0 < l$, colloid formation is controlled by l_0, and l determines the kinetics at longer times (colloid destruction). In the opposite case, $l_0 > l$, it is the sink scale which controls the F annihilation kinetics since defects become trapped *before* they have a chance to meet each other during random walks. The fact that the colloid band is not already formed at $n_0 \approx 10^{17}\,\mathrm{cm}^{-3}$ indicates that l is not very much smaller than l_0. Dislocations, grain boundaries and impurities are likely to be the main internal sinks for the F centers.

In this paper, we use the simplest model of point unsaturable sinks. Its concentration, n_T, determines the sink scale l. The F-center kinetics is formulated as follows. (i) Single F centers perform random walks between the nearest lattice sites characterized by the diffusion coefficient $D(T)$. We fixed the activation energy $E_a = 3.5\,\mathrm{eV}$ and varied the preexponential parameter D_0, in order to reproduce semiqualitatively the experimental kinetics. It should be noted that $D_0 = 10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ is close to the maximum observed value. Thus, it is not realistic to significantly decrease E_a and to compensate with a corresponding increase of D_0. (ii) NN F centers attract each other, which is characterized by the interaction energy ε associated with the elastic attraction of the two close defects due to the overlap of the relevant lattice deformation fields.[5] Due to its short-range nature, the defect interaction is modeled on the lines of the Ising model (NN interaction). (iii) Clusters of F centers are *dynamic* formations. Any F center on the periphery can detach from the cluster. The delicate balance between aggregation of defects into colloids and colloid destruction at higher temperatures is controlled by the dimensionless factor ε/kT. The probabilities of jumps between two sites on the defective lattice are determined not only by the diffusion activation energy, E_a, characteristic of the perfect lattice, but also by the difference of the defect *interaction* energies with nearest neighbors in these two sites. (iv) Those F centers which turn out to be NN's of sinks (traps) instantly disappear. Traps with concentration n_T are randomly distributed over the sample.

Summing up, we have only three key parameters—D_0, ε, and n_T—which makes the solution of the problem quite straightforward. Our previous experience with similar problems suggests that the kinetics depend very much on the value of the defect interaction energy ε, which is typically quite small, of the order of 0.03 eV.[5,6] The small value of this parameter is also supported by the experimental data in Fig. 1: the F center concentration drops to zero near T_2, whereas the intensity of the colloid band reaches its maximum around 1600 K when the F center concentration is reduced by only ≈20%. This means that not every encounter of two F centers results in their aggregation, and defect pairs (dimers) easily separate. This is why only a fraction of the F centers aggregate into very loose clusters. The strong sensitivity of the kinetics with the interaction parameter ε makes it possible to determine its value quite precisely.

Calculations were performed using the computer code KINETICA described in detail in Ref. 7. This code was earlier successfully applied to a number of problems, including accumulation of Frenkel defects under irradiation of ionic solids[7] and catalytic surface reactions.[8] The most important calculated properties include: (i) concentrations of single and dimer F centers, (ii) concentration of colloids (defined as clusters containing more than three defects), (iii) mean colloid size and number of defects therein, all as a function of temperature. Not going into details, it should be noted here that we use microscopic formalism treating all elementary

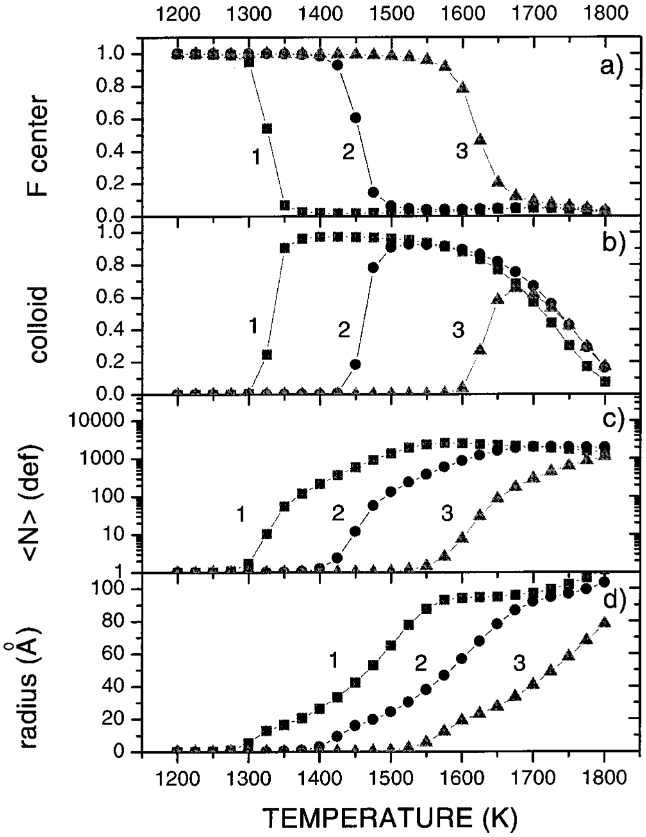

FIG. 2. Calculated annealing kinetics for a defect interaction energy of 0.04 eV, $n_0 = 10^{18}\,\mathrm{cm}^{-3}$, and $n_T = 10^{17}\,\mathrm{cm}^{-3}$. Curves 1, 2, and 3 correspond to the diffusion pre-exponential factors $D_0 = 10^{-3}$, 10^{-4}, and $10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, respectively. Figure 2(b) gives a fraction of all F centers aggregated into colloids.

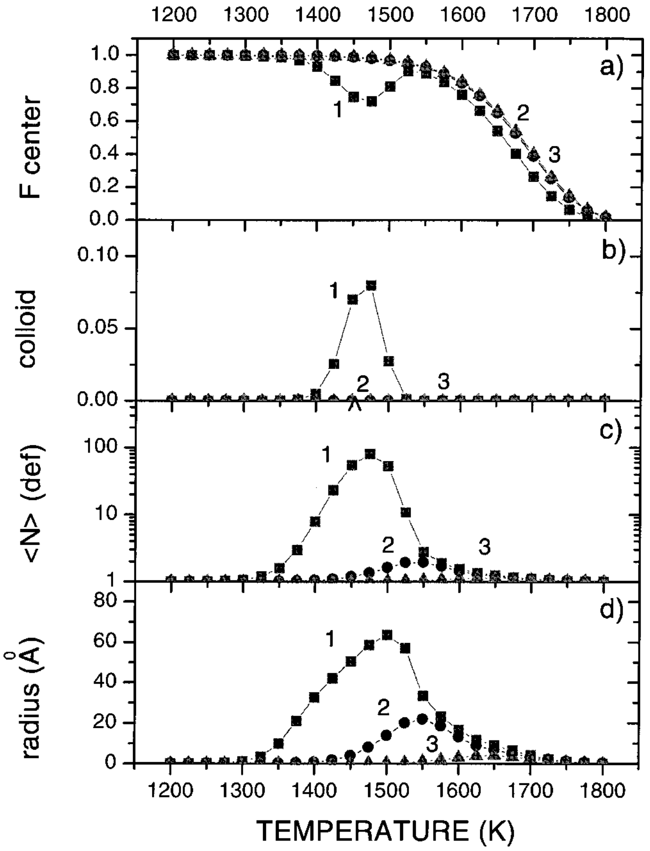

FIG. 3. Calculated annealing kinetics for $\varepsilon = 0.03\,\mathrm{eV}$, $n_0 = 10^{18}\,\mathrm{cm}^{-3}$, and $n_T = 10^{17}\,\mathrm{cm}^{-3}$. Curves 1, 2, and 3 correspond to the diffusion preexponential factors $D_0 = 10^{-3}$, 10^{-4}, and $10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, respectively.

processes at atomic scale. In this theory[6] the reaction kinetics for the macroscopic concentrations of F centers, traps and empty sites n_λ ($\lambda = F,T,0$, respectively) could be schematically presented by nonlinear kinetic equations of the following type:

$$\frac{dn_\lambda}{dt} = G_\lambda(n,K),$$
$$\frac{dK_{\lambda\mu}(r,t)}{dt} = J_{\lambda\mu}(n,K), \tag{1}$$

where λ, μ stand for the F centers, traps and empty sites, sets of K describe spatial correlations between λ- and μ-type defects, and G, J are complicated functionals of both defect concentrations and their spatial distributions. A qualitatively different feature of this approach (described in detail in Ref. 6)—unlike the usual macroscopic rate equations—is a direct incorporation of the effects of relative spatial distribution of the F centers which is not assumed to be random. As a result, the reaction rates becomes dependent on both time and spatial distribution of the F centers.

Another feature of our theory is the incorporation of the defect elastic interaction which considerably reduces the average mobility of the F centers due to their dynamical aggregation. As a result, our kinetic equations contain functionals G and J with joint correlation functions, unknown in the usual rate-equation approach. This makes our kinetic equations strongly nonlinear and complicated.[7] In conclusion of this section it should be mentioned that the F center annealing under study cannot be characterized by any certain order of the kinetics since the reaction rates now are time-dependent, and, unlike usual simple mono- or bimolecular reactions, here we have a competition of the reversible F center aggregation and their irreversible annihilation at traps, which are treated on equal ground in our model.

III. RESULTS

In our calculations we fixed the initial concentrations of F centers, $n_0 = 10^{18}\,\mathrm{cm}^{-3}$, and traps, $n_T = 10^{17}\,\mathrm{cm}^{-3}$, as well as the diffusion energy $E_a = 3.5\,\mathrm{eV}$. The variable parameter is the defect interaction energy ε. Figures 2 and 3 show the results of the calculations for $\varepsilon = 0.04\,\mathrm{eV}$ and 0.03 eV, respectively. The three curves in each window correspond to three different values of the diffusion preexponential factor D_0. As indicated in the figure captions, from one curve to the next, the diffusion coefficient changes by one order of magnitude. The results in Fig. 2 were obtained for a strong F-center attraction: F centers aggregate very abruptly as soon as they are mobile and the colloid radius is not a bell-shaped

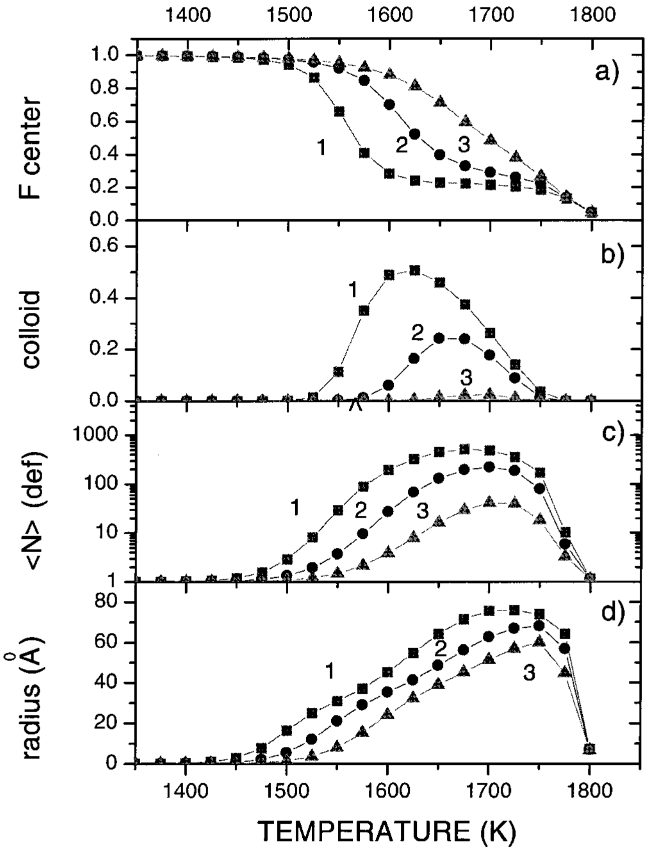

FIG. 4. Calculated annealing kinetics for $\varepsilon = 0.035\,\mathrm{eV}$, $n_0 = 10^{18}\,\mathrm{cm}^{-3}$, and $n_T = 10^{17}\,\mathrm{cm}^{-3}$. Curves 1, 2, and 3 correspond to the diffusion preexponential factors $D_0 = 10^{-4.25}$, $10^{-4.5}$, and $10^{-4.75}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, respectively.

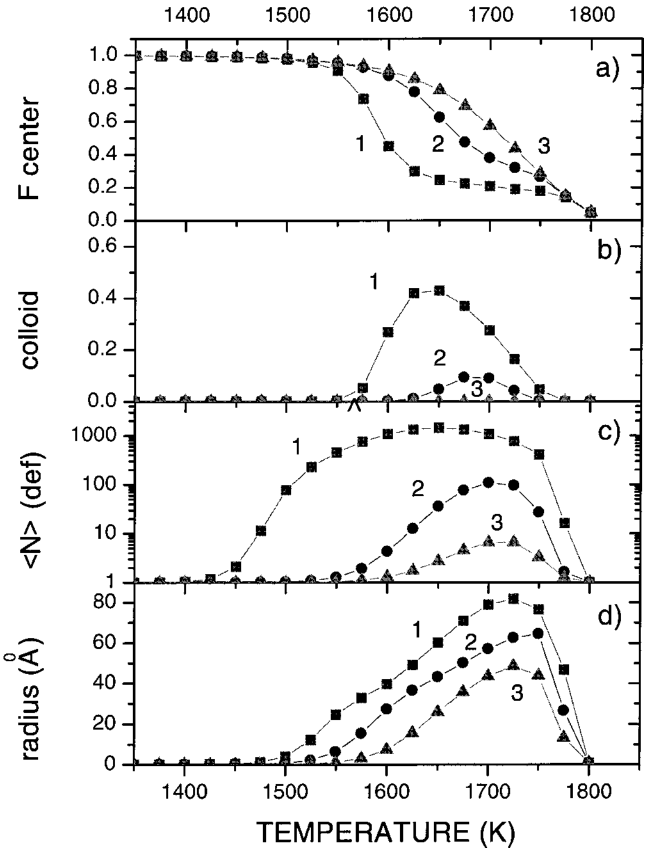

FIG. 5. Calculated annealing kinetics for $\varepsilon = 0.035\,\mathrm{eV}$, $n_0 = 10^{17}\,\mathrm{cm}^{-3}$, and $n_T = 10^{17}\,\mathrm{cm}^{-3}$. Curves 1, 2, and 3 correspond to the diffusion preexponential factors $D_0 = 10^{-4.25}$, $10^{-4.5}$, and $10^{-4.75}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, respectively.

function of the temperature, which contradicts the experimental findings. Curves 1 to 3 show that diminishing the *F*-center mobility by one order-of-magnitude increases the colloid formation temperature by 150–200 K. Even for such a large mutual attraction energy, the *F* centers are not completely bound in colloids: Figs. 2(c) and 2(d) show that there is some redistribution of *F* centers among colloids of different sizes due to a dynamic detachment-attachment process. As a result, the mean colloid radius and the number of defects therein grow.

A relatively small variation of the attraction energy leads to qualitative changes. For $\varepsilon = 0.03\,\mathrm{eV}$, the *F*-center annihilation takes place in a wide temperature interval of 300–400 K [Fig. 3(a)], in better agreement with the experimental results. However, the colloid formation turns out to be a very inefficient process and the colloids contain very small number of defects. Large colloids no longer grow at the expense of small colloids. They dissolve and the released *F* centers prefer to go to traps. Obviously, the true situation lies in-between the two cases shown in Figs. 2 and 3. In Fig. 4 we present results for the intermediate value of $\varepsilon = 0.035\,\mathrm{eV}$, and a smaller variation of the diffusion preexponential factor. Here, curves 2 resemble the experimental data: the temperature interval for the *F*-center decay is 300 K, and the peak temperature of the colloid formation and colloid radius curves also resemble those of the experiment. In addition, the colloid formation curve reveals a bell-shaped temperature dependence, with 25% of the *F* centers immersed in the aggregates. This translates to a typical colloid radius of about 70 Å containing a few hundred *F* centers. This result is consistent with experiments using microdiffraction, x-ray microanalysis, and high resolution electron microscopy, which demonstrated that the observed rectangular defects are nanocavities with their walls plated with magnesium.[2]

For the same D_0 preexponential factor, decreasing the initial *F* concentration by only one order of magnitude (Fig. 5) results in a reduction by a factor of 2–3 of the magnitude of the colloid formation [see curve 2 in Figs. 4(b) and 5(b)]. This result indicates that most of the mobile *F* centers are effectively trapped before they have a chance to aggregate.

IV. DISCUSSION AND CONCLUSIONS

The model in the present study provides a basis for diffusion-controlled aggregation of the *F* centers in thermochemically reduced MgO single crystals. Coupled with experimental data, the model leads to three basic conclusions: (i) the pairwise interaction energy between two nearest *F* centers is one of the key factors of the colloid formation kinetics (a similar conclusion was drawn for the *F*-center accumulation under irradiation of strongly ionic solids[5,7]); (ii) *F* centers do not reach the external sample surface but annihilate at internal defects (dislocations, subgrain boundaries and impurities); (iii) due to an effective trapping-aggregation competition Mg colloids can only be observed in crystals with very high initial *F*-center concentrations $(>10^{18}\,\mathrm{cm}^{-3})$.

Despite the fact that in our microscopic theory we use the only interaction parameter—the *pairwise F* center attraction energy ε—the interaction energy between any single *F* center attached to the cluster of *F* centers is proportional to the number of its nearest neighbors and thus depends not only on the radius of the cluster (colloid) but also on its shape, which is properly incorporated into our theory. The efficiency of this approach was demonstrated in our recent study of metal colloid growth and Ostwald ripening of small colloids into large colloids in electron irradiated LiF.[9]

It should be stressed that presented here kinetic theory is the first successful attempt of semiquantitative modeling of nanovoid formation in MgO. Further thermodynamical analysis is important for the understanding in detail an interaction of the mobile *F* centers with dislocations (e.g., Ref. 10).

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