

Thermal-annealing studies of defects in lithium fluoride after electron-beam irradiation

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(Received 9 July 1990)

We have bombarded single-crystal LiF surfaces with 400-eV electrons at fixed target temperatures between 330 and 470 K and varied the irradiation time between 30 and 4200 sec. After irradiation we heated the crystals up to 750 K and simultaneously recorded the Li desorption. Interpreting the amount of desorbed Li atoms as a measure for frozen electron-center defects and Li agglomerates in the crystal, we were able to obtain an activation energy for the thermal migration of the H centers of about 0.13 eV. Investigations, where the bombarding time has been varied, indicate efficient H -center trapping processes and different lifetimes for H -center clusters of different sizes in the crystal. In addition, we found evidence for a substantial formation of F -center agglomerates under the surface and Li islands on the surface.

I. INTRODUCTION

Ionizing radiation has long been known to damage alkali halides and since the late 1960s the damaging process, which leads to the formation of H and F centers, is basically understood in terms of an excitonic mechanism.^{1,2} Whereas H centers become mobile at temperatures as low as 40 K [in LiF they become mobile at 60 K (Ref. 3)], F centers are generally much less mobile up to a temperature as high as room temperature (RT), due to the higher activation energy for their diffusion [$Q_F \approx 0.8$ eV (Refs. 4 and 5)]. Therefore, at temperatures higher than RT, F and H centers are unstable. Several possibilities exist for their stabilization. Their existence then can result in a substantial contribution to desorption beyond bombardment.

(i) F centers formed at the surface or having diffused to the surface will decay irreversibly in neutralizing surface alkali-metal ions.⁵ At temperatures close to the melting point of the alkali metal (Li, 180°C), the alkali-metal atoms can aggregate into islands. The vapor pressure $p(r)$ of these small islands is size dependent and can be calculated with the Kelvin equation, which yields the result that small islands evaporate faster than larger ones.⁶

(ii) F centers may form aggregates in the bulk of the crystal. The clustering process of F centers has been investigated by many authors,^{4,7,8} and is—in contrast to the aggregation process of H centers—well understood. In the following we will focus our attention on various clustering processes of H centers.

(iii) If an H center reaches the surface, it will decay and emit a neutral halogen atom. It is now accepted from electron-microscope,⁹ optical,¹⁰⁻¹⁴ and Raman-scattering studies¹⁵⁻¹⁸ that halogen interstitials form interstitial halogen clusters under high-dose irradiation. The most important problem associated with interstitial centers is the determination of their structure.

Kanzig and Woodruff¹⁹ have shown that the H center is an X_2^- molecular ion associated with two neighboring anions, located at an anion site and oriented along the

$\langle 110 \rangle$ direction (in LiF the H center lies along the $\langle 111 \rangle$ direction¹⁹). Typical migration energies of H centers are about 0.1 eV.^{10,20} The work of Hobbs *et al.*,⁹ in which interstitial-halogen-cluster formation was studied with an electron microscope, has contributed substantially to our understanding of the final configurations of the primary H centers at high defect concentrations at elevated temperatures. According to Hobbs *et al.*,⁹ two H centers form a halogen molecule occupying a vacancy pair, thus providing an anion and cation which form part of a perfect interstitial loop. The efficiency of H -center-cluster generation increases with increasing temperature, as long as the clusters are stable. In LiF, molecular fluorine has been identified by Knutson *et al.*²¹ after heavy neutron irradiation. These molecular-fluorine centers proved to be thermally stable up to 300°C. Trinkhaus *et al.*²² have interpreted their data of x-ray scattering experiments performed on LiF at RT in terms of interstitial halogen clusters. In NaCl the V_2 band, which corresponds to a di-interstitial center (probably a Cl_3^- molecule^{1,23}), annealed at 200°C,²⁴ and in KCl the V_3 band was thermally stable at least up to 60°C.²⁵ (The structure of the V centers will be discussed below.) These results prove the high stability of some H -center clusters at elevated temperatures.

Itoh²⁶ and Aguilar *et al.*²⁷ have interpreted data from optical studies in the spectral region of the V bands (uv regime) in terms of different lifetimes of the interstitial clusters as a function of their size. Itoh²⁶ assumed an unstable interstitial cluster consisting of an odd number of H centers. Kowaczyk and Damm²⁸ have investigated the V bands of doped KCl crystals after γ -ray irradiation. They obtained the result that for low irradiation doses the V_2 band dominates, whereas for high doses the peak shifted to shorter wavelengths (V_3 band) probably due to the bigger size of the interstitial centers (see Raman-scattering experiments below). Lopez *et al.*²⁹ have obtained very similar results. Some groups^{15,16,23,17,18} have investigated several alkali-metal halides (e.g., KI, KBr) after x- and γ -ray irradiation by Raman-scattering

methods, which is a valuable tool to obtain information about the structure of the nonparamagnetic V centers.

For low irradiation doses, X_3^- molecules (X =halogen) are formed. We will refer to this as stage I. For high irradiation doses, the fraction of X_M^- ($M=5,6,7,\dots$) and finally $(X_2)^n$ ($n=1,2,3,\dots$) (stage III) increased, which probably corresponds to the halogen agglomerates observed by Hobbs *et al.*⁹

Performing optical-absorption measurements simultaneously,²³ or comparing the results with optical measurements performed under similar conditions¹⁸ yields the result that the X_3^- molecules correspond to the V_2 and V_4 bands in the case of KI and KBr, respectively,¹⁸ whereas the $(X_2)^n$ aggregates probably correlate with the V_3 band, at least in the case of KBr.¹⁷ The fact that V_3 centers are more stable than V_2 or V_4 centers²⁰ is consistent with the identification mentioned above.²³ Elango and Nurakhmetov^{12,13} identified the V_2 and V_4 bands as Br_3^- molecules, occupying two anion and one cation sites.

II. EXPERIMENTAL METHOD

In most measurements reported so far, optical-absorption techniques are used to obtain information about the yield of the generated defects in the crystal by photon, or electron irradiation.^{7,26,28} With this technique it is possible to derive quantitative results about F centers, F -center clusters, or V centers. As mentioned before, the Raman-spectroscopy technique allows one to determine the structure of the nonparamagnetic V centers.

In the experiments presented here, we have used a different experimental approach based on the study of desorbed neutral atoms to obtain information about the total yield of electron-center defects (F centers, colloids, etc.) and Li in the crystal. For this purpose we irradiated our targets at temperatures not higher than 190°C. At 190°C the vapor pressure of Li from Li metal corresponds to an evaporation rate of 10^{-4} monolayer (ML)/sec, which amounted in our detection sensitivity to less than 1 count/sec. After irradiation we heated the target up to 450°C (Fig. 5). The heating rate was 1–0.4 K/sec. This annealing process now forces all the Li on the surface, which has been formed during irradiation or due to the decay of F -center clusters during the annealing process, to desorb. During the heating process we recorded the Li^0 desorption as a function of time (temperature).

The integral area under the desorption peak as shown in Fig. 1 now can be regarded as a measure for the number of electron-center defects (total number of F - M centers) and Li in the crystal. It will be demonstrated later in the discussion that this assumption is reasonable. It turned out that the area under the desorption peak almost did not depend on the conditions of how the heating was performed. This reflects a negligible recombination rate of F and H centers during the heating process. Only when we heated extremely slowly (5 K/min), was the integral area up to 10% higher for long irradiation times than in the case of high heating rates. This is probably due to the fact that the maximum of the desorption peak is shifted to higher temperatures under fast heating. At

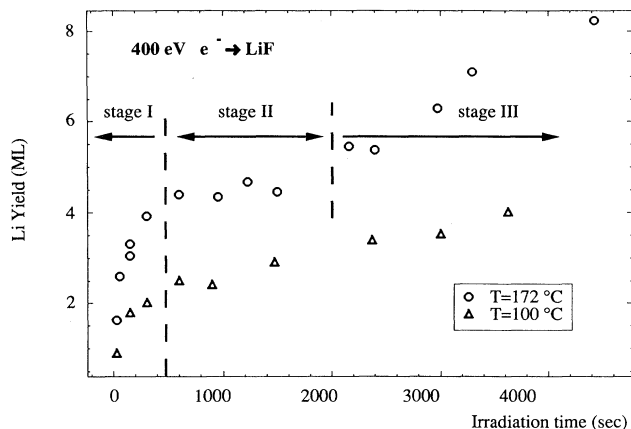


FIG. 1. The calibrated integral over a desorption peak as a function of irradiation time ($16 \mu\text{A}/\text{mm}^2$) exhibits three stages for high irradiation temperatures (circles). For low irradiation temperatures (100°C, triangles) only two stages can be identified within the investigated irradiation times.

temperatures higher than 300°C,²¹ the H -center clusters are more unstable and, therefore, the recombination increases during the process of heating.^{21,24} This can explain why the desorption yield is lower for high heating rates.

All the data presented here were obtained under identical experimental conditions (high heating rate). Slow heating experiments were only performed in order to calibrate the sensitivity of our quadrupole mass analyzer. This had to be done, since for high heating rates the temperature of the surface was not well defined in our experimental setup (insulator properties of the crystal).

After electron irradiation, a Li overlayer will form on the surface of the LiF crystal.^{30–32} At the beginning of the subsequent heating process, only the Li on the surface desorbs. This fact can be used to calibrate the detection, as described in the following. The Arrhenius plot of this low-temperature tail of the desorption peak can be used to obtain the activation energy of the Li desorption.

We obtained typical activation energies from 1 to 1.6 eV, depending on the duration of bombardment and, therefore, on the Li coverage on the surface.⁶ For irradiation times around 20 min, the activation energy turned out to be 1.6 eV, which is the activation energy for Li evaporation from Li metal. As the evaporation rates (ML/sec) of Li from Li metal as a function of the temperature is known from the literature,³³ we are able to calibrate our detection system using this low-temperature tail of the desorption peak, where the Li desorption is due to Li evaporation from Li metal, as shown before. We obtained a detection efficiency for the quadrupole in our setup of 2×10^{-4} counts/desorbing-atom.

III. EXPERIMENTAL SETUP

Single-crystal surfaces were bombarded with 400-eV electrons at different target temperatures (330–470 K), and the electron current was varied between 7 and 17

$\mu\text{A}/\text{mm}^2$. The angle of incidence of the electron beam was 45° with respect to the target normal. The beam diameter was about 2 mm. Ground-state Li atoms have been measured with a quadrupole mass analyzer. The UHV system maintained a base pressure of less than 1×10^{-9} Torr. The crystals have been cleaved in air and cleaned in the vacuum system by prolonged heating at 400°C . The temperature was measured with a thermocouple, which was thermally connected to the surface of the crystal and to the target holder.

IV. RESULTS

Information about "frozen" defects can be obtained by two different types of experiments, which are presented in the following. In these measurements we have varied the irradiation time and temperature.

A. Variation of the irradiation time for bombarding temperatures lower than 200°C

In Fig. 1 we can see a typical result, where the total desorption yield is plotted versus the bombarding time. Three stages can be identified for temperatures above 150°C . For irradiation times of a few minutes, the desorption yield saturates. In the following we will refer to this regime as stage II. The higher the bombarding temperature or the currents are, the sooner and more pronounced the (integrated) signal increases again for long irradiation times. For long bombarding times the maximum of the peak shifts to higher temperatures (Fig. 2), whereas the beginning of the desorption (low-temperature tail of the desorption peak) does not shift significantly.

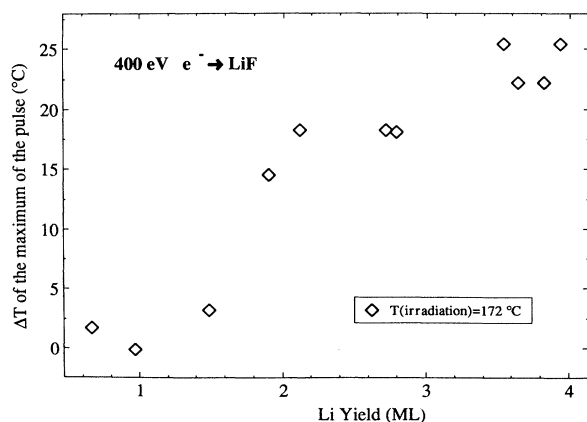


FIG. 2. Shift of the maximum of a desorption peak to higher temperatures for bombarding at irradiation temperatures lower than 200°C (172°C). The temperature is given relative to the data point, which exhibits the lowest temperatures of its maximum.

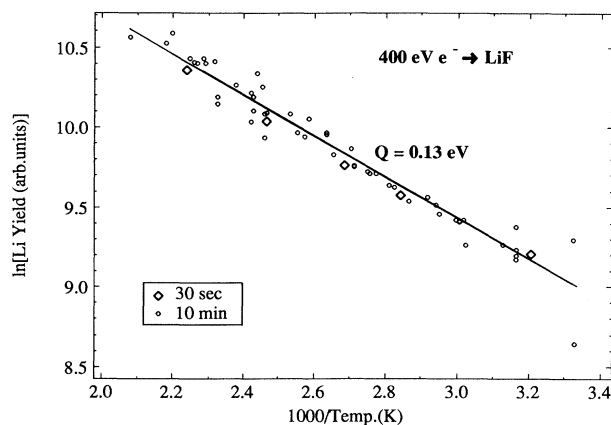


FIG. 3. Arrhenius-type plot of the temperature dependence of the total Li yield after 30 sec and 10 min irradiation with $\sim 14 \mu\text{A}/\text{mm}^2$, respectively. In the former case, the integral over the desorption peaks has been multiplied by a constant factor.

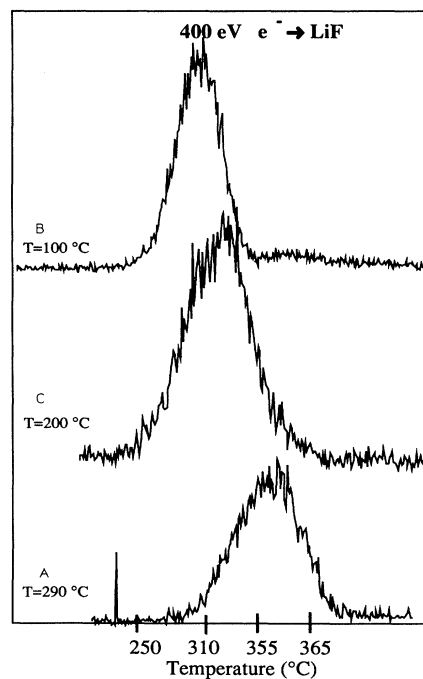


FIG. 4. Annealing spectrum after irradiation at 290°C (curve A), 100°C (curve B), and 200°C (curve C). For irradiation temperatures lower than 200°C , only the maximum shifts to higher temperatures ($B \rightarrow C$), but the threshold of desorption is not shifted significantly. After irradiation at 290°C and cooling down to 190°C (cooling process took several minutes), spectrum A was recorded: The whole peak was shifted to higher temperatures.

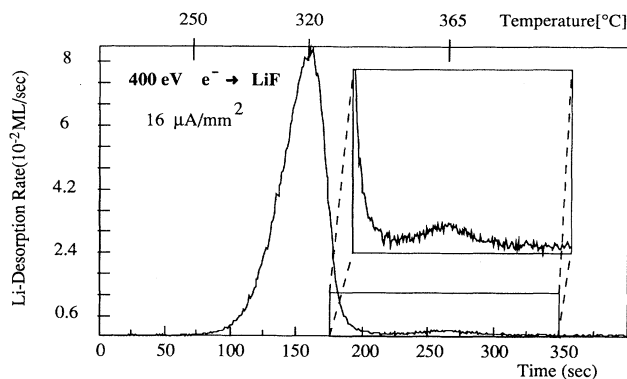


FIG. 5. After electron irradiation (400 eV, $16 \mu\text{A}/\text{mm}^2$) for 5 min at 150°C , we heated ($\sim 1\text{--}0.4 \text{ K}/\text{sec}$) the crystal up to 450°C . The inset shows the small second peak enlarged.

B. Variation of the bombarding temperature

Figure 3 shows an Arrhenius plot of the desorption yield at a fixed irradiation time. The duration of bombardment was 30 sec and 10 min, respectively. The Arrhenius plot yields an activation energy of 0.13 eV in the investigated temperature regime from 60 to 190°C . The activation energy is independent of the bombarding time for irradiation times shorter than 10 min (irradiation times longer than 10 min were not investigated).

We have also performed experiments where we irradiated the target at temperatures higher than 200°C and cooled the target to 190°C after irradiation. We can clearly see how the whole peak shifts to higher temperatures (Fig. 4). Taking a closer look at Fig. 5 (inset), we conclude that the annealing experiments exhibit a second peak. This peak does not show any temperature dependence in the regime between 60 and 190°C . This second maximum between 350 and 360°C occurs only for long bombarding times (10 min and more), and its integral area increases monotonically with irradiation time. For higher bombarding temperatures, the wings of the first peak completely bury the small second peak.

V. DISCUSSION

In our analysis we will not consider recombination of F and H centers during the heating process, as optical-absorption spectroscopy, thermoluminescence, and hardening measurements show that the recombination becomes significant only when the H -center clusters disintegrate,²⁷ or disperse.²⁴ During the heating process the latter case becomes more and more relevant, as the H -center clusters have a higher probability to disperse at elevated temperatures. A larger number of dispersed H -center clusters represent a better target for F centers, and therefore the recombination rate increases.²⁴ In LiF this process seems to become relevant at temperatures higher than $\approx 300^\circ\text{C}$.²¹ According to Knutsen *et al.*²¹ annealing for 30 min at 350°C resulted in a 40% decrease of molecular-flourine content (whereas after annealing 30 min at 300°C there was a 10% increase in the molecular-

flourine content). Therefore, as the heating process lasted only a few minutes in our experiments, the decrease of the molecular-flourine content at temperatures where most of the electron-center defects desorb (Fig. 5, $T \leq 350^\circ\text{C}$) is probably negligible. As already discussed in Sec. II, the fact that the integral area under the desorption peak hardly depends on the heating rate is a clue that our assumption is reasonable. Of course, a minimal influence of the recombination cannot be excluded.

A. Interpretation of the temperature dependence of the integral area under the desorption peaks

As mentioned in Sec. IV B, the temperature dependence involves an activation energy of 0.13 eV, which is close to the activation energies Q_H for the migration of H centers in other alkali-metal halides.^{7,20} For elevated temperatures the rate of F - H pair generation increases exponentially with an activation energy of Q_H .² The question arises of whether the temperature dependence observed in our experiments is due to the primary generation process of F -center- H -center pairs or due to a secondary process, as many processes involve H -center diffusion and, therefore, probably an activation energy of Q_H . As for short bombarding times (yield lower than 1 ML, linear part of stage I in Fig. 1) the recombination rate of H and F centers may be neglected; the temperature dependence in this case is simply governed by the primary defect-generation process. This process involves Q_H and we can maintain that

$$Q_H = 0.13 \text{ eV} .$$

However, this value is very close to activation energies for H -center migration in LiF obtained by other authors, such as 0.11 eV, which Durand *et al.*⁷ obtained by M -center-interstitial recombination experiments, and 0.138 eV, obtained by Yabe.³⁴

The fact that the temperature dependence after an irradiation time of 10 min yields the same activation energy can be explained by secondary processes. One possible reason could be that the trapping of H centers is a function of their mobility: As more H centers are trapped at higher temperatures, the recombination rate decreases because, for every trapped H center, one F center survives.⁴

B. Discussion of the progress of the integral area as a function of the irradiation time

For reasons of simplicity and phenomenological similarity we refer to this measurement as coloring curves, although this term is generally used for F -center concentrations as a function of the irradiation time.

(i) Lopez *et al.*²⁹ and Kowalczyk and Damm²⁸ have investigated the V -band regime of x-ray-irradiated NaCl and γ -ray-irradiated KCl, respectively, as a function of the irradiation time and doping with divalent impurities at RT. They observed that the F -center concentration increases again after saturation. The lower the concentration of impurities, or the higher the dose rate, the less pronounced the saturation regime (stage II). They refer

to the regime before the saturation regime as stage I (linear part of the growth curve), and to the regime after the saturation of the F -centers as stage III. Kowalczyk and Damm simultaneously investigated the V -band regime. They observed that for small irradiation times the V_2 band (and for long irradiation times the V_3 band) dominates.

(ii) Aguilar *et al.*²⁷ simulated these experimental results assuming that, during irradiation, interstitial halogen clusters are formed whose stability is a function of their size. During stage II (saturation regime) unstable clusters are formed. The decay of these unstable centers increases the concentration of free H centers and therefore the recombination rate between H and F centers. For higher irradiation doses the fraction of stable interstitial halogen clusters increases and therewith the recombination rate starts to decrease again.

The similarity between our coloring curves and the "real" coloring curves (F -center concentrations), which Lopez *et al.* or Kowalczyk and Damm obtained by optical methods, is striking. They obtained their results at RT, where only a negligible fraction of the F centers due to their low mobility agglomerates. Therefore, the concentration of the free F centers is approximately the concentration of the total number of electron-center defects. In our experiments the total yield of the desorbed Li originates from Li on the surface of the crystal, which has been formed during irradiation, and from F -center clusters, which decay during the annealing process.

It is important to point out that our experiments can be compared to those of Kowalczyk and Lopez only if the major contribution of the total yield of the generated electron-center defects and Li is stored in the crystal during irradiation in the form of colloids or F -center aggregates. Since we assume that Li on the surface is stable with respect to recombination with H centers, a comparison would not be possible, if the major contribution were Li on the surface of the crystal.

The shape of the coloring curves cannot be explained by assuming that (i) a substantial metal overlayer is formed, which would decrease the defect generation, because the electrons would be prevented from penetrating below the surface. (This model then could not, for instance, explain the increase of the signal in stage III); or (ii) the metal overlayer conserves the H centers in the crystal and, therefore, increases the recombination rate (this model does not consider interstitial clusters). This model fails to explain the fact that the signal, as observed, saturates for 3 ML and not for 1 ML for irradiation at 172 °C. In addition, it cannot explain the increase of the signal in stage III as well.

We propose that the shape of our coloring curves (Fig. 1) can be explained by assuming that interstitial halogen clusters are formed and that the stability of these interstitial clusters is size dependent.²⁷ During the first stage F and H centers agglomerate in the bulk and Li is formed on the surface. The interstitial clusters in this stage are probably, in analogy to other alkali-metal halides, F_3^- molecules.^{17,18,23} As the number of traps for the H centers is constant,^{4,9} the interstitial halogen centers begin to grow in size and F_n^- ($n=4,5,6$) are formed. As

X_4^- centers have not yet been observed in other alkali-metal halides,²³ this center is probably unstable and therefore decays, which results in an increase of free H centers. These free H centers recombine with free F centers or with F centers in agglomerates. The enhancement of the recombination rate is reflected in the decrease of the yield in stage II. For high doses (stage III) the fraction of V centers, which managed to become stable by trapping another H center [probably X_n^- or $(X_2)^m$ centers, with $n \geq 5$], increases. Therefore, at high doses the yield increases again, because the recombination of F and H centers decreases due to more stable V centers (stage III). The observation that stage III does not occur for a bombarding temperature of 100 °C in the investigated irradiation times may be due to the overall lower generation rate of defects.²⁷

Kowalczyk and Lopez have obtained these three stages only for very low doses ($\approx 10^{19}$ eV/cm³). For higher doses they have only identified stage III (a monotonic increase of the signal). The energy-deposition rate in our experiments was about 10^{22} eV/(cm³ sec), without considering the diffusion of the F centers but only assuming a penetration depth of 400 eV for electrons [150 Å (Ref. 35)].

At temperatures above 100 °C the H centers and even F centers are very mobile. In NaCl, for instance, it takes about $\tau = (100 \text{ \AA})^2 / D_F \sim \text{msec}$ (D_F = diffusion coefficient for F centers) for an F center to diffuse 100 Å.⁴ Therefore the average diffusion length of the F centers (and of course the H centers) is much bigger than the penetration depth of the electrons for irradiation times up to 4500 sec. This would result in a corresponding lower-energy-deposition rate. As mentioned above, the shapes of the "coloring curves" suggest that the major fraction of the generated electron-center defects is bound in the crystal in the form of agglomerates during irradiation. We have performed further experiments in order to prove effective F -center agglomeration.

C. Further experimental evidence for the formation of F -center agglomerates in LiF

We have irradiated the crystal at temperatures higher than 200 °C in order to find evidence for electron-center agglomerates under the surface for temperatures higher than 200 °C. We have examined two properties.

(i) The maximum of the desorption peak shifted to higher temperatures.

(ii) The desorption started at higher temperatures.

The shift of the maximum may be explained by the formation of Li islands, or F -center clusters as well. This is due to the increase of the average radius of the agglomerates and islands, as small islands or agglomerates evaporate during irradiation and cooling. The higher threshold for the desorption cannot be due to islands. After long irradiation times at temperatures lower than 200 °C, which resulted in a maximum of one ML of Li on the surface³¹ (activation energy of the low-temperature tail, 2.6 eV), the signal increased at lower temperatures than in the case of irradiation at temperatures higher than 200 °C. As 1.6 eV is the highest possible activation energy for the evaporation of Li islands, the higher

threshold should be due to *F*-center agglomerates. Betz^{30,36} and others have studied delayed emission of Li after irradiation of LiF and observed decay times of minutes after electron bombardment at $\sim 300^\circ\text{C}$, which according to our calibration corresponds to several ML of Li under the assumption that the delayed fraction is due to evaporation of islands on the surface. According to the experiments of Wurz and Becker,³¹ at most 1 ML can be formed on the surface, and, therefore, the delayed emission must originate mainly from the bulk.

We have also observed a shift of the maximum of the desorption peak for irradiations under 200°C (Fig. 2). The temperature at which the maximum of the desorption peak occurs increases monotonically with increasing yield. The activation energy of the low-temperature tail of the heating peaks varies between 0.8 and 1.6 eV, which is mainly due to the increasing average radius of the islands on the surface of the crystal. We obtained an activation energy of 1.6 eV after about 15–20 min of irradiation (170°C). The shift of the maximum to higher temperatures for irradiation times longer than 20 min is further evidence for electron-center agglomerates in the bulk for irradiation temperatures lower than 200°C , as at most 1 ML can be formed on the surface.

In this context the question arises as to what degree might the second peak in Fig. 5 be caused by agglomerates and, if so, what kind of agglomerates. This second peak must be caused by rather stable centers, since it occurs at higher temperatures than the first peak. Under the assumption that the low-temperature tail of the first peak is due to the disintegration of Li islands on

the surface of the crystal, it is very probable that this second peak originates from the disintegration of agglomerates in the bulk. We have observed the occurrence of the second peak down to RT. Small clusters are formed at temperatures as low as room temperature (*M* and *R* centers).⁷ Because *M* centers do not exhibit a constant-temperature behavior as does the second peak (see Sec. IV), probably the *R* centers, etc., are involved in the second peak. Optical-absorption spectroscopy in combination with annealing-technique measurements would be very valuable in this case. In addition to this fact, the integral areas under the second peak are very similar in size compared with the small peaks, which occur at the delayed emission of ground-state Li atoms after turning off the electron beam at high temperatures (400°C).³⁰ We have conducted our experiments under very similar conditions (same quadrupole, similar electron currents, etc.). Betz *et al.*³⁰ have interpreted these delayed peaks as being a consequence of the disintegration of colloids, or small *F*-center clusters. In addition, they have not found these delayed peaks at temperatures below 360°C , because, at these temperatures, the clusters are probably thermally stable and therefore cannot disintegrate.³⁶ This coincides quite well with the appearance of our second peak at 360°C .

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support by the Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung (Project Nos. 5833 and 6797).

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