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F CENTER AGGREGATION KINETICS IN LOW-ENERGY ELECTRON IRRADIATED LiF

N. Bouchaala,[a] E.A. Kotomin,[a,b] V.N. Kuzovkov[b,c] and M. Reichling[a,*]

[a]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
[b]Institute of Solid State Physics, 8 Kengaraga Str., 1063 Riga, Latvia
[c]Institut für Theoretische Polymerphysik, Universität Freiburg, 79104 Freiburg, Germany

Results of experimental and theoretical studies describing aggregation of F centers after irradiation and subsequent heating of LiF are presented and analysed. Samples were irradiated in UHV for 30 min with 2.5 keV electrons at a temperature of 300 K and then heated at a rate of 1.5 K min^{-1}. The evolution of F centers from single defects into metal colloids was monitored by optical extinction spectroscopy. The concentration of F centers is found to decrease monotonously for temperatures above 360 K and to fall below the limit of detectability at about 450 K. Experimental data are compared to results of a microscopic theory of F and H center interaction and aggregation. This theory predicts the activation energy for single F center diffusion to be around 1.5 eV and demonstrates the key role of defect mutual attraction for the aggregation kinetics. © 1998 Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

It is well known that the primary radiation defects in ionic solids − F centers (electron trapped by an anion vacancy) and H centers (interstitial halide atoms) − aggregate under intensive irradiation at temperatures high enough to allow defect diffusion. This leads to the formation of alkali metal colloids (see [1] and references therein) and this process is generally believed to occur via diffusion-controlled aggregation of single F centers. Their smallest aggregate centers [F$_2$(M), F$_3$(R) two and three anion vacancies with trapped electrons] can be identified by characteristic optical absorption bands, whereas large aggregates transform into metal colloids with a broad optical extinction band. Intensive optical studies of the F-center small aggregates and metal colloids were done so far for many alkali and alkaline-earth halides [1]. Coloured LiF crystals are of special interest since they provide excellent thermal stability of complex colour centers and are used, e.g. for dosimetry [1] and laser applications [2, 3]. Despite numerous experimental studies of the F center aggregates produced in LiF under different kinds of irradiation [2–7], the kinetics of the F center aggregation leading to the metal colloid formation is not well understood. In particular, there is uncertainty in the experimental (indirect) estimates of the activation energies for the single F center activation energy for diffusion hops. We are aware of the two different values published in the literature, namely 0.66 eV and 0.85 eV [3]. In this paper we present results of the F center aggregation kinetics in LiF upon irradiation with low energy electrons and try to elucidate the process of Li colloid growth during annealing experiments in some detail. For this purpose we combine experiments with theory, in order to obtain the magnitude of the F center diffusion energy and to study the role of defect interaction in the aggregation kinetics.

2. EXPERIMENTAL PROCEDURE

Experiments were performed on LiF single crystals cleaved in air along their natural (1 0 0) cleavage direction

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* Corresponding author. E-mail: reichling@physik.fu-berlin.de

and introduced into an ultra-high vacuum chamber. Crystals had dimensions of $20 \times 20 \times 5$ mm^3 and were mounted in a copper sample holder that could he heated to temperatures up to 650 K by resistive heater elements and cooled down to 200 K by a liquid nitrogen supply. The sample holder was designed as a frame allowing light transmission through most of the 4 cm^2 surface area. Transmission spectroscopy experiments were performed with monochromatized light from a Xe high pressure lamp and two photodetectors sampling a small fraction of the incident and transmitted light. Absolute calibration for calculating the optical density of the irradiated sample was accomplished by reference measurements performed prior to electron irradiation and with the sample removed from the optical path. By this referencing procedure, extinction from the bare substrate and vacuum chamber windows as well as the wavelength dependence of the light spectrum and intensity fluctuations were effectively removed and spectra shown here solely represent changes in optical density introduced by electron irradiation. Optical spectra were measured from 1.5 to 6.5 eV photon energy. For irradiation with 2.5 keV electrons we used a source providing a current density of 100 μA cm^{-2} where the current was homogeneously distributed over a spot of 4×4 mm^2 at the sample surface. The irradiation time was 30 min. Optical transmission was measured in the center of this spot over about half of the area covered by the electron beam. The aim of the present study was to monitor the evolution of F centers and metal colloid formation during sample heating after irradiation at 300 K. After irradiation, crystals were heated at a rate of 1.5 K min^{-1} and a series of consecutive spectra was taken to observe the time evolution of the optical extinction.

3. EXPERIMENTAL RESULTS

A typical series of absorption spectra displayed in Fig. 1 shows that at low temperatures F and M centers are predominant. We observe neither the H centers (absorption band at 3.6 eV) since they are highly mobile at these temperatures, nor their aggregates (since the latter, the so-called V$_3$ centers, have absorption at much higher energies of about 10 eV [9]). Figure 1 clearly demonstrates that during the heating the F centers and dimer-, trimer-centers transform into a broad band at 2.9 eV associated with Li metal colloids [4]. The F-type center aggregation is accelerated above 360 K and is completed at 490 K. Three stages of this process could be distinguished. First, between 300 K and 360 K a weak and broad background band centered at 2.5 eV arises. Then, between 360 K and 415 K two bands grow: a strong and sharp extinction band at 2.9 eV as well as a
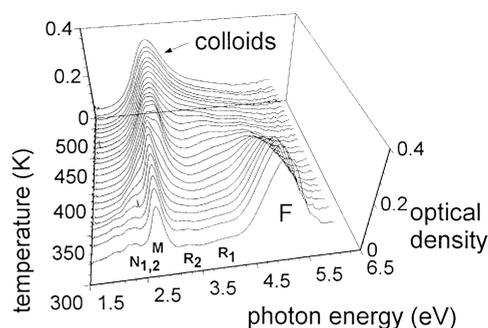

Fig. 1. Development of optical colloid extinction spectra during heating of a LiF crystal after 30 min of electron irradiation with 2.5 keV electrons, with a dosage density of 180 mC cm^{-2} at 300 K crystal temperature. Positions of isolated (F), dimer (M) and trimer (R) electron centers are shown.

rather flat and broad band at 4.5 eV. Finally, above 415 K the 2.9 eV band considerably broadens, whereas the F and M bands completely disappear. At 490 K the aggregation process is completed and up to 550 K only small changes in peak position (from 2.88 eV to 2.92 eV) and half-width (from 1.4 eV to 1.2 eV) of the colloid band are observed. The observed shape of the latter, having a background growing with the photon energy is typical for the extinction due to spherical metal colloids, which can be calculated from the Mie theory [10, 11]. Mie theory has been successfully applied to the analysis of colloid extinction bands in many alkali halides and alkaline earth fluorites. In particular, in [12] we recently found for CaF$_2$ that except for the very early stages of heating, experimentally observed spectra could well be fitted by Mie bands, indicating that it is justified to approximate colloids as spherical metallic particles and their size distribution is rather sharp. In the case of CaF$_2$, we could extract the mean colloid radius and the area density of metal from the fitted curves. However, for the LiF data shown above the optical absorption bands cannot well be fitted by a simple Mie theory. Most probably, this is caused by a non-spherical shape of Li metal colloids, which is in agreement with earlier conclusions that these colloids have a platelet morphology [4, 13]. The great difference of CaF$_2$ and LiF crystals is that in the former the free Ca metal lattice almost perfectly matches its sublattice in CaF$_2$, whereas in LiF the Li sublattice constant is much smaller than for a free Li metal (the difference in a volume of the unit cell is as big as 25%) an also the crystalline structure is different. Unclear is also the nature of the bands at 2.5 eV and 4.5 eV arising at the first and second stages of the aggregation process. The latter was associated by Lobanov [14] with F-center perturbed by a Li atom nearby forming a pre-colloid center. Despite the difficulties in interpreting the final colloid spectra, clear
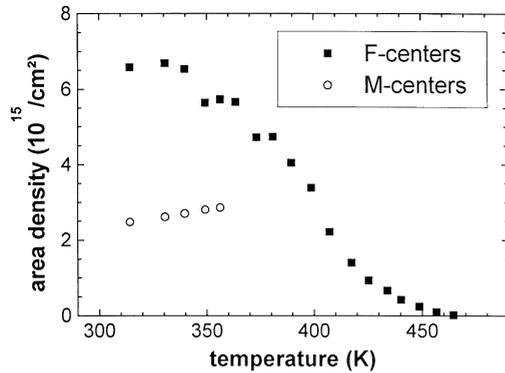
Fig. 2. Temperature dependent evolution of the F and M center concentrations as derived from the data in Fig. 1.

monitoring of the temperature dependent F and M center concentrations is possible using the Smakula relation [15].

Figure 2 shows the development of F and M center concentrations with temperature upon heating. In particular, the F centers decay slowly from 350 K to 450 K. The initial F center concentration can be estimated as the ratio of the area density to the electron penetration depth (about 10^3 Å for 2.5 eV electrons [16]) which gives 6×10^{20} cm^{-3}. We will use these results for a comparison with theoretical calculations presented below.

4. THEORETICAL MODELLING

For the interpretation of the experimental observations, we applied a recently developed defect aggregation theory [17, 18] based on a microscopic formalism treating elementary processes at atomic scale and using only several basic defect parameters like diffusion energies and interaction energies. In our calculations we consider the creation of F and H centers with a given dose rate and their recombination when, during their random walks in a lattice, defects approach each other to within the nearest neighbour (NN) distance. Defect interaction is incorporated in our model via NN attraction energies between similar defects E_{FF} and E_{HH}.

In our model the kinetics of the F, H center macroscopic concentrations C_F and C_H could be schematically presented by non-linear equations of the following type

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = G(C_i, C_j, K_{ij})$$

$$\frac{\mathrm{d}K_{ij}}{\mathrm{d}t} = J(C_i, C_j, K_{ij}),$$

where i, j stand for the F, H centers, K_{ij} describe spatial correlations between defects of ith and jth type (see

below) and G, J are complicated functionals of both defect concentrations and their spatial distributions.

A qualitatively new feature of our microscopic (atomistic) theory compared to several previous (macroscopic or mesoscopic) approaches is a direct incorporation of the effects of relative spatial distribution of similar (F–F, H–H) and dissimilar (F–H) defects, which is done in terms of three kinds of the joint correlation functions, $K_{FF}(r,t)$, $K_{HH}(r,t)$ and $K_{FH}(r,t)$ [17] entering equations above. As we have shown earlier, spatial correlations of the F and H centers turn out to be closely related and strongly affect reaction kinetics. For instance, the aggregation of F centers results in a decrease of the concentration of close F, H pairs and thus increases their average distance, as compared to the random defect distribution. In turn, this strongly reduces the rate of the F, H recombination. Another new feature of this theory is the incorporation of defect interactions into diffusion-controlled kinetics, which qualitatively changes the defect average mobility due to similar defect aggregation and thus the reaction kinetics under study. As a result, our kinetic equations containing functionals G and J, unlike previous simple theories, turn out to be strongly non-linear. In fact, we solve a set of 35 coupled equations for the macroscopic defect concentrations, joint correlation functions, effective interaction potentials, etc. We have no space to present them in this short communication, see for details [17–19].

The input parameters for colloid growth simulations are activation energies for diffusion, E_F and E_H and attraction energies between defects, as defined above, as well as the temperature and defect production rate (which in present experiments is estimated as 10^{17} cm^{-3} s^{-1}). The activation energy for H center diffusion in LiF is 0.15 eV [20] whereas for the F centers the relevant energy is uncertain. This is why we have modelled the F aggregation kinetics varying the F center activation energy from 1 to 1.5 eV. The attraction energies determining F and H center attachment/detachment to/from similar-particle aggregates are even less well known. Calculations of the elastic interaction between two nearest F or H centers in KBr yield an attraction energy of about 0.04 eV [21]. This value we also used in our calculations as an initial guess. For simplicity we assume that similar particle interactions are equal for different defects, i.e. $E_{int} = E_{FF} = E_{HH}$.

We calculated the time development of both, electron and hole defect total concentrations (which are densities of all defective lattice sites, i.e. the total concentration of F-type centers is nothing but a combination of single, dimer, trimer and higher aggregate concentrations), $n_F(t) = n_H(t)$, as well as concentrations of single (isolated) defects (no other defects in NN lattice sites) and dimer defects (two similar defects are NN). Larger
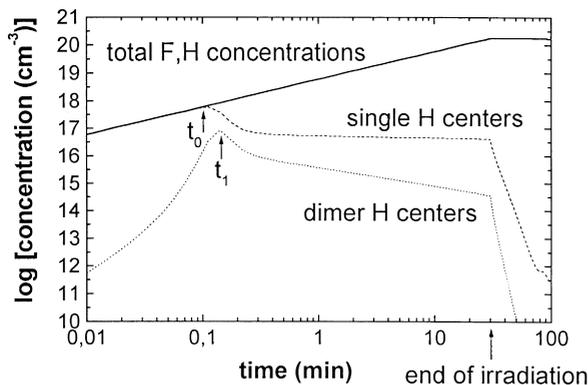
Fig. 3. Prediction of the F and H center and aggregate center concentrations when a defect production rate of 10^{17} cm^{-3} s^{-1} is assumed during 30 min of irradiation at 300 K crystal temperature.

aggregates are characterized by the integral values of the number of particles N_F, N_H therein and their radii R_F and R_H. Large aggregates of F centers are metal colloids.

During irradiation at 300 K the H centers are quite mobile. The temporal evolutions of the total H-type center concentration, as well as single H and dimer H_2 centers are plotted in Fig. 3. It is seen that due to fast aggregation of the H centers at the very early stages of irradiation the concentration of H_2 centers rapidly increases and approaches that of single H centers. This is why at a short time t_0 the H center concentration begins to decrease. Intensive H-aggregation leads to an almost simultaneous decrease of the density of H_2 centers due to a growth of larger H aggregates at time t_1. This process is greatly enhanced by sample heating after irradiation.

In turn, up to 100 min all F centers are immobile and thus remain single. Their concentration grows linearly with irradiation time (Fig. 3) exceeding 3×10^{20} cm^{-3}, i.e. several percent of the fluorine lattice sites are occupied by F centers. This is in agreement with our experimental data. F center aggregation begins only after sample heating up to 350 K. In Fig. 4 we have plotted the decay of the total F-type defect concentration (A) and concentration of the single F centers (B) for three activation energies of diffusion, varying from 1 eV to 1.5 eV and assuming a defect interaction energy of 0.04 eV. Calculations for 1 eV diffusion energy yield a very sharp F center decay clearly contradicting the experimental data in Fig. 2. For the 1.2 eV and 1.5 eV diffusion energies the F center concentration decays much smoother and the temperature range agrees well with experimental data.

Calculations of the aggregate radius and of the number of F centers inside show that for a diffusion energy of 1.5 eV both quantities grow intensively above 350 K reaching a radius of 22 nm with a concentration higher than 10^5 at 425 K. Calculations for the F center
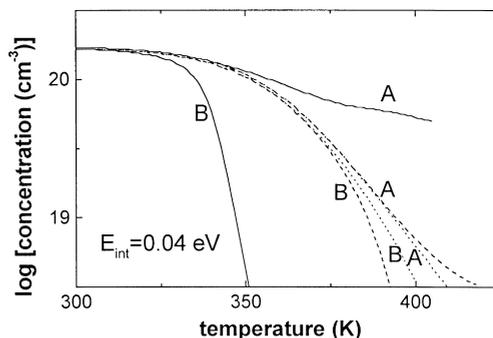

Fig. 4. Calculated development of the total concentration of all kinds of the F-type centres (full lines), of F-type (A) and single F centers (B) during heating. The three activation energies used for F center diffusion are: 1 eV (solid lines), 1.2 eV (dashed lines) and 1.5 eV (dotted lines). The attraction energy between defects was assumed to be 0.04 eV.

activation energies of 1.2 eV and 1.5 eV (Fig. 4) predict a considerable decay of the total F center concentration due to a recombination of a considerable fraction of the isolated F centers with aggregates of the H centers, which happens when mobile F centers start random walks instead of joining other F centers or their aggregates. Experiment does not yield significant information about this since we do not observe H centers. Probably, in reality most of the H centers are not accumulated in loose aggregates in the bulk, as is assumed in our model, but disappear in dislocation loops and probably a large portion of them is desorbed from the surface.

Figure 5 demonstrates how strongly the interaction energy between the defects affects the F center aggregation kinetics; an interaction energy increase by 25 to 30% (A–B–C) shifts the F center decay temperature up by 50 K. Obviously, this is a result of the F center recombination with mobile H centers escaped
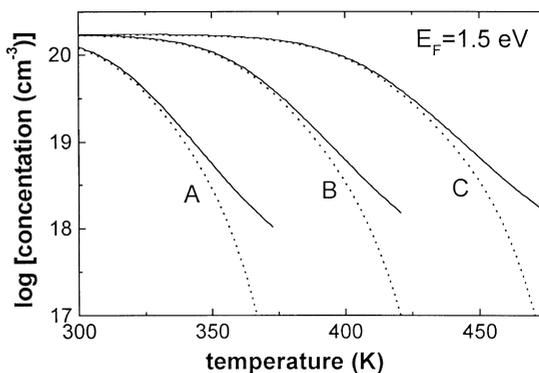

Fig. 5. Calculated development of the total concentration of the F-type (full lines) and single F centers (dotted lines) for three attraction energies between defects: 0.03 eV (A), 0.04 eV (B), 0.05 eV (C) and a diffusion of 1.5 eV.

from their aggregates: the higher an attraction energy between defects inside the H aggregate, the stronger defects are bound to each other and respectively, the higher the temperature at which a fraction of them can be released from the aggregates and recombine with the F centers.

In summary, in LiF − unlike CaF$_2$ − F centers are very stable; their transformation into Li colloids occurs in the temperature range from 350 to 450 K. Colloids probably have non-spherical shape and this is why they cannot be described by a simple Mie theory.

The F center recombination/aggregation kinetics and the relevant metal colloid formation depend on both the F center mobility (controlled by the activation energy for diffusion) and the defect attraction energies inside aggregates of F and H centers (E_{FF} and E_{HH}, respectively). In irradiated LiF crystals the F center recombination/aggregation kinetics is affected by the presence and thermal stability of the H center aggregates which will be analysed in detail in a separate paper.

From a comparison of theory (Figs 4 and 5) with the relevant experimental data (Figs 1 and 2) the conclusion can be drawn that the activation energy for the single F center diffusion is at least 1.5 eV, much larger than in previous indirect estimates putting it below 1 eV.

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