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Kinetics of *F* center annealing and colloid formation in Al$_2$O$_3$

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Abstract
The diffusion-controlled kinetics of the *F* center annealing in Al$_2$O$_3$ (sapphire, corundum) is simulated theoretically for the two regimes: after neutron irradiation when the immobile *F* centers are annihilated with complementary defects -- mobile interstitial oxygen ions, and in thermochemically reduced (additively colored) crystals where mobile *F* centers aggerate and create the metal colloids. A comparison of the experimental and theoretical kinetics allowed us to estimate the migration energies for the *F* centers and interstitial oxygen ions. It is obtained that the pre-exponents in diffusion coefficients for defects in different neutron irradiated samples can vary by two orders of magnitude which is attributed by presence of numerous traps for mobile interstitial oxygen ions.

Keywords: sapphire (Al$_2$O$_3$); fusion reactors; *F* centers; annealing; diffusion; neutrons; thermochemical reduction; metal colloids

1. Introduction

Al$_2$O$_3$ (sapphire, corundum) is a promising material for fusion reactors, e.g. for components such as breeder blanket and diagnostic windows [1]. Hence, there is a great interest in its radiation resistivity, nature of the radiation damage, structure and characteristics of the point defects it sustains upon exposure to high energy particles (neutrons, ions, protons etc) [2-12]. Among a large family of point defects formed in Al$_2$O$_3$ [2,4,13-15], *F* and *F*$^+$ centers (oxygen vacancy V$_o$ with two or one trapped electrons, respectively) are known as simplest primary point defects whose optical properties were studied in details [2,4,16]. In particular, there are numerous experimental measurements of the *F* center accumulation kinetics as a function of dose rate and temperature as well as their post-radiation subsequent temperature annealing [2-9, 11,12]. Thus, this is very important to predict/simulate the kinetics of defect accumulation under neutron irradiation as well as long-time defect structure evolution.

At moderate radiation doses and temperatures, the kinetics of the *F* center accumulation and subsequent annealing is controlled by their recombination with much more mobile interstitial oxygen ions (complementary Frenkel defects). Instead, at high irradiation doses (defect concentrations typically, of the order of 10^{19}cm^{-3}) and/or high temperatures the primary defects begin to aggregate, giving rise to colloids [6,11,17-20].

Another way to produce metal colloids is a high-temperature heating of thermochemically reduced (TCR) oxide crystals, as was demonstrated in the case MgO [21,22]. Note, that no colloid formation has been observed in sapphire under photo-excitation (photo-bleaching) of the *F* centers in both neutron- and thermochemically reduced MgO [23-25], unlike observations in alkali halides [20].

A study of metallic colloids in sapphire is especially important since they are related to material degradation. However, the kinetics of colloid formation here is studied much less than in similar MgO crystals [26] or alkali halides [17-20, 27]. Note also that the characteristic temperatures of the *F* center annealing in neutron irradiated and TCR samples greatly differ [4, 8, 28]: ~500K and ~1600K, respectively, due to large difference in temperatures at which the interstitial oxygen ions and the *F* centers begin to migrate (and the respective migration energies).

In this paper, we simulated theoretically the kinetics of the *F* center annealing as a function of temperature in the two regimes: after neutron irradiation, as a result of their recombination with mobile interstitial oxygen ions, and in thermochemically reduced samples containing only the *F* centers. Based on the comparison with the experimental kinetics, the defect migration and interaction energies are obtained.

2. Theoretical method

One of the main theoretical approaches to the kinetics of radiation damage is based on the rate equations (e.g. [29]) which take into account defect production and recombination but neglect similar defect aggregation and spatial inhomogeneities in defect distribution. In particular, such approach cannot study the kinetics of colloid formation. Another disadvantage is use of many phenomenological parameters—reaction rates—which should be estimated from experiments or theoretical calculations. We developed the alternative approach based on the formalism of *joint correlation functions* of spatial distribution of similar (*F-F* centers) and dissimilar (Frenkel pair of defects: the *F* center – interstitial O_i ions) [30] which is much better suited for the study of defect kinetics and aggregation.

The atomistic model of radiation damage takes into account the following steps:

- Frenkel defect production (e.g. *F* center- O_i pair in sapphire or other oxide material),
- Defect migration with the diffusion coefficient determined by the activation energy E_a and pre-exponent D_0,

- Similar (*F-F*) defect mutual attraction with the energy ε when they approach each other to nearest neighbor distance
- Dissimilar defect recombination upon mutual approach within the critical radius a_0
- Post-irradiation annealing with linear increase of temperature

The main calculated properties are

- Change with time (temperature) of concentrations of single-, dimer-, trimer- defect aggregates and colloids
- The size of colloid and number of defects therein
- The effective diffusion coefficient of defects in aggregates

A similar model was successfully used by us earlier for analysis of the LiF and CaF_2 metallization under low energy electron irradiation [31, 32].

3. Results

3.1.   TCR sapphire

We started with the modeling of Al colloid formation during the *F* center annealing in TCR sapphire, in order to reproduce experimental data [4, 28]. As shown in Fig.1, the *F* center annealing kinetics is controlled by its migration (E_a) and interaction (ε) energies. From a comparison with experiments (dotted points) , we extract their values: E_a=4.5 eV, ε= 0.08 eV. An increase of the migration energy by 0.2 eV leads to a considerable annealing temperature shift (200 K) to higher temperatures. The binding energy plays a key role in defect aggregation and colloid formation.

Fig. 2 shows that the *F* center annealing is accompanied by the intensive growth of the colloids at temperatures where the *F* centers are annealed. If the binding energy between the *F* center is small (<0.04 eV), colloids are dissolved at high temperatures. The typical colloid size for optimized parameters (E_a=4.5 eV, ε= 0.08 eV) is predicted to be quite small (10-20 Å); the average number of defects in each colloid only ~100-200 (Fig. 3). This explains why optical measurements [6, 11] show very broad band (which follows from Mie theory).

3.2.   Neutron irradiated sapphire

   The kinetics of the *F* center annealing after neutron irradiation was simulated as the bimolecular process [30] with equal concentrations of the *F* and O_i defects. It is controlled practically by the interstitial oxygen ion mobility which is much higher than that of the *F* centers. Fig. 4 shows fitting of the theoretical curves to four experiments done for neutron irradiated sapphire, in all cases annealing begins at temperatures 500-600K where both *F* and F^+ centers are still immobile [8]. Note that the experimental curves of the *F* center thermal annealing are slightly differ due to different neutron dose received by the samples and therefore different *F*

center concentration therein. Say, in Ramirez et al study [8], the irradiation dose was up to 1.4 x 10^{17} n/cm^2, while in Vila et al report [33], the neutron dose was higher ($\sim 10^{18}$ n/cm^2).

The shape of the annealing curves is determined by two control parameters: E_a and X which is

$$X = N_0 \, a_0 \, D_0 \, / \, \beta, \qquad\qquad\qquad (1),$$

N_0 is initial defect concentration, a_0 recombination radius, D_0 diffusion pre-exponent, and β heating rate. Assuming standard parameters $N_0 = 10^{17}$cm^{-3}, $a_0 = 10$ Å, $D_0 = 10^{-3}$ cm^2 s^{-1}, $\beta = 10$ K/min, one gets the estimate X= 10^8 (K^{-1}). However, fitting of the experimental curves gives much smaller X values (see Fig. 4 caption) which also differ by two orders of magnitude for different curves. This could be interpreted as a reduction of the diffusion rate due to interstitial oxygen ion trapping by impurities. The calculated migration energies also differ considerably, ranging from 0.8 eV down to 0.35 eV. This could be also partly related to trapping effects. Note that in recent experiments on neutron irradiated sapphire [34] even smaller annealing energies, 0.2-0.3 eV were reported, which hardly could be defect diffusion but more likely defect de-trapping energies.

4. Conclusions

A comparison of the calculated and experimental annealing kinetics for the *F* centers in neutron irradiated and thermo-chemically reduced samples allowed us to estimate the migration energy of interstitial oxygen ions and that for the *F* centers as ~0.8 eV and ~4.5 eV. These estimates could be checked by means of further atomistic defect calculations. Of special interest is a study of defect migration energies in different charge states since the fitted energies considerably differ from available calculations, e.g. our fitted 4.5 eV for the *F* centers and 1.85 eV [35] calculated for double charged oxygen vacancy. It was also shown, that the activation energy for cation intersitial *Al$_i$* diffusion is about 0.3 to 0.4 eV [36] which could be relevant for understanding experimental data in Fig.4.

Theoretical calculations could be also very useful for a study of the interstitial oxygen ion trapping by impurities (e.g. Mg). The Al colloids are predicted to be quite small, 10-20 Å, in agreement with available experiments [6,11]. Large dispersion (two orders of magnitude) in the pre-exponential factors of the interstitial oxygen diffusion could arise due to presence of numerous traps (impurities and structural defects) in studied sapphire samples. Note that this is one of few first attempts to quantify the kinetics of the defect annealing in sapphire which needs further detailed analysis.

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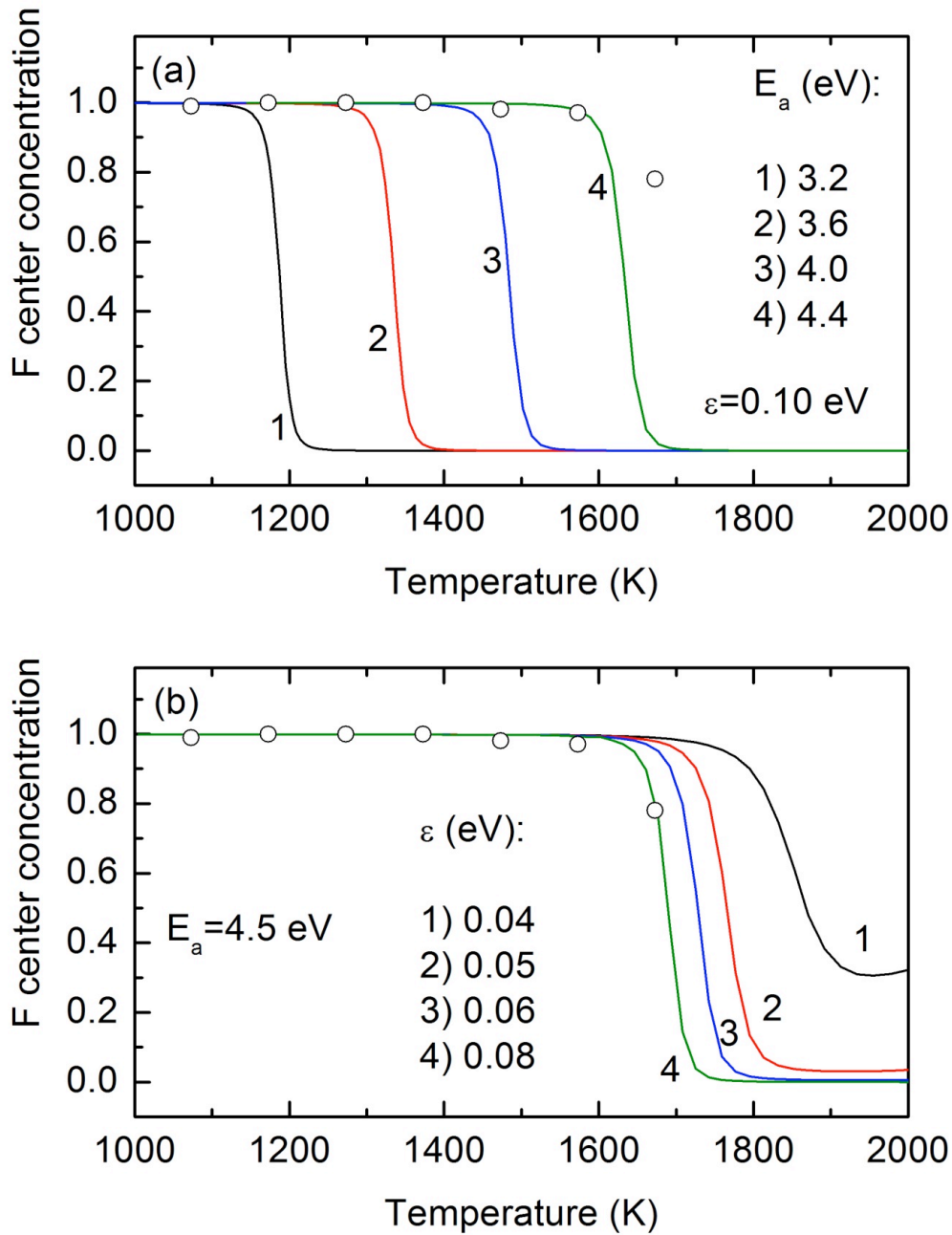
Figures

Fig.1. The kinetics of *F* center annealing in thermochemically reduced sapphire as a function of the defect diffusion energy E_a (upper window) and mutual attraction ε (window below). The best agreement with experiments corresponds to E_a=4.5 eV, ε= 0.08 eV. Initial defect concentration 10^{18} cm^{-3}. Point are experimental data (ref. [4]).
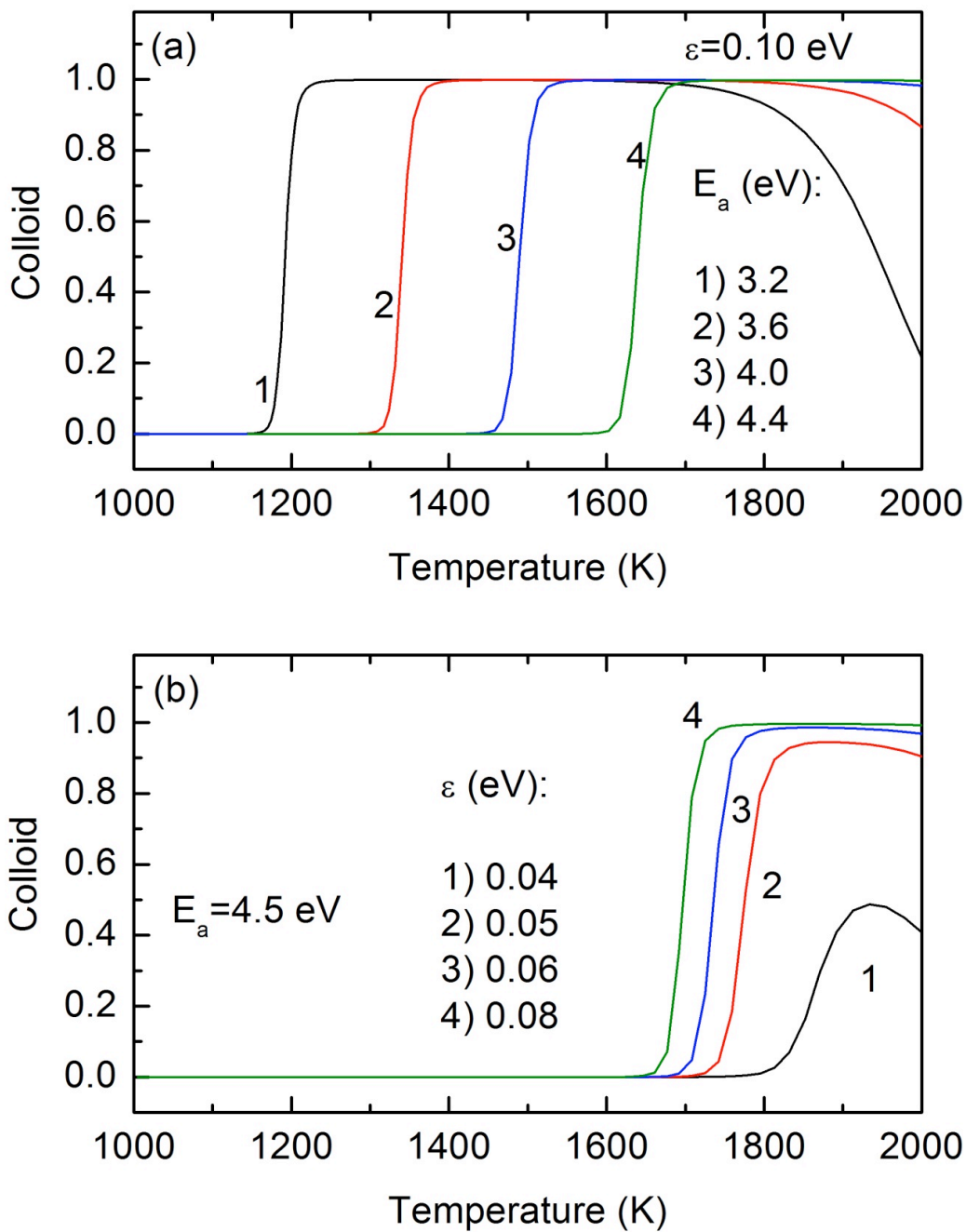
Fig.2. Growth of Al colloid relative concentration as a function of *F* center diffusion and interaction energy.
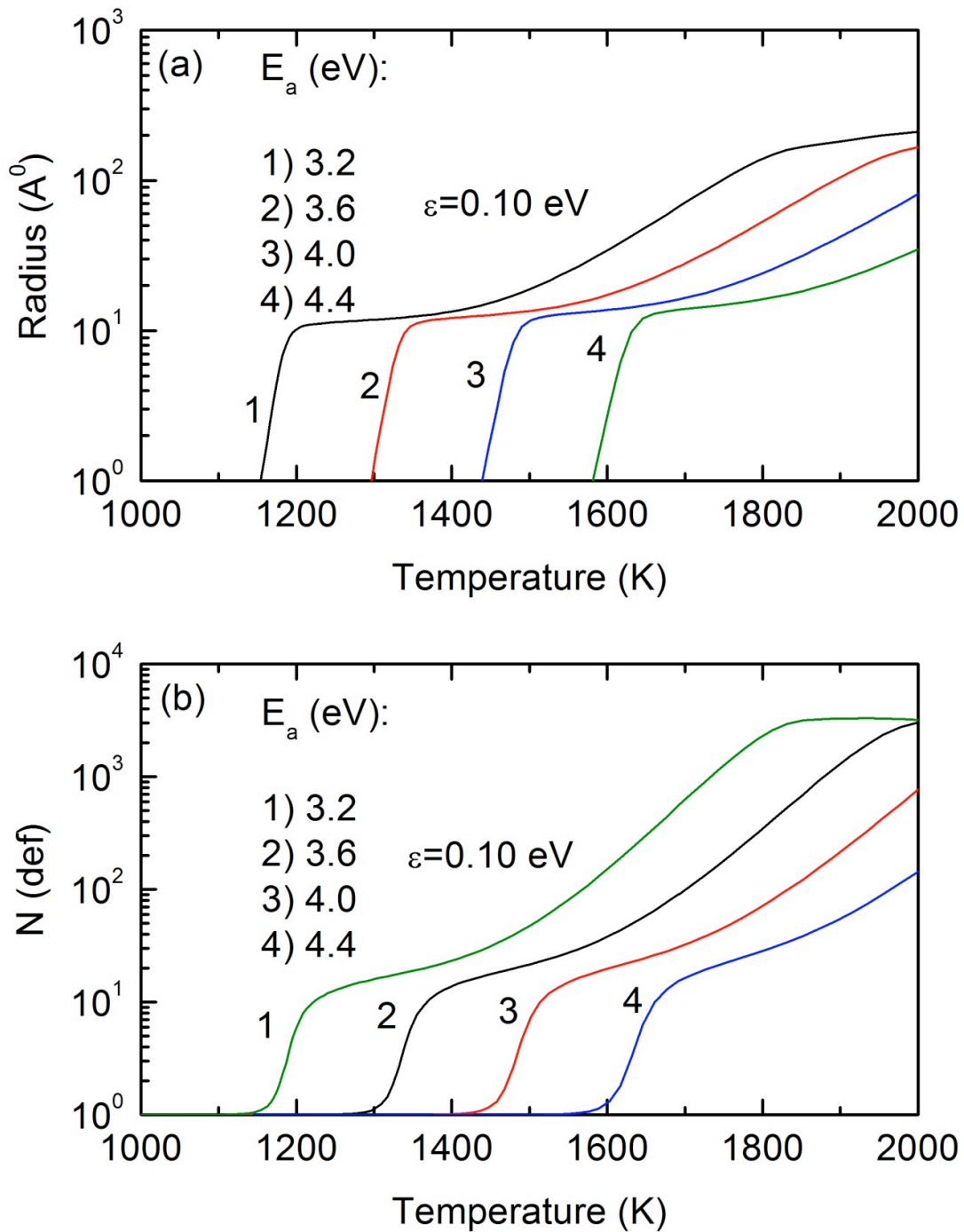
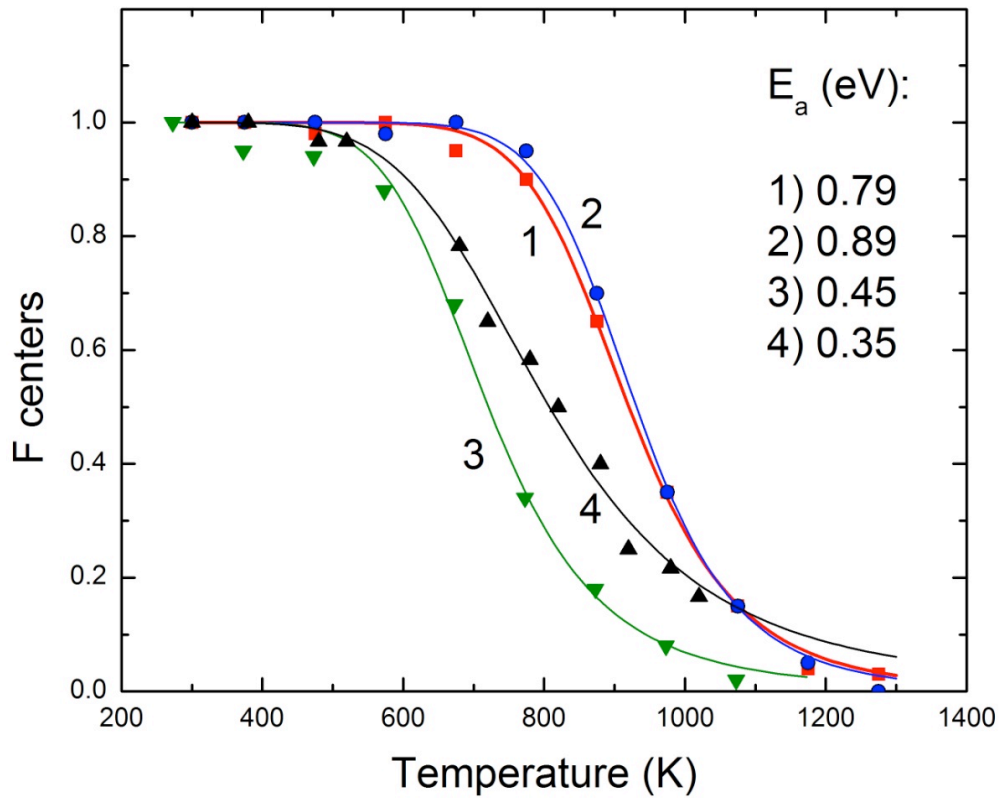**Fig.3**. Calculated colloid radius as a function of the F center migration energy and number of defects therein.

Fig.4. The kinetics of *F* center annealing in neutron irradiated samples (1,2- ref.[8] for the *F* and *F*⁺ centers , 3-[4] for *F*⁺ centers , 4-[33]). The effective fitted migration energies are shown in the legend. The effective pre-exponential factors are: X= 21.5 (1); 70.0 (2); 1.4 (3) and 0.11 (4) (see the text for explanation).