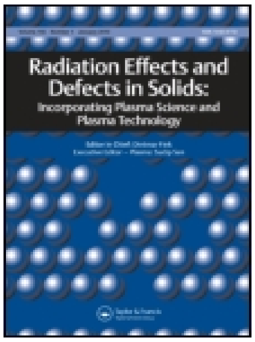

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ELECTRON STIMULATED DESORPTION THRESHOLDS FOR EXCITED ATOMS DESORBED FROM ALKALI-HALIDES

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We have investigated the thresholds for the generation of desorbed excited alkali atoms under electron bombardment for LiF, KCl and KBr in the energy range from 10 to 120 eV, and from room temperature up to 450°C. The dependence of the yield of excited atoms on the electron energy shows features which are in good agreement with the excitation energies of alkali core-excitons in the alkali-halide crystal. This suggests the production of an alkali core-exciton as an initial step for the desorption of excited alkali metal atoms under electron bombardment. The dependence of the yield of excited alkali atoms on either the temperature of the crystal or the electron density in the irradiated surface area gives additional support for that model.

INTRODUCTION

The interaction of electrons and photons with alkali-halides remains of strong current interest. Neither the desorption of neutral ground-state atoms[1–4] nor of excited atoms and ions is very well understood. In particular, there exists no general agreement about the generation of excited atoms and ions in the literature.[5–8] As the neutral ground-state atoms are the main fraction of the desorbed particles, their generation mechanism will be discussed briefly. The current understanding of neutral ground-state desorption is that the mechanism is based on the generation of a self-trapped exciton on a halogen site.[1–4] This excited state can decay by inducing a replacement collision sequence along the chain of halogens in the ⟨110⟩ direction. The process leads to the emission of a halogen atom either directly as a consequence of the replacement collision sequence or later by diffusion of defects to the surface. As these defect processes only take place in the halogen sublattice, an alkali metal enrichment results in the near surface layer. According to this model the alkali atoms evaporate thermally from the crystal, provided the vapor pressure of the alkali metal is sufficiently high. Otherwise the formation of a metal layer prohibits any further desorption process. Later on in this paper this model will be referred to as the valence excitation mechanism.

Excitation or ionization of atoms desorbed from alkali-halides can be due to the following processes: (i) Atoms desorbed by the valence excitation mechanism can be excited or ionized in the gas phase either by secondary electrons[6] or by the primary electron beam.[5] (ii) Core-hole excitations of surface or near surface atoms leads via Auger decay to direct emission of excited atoms or ions.[7] (iii) Neutral ground-state atoms produced by the decay of core-hole excitations of surface or near surface atoms (similar to (ii)) are excited or ionized either by secondary electrons (Auger electrons) or by the primary electron beam.

The core-hole excitation mechanism is referred to as the Knotek–Feibelman mechanism in the literature[9,10] when it is used to explain desorption of ions in maximum valency systems. The incident electron creates a core-exciton or a core-hole. Both excited states can decay via an inter- or intra-atomic Auger transition depending whether the core-hole or core-exciton is located on the cation or anion, respectively. This leaves the halogen anion in a singly or multiply positively charged state, since the only available electrons are located on the anion. Consequently, Coulomb repulsion leads to the emission of halogen and alkali ions. Core hole excitation may also lead to the emission of neutral particles when the system is left in a repulsive or energetic state.

Some authors have suggested that the major if not exclusive contribution to the observed yield of excited state neutrals and ions is due to gas phase excitations by the primary electron beam or by secondary electrons.[6,11] Recent measurements strongly suggest, that the desorption of ions from alkali-halides is caused by a process different from gas-phase excitation, namely by the creation of an alkali core-hole as a first step in the desorption process of ions.[8] It is the aim of this paper to provide conclusive experimental data to elucidate the mechanism responsible for the emission of excited states. Therefore, we measured ESD-thresholds of excited alkali atoms from LiF, KBr and KCl at various target temperatures. This is compared to existing photon stimulated desorption (PSD) and electron stimulated desorption (ESD) data of neutral ground-state and excited-state atoms and ions. Our data suggest that the emission of excited state neutrals is correlated with the formation of alkali core-holes and does not require invoking gas phase excitation.

EXPERIMENTAL PROCEDURE

A 10 eV to 120 eV electron beam with currents up to 30 μA was used to bombard alkali-halide single crystal surfaces. The electron beam axis was incident on the target at 45°. The bombarded area had dimensions of approximately 2 by 4 mm. Careful investigations have been done to measure the profile of the electron beam. Radiation of excited states was collected by a MgF_2 lens into a high resolution one meter grating monochromator viewing the crystal along the surface normal. The UHV-system maintained a base pressure of less than 3×10^{-10} torr during the measurements. All investigated crystals have been cleaved in air and cleaned in the UHV-system by baking at 200°C overnight. The sample temperature was varied between 20°C and 450°C. Sample charging, which is a crucial problem with insulators especially at low temperatures, was largely reduced by placing a Mo-mesh with a transmission of 80% over the crystal surface and by using low current densities. Nevertheless, special care had to be taken when changing the electron energy, as the signal reached a steady-state value only after a few minutes. This was ascribed to the migration time of previously produced defects to the surface. Background radiation originating from bulk luminescence from the crystal, from the sample-furnace and from the electron gun filament was measured carefully for each data point and subtracted from the absolute count-rates. Uncertainties in the electron energy are due to the work-function of the cathode and the work-function of the crystal.[10]

RESULTS AND DISCUSSION

According to the valence excitation mechanism excess metal atoms accumulate on the alkali-halide crystal surface. Therefore, two regimes can be distinguished. (a) Below a certain temperature the evaporation rate is too low to cause significant desorption and an excess metal layer is produced. (b) The evaporation rate is high enough that each excess metal atom evaporates immediately.[12] The vapor pressure is governed by the crystal temperature and changes by several orders of magnitude in the investigated temperature range. Unfortunately the vapor pressure of K[13] is so high that considerable evaporation already occurs at room temperature.[14] For K there are no excess metal atoms on the surface above 100°C.[15] Only the vapor pressure for Li[13] is low enough to allow a surface enrichment of Li on a LiF crystal up to 250°C.[16] Therefore, our efforts concentrated on LiF since we anticipated more convincing results as far as the involved desorption mechanisms are concerned.

a) *LiF*

The correlation of the yield of neutral ground-state Li atoms by ESD from LiF with the vapor pressure of the Li metal has been shown previously.[17] The ESD yield follows the evaporation rate giving a detectable amount of neutral ground-state atoms above 250°C and rising exponentially until 400°C, where the desorption of ground-state Li atoms is only governed by the electron flux and not limited by the evaporation rate anymore.[16,17] Below 250°C no neutral ground-state desorption of Li was found under electron bombardment,[17] which could be attributed either to a lack of sensitivity of the Laser Induced Fluorescence measurement, or the presumably higher energetic deexcited Li* atoms are detected with less efficiency, because of the narrow bandwidth of the cw dye-laser. Although, detection of optical emission is more sensitive, we would expect the temperature dependence of the yield of excited states to be proportional to the yield of ground-state atoms if the excited atoms desorb by the same mechanism as the ground-state atoms and are subsequently excited in the gas-phase. However, this is not observed in our experiment as can be seen in Figure 1, where the ground-state yield increases three orders of magnitude in the temperature range from 250°C to 400°C, compared to an increase of the yield of excited states of merely one order of magnitude. A rough estimate of the detection efficiency gives a yield of 10^{-8} excited Li atoms per incoming electron at 150°C.

In order to investigate, if different processes are involved in these two temperature regimes, we measured the energy dependence of excited Li atoms at two temperatures: at room temperature, which is in the first regime, where no evaporation of ground-state atoms occurs and at 360°C, where there is negligible limitation for desorption of neutral ground-state atoms by evaporation. For both temperatures the energy dependences exhibit similar shapes, which suggests that there is only one underlying physical process over the whole investigated temperature range. As can be seen in Figure 2 there is an onset at around 60 eV for both temperatures. This 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.[18] In photon stimulated desorption experiments the same dependence for the positive ion yield of Li and F on the photon energy was found.[19,20] Minor structure in the curve above 80 eV is not reproducible and is attributed to sample charging. No enhancement of the yield of excited Li atoms can be correlated with the core-hole levels $F^-(2p)$ at 14.2 eV[21]

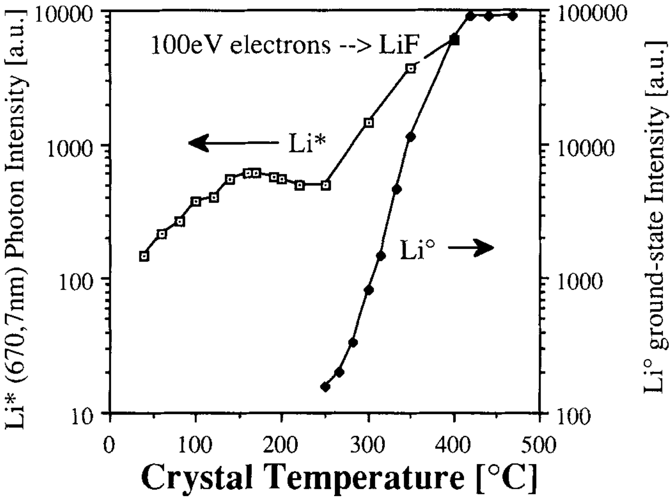

FIGURE 1 The dependence of the Li* (670.7 nm) upon the crystal temperature is compared with the Li^0 yield from Ref. 7, for electron bombardment with 100 eV and 500 eV, respectively.

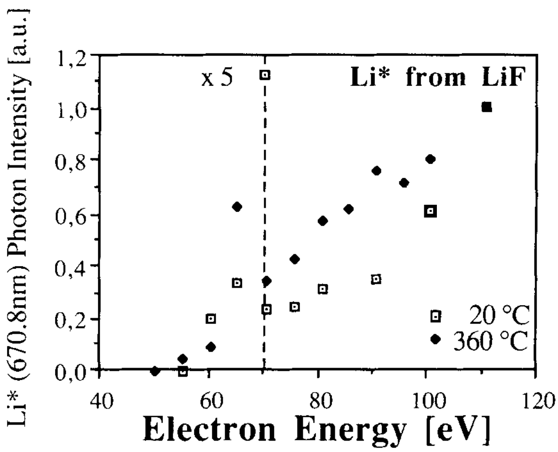

FIGURE 2 The dependence of desorbed Li* from LiF on the electron energy is plotted. Apparently, the onset is observed at around 60 eV. Minor structures at higher electron energies are not reproducable and therefore attributed to sample charging.

and $F^-(2s)$ at 38.2 eV.[18] Additionally, a pronounced peak in the excited Li atom emission under photon irradiation at a photon energy of 61.5 eV was measured,[14,22] suggesting excitation of the core-electron to a discrete level rather than excitation to the continuum of the conduction band. These structures strongly favor a mechanism involving the creation of a core-exciton as initial step for the desorption of excited Li atoms from LiF. According to these first measurements we propose that the primary event is the creation of a core-exciton in an alkali ion by an incoming electron. During the following inter-atomic Auger transition the hole is filled by an electron from the valence band. The alkali ion, which desorbs from the surface, can capture an electron into an excited state. This process will be explained in more detail in the conclusions.

In the temperature range up to 250°C the emission of excited Li atoms is sufficiently explained by this model. Above 250°C there are two possible explanations. Firstly, the alkali metal enrichment on the crystal surface is not a homogeneous layer, but the excess metal atoms aggregate to three-dimensional islands above the melting point of the alkali metal, i.e. 180°C for Li, as seen in previous experiments.[15,23] Only on a clean crystal between these islands emission of particles due to the core-hole excitation mechanism is possible. Therefore, the emission of excited atoms is prohibited in the area covered by these islands. With increasing temperature more and more pure alkali-halide crystal surface is exposed, because of increased evaporation and increased aggregation of Li atoms above the melting point of the alkali metal.[15,23] Thus, the desorption yield of excited atoms is enhanced at higher temperatures. As one impinging electron is sufficient for the desorption of an excited alkali atom, a linear dependence of the yield of excited Li atoms on the current density is expected.

Secondly, the evaporation increases the density of ground-state Li atoms in front of the crystal. These additional atoms can be excited by secondary electrons in the gas phase. The creation of secondary electrons and the evaporation as a consequence of defect generation are not correlated, but both depend on the current density. Therefore, the yield of excited Li atoms should increase proportionally to the square of the current density, at least in the temperature regime where evaporation is not limiting the desorption process. As it is outlined above, the two proposed models can also be distinguished by measuring the yield dependence on the current density. Figure 3 shows the results for two crystal temperatures, at room temperature and at 380°C. In both cases a linear

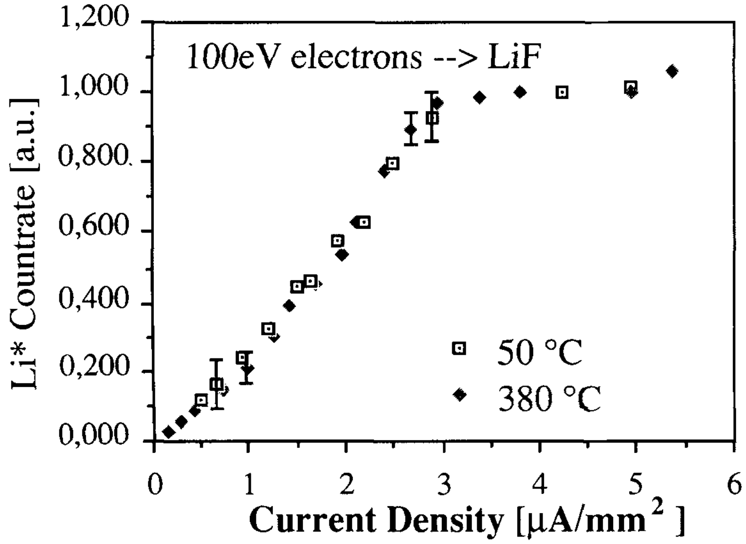

FIGURE 3 The dependence of the Li* yield on the current density of 100 eV electron irradiation is plotted for 50°C and 380°C. Both curves are normalized to one and the actual sizes can be deduced from Figure 1. In the saturation area sample charging influenced the signal and caused a larger uncertainty. The straight lines are meant to guide the eye.

dependence on the current density up to 2.9 $\mu A/mm^2$ has been found and the saturation of the yield of excited Li atoms at higher current densities is the same. Saturation will occur when all available sites for core excitation in the surface region are excited. As the number of these sites per surface area is a property of the crystal and does not change with temperature, the current density value, above which saturation is reached (2.9 $\mu A/mm^2$), remains unchanged for different temperatures. Not only the similarity of the shape but also the linearity of the dependence are in favor of the core-exciton process. The two temperature regimes (below and above 250°C) are represented by the two selected temperatures. This is additional evidence that there is only one mechanism involved for the generation of excited states by ESD in the whole temperature range for our experimental conditions.

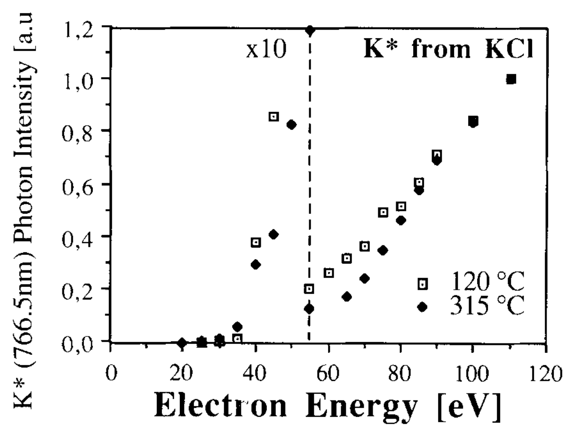

FIGURE 4 The dependence of desorbed K* from KCl on the electron energy is plotted for 120°C and 315°C. The onset is observed at 35 eV.

b) *KCl and KBr*

As the vapor pressure for K is so high in the investigated temperature range,[13] there is always considerable evaporation. Although our measurements were performed at different temperatures all are located in the second regime. For KCl and KBr the energy dependences of the excited K atoms are shown in Figures 4 and 5, respectively. Clearly the onset at 35 eV for both materials can be seen, again correlating with the $K^+(3s)$ core-exciton at 35.8 eV.[24] The K^+ core-exciton limit for $K^+(3p)$ at 11.21 eV seems to have no effect on the yield of excited K atoms. Also no correlation is found with Cl^- core-holes, $Cl^-(3p)$ at 9.3 eV and $Cl^-(3s)$ at 26.0 eV and the Cl^- exciton limits at 7.16 eV and 23.9 eV, respectively.[21] In case of KBr a small influence of sample charging in the range of few eV seems to be the reason for the shift of the lower temperature plot towards higher energies.

For KCl the dependence of the excited alkali atoms on the current density is shown in Figure 6. Equal to Li from LiF (Figure 3) a linear dependence up to a saturation value of 1.9 $\mu A/mm^2$ is found. The formation of three-dimensional islands was also found for KCl and KBr[15,23] to occur above the melting point of the alkali metal.

Finally, it has to be mentioned that all energy dependent measurements were carried out using current densities well below the saturation regime.

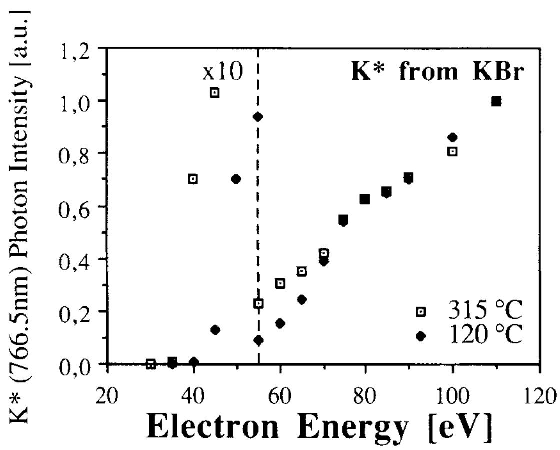

FIGURE 5 The dependence of desorbed K* from KBr on the electron energy is plotted for 120°C and 315°C. The onset is observed at around 35 eV, and shifted to higher energies in the lower temperature plot due to sample charging.

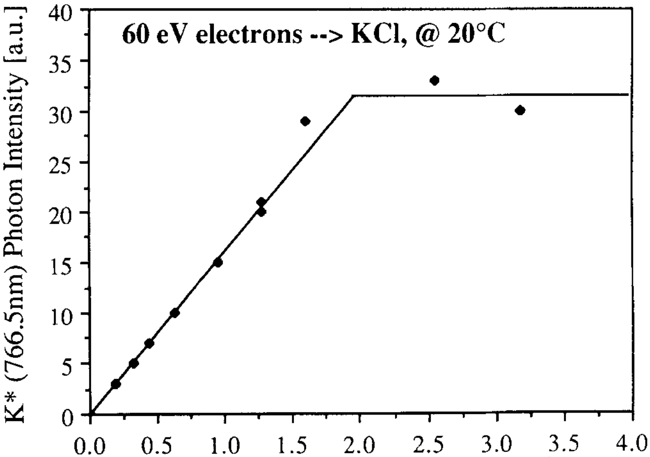

FIGURE 6 The dependence of the K* yield on the current density of 60 eV electron irradiation is plotted for 20°C. In the saturation area sample charging influenced the signal and caused a larger uncertainty. The straight lines are meant to guide the eye.

CONCLUSIONS

Based on our experimental results we propose a generation mechanism for excited alkali atoms, which is also consistent with data from other authors. This mechanism consists of the following steps:

a) Provided that the primary electron has sufficient energy, the incident electron creates a core-exciton on the alkali-ion lattice site.

b) 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,[9,10] as the excess energy is used for the release of valence electrons originally located on the anion. The electron, which was bound to the core-hole, can be (i) released into the conduction band, (ii) trapped in a surface exciton,[23,25] (iii) trapped in a surface state.

c) On the surface the alkali ion captures an available electron, presumably from a location mentioned above, into an excited state or the ground state.

d) Due to repulsive forces[27] the excited alkali atom leaves the surface with an energy, which we expect to be higher than thermal.

e) Decay of the excited atomic state in front of the crystal.

The linear current dependence of the desorption yields we found for excited Li atoms desorbed from LiF and also for excited K desorbed from KCl and KBr (see Figures 3 and 6) is in good agreement with measurements on NaCl and KCl done by Pian *et al.*[7] and Na desorbed from NaCl done by Tolk *et al.*[26] This is in contrast to the quadratic current density dependence of the yield of excited alkali atoms found by Walkup *et al.*[6] and by Postawa *et al.*[5] A possible explanation for this discrepancy is that these authors used much higher electron energies in their measurements, resulting also in a higher penetration depth of the primary electrons. The positively charged halogen resulting from the Auger deexcitation of the core-hole can only lead to the ejection of a particle if it is located in the first or second atomic layer.[27] In the bulk, the lifetime of the positively charged halogen is too small to gather enough kinetic energy to leave its original lattice site or impart kinetic energy to an adjacent cation. The need for a defect enriched surface for positive ion desorption was also suggested by other authors.[27,28] The existence of minority sites either intrinsic or radiation induced has been observed in recent PSD experiments,[29] too.

As shown experimentally[8] and also by theoretical calculations,[27] desorption of ions from LiF under electron bombardment can be explained by a similar mechanism involving a core-hole instead of a core-exciton as initial step of the desorption process. The ejected ions exhibit a non-thermal energy distribution,[8] which is in disagreement with gas phase excitation of desorbed neutral ground-state atoms. However, Walkup *et al.*[6,29] found thermal energy distributions of desorbed excited alkali atoms from LiF and NaCl. We believe that these measurements were done under experimental conditions, where gas phase excitation due to the primary electron beam is the principle contributor to the yield of excited atoms. Furthermore, for LiF as well as KCl and KBr we did not observe any pronounced changes in the secondary electron yields for electron energies near the thresholds for excited atoms. Thus, the only way to explain the observed thresholds by means of excitation in the gas phase would be to assume a similar increase of the ground-state yield at these energies. However, according to the valence excitation mechanism for the desorption for neutral ground-state atoms thresholds are expected at approximately 10 eV.[1-4] The similarity between the optical emission spectrum under electron irradiation of alkali-halide crystals at elevated temperatures with an electron impact induced spectrum in alkali vapour was used to emphasize excitations in the gas phase in front of the crystal by primary[11] or secondary electrons[6] in this temperature regime. But, according to our model the excited levels of an alkali atom are populated in a similar way. Therefore, the similarities with an electron impact spectrum are not surprising and the argument mentioned above[6,11] is not conclusive. The distinction in two temperature regimes is not necessary any more, as we have one process in the whole temperature range.

In addition, gas phase excitation processes will always take place, but will give a significant contribution to the yield of excited states only at experimental conditions with a high desorption rate of neutral ground-state atoms (high temperature and high electron current densities).

Previous measurements have been done under different experimental conditions, e.g. at current densities which are located in the saturation regime seen in Figure 3 and at higher primary electron energies.[6,7] Additionally, these measurements were performed at high crystal temperatures to reduce sample charging,[6,7] where evaporation is the dominating process. Thus the conclusions drawn from these measurements are limited to the range of these investigations. We do not rule out gas-phase excitation in principle, but argue that for our experimental conditions it is a minor if not negligible contribution to the flux of excited Li atoms desorbed from LiF under electron bombardment.

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