Role of *F*-Center Diffusion in the Electron-Stimulated Desorption of Metal Atoms from Alkali Halides

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Measurements of the time history of ground-state neutral-lithium desorption from LiF during pulsed electron irradiation have resulted in a new model for the lithium desorption mechanism. We show that the slow diffusion to the surface of bulk *F* centers created by the electron beam is the rate-controlling factor responsible for most of the time history of the lithium desorption rather than the thermal evaporation of the metal from the surface. Comparison between theoretical and experimental time dependences yields values for the *F*-center diffusion constant and its activation energy for diffusion.

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We report measurements of the time dependence of electron-stimulated desorption (ESD) of neutral ground-state Li (Li^0) from a LiF (100) surface during electron-beam irradiation. The new experimental result is that the emission of Li^0 persists for at least seconds after the excitation pulse. By contrast, the neutral-excited-lithium (Li^*) desorption is extremely fast (less than 100 nsec).[1] The contrasting time scales suggest that Li^* and Li^0 are produced by completely different mechanisms and led us to a reconsideration of the delay mechanism presented in the literature for metal-atom desorption from the alkali halides.[2,3] We find that the persistence of the Li^0 emission after a pulse can be explained in terms of the slow diffusion of bulk *F* (*Farben*) centers (an electron trapped in a halogen vacancy) created by the electron beam. A quantitative model which describes the bulk diffusion of the *F* centers and their surface conversion to desorbed Li atoms is used to extract from the data the *F*-center diffusion hopping rate and activation energy, as well as an *F*-center surface residence time. This is the first time that *F*-center bulk diffusion has been connected with delays in metal-atom desorption from alkali halides and our results contrast with the generally accepted notion that the thermal desorption of the metal atom from the surface is responsible for the delays.[2,3] While surface effects are also important, especially at very low temperatures, the data show that at high temperatures the delay in the metal-atom signal is entirely due to the *F*-center diffusion time.

The production of *F* centers in alkali-halide crystals—whether by the electrolytic injection of electrons, by the immersion of the crystals in a vapor of their metal (additive coloration), or by irradiation with x rays, neutrons, or electrons—has been studied for many years.[4] In the additive coloration process, for example, a metal atom from the vapor produces an *F* center in the crystal. The irradiation of alkali halides by photon or particle beams which can excite crystal electrons across the band gap produces a much-studied series of very fast (nanosecond) electronic transitions which lead to the production of separated *F*-center and *H*-center pairs. An *H* center, also labeled a crowdion, is an interstitial neutral halogen atom crowded among the halogen ions along a ⟨110⟩ crystal direction. Relative to the crystal, both the *F* and *H* centers are charge neutral.

In experiments conducted over the past two decades it has been established that the *H* centers are the source for halogen-atom electron-stimulated desorption.[5,6] Since the *H* center is extremely mobile at room temperature, halogen atoms desorb within a few milliseconds of excitation.[7] The desorption of alkali-metal atoms is known to produce a Maxwell-Boltzmann velocity distribution at the crystal temperature,[8,9] and until the experiments reported here, it was thought that they also desorbed in times of the order of milliseconds or less.[7]

Our experimental setup has been discussed previously.[10] An electron beam is incident along the surface normal on a clean, optically transparent LiF target at $\sim 6\times10^{-10}$ Torr. The LiF (100) target surface was cleaved prior to introduction into the vacuum system and then cleaned by repeated cycles of heating to 500 °C and electron bombardment. For the measurement of Li^0 yields, a laser beam was made to impinge from the back of the sample, collinear with the electron gun, with a strength of 85 μW. The Li^0 atoms are excited by the laser and their decay at ~ 2 mm in front of the sample is detected by optical elements.

Analysis of the electron pulse shows that it has a slow time rise but that its cutoff is sharp (between 100 and 400 nsec). For this reason we will analyze the effects of the sharp turnoff of the beam. Timing of the fluorescence relative to the electron pulse was achieved by use of a time-to-amplitude converter or a multichannel analyzer for dwell times ranging from 10^{-8} to 10^{-5} sec. We did not analyze the velocity of the emitted Li^0 particles prior to the timing of their fluorescence. The reason for this is that if we assume a Maxwell-Boltzmann velocity distribution for the Li^0 atoms, as in other alkali halides,[8,9] the velocity spread can be converted to a spread in time which is smaller than our counting dwell times. The experiments reported here were carried out at 628, 699, and 826 K with use of a 200-eV electron beam chopped in a square-wave fashion. The high temperatures minimized the effects of charging on the electron beam energy. The Li^0 yield following electron-beam turnoff is shown in Fig. 1 for a sample temperature of 699 K. The square-wave pulse repetition rate was 3.74 ms. These data will be compared with theory after the model is introduced and the necessary notation developed. In a separate experiment we completely turned off a 400-eV electron beam and with the sample at 675 K observed the decay of the Li^0 yield. The time required for the yield to drop to 10% of its maximum value prior to turnoff was 200 sec.

The desorption mechanism that we propose is illustrated in Fig. 2. First, the electron beam produces a one-dimensional distribution of *F*-center–*H*-center pairs and the *H* centers rapidly leave the crystal. Second, each *F* center diffuses to the surface where it creates a neutral Li atom. Third, the neutral Li atom thermally desorbs. The mechanism is similar to that in additive coloration. The parameters of the model are a bulk hopping rate W and a surface residence time equal to the inverse of a rate constant γ. The model takes into account the time history of the electron beam. It also uses a depth distribution of defects created in the bulk, previously tested for desorption of halogens,[11] and an experimental range of 61.8 Å for 200-eV electrons.[12] The incorporation of the concepts outlined above into a calculation which can be compared to experiment is somewhat complicated. It is described at length by Green *et al.* In the next two paragraphs we describe the physics of the problem and give a simple example of how the model results in equations that can be compared to experiment.

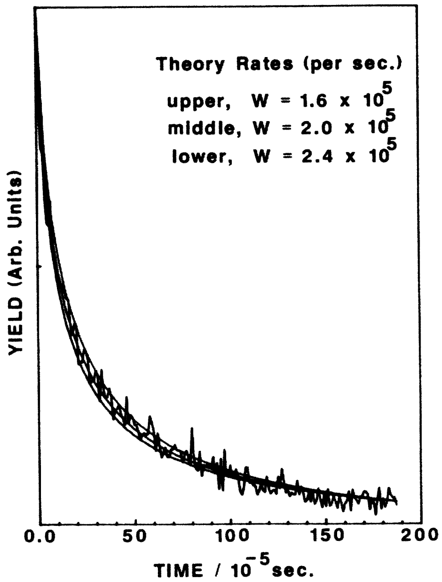

FIG. 1. Time dependence of the drop of the Li^0 yield for a sample temperature of 699 K. The smooth curves correspond to our theoretical fits to the data using different values of the *F*-center hopping rate W and a fixed value of the surface residence time $1/\gamma = 1.67\times10^{-6}$ sec.

To understand the physics we need to compare the delay caused by the surface residence time $1/\gamma$ to the diffusion time $t_d = (\bar{x}_0)^2/2W$ for the F center to reach the surface from the average penetration depth $\bar{x}_0$, measured in units of the crystal lattice constant ($\bar{x}_0 = 6$ for 200-eV electrons[13]). Here W is the bulk *F*-center hopping rate. The importance of $1/\gamma$ and t_d in the time behavior of the desorption can be best illustrated by consideration of each process independently. If the F center is created in the surface the Li atom can desorb without bulk diffusion and therefore the desorbed Li^0 flux following surface energy deposition decays exponentially with rate γ. For F centers created in the bulk, the surface concentration of F centers is governed by the Green's function for bulk diffusion, which leads to an asymptotic $t^{-3/2}$ power law for the *F*-center concentration. In general we have both surface desorption and bulk diffusion. Intuitively, it is

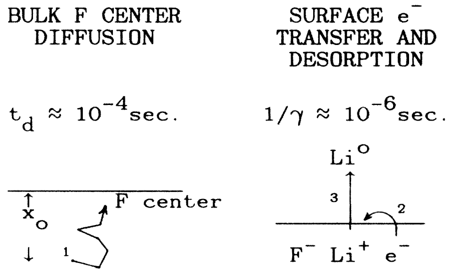

FIG. 2. Mechanism for electron-stimulated desorption of Li^0 from LiF: (1) Electrons penetrate a distance x_0 into the bulk and create F centers which diffuse to the surface in a time t_d. (2) The *F*-center electron is captured by a Li ion. (3) The neutral Li atom desorbs. The time required for steps 2 and 3 is the surface residence time $1/\gamma$ which is much smaller than t_d at the temperatures and electron penetration depths used here.

clear that since an exponential decays faster than any given power law, the dependences of the yield at short and long times are mostly governed by surface desorption (γ) and bulk diffusion (W), respectively.

To illustrate the nature of the solutions to this diffusion problem and their subsequent use in comparison with the data we will assume that the surface desorption time is negligible compared to t_d. In this case, for a square electron-beam excitation pulse which produces one F center at a depth x_0 between time $t=0$ and $t=t_0$, the desorbed Li atom flux $\Phi(t)$ is given by

$$\begin{aligned}
&\Phi(t)=f(t)\equiv(1/t_0)\operatorname{erfc}([t_d/2t]^{1/2}), \\
&\qquad\qquad\qquad\qquad 0\leq t\leq t_0, \\
&\Phi(t)=f(t)-f(t-t_0), \quad t_0\leq t\leq\infty, \\
&\Phi(t)\rightarrow(t_d/2\pi t^2)^{1/2}, \quad t\rightarrow\infty,
\end{aligned}\tag{1}$$

where erfc is the complementary error function. Equation (1) exhibits the rise and fall of the desorbed Li flux as a result of F-center production by the electron beam as well as the asymptotic $t^{-3/2}$ behavior which represents the probability of first arrival[14] at the surface at times $t >> t_d$. The use of an infinite surface desorption rate in Eq. (1) is consistent with the experimental data for the temperatures of 826 and 699 K. At low temperatures (for example 628 K), $\gamma=\infty$ is incompatible with the experimental data and the full theory is required.[13] Since the electron beam creates F centers over a distribution of depths x_0, Eq. (1) has to be summed numerically over this distribution in order to be compared with the experimental data. For the general case when γ and W are finite, the solutions to the diffusion equation are similar to those in Eq. (1) except that complex error functions are obtained. Also, the asymptotic behavior is identical. The depth distribution of defects and the time history of the electron beam must again be taken into account.

Returning to Fig. 1 we can now compare the time dependence of the ESD Li^0 yield for a temperature of 699 K with curves from the model which provide the best-fit value for W and its upper and lower bounds. The fitting is accomplished by adjustment of the values of the bulk hopping rate W and the surface desorption rate γ. Since the absolute value of the yield and the background level are not known, the theoretical curves were normalized to the experimental data at the beginning and end of the beam-off period. We find best fits of $W=2\times10^5$ sec^{-1} and $\gamma\geq1\times10^5$ sec^{-1} for 699 K. The corresponding delays are $t_d=0.9\times10^{-4}$ sec and $\gamma^{-1}\leq10^{-5}$ sec, which implies that at this temperature bulk diffusion is the rate-limiting step. The determination of the best fit is unique within the bounds specified since γ and W mostly affect the yield at short and long times, respectively. In particular, the assumption that the decay is governed solely by surface evaporation of a Li-rich layer[2,3] would result in a finite γ of the order of 10^3 sec^{-1}, an infinite W, and a consequent exponential behavior which does not fit with the data. Very similar results are obtained at 826 K where we find $W=1.2\times10^6$ sec^{-1} and $\gamma\geq2\times10^5$ sec^{-1}. For 699 and 826 K an infinite value of γ is compatible with the data.

We have also fitted experimental data for decay times of Li^0 desorption at 628 K and find $W=5.4\times10^4$ sec^{-1}. At 628 K the surface rates are slow enough to obtain a finite value of $\gamma=0.7\times10^5$ sec^{-1}. Values of γ larger than 3.0×10^5 sec^{-1} do not fit the data. This demonstrates that in general it is essential to take the surface processes into account.

The values of W given above result in a temperature dependence given by $W=W_0\exp(-U/kT)$, where W_0 is a preexponential, k is Boltzman's constant, T is the absolute temperature, and $U=0.7\pm0.3$ eV. A plot of $\ln(W)$ vs $1000/T$ is shown in Fig. 3. It is important to compare these results with previous data on LiF. The activation energy for F-center diffusion has not been measured directly. To determine if the value of 0.7 eV obtained for the activation energy of the bulk defect is compatible with the assignment of the F center as the bulk defect we will use the model of Kalnin and Itzkovich.[15] This model is designed to explain F-center diffusion at temperatures where the number of thermally produced vacancies is smaller than those produced by divalent metal impurity ions (the extrin-

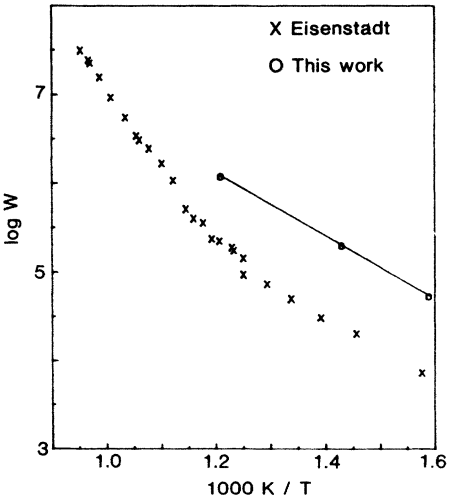

FIG. 3. Arrhenius plot of our best fits for the F-center bulk hopping rate W and the data of Eisenstadt (Ref. 16) on the cation-vacancy diffusion rate in LiF. As described in the text, the similarity of the activation energies in the low-temperature regime (0.7 eV) is consistent with the assignment of an F center as the bulk defect responsible for the desorption.

sic impurity regime). For low impurity densities, their model implies that the *F*-center hopping rate is proportional to the product of the density of divalent impurity ions and the cation-vacancy hopping rate. For this reason, if the diffusing entity is an *F* center, the activation energies for *W* and the cation-vacancy diffusion constant should be equal. As is seen from Fig. 3, the activation energy for *W* and that of the cation vacancy diffusion[16] are the same.

Another test of the diffusion constant may be obtained by our using it to calculate the number of divalent metal impurity ions, again using the model of Kalnin and Itzkovich.[15] At 699 K the diffusion constant obtained here is 3.2×10^{-10} cm^2/sec, while from the work of Haven[17] the cation-vacancy diffusion constant at that temperature is 7.7×10^{-7} cm^2/sec. The model of Kalnin and Itzokovich would then imply a density of 2×10^{16} divalent ions/cm^3 in our sample. Since the crystal is in the extrinsic regime the impurity density given above should be larger than that of thermally induced, intrinsic cation-anion vacancy pairs. At 699 K, the latter density is about 7×10^{15} cm^{-3} (Ref. 16). Thus, the assignment of the diffusing defect in the model as an *F* center is consistent with the available data.

In summary, we have made new time-resolved measurements of ESD of Li^0 from a LiF (100) surface. The time dependence of the flux in the beam-off period is consistent with the delay observed in the metal desorption, being primarily due to the diffusion of *F* centers produced in the bulk by the electron beam. At the high temperatures discussed here, the surface desorption rate, by contrast, is very fast and only affects the flux at very early times. This new insight into the mechanism for metal-atom desorption suggests a number of new directions for experimental and theoretical work.

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