Time dependence of desorbed ground-state lithium atoms following pulsed-electron-beam irradiation of lithium fluoride

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Recent experiments have shown that during the irradiation of lithium fluoride crystals by a chopped electron beam the signal of desorbed ground-state lithium atoms continues for times up to seconds in the beam-off period. A quantitative model is presented which connects the desorption of lithium atoms with the diffusion of lithium fluoride F centers to the surface. The model thus introduces a new source of time delay (F-center diffusion) in the desorption of ground-state metal atoms from alkali halides. Formerly it has been supposed that the delay occurred entirely during the surface desorption step. The model fits the experimental data very well, and should be applicable to other similar systems. For the cases considered here, F-center diffusion turns out to be the primary source of delay in the Li-atom signal. The model suggests some new directions for investigation.

I. INTRODUCTION

Recent experiments by Loubriel, Tolk, and their collaborators have shown that during the irradiation of LiF crystals by a chopped 200-eV electron beam, the signal of desorbed ground-state lithium atoms (Li) continues for at least seconds in the beam-off period.[1] This is to be compared with the case of ground-state-halogen desorption where time scales of the order of milliseconds or less are observed.[2] In the work described below, a quantitative model is developed which connects the Li desorption from the hot LiF surface with the diffusion of F centers to the surface. In order to put the model into a suitable perspective, the current view of electron and photon-induced halogen desorption must first be summarized. We follow the description of Szymonski[3] and that of Agullo-Lopez and Townsend.[4] These descriptions are based on more than a decade of electron- and photon-stimulated-desorption research on alkali halides, and Refs. 3 and 4 cite many of the most significant papers.[5] It will be seen from these that, although the mechanism of desorption seems to be well understood in its main qualitative outlines, there is yet much to understand about all the quantitative reaction mechanisms involved. References 3 and 4 are not in complete agreement on some details of the halogen-desorption process. Our model is based, however, on ideas common to both descriptions.

Following Refs. 3 and 4, in a typical desorption experiment, the electron or photon beam deposits energy to a depth up to several hundred angstroms, the most important end result of which is the production of electron-hole pairs. The holes are self-trapped within picoseconds, leading to the formation of V_K centers (an F_2^- molecular ion replacing two F^- ions). On a time scale of about ten nanoseconds, the electrons in the system are captured by the V_K centers to form self-trapped excitons (STE), and are also captured by whatever preexisting acceptor defects and impurities are in the crystal at the time of irradiation. The STE decay in times of the order of nanoseconds and a decay channel of substantial probability leads to the formation of F-center—H-center pairs, some of which annihilate mutually, and some of which separate to lead independent lives. An F center is an electron occupying the normal place of a negative halogen ion. An H center is an interstitial neutral halogen atom crowded amongst the negative halogen ions along a $\langle 110 \rangle$ line to form what is also known as a "crowdion."

According to Refs. 3 and 4, the release of the interstitial halogen atoms from H centers arriving at the surface is the source of halogen desorption. The H centers start their travels in a replacement sequence along the $\langle 110 \rangle$ directions containing the F center of the F-H pair. If this collision chain intersects the surface, a nonthermal halogen atom can be ejected on a time scale of less than 0.0001 sec.[2] Otherwise, the H center can thermalize and diffuse around the crystal until it is annihilated, trapped in the crystal, or reaches the surface and releases a thermal halogen atom. It is generally agreed that, when the crystal surface has become nonstoichiometric, excess metal atoms are formed; at sufficiently high temperatures the metal atoms desorb.[6-8] The electronic mechanism by which the metal atoms form is not understood at present, but the presence of Li metal in the surface region of electron-irradiated LiF at temperatures below 588 K appears to be well established; above this temperature, the Li-metal signals disappear,[8] probably due to rapid desorption.

In this paper we accept the description of the halogen desorption mechanism sketched above but we note that since an H center incorporates an interstitial halogen atom, the release of its atom does not change the stoichiometry of the surface. The lack of stoichiometry resides in the F centers. Therefore, before the surface can

become nonstoichiometric, the F centers must diffuse from their place of creation to the surface. Since H centers are very mobile compared to F centers, it is appropriate to consider that the F-center diffusion takes place for the most part after the halogen atoms have left the crystal. This is the physical basis of our model. Thus, the model adds a new source of delay to delays occurring at the surface during the desorption step. This is the delay due to F-center diffusion. The phenomenon of F-center diffusion at high temperatures is not completely understood at present, although several plausible diffusion mechanisms have been developed.[9-11] Radiation-induced F centers, and the coloring they produce in alkali-halide crystals, have been a source of fascination for over fifty years. For this reason, it is very pleasing that the new measurements[1] have uncovered their participation in the electron-stimulated desorption process.

Given the lack of a complete theory for the events described above, the model presented below is limited to just those features which appear to be essential. The model allows for an energy deposition profile which is translated into an independent F-center production profile of the same shape.[12] The F centers diffuse in the semi-infinite solid in which their concentration is a function only of the distance from the surface. An F center which reaches the surface can either hop back into the bulk or, in an unspecified way, be annihilated while producing a metal atom which can desorb. The disappearance of the F centers and the desorption of the metal atoms are treated using first-order kinetics. The bulk diffusion constant, the back-hopping frequency, the F-center rate constant to make a metal atom, and the metal-atom evaporation-rate constant are temperature-dependent parameters of the theory. The F center may also have an effective lifetime for destruction in the bulk which, according to our comparison with the experimental data, appears to be infinite, apart from the F-center participation in the desorption process at the surface. Thus, each F center left in the crystal after the departure of the halogen atoms disappears only in connection with the desorption of one ground-state metal atom.

In Sec. II the Green's function for the time-dependent problem is obtained as a Laplace transform and its inverse. This is convoluted numerically with the space deposition profile and with the electron or photon pulse shape in time. The results of the model are compared with experiment by seeking the best fit in the space of the model parameters. The results are discussed in Sec. III. It is fortunate that despite all the uncertainties inherent in the theory, the diffusion process leads to a distinctive desorption time dependence which lends credence to our basic assumptions. The Green's function for the problem is asymptotically proportional to the negative 1.5 power of the time. This allows the metal-atom desorption to proceed on the long time scales observed experimentally.

II. DIFFUSION MODEL

We derive here the Green's function for an F center initially at distance x_0 from the surface diffusing to the surface where it creates a Li whose presence is observed. The

equations are linear in the limit of low F-center concentration so that response to pulses of finite duration and arbitrary initial spatial configuration is readily computed once the Green's function is known. Although the F center undergoes a three-dimensional random walk, the macroscopic spatial variation is one dimensional for the geometry considered here. The process of migration through the bulk, hopping on and off the surface, and production of Li is assumed to be described by the following system of one-dimensional equations:

$$\frac{\partial P(x)}{\partial t} = D\partial^2 P(x)/\partial x^2 - P(x)/\tau, \quad x > a \tag{1}$$

$$\frac{\partial P(a)}{\partial t} = Da^{-1}\partial P/\partial x \mid_{x=a+} - Da^{-2}P(a)$$

$$+ W_1 P(0) - P(a)/\tau, \tag{2}$$

$$\frac{\partial P(0)}{\partial t} = -W_1 P(0) + Da^{-2}P(a) - (\Gamma + \tau^{-1})P(0), \tag{3}$$

$$\frac{\partial L_0}{\partial t} = \Gamma P(0) - \gamma L_0, \tag{4}$$

where terms have the following meaning. $P(x)$ is the deviation of F-center concentration from its thermal equilibrium value at a distance x from the surface plane $x = 0$, and L_0 is the above-equilibrium concentration of Li at the surface. $P(x)$ and L_0 of course are functions of time although t is not shown as an argument. D is the bulk F-center diffusion coefficient, and W_1 is the rate for the F center to hop back off the surface into the bulk. Rapid diffusion on the surface and/or a barrier to reentry from the surface may make W_1 be considerably less than Da^{-2}, the rate for hopping onto the surface (assumed to be the same as the rate for hopping a distance a in the bulk); and in general we allow for the on-off surface rates to be different which necessitates the intermediate Eq. (2), in which a is one hop distance perpendicular from the surface. At the surface an F center is annihilated to form a Li at the rate Γ, and the Li may desorb at a rate γ. Finally, τ is the lifetime of the F center, assumed to be the same at the surface and in the bulk for processes other than Li production at the surface. The possibly complex dynamics associated with reentry of the F center into the bulk and production of Li are assumed here to be describable by the phenomenological rate constants W_1 and Γ.

Equations (2) and (3) effectively provide boundary conditions at the surface $x = 0$ to which the diffusion solution to Eq. (1) is matched. The other surface is taken to be at ∞ in correspondence with the experimental conditions that the observing times are much less than the time for an F center to reach the far surface. The initial conditions are $P(x) = \delta(x - x_0)$, $L_0 = 0$; and the system is readily solved by using Laplace transform techniques. Equation (1) becomes

$$(s' - D\partial^2/\partial x^2)\widetilde{P}(x) = \delta(x - x_0), \quad x, x_0 > a \tag{5}$$

where the tilde above a quantity indicates its Laplace transform with respect to the variable s, e.g.,

$$\widetilde{P}(x) = \int_0^\infty P(x,t)e^{-st} dt,$$

and $s'=s+\tau^{-1}$. The solution to Eq. (5) which is finite at the far surface $x \to \infty$ is

$$\tilde{P}(x)=Ae^{-\kappa x}+(1/2D\kappa)e^{\kappa(x-x_0)} , \qquad (6)$$

for $x < x_0$, where $\kappa=(s'/D)^{1/2}$ and A is a constant to be determined by matching to the conditions of Eqs. (2) and (3). The second term on the right-hand side of Eq. (6) results from matching to a decaying $e^{-\kappa x}$ solution for $x > x_0$ with the conditions that at x_0, $\tilde{P}(x)$ be continuous and $\partial \tilde{P}/\partial x$ have a discontinuity $1/D$, obtained from integrating both sides of Eq. (5) over the δ function. Observing times and the lifetime τ are very long compared with the bulk hopping time a^2/D. Hence we have $s' \ll D/a^2$, equivalent to $\kappa a \ll 1$. The solution for the main quantity of interest, the Li concentration L_0, which results from using Eq. (6) in the Laplace-transformed equations (2)—(4)—each of which has a zero initial condition term on the right-hand side, in contrast to Eq. (5)—and keeping only first order in $\kappa a =(s'a^2/D)^{1/2}$ is

$$\tilde{L}_0=\frac{a^{-1}e^{-\kappa x_0}}{s'+\Gamma+W_1\kappa a}[\Gamma/(s+\gamma)] . \qquad (7)$$

The factor a^{-1} occurs because $P(x)$ and L_0 are defined as one-dimensional probability densities with dimensions cm^{-1}.

The complete time dependence obtained from inverting the Laplace transform in Eq. (7) is treated in detail in following sections; but we discuss here the general physical content. First note from Eq. (4) that the term multiplying the quantity in square brackets [ ] is the surface F-center concentration $\tilde{P}(0)$. Hence Eq. (7) expresses the fact that the Li concentration is obtained by convoluting the rate of production from F centers at the surface with the loss by desorption. That is,

$$L_0(t)=\Gamma \int_0^t P(0,t')e^{-\gamma(t-t')}dt' , \qquad (8)$$

as follows from the convolution property, and we henceforth focus attention on $P(0,t)$ as inferred from inverting its transform. The inverse transform of $e^{-\kappa x_0}$ is

$$F(x_0,t)=x_0(4\pi Dt^3)^{-1/2}\exp(-x_0^2/4Dt) ,$$

which is recognized as the first passage probability[13] that a random walker starting at $x=x_0$ first arrives at $x=0$ at time t. (For this and subsequent discussion, we take the bulk lifetime $\tau \to \infty$ so that $s'=s$.) Thus in the limit of $W_1 \ll \Gamma$ for which there is negligible probability for the F center to return to the bulk before being annihilated, $P(0,t)$ is given, similar to Eq. (8), as the convolution between the first-passage $F(x_0,t)$ and the exponential decay at rate Γ to produce Li. First passage is appropriate in this instance since the F center annihilates on its first visit to the surface. A major prediction of the model is that for times long compared with that to diffuse to the surface, i.e., $x_0^2/4Dt \ll 1$, and long compared with the relaxation times γ^{-1}, Γ^{-1} ($s \ll \gamma, \Gamma$) the desorbed flux has a $t^{-3/2}$ decay given explicitly by $a\gamma L_0(t)=x_0(4\pi Dt^3)^{-1/2}$. This assumes the initial F-center production at x_0 takes place in a very short pulse, so one does not have to worry about the problems associated with finite-duration pulses

treated in the following sections.

The other limit $W_1 \gg \Gamma$ also has a simple interpretation, although it is probably not as physically relevant. If Γ can be neglected in the denominator of Eq. (7), one has $\exp(-\kappa x_0)/\kappa$ which is proportional to the Laplace transform of $(Dt)^{-1/2}\exp(-x_0^2/4Dt)$, in turn proportional to the normal random-walk probability $R(x_0,t)$ of finding the F center at time t a distance x_0 from its starting point. $R(x_0,t)$ differs from the above first-passage probability $F(x_0,t)$ in that $R(x_0,t)$ includes subsequent returns to x_0, which is to be expected for large W_1 and small Γ. The resulting $t^{-1/2}$ dependence for $x_0^2/4Dt \ll 1$ is generally more familiar than the $t^{-3/2}$ decay of $F(x_0,t)$. In neither limit is $P(0,t)$ given by simple exponential decay. The reason is that we are always tacitly assuming $X^2 \gg Dt$, where X is the total sample thickness. In this case, a quasi-steady-state solution $P(0,t)=X^{-1}e^{-\Gamma t}$, which would reflect a uniform F-center distribution throughout the sample, does not have time to materialize no matter how small Γ is. Such would be the small-Γ, thin-sample solution in the opposite limits $X^2 \ll Dt, D/\Gamma$, assuming the F center could reflect from the far surface.

We now take up the problem of inverting the Laplace transform in Eq. (7). One way to proceed, as indicated above, is to apply the convolution theorem to its three factors. However, in view of the subsequent numerical convolutions required to introduce the space and time dependencies of the electron- or photon-energy deposition, it is desirable to get as far as possible using purely analytical methods.[14] This can be done by factoring the denominator in Eq. (7) into products of the form $s^{1/2}+c$, where c is a constant. Then standard techniques allow one to express the inverse Laplace transform of $\tilde{L}_0$ in terms of the error function of a complex argument.[15]

Returning to Eq. (7) and considering its meaning for the three-dimensional solid, we note that $aL_0(t)$ corresponds to the number of lithium atoms per unit area on the surface and that $\gamma aL_0(t)$ corresponds to the number of lithium atoms leaving the surface per unit area per unit time, for one F center created per unit area at depth x_0 in a pulse with a Dirac δ-function time dependence $\delta(t)$. Following Ref. 12, the number of F-center—H-center pairs produced per unit volume per unit time at depth x_0 by electrons is taken to be $I/(AeE_F)$ times $dE/dx(x_0)$, where dE/dx is the medium stopping power, I is the electron current, e is the electronic charge, A is the electron-beam cross-sectional area, and E_F is the phenomenological energy to create a separated F-center—H-center pair. We use the simple shape for dE/dx shown in Fig. 1 of Ref. 12. For photons an exponential distribution based on the attenuation coefficient is used. The time dependence of the electron or photon pulses can be described in any convenient way, since the convolutions of the Green's function with the source in space and time are done numerically. The space integration was done approximately as a sum over contributions from atomic planes spaced by half a lattice constant, with weights determined by dE/dx. The time integration was done using the GAUS8 subroutine from the Laboratories' mathematical library. In the case of a series of identical pulses, the contributions

from previous pulses to the desorbed atom flux during and following the n-th pulse are included. The treatment of the spatial distribution is crude. The evaluation of the spatial integral is easily made more accurate, but obtaining the correct dE/dx for low-energy electrons in LiF would be very difficult.

When $\tau = \infty$, each F center produced must eventually produce just one desorbed metal atom. This follows from the fact that the integral of the desorbed atom flux $\gamma a L_0(t)$ from time zero to infinity is equal to $\gamma a \tilde{L}_0(s = 0)$, which by Eq. (7) is equal to unity. Thus the integral of the computer-generated metal-atom flux for a given electron pulse must yield a number of metal atoms equal to the number of F centers created. This provides a check on the numerical procedures. In addition, in a steady-state calculation, where the electron or photon beam is turned on at $t = 0$, the flux of desorbed metal atoms eventually approaches the F-center creation flux.

This section will now be concluded with a discussion of the input data for the model. We use a lattice constant equal to 4.028 Å and a density of 2.635 g/cm^3. The electron range $R(E)$ is taken from the work of Bronshteyn and Protsenko.[16] In measurements on LiF between 1 and 4 keV they find

$$R(E) = 500[E(\text{keV})]^{1.3} \text{ Å} , \tag{9}$$

where E is the electron energy in keV. The electron range is required for the specification of the approximation for dE/dx.[12] The other parameters needed from Ref. 12 are $h = 0.7$ and $f = 0.25$. The value of E_F was not used in the comparisons with experiment since the experimental data are not obtained on an absolute scale. For the purpose of estimating F-center densities produced by 200-eV electrons, we somewhat arbitrarily used an F-center production efficiency of 300 eV/(F center), obtained by extrapolating the LiF data in Fig. 3 of a paper by Lord.[17]

III. COMPARISON BETWEEN THEORY AND EXPERIMENT, AND DISCUSSION

The experiments[1] with which the theory will be compared were carried out with a nominally square-wave chopped beam of electrons whose energy was 200 eV. The beam current and beam cross section were about 0.0001 A and 0.0025 cm^2, respectively. For the measurements at 699 K the pulse repetition rate was 3.74 msec; for the measurements at 628 K the pulse repetition rate was 6.74 msec. The rising portion of the square pulse is not particularly fast; the fall to zero occurs in about 100 nsec.

The experiments were carried out at elevated temperatures to obtain larger lithium yields and to minimize charging. The effect of charging on the stability and focusing properties of the electron beam is monitored directly by looking at the fluorescent spot on the sample. We have good stability and focusing down to beam voltages of about 90 V and temperatures of about 473 K. It is our belief that such voltage differences as may exist in the region of electron beam energy deposition do not influence the F-center diffusion significantly.

The experimental setting described above allows several useful theoretical conclusions to be drawn. The electron range is 62 Å and the average value of x_0 from the dE/dx model described in Sec. II is 24 Å. From the electron range and beam cross section, the one-dimensional treatment is seen to be appropriate. The maximum temperature of 699 K implies that the concentration of point defects in the crystal before irradiation is most likely dominated by impurities.[18] At 699 K the equilibrium concentration of anion and cation vacancies in the pure crystal would be about 7×10^{15} cm^{-3}.[19] From the information given in Sec. II, we can estimate the density n_F of independent F-center—H-center pairs produced during a 1.87-msec pulse. Neglecting any losses, we obtain approximately 5×10^{20} pairs per cm^3. Since the number N of halogen sites per cm^3 is 6.12×10^{22}, the concentration of F centers created is about 1%.

In principle, F-center loss due to the statistical formation of M centers (from the production of an F center on a nearest-anion-neighbor site to a preexisting F center), as well as the ionization of newly formed F centers by the electron beam, will result in a time dependence for F-center production different from that of the incident electron beam. The magnitude of these effects is estimated next. The density of M centers produced by the statistical mechanism is given by $6(n_F)^2/N$.[20] The ratio of the M-center density to the F-center density is therefore approximately 6%, corresponding to a 12% F-center reduction. At the crystal temperatures of concern here, the M center should be the most numerous F aggregate center composed of a few F centers, and the tendency toward thermodynamic equilibrium is toward the decomposition of these centers.[21] The ionization of the F centers by the electron beam during their production gives rise to an additional production of M centers. The F-center ionization cross section Q is not known and so we estimate it to be equal to that for the ionization of Li, since the F-center and Li ionization potentials are not very different. Taking Q from Ref. 22 and averaging over the slowing down energies from the dE/dx model, we obtain a mean F-center ionization loss rate of 59 per sec. The newly produced α center (fluorine-ion vacancy) will combine with an F center to form an M^+ center on a time scale of the order of 0.05 μsec. Then the M^+ center will capture a conduction electron to form an M center on a very rapid time scale.[23] The net result is that F centers disappear at a rate about equal to twice the postulated F-center ionization rate. A 10% reduction in the F-center population is estimated to occur. In the calculations carried out here all F-center loss processes have been neglected, and the time dependence of the independent F-center density is taken to be that of the incident electron beam.

The model described in Sec. II involves two surface processes about which no information is available at present: the formation of a metal atom from an F center (rate Γ) and the evaporation of the metal atom (rate γ). In addition, the back-hopping rate W_1 is unknown. We assume that the back-hopping rate will not exceed the bulk hopping rate W. Here W corresponds to D/a^2 in the notation of Sec. II, and is equal to D divided by the square of the crystal lattice constant. If Γ is much larger than W, the back-hopping rate becomes irrelevant, as can be seen from Eq. (7). We have chosen to consider two

cases of the model for comparison with experiment. In the first, the metal-atom evaporation is assumed to be the rate-limiting surface step. Thus, Γ is taken to be infinite so that the back hopping is irrelevant. The parameters W and γ are then chosen to fit the experimental data. In the second, the formation of the metal atom is the rate-limiting step. Therefore γ is taken to be infinite, and the parameters W, Γ, and W_1 are fitted to the data. In this case, the F center may reside on the surface long enough to hop back, but once the metal atom is formed, it evaporates immediately. The F-center bulk lifetime τ is taken to be infinite.

The experimental data are not normalized on an absolute scale and the background level is not known. For this reason, the theoretical data are fitted, using a linear transformation, to the first and last points of the experimental data for the decay period when the electron beam is off. In order to treat the rising portion of the desorbed Li signal, the time dependence of the rising portion of the electron pulse must be known. At present, it is not. In one test calculation it was found that with the parameters determined from the falling portion of the Li signal, a reasonable assumption for the shape of the electron pulse led to a good fit to the rising portion of the desorbed Li signal. At 699 K, for each electron-energy deposition pulse 71% of the Li atoms desorb during the beam-on period, 15% desorb during the next beam-off period, and the rest desorb later.

Figures 1 and 2 show the fitting of the experimental Li flux by the theory with Γ set equal to infinity (W_1 irrelevant) for crystal temperatures of 699 and 628 K, respectively. The upper and lower curves were used to obtain estimates of the limits to be assigned to the value of the bulk hopping frequency W. The central curves represent our best fits for W and correspond to
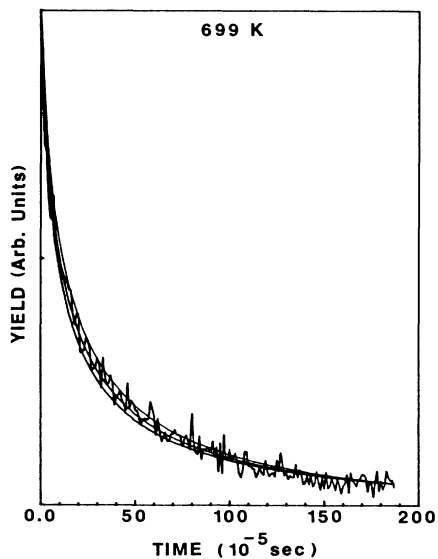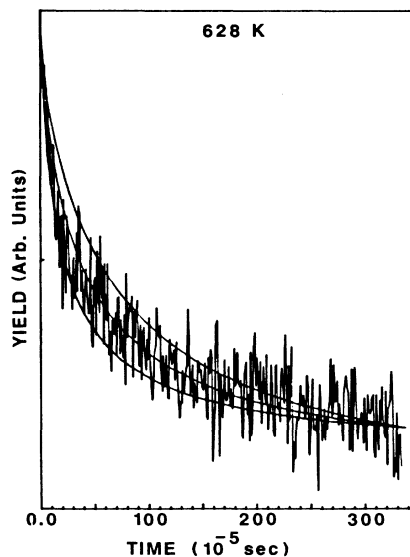

FIG. 2. Desorbed Li yield at 628 K. The square-wave pulse repetition rate was 6.74 msec. The yield following beam turnoff is shown. The upper, middle, and lower curves correspond to theoretical fits with $W = 2.6 \times 10^4$, 5.4×10^4, and 1.2×10^5 sec^{-1}, respectively. The value of γ is 0.7×10^5 sec^{-1}.

$$W = 2 \times 10^{10} \exp(-U/k_B T) \text{ sec}^{-1} ,$$

with $U = 0.7$ eV. Here k_B is Boltzmann's constant and T is the absolute temperature. For the parameter range of interest here the desorption is almost diffusion limited, and the latter half of the curves are quite insensitive to the value of γ. As shown in Sec. II, the tail of the distribution depends only on the ratio $x_0/D^{1/2}$ so one can find the value of W very easily. The value of γ influences the first half of the curves primarily, as is shown in Fig. 3
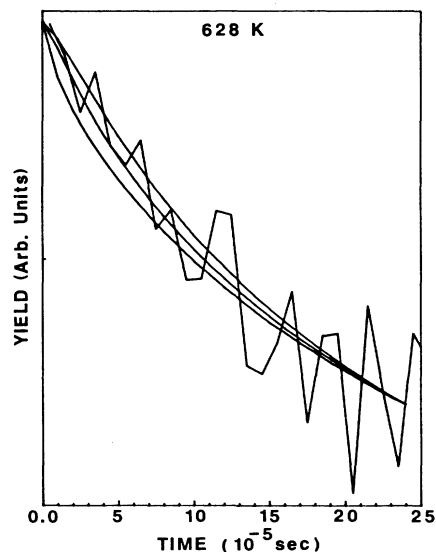

FIG. 1. Desorbed Li yield at 699 K. The square-wave pulse repetition rate was 3.74 msec. The yield following beam turnoff is shown. The upper, middle, and lower curves correspond to theoretical fits with $W = 1.6 \times 10^5$, 2.0×10^5, and 2.4×10^5 sec^{-1}, respectively. The value of γ is 6×10^5 sec^{-1}.

FIG. 3. Desorbed Li yield at 628 K. As in Fig. 2 but for short times after beam turnoff. The upper, middle, and lower curves correspond to $\gamma = 0.4 \times 10^5$, 0.7×10^5, and 3.0×10^5 sec^{-1}, respectively. The value of W is 5.4×10^4 sec^{-1}.

which provides some bounds on γ for the 628-K data. At 699 K, any value of γ greater than that given fits the data equally well. The lowest value of γ consistent with the data at 699 K is 1×10^5 sec^{-1}. Along with the largest value 3×10^5 sec^{-1} for 628 K, this leads to a lower bound for V of -0.6 eV, where we write $\gamma = \gamma_0 \exp(-V/k_B T)$ and γ_0 is a constant.

We now consider the alternate interpretation, in which γ is taken to be infinite. The same fits just discussed apply with W_1 set equal to zero and γ replaced by Γ. We have also searched for fits to the data with W_1 set equal to W. When the F center can hop back into the bulk, the desorption process is retarded compared to the case when W_1 is zero. The buildup of the desorbed flux is slower while the electron beam is on so that at the time the beam is turned off the flux is at a lower value. Since the back hopping continues to retard the departure of the metal atoms from the crystal after the electron beam is turned off, the desorbed flux, with back hopping, soon exceeds that for no back hopping. Compared to the best-fit cases for $W_1 = 0$, the excess for the latter three-fourths of the beam-off period is about 6%. When the curves are renormalized to fit the experimental data, the effect of back hopping shows up as an increase of about 2% for times close to the electron-beam turnoff time and gradually smaller increases at larger times. The effect is small and within the upper curve shown in Figs. 1 and 2. With $W_1 = W$, one can come closer to the best-fit curves by increasing either W or Γ somewhat. The most extreme deviation of the parameters from the best-fit results, within the bounding curves shown in Figs. 1 and 2, was found for 699 K. We obtained $W = 3 \times 10^5$ sec^{-1}, $\Gamma = 3 \times 10^5$ sec^{-1}, $W_1 = W$. This choice results in a curve which is about 2% high near the early times and about 0.5% low at later times. In summary, back hopping does not play a very big role in the interpretation of the present data, which are consistent with W_1 being zero.

We should point out briefly what happens if one tries to fit the 699-K experimental data with the prior assumption that the diffusion time $x_0^2/4D$ is very short (for example, 1 μsec) compared to the Li atom surface desorption time (necessarily of the order of milliseconds). For very large γ the theoretical curve lies below the data in Fig. 1, and for very small γ it lies above the experimental data. For any intermediate value the theoretical curve crosses the data just once. It is impossible to fit both the short- and long-time behavior on this assumption.

It is important to see if the diffusion constant D attributed to the F center in the model is in agreement with values determined independently. This poses a problem for LiF which cannot be colored either additively or electrolytically,[24] and for which there is no value applicable to our temperature range.[25] Reference 10 describes F-center diffusion models applicable to temperatures above 700 K, while Ref. 9 tests a model designed for lower temperatures on F-center diffusion in KCl. In this model, which is based on the presence of divalent impurities, the F-center hopping is speeded up by the presence of cation vacancies which thereby enhance the F-center diffusion when the cation vacancy is within a distance r_0 of the F center. In the limit of low impurity density, the F-center diffusion

constant is proportional to the number of impurity ions inside r_0, and to the cation vacancy diffusion constant. The measured activation energy for the cation mobility in the extrinsic regime in LiF is close to 0.7 eV,[18,19,26] the value obtained here. At 699 K the diffusion constant obtained here is 3.2×10^{-10} cm^2/sec, while from Ref. 19 the cation vacancy diffusion constant is 7.7×10^{-7} cm^2/sec. From Ref. 9, this implies a divalent ion impurity density of about 10^{16} cm^{-3}. This value is compatible with the value 7×10^{15} of thermally produced vacancy pairs per cm^3 for the pure crystal given earlier. Thus the identification of the diffusing defect in the model with the F center is consistent with the available experimental and theoretical evidence.

Since we cannot place useful bounds on the value of γ obtained at 699 K, it is not possible to compare the value obtained for the activation energy V with other results.[6] Within the framework of the model in the one-step form used here (either γ or Γ is infinite) V is the barrier height in the transition between a surface F center and an evaporated metal atom outside the crystal, which thereby acquires new F$^-$ and Li$^+$ surface vacancies. This transition is the inverse of that occurring in the reaction of Li metal vapor with LiF in the additive coloration process. Since LiF cannot be additively colored, experimental data are not available.

After the experimental data for temperatures of 628 and 699 K had been analyzed as described above, a file of 826-K data was analyzed. This higher temperature is at the knee between the intrinsic and extrinsic regimes in the paper of Eisenstadt,[18] and corresponds to a thermal vacancy pair density of about 2×10^{17} cm^{-3}.[19] The desorbed flux data were fit with $W = 1.2 \times 10^6$ sec^{-1} and $\gamma \geq 2 \times 10^5$ sec^{-1}. These values are compatible with the results for 628 and 699 K, and again lead to an activation energy of 0.7 eV.

An effect of irradiation on LiF should be mentioned which may be important but which has not been considered here. This is the possible formation of large F-center clusters containing hundreds of F centers at impurity sites.[27] In the experiments described in Ref. 27, F centers were produced by x irradiation over many hours at temperatures up to 600 K, and it was found that a substantial fraction of the total F-center production went into F-center clusters with a cluster density of the order of 10^{16} clusters per cm^3. The clusters were studied by small-angle x-ray scattering. It is not known whether such clusters are produced on the short time scales involved in the present experiments, but the originally transparent crystals are cloudy in appearance after the experiments have been conducted. The formation of clusters would reduce the number of F centers arriving independently at the surface; the formation of surface clusters could alter the Li desorption kinetics.

At the temperatures of interest here, there should be no Li observable as metallic Li in the crystal surface region.[8] However, at temperatures below 688 K metallic Li should make its appearance,[8] and one may hope for some interesting new experimental and theoretical results on the time dependence of desorbed Li. Perhaps it will also be possible to observe the large F-center clusters mentioned

above, and if they are found, connect them with the formation of metallic Li.

IV. CONCLUSIONS

We have developed a quantitative model of the experimentally observed delays in the flux of desorbed ground-state Li atoms following the irradiation of LiF by a pulsed 200-eV electron beam. The use of the model to analyze the experimental data for three temperatures in the impurity-dominated regime shows that the main source of delay in these experiments is the time required for F centers produced in the bulk to diffuse to the surface. A secondary source of delay, relatively more important at lower temperature, is connected with the rates for the surface processes that convert the newly arrived F center into a desorbed metal atom. Formerly this was thought to be the only source of delay.

The model suggests some interesting new directions for future research. By changing the electron-beam energy and by using photons, one can create the F centers at different depths and thereby change the time needed for the F centers to reach the surface. At large times the desorbed flux is proportional to $\bar{x}_0/D^{1/2}$, where $\bar{x}_0$ is the average deposition depth, which in turn is proportional to

the electron range. Studies of desorbed flux versus electron energy at fixed temperature should provide a severe test of the F-center production model, especially the range-energy relation. In the present case extrapolation from 1 keV to 200 eV has been employed, a very dangerous extrapolation indeed. By doping the crystal with divalent metal ions, it should be possible to increase the diffusion constant according to the theory of Ref. 9. By going to very high temperatures, it should be possible to reach the intrinsic regime of diffusion. By going to temperatures below 688 K, surface metallic Li should influence the desorption process. And, of course, it would be of great interest to have experimental data for other alkali halides.

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