

## ENERGY THRESHOLDS AND DELAYED EMISSION FOR ELECTRON-STIMULATED DESORPTION OF NEUTRAL GROUND- AND EXCITED-STATE Li ATOMS FROM LITHIUM FLUORIDE

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We have bombarded single-crystal surfaces of LiF with 5–500 eV electrons at different target temperatures (300–800 K) and the temperature dependence of the yield of ground- and excited-state Li atoms was studied. Measuring the electron energy threshold for desorption of Li\* we found an onset for desorption of Li\* around 60 eV, which correlates well with the Li<sup>+</sup> core-exciton levels of Li<sup>+</sup> in LiF. Based on these findings we propose a Knotek–Feibelman-like mechanism for the desorption of excited Li atoms from LiF initiated by Li core electron excitations (core excitons). On the other hand, we found the threshold for desorption of Li<sup>0</sup> atoms to be much lower, around 12 eV. This is explained with a process involving valence band excitation and subsequent F- and H-center formation. In related experiments we have studied the delayed emission of ground-state atoms after turning off the electron beam, which can be explained in terms of F-center production by the primary electron beam, Li metal colloid formation and the subsequent evaporation and diffusion of Li to the surface, resulting in metal desorption.

### 1. Introduction

Electron-stimulated desorption (ESD) from alkali halides has been studied for more than 20 years. Although the main mechanism leading to the desorption of halogen atoms and consequent evaporation of the alkali metal atoms is well understood, many questions on the detailed mechanism are still open [1–4]. One problem, which has been addressed recently in numerous investigations, is the emission of excited and ionized alkali atoms under electron bombardment of alkali halides [2,5–15]. Two possible mechanisms have been proposed: (1) emission due to an intrinsic desorption process via inelastic energy transfer, usually assumed to start with the creation of an alkali core hole/exciton as the initial step [8,11–13], and (2) gas phase excitations of desorbed neutral ground-state atoms by the primary electron beam or by secondary electrons [2,5,6,9,10]. To get further insight into this problem energy threshold measurements for ESD from LiF were performed for ground- and excited-state Li atoms.

Recent measurements by Green et al. [14] on delayed emission of alkali atoms from LiF after the bombarding electron beam was interrupted have been explained in terms of F-center diffusion to the surface, followed by Li evaporation. We have performed similar measurements on an expanded time scale (delayed emission up to seconds) and will explain them in terms of alkali metal colloid formation [15–17] and subsequent slow disintegration of these colloids with time. In these measurements two contributions to the emitted Li<sup>0</sup> flux can be distinguished: (1) a prompt contribution (delay time

less than ms) and (2) a delayed contribution (delay time in the order of seconds).

### 2. Experimental setup

Single-crystal surfaces of LiF were bombarded with 5–500 eV electrons at different target temperatures (300–800 K). The angle of incidence of the electron beam was 45° with respect to the target normal. The bombarded area had dimensions of approximately 2 mm by 4 mm. Total electron current in the threshold measurements was kept constant at 10  $\mu$ A independent of electron energy. Radiation of excited states was observed with a 1 m grating monochromator viewing the crystal along the surface normal.

Ground-state Li atoms have been measured with a quadrupole mass analyzer.

The UHV system maintained a base pressure of less than  $3 \times 10^{-10}$  mbar during the measurements. The crystals have been cleaved in air and cleaned in the vacuum system by prolonged heating at 250°C. To avoid sample charging, which is a crucial problem with insulators at low temperatures, a Mo-mesh with a transmission of 80% was placed over the crystal surface in some measurements. In the delayed measurements the electron beam was prevented from reaching the target by applying a negative electrical extraction voltage within less than 1 ms.

### 3. Results and discussion

The interaction of electrons with an alkali-halide lattice is essentially restricted to the halogen sublattice and has recently been summarized by Williams [1]. The first step leading to desorption is the generation of an electron-hole pair out of the valence band, by absorbing energy to overcome the band gap. The hole becomes self-trapped after less than 1 ps, forming a self-trapped hole (STH), and transforms together with a conduction band electron into a self-trapped exciton with high efficiency. The self-trapped exciton (STE), which already can be imagined as a nearest-neighbor pair of an F-center (electron on a halogen (fluorine) vacancy) and an H-center ( $F_2^-$  molecule) can now decay via three decay channels: (1) by radiative recombination restoring the lattice; (2) via a focused collision replacement sequence in which the H-center moves away from the F-center and carries kinetic energy in the order of 1 eV; if the H-center intersects the surface it will decay and emit a neutral halogen atom; thus the lattice is restored except for the F-center at the original site of the STE; (3) the H-center can thermally diffuse away from the F-center and again, if it reaches the surface, emission of a neutral halogen atom takes place. While H-centers are mobile and will already diffuse at temperatures as low as 30 K, F-centers diffusion only takes place at temperatures of a few hundred K.

F-centers formed at the surface or having diffused to the surface will decay in neutralizing an alkali atom, thus forming an alkali overlayer at the surface. Therefore excess alkali metal atoms will accumulate at the crystal surface and four temperature regimes can be distinguished (see fig. 1):

- (1) At low temperatures, for which the vapor pressure of the alkali metal is negligible, no alkali evaporation ( $Li^0$ ) takes place and a surface metal film will develop and finally prevent further halogen emission. For LiF this is typically the case below 450 K at all bombarding energies.

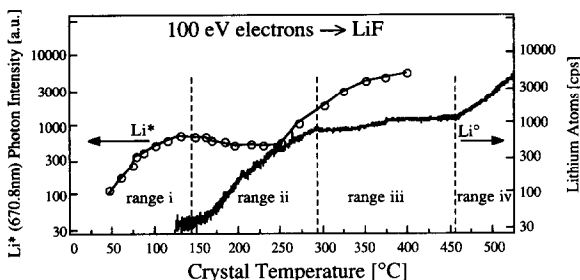


Fig. 1. The dependence of the  $Li^0$  and  $Li^*$  signal upon the crystal temperature during 100 eV electron bombardment of LiF. Four temperature regimes can be distinguished.

- (2) As the temperature is increased, Li atoms can evaporate from the surface and an exponential increase in the yield is observed. The desorption flux is limited only by the evaporation rate in this regime.
- (3) As soon as the evaporation rate becomes larger than the Li metal formation rate at the surface a constant yield can be observed, even with increasing temperature.
- (4) At even higher temperatures, above 750 K, thermal evaporation from the alkali halide becomes measurable and dominates the emission flux at temperatures above 800 K. Separate measurements for an unbombarded surface verified this point. In the case of NaCl a similar temperature dependence was observed; however, evaporation already becomes dominant at temperatures above 600 K.

For the yield of excited neutral  $Li^*$  atoms (670.8 nm) a very different behaviour with temperature was observed [11]. A significant yield of  $Li^*$  is already found at room temperature, exhibiting a maximum around 420 K, followed by a strong increase similar to ground-state Li atoms (see fig. 1). Although detection of optical emission is more sensitive than detection of ground-state atoms using a quadrupole, the yield of ground-state atoms shows an increase with temperature by more than two orders of magnitude as compared to one order of magnitude for the excited yield. Similar experiments using photon-stimulated desorption (PSD) of  $Li^*$  from LiF [18] and  $Na^*$  from NaCl [19] also show a clear anticorrelation between the excited- and the ground-state yield with temperature. On the other hand, we did not observe significant changes in the secondary-electron yield with temperature. All these observations cannot be explained in terms of post-excitation of emitted ground-state atoms in the gas phase by secondary electrons or the primary-electron beam [2,5,6].

To obtain further insight, energy threshold measurements were performed both for ground- and excited-state Li atoms and are shown in fig. 2. The threshold behaviour for excited Li atoms is shown at two different target temperatures (290 and 630 K). In both cases the same energy threshold value with an onset around 60 eV was observed. This energy correlates with the  $Li^+$  core exciton levels of  $Li^+$  ( $1s \rightarrow 2s$ ) at 60.8 eV and for  $Li^+$  ( $1s \rightarrow 2p$ ) at 61.9 eV of Li in LiF. No enhancement of the yield of excited Li atoms could be correlated with the core hole levels  $F^-(2p)$  at 14.2 eV and  $F^-(2s)$  at 38.2 eV. In a similar manner, measurements for the onset of excited  $K^*$  emission from KCl and KBr [11] could be correlated with the  $K^+(3s)$  core exciton.

For the energy threshold of ground-state Li atoms we found an energy around 13 eV. This value corresponds well with the measured band gap in LiF of 14.2 eV, thus confirming that the first step in the desorption

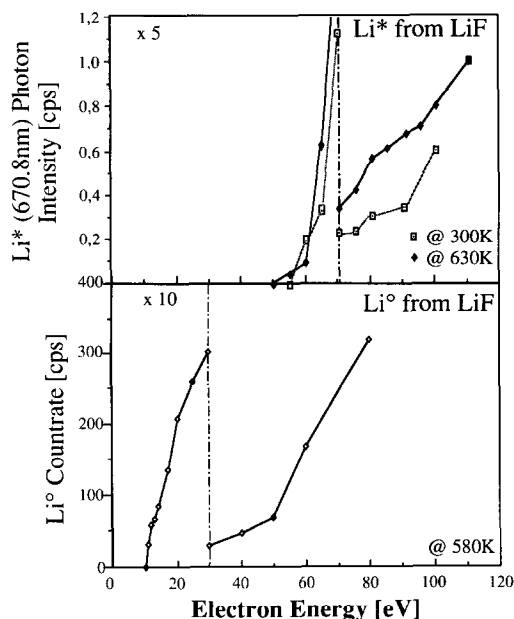


Fig. 2. The dependence of desorbed  $\text{Li}^*$  and  $\text{Li}^0$  from LiF on the electron energy. The onset is independent of target temperature around 60 eV for  $\text{Li}^*$  and around 13 eV for  $\text{Li}^0$ .

process of ground-state atoms is the formation of an electron-hole pair out of the valence band. We do not see any drastic yield increase in the ground-state signal around 60 eV, the onset of the excited yield production. This indicates the presence of two distinct desorption processes for ground- and excited-state atoms.

Based on our experimental results we have to exclude secondary gas-phase excitation processes for the creation of excited Li atoms and propose the following Knotek-Feibelman-like [20] mechanism:

- (1) Provided the primary electron has sufficient energy, the incident electron creates a core exciton on the alkali site. This is supported by the threshold measurements (fig. 2) for LiF, but also for KBr and KCl.
- (2) This core exciton decays via an interatomic Auger transition from a neighboring anion. Consequently, the anion is left in a singly or multiply positively charged state, as the excess energy is used for the release of valence electrons originally located on the anion. The electron itself, which was bound to the core hole, can be released into the conduction band, trapped in a surface exciton or trapped in a surface state.
- (3) Due to Coulomb repulsion the Li ion is ejected and, on leaving, captures an electron, presumably from a location mentioned above, into an excited state. Therefore the ionic bond to the crystal no longer exists, and the excited alkali atom leaves the surface. Our model is supported by calculations of the ejection

process from an ideal alkali halide surface [7,8]. Contradicting calculations indicate that ion emission is impossible as the lattice relaxation is faster than Coulomb repulsion [9,10]. Furthermore, energy thresholds for the emission of Li and F ions from LiF under ESD and PSD have been found to be identical [12,13].

A process as depicted above should result in non-thermal energies for excited or ionized particles. Experimental results are contradictory [6,13].

In an additional set of experiments we have studied delayed emission of Li from LiF after the electron beam was turned off. Contrary to experiments by Green et al. [14] the main emphasis was on delayed emission in the time range of 0.1 to 10 s. Bombarding electron energies were in the range from 50 to 400 eV and temperatures from 600 to 750 K. As the main feature, two contributions to the emitted  $\text{Li}^0$  flux are observed for all energies and temperatures:

- (1) A prompt contribution, for which the signal drops faster than our time resolution (20 ms). In the work by Green et al. [14], which was performed in a time range of  $10^{-3}$  s (resolution  $10^{-5}$  s) the prompt contribution has been studied and interpreted as F-center diffusion to the surface.
- (2) A delayed emission with decay rates in the order of seconds. For temperatures above 750 K the prompt signal becomes more and more dominant. The ratio of the two contributions was essentially constant with energy.

A peak in the delayed-emission signal is observed (fig. 3) at temperatures around 700 K for short bombardment times at current densities in the order of  $10^{14}$  electrons/( $\text{cm}^2$  s). This peak could be observed at

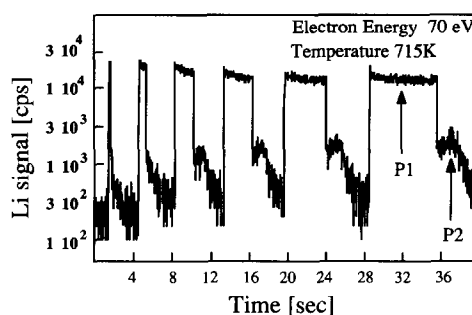


Fig. 3. Delayed emission of  $\text{Li}^0$  from LiF after the electron beam is repeatedly interrupted. The electron current density was  $10^{14}$   $\text{e}^-/(\text{cm}^2 \text{ s})$ . After each interruption of the electron beam the signal shows a prompt decrease followed by delayed emission in the order of seconds. With increasing bombardment time a peak ( $P_2$ ) in the delayed emission becomes apparent. With further increasing bombardment time the peak slowly disappears again; however, delayed emission falls off with a larger time constant. If the target is irradiated for a few seconds after a break following long bombardment, the peak ( $P_2$ ) reappears.

all bombarding energies but was dependent on the current density. With increasing electron dose the peak becomes less pronounced and disappears for long electron bombardment times.

We will explain the observed behaviour of delayed emission by the occurrence of colloids. At high irradiation doses, alkali metal colloid formation is a general phenomenon in ionic crystals [15–17]. At a few hundred K, when F-centers become mobile, F-center aggregation starts and leads to alkali metal colloid formation. However, at even higher temperatures the colloids will again disintegrate due to Li evaporation from the surface of the colloids [15]. There exists an equilibrium between condensation and disintegration at any temperature where colloids are present. This is a slow process and the final size distribution of the colloids after bulk irradiation will develop only after hours (ripening process).

During electron irradiation F-centers are formed in a near-surface layer of about 10 nm. We have two loss channels for F-centers: (1) aggregation leading to colloid formation, and (2) diffusion to and trapping of F-centers at the surface followed by Li evaporation, which leads to prompt Li evaporation (prompt emission).

As soon as irradiation is stopped, no more F-centers are produced. The only remaining process leading to Li emission is disintegration of colloids and diffusion of Li to the surface followed by evaporation (delayed emission). As delayed emission is due to colloids, we have to expect the same temperature dependence as for colloid formation, which is confirmed by our measurements. At 670 K the ratio delayed/prompt emission was about one, decreasing for higher as well as for lower temperatures. The details of the time dependence in delayed emission reflect the interplay of colloid formation, ripening, disintegration and diffusion of Li to the surface.

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