



# Diffusion-controlled annihilation and aggregation of F-centers in thermochemically reduced MgO crystals

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## Abstract

The dynamics of F-center (an oxygen vacancy which has trapped two electrons) aggregation in thermochemically reduced MgO single crystals with an exceptionally high F-center concentration ( $6 \times 10^{18} \text{ cm}^{-3}$ ) is discussed. A theory of the Mg 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. © 2002 Published by Elsevier Science B.V.

**Keywords:** F centers; Thermochemically reduced MgO; Defect aggregation; Metallic colloids

## 1. Introduction

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 the first 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,  $n_0 \approx 6 \times 10^{18} \text{ cm}^{-3}$ . The formation of an extinction band centered at  $\approx 3.6 \text{ eV}$ , 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

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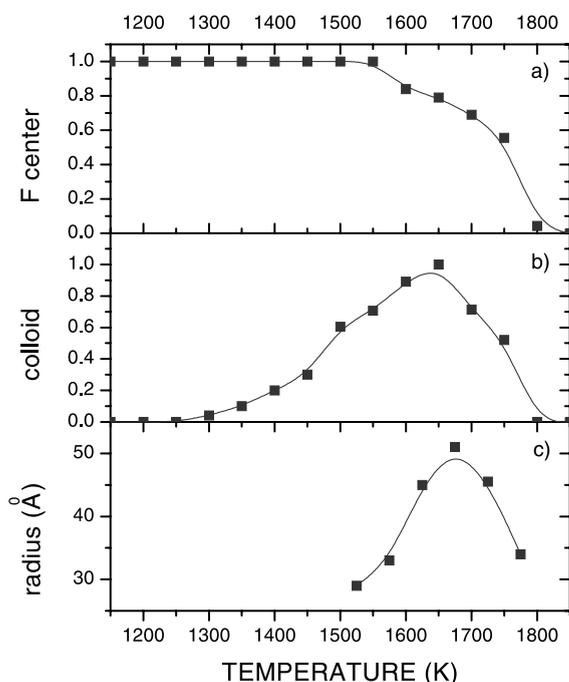


Fig. 1. Experimental kinetics of single F-center concentration decay (a), Mg colloid growth (b) and colloid radius (c) estimated based on Mie theory,  $n_0 = 6 \times 10^{18} \text{ cm}^{-3}$  [2].

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 fractional decay [3]. We have proposed that for MgO crystals with low and intermediate F-center concentrations ( $<10^{17} \text{ cm}^{-3}$ ) 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 ( $>10^{18} \text{ cm}^{-3}$ ), 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 3.5 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 first simulations the nanocavity formation process.

## 2. Model

In order to develop a model of metal colloid formation, we will first analyze the experimental data. Fig. 1 shows that the F-concentration decay and considerable growth of the Mg-colloids start around the temperature  $T_1 \approx 1500 \text{ K}$ , whereas complete destruction of both single F centers and colloids takes place at  $T_2 \approx 1800 \text{ K}$ . 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 lattice (NN) sites. The resulting F-aggregates ( $F_2$ ,  $F_3$ , etc.) ultimately lead 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  $\tau$  seconds have to diffuse the distance  $l_0 = (D(T)\tau)^{1/2}$ ; here  $D = D_0 \exp(-E_a/kT)$  is the diffusion coefficient,  $E_a$  the activation energy, and  $D_0$  the pre-exponential factor. Using the above-mentioned  $E_a$  estimate of 3.5 eV, a typical value of  $D_0 = 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ , and  $n_0 = 10^{18} \text{ cm}^{-3}$ , we obtain  $\tau = 10 \text{ min}$ , 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  $d \approx 0.1 \text{ cm}$  (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  $l_0 = 10^{-6} \text{ cm}$  and  $d = 0.1 \text{ cm}$  differ by five orders of magnitude. Thus, at these temperatures (1500–1800 K) mobile F centers do not have a chance to reach the external sample surfaces and can only annihilate at internal sinks.

In this paper, we use the simplest model of point unsaturable sinks. 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  $E_a = 3.5 \text{ eV}$  and varied the pre-exponential parameter  $D_0$ , in order to

reproduce semi-qualitatively the experimental kinetics. It should be noted that  $D_0 = 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  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  $\varepsilon$  associated with the elastic attraction of the two close defects due to the overlap of the relevant lattice deformation fields [5,6]. 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  $\varepsilon/kT$ . 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 of sinks (traps) instantly disappear. Traps with concentration  $n_T$  are randomly distributed over the sample. Thus, we have only three key parameters –  $D_0$ ,  $\varepsilon$  and  $n_T$  – which makes the solution of the problem quite straight-forward.

Calculations were performed using the computer code KINETICA described in detail in [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. Without going into details, it should be noted here that we use microscopic formalism treating all elementary processes at atomic scale. A qualitatively new feature of our approach (described in detail in [6]) – unlike the usual macroscopic rate equations – is a direct incorporation of the effects of relative spatial distri-

bution of the F centers which is not assumed to be random. As a result, the reaction rates become dependent on both time and spatial distribution of the F centers.

### 3. Results

In our calculations we used the experimental initial concentrations of F centers,  $n_0 = 10^{18} \text{ cm}^{-3}$ , and an estimate for traps,  $n_T = 10^{17} \text{ cm}^{-3}$ , as well as the diffusion energy  $E_a = 3.5 \text{ eV}$ . The main variable parameter is the F center attraction energy  $\varepsilon$ . A relatively small variation of the attraction energy leads to qualitative changes in aggregation kinetics. For  $\varepsilon = 0.03 \text{ eV}$ , the F-center annihilation takes place in a wide temperature interval of 300–400 K, in 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.

In Fig. 2 we present results for the optimised value of  $\varepsilon = 0.035 \text{ eV}$ , accompanied by a variation of the diffusion pre-exponential factor. 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 value is consistent with analytical electron microscopy observations of nanocavities with their walls plated with magnesium [2]. It should be stressed that use of the same  $D_0$  pre-exponential factor, but decreasing the initial F concentration by only one order of magnitude results in a reduction by a factor of 2–3 of the efficiency of the colloid formation. This indicates that most of the mobile F centers are effectively trapped before they have a chance to aggregate.

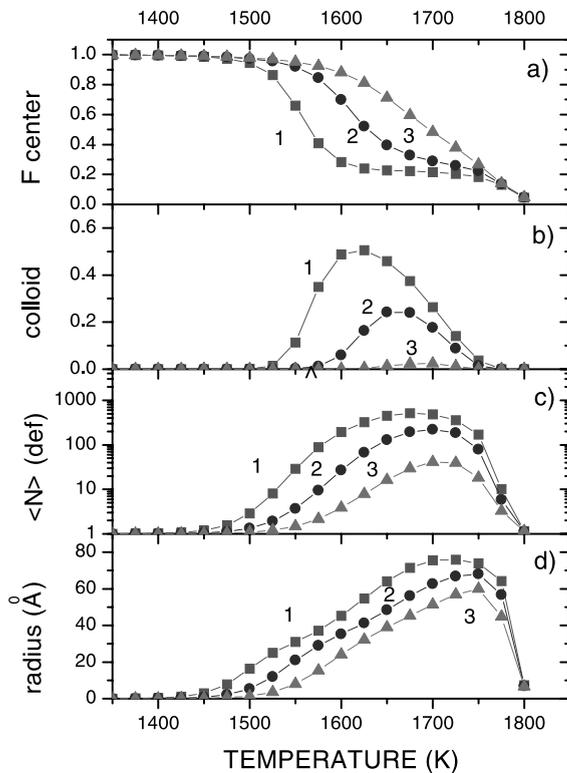


Fig. 2. Calculated F center annealing kinetics (a), the fraction of all F centers aggregated into colloids (b), a mean number of F centers in colloid (c), and its mean radius (d). The F center attraction energy  $\varepsilon = 0.035$  eV,  $n_0 = 10^{18}$  cm $^{-3}$  and  $n_T = 10^{17}$  cm $^{-3}$ . Curves 1, 2 and 3 correspond to the following diffusion pre-exponential factors  $D_0 = 10^{-4.25}$ ,  $10^{-4.5}$  and  $10^{-4.75}$  cm $^2$  s $^{-1}$ , respectively.

#### 4. Conclusions

Our model 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 ionic solids [5,7]); (ii) F centers do not reach the external sample surface but annihilate at internal defects (disloca-

tions, 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 ( $>10^{18}$  cm $^{-3}$ ). The efficiency of this approach was also demonstrated in our recent study of metal colloid growth and Ostwald ripening of small colloids into large colloids in electron irradiated LiF [9].

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