Different Processes for Desorption of Ground- and Excited-State Atoms Under Electron Bombardment of Alkali-Halides

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Abstract. Single crystal surfaces of LiF were bombarded with 5 to 500eV electrons at different crystal temperatures (300-800K). The temperature dependence as well as the energy dependence of ground- and excited-state alkali atoms were studied. These measurements strongly suggest different mechanisms for the desorption of ground- and excited-state alkali atoms. An excitation of a valence electron into the conduction band and subsequent decay of the formed excited state into an F-H pair will finally lead to the desorption of a ground-state atom, which is well established in the literature. The creation of a core-hole on an alkali lattice-site close to the surface followed by an inter-atomic Auger decay of that core-hole leads to emission of excited alkali atoms and ions. The measurement of the threshold energies for ground- and excited-state alkali atom desorption is a major piece of evidence. The threshold energies are found at 13 and 60eV for the desorption of ground- and excited-state atoms, respectively. This agrees very well with the band gap of 14.2eV and the core-hole excitation of $Li^+(1s \to 2s)$ at 60.8eV and for $Li^+(1s \to 2p)$ at 61.9eVand is clear evidence for a surface intrinsic process for the generation of excited alkali atoms and will be discussed together with the underlying experimental results.

1. Introduction

The interaction of electrons and photons with alkali-halides remains a field of strong current interest. The concept for desorption of neutral *ground-state* atoms is generally agreed on [1-4], discussion being confined to selected topics [e.g. 5]. The situation is worse in the case of the desorption of *excited* atoms and ions from alkali-halides. Conflicting models and experimental results are currently debated in literature [6-9]. In the following we will refer to ground-state atoms as Li^0 and to excited atoms as Li^*. As the Li^0 atoms are the main fraction of the desorbed particles, we will review their generation mechanism briefly.

The mechanism for ground-state desorption is based on the generation of a self-trapped exciton on a halogen lattice site [1-4]. This excited state can decay by inducing a replacement collision sequence along the chain of halogen atoms in a <110> direction, which separates the H-center from the F-center by some lattice constants. The process can lead either to prompt emission of a halogen atom if the range of the replacement collision sequence extends beyond the distance to the surface, or to delayed emission due to diffusion of H-centers to the surface. As these defect processes

Springer Series in Surface Sciences, Vol. 19
Desorption Induced by Electronic Transitions, DIET IV
Editors: G. Betz · P. Varga

only take place in the halogen sublattice, an alkali metal enrichment results in the near surface layer when the remaining F-centers diffuse to the surface [10]. 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 inhibits further desorption.

Basically, there have been two explanations for desorption of excited or ionized atoms from alkali-halides: Firstly, gas-phase excitation of desorbed neutral ground-state atoms by the primary electron beam or by secondary electrons. This accounts for some experimental results [7,8]. Secondly, emission of excited atoms due to a surface intrinsic process via inelastic energy transfer, assumed to start with the creation of an alkali core-hole/exciton as the initial step. Experimental data which can be interpreted by this mechanism have been found for excited atoms [6,9] and ions [11]. It is the aim of this paper to solve this controversy by presenting new experimental data for the desorption of ground- and excited-state atoms.

2. Experimental

LiF single crystal surfaces have been bombarded with electrons of 5eV to 500eV energy and with currents up to 30μA. The electron beam axis was incident on the crystal at 45°. The bombarded area had dimensions of approximately 2 by 4mm. Uncertainties in the electron energy are due to the work-function of the cathode and the work-function of the crystal [12]. 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. Ground-state atoms have been measured with a quadrupol mass analyzer also viewing the crystal along the surface normal.

The UHV-system maintained a base pressure of less than $3x10^{-10}$ torr during the measurements. All investigated crystals have been cleaved in air and cleaned in the UHV-system by baking at 400°C overnight. The sample temperature was varied between 20°C and 500°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.

3. Experimental Results

As already discussed in the introduction, the evaporation rate of the alkali metal plays an important role in the process of alkali atom desorption. We distinguish three ranges in the temperature dependence of the desorption yield of Li ground-state atoms from LiF (Fig. 1): i) Due to a negligible evaporation rate at low crystal temperatures no desorption of alkali atoms occurs, and alkali metal accumulates on the crystal surface [10]. ii) The desorption rate increases, limited by the exponentially rising evaporation rate. An increase in the electron flux will not lead to an increase of the desorption rate. iii) A plateau in the temperature dependence of the desorption

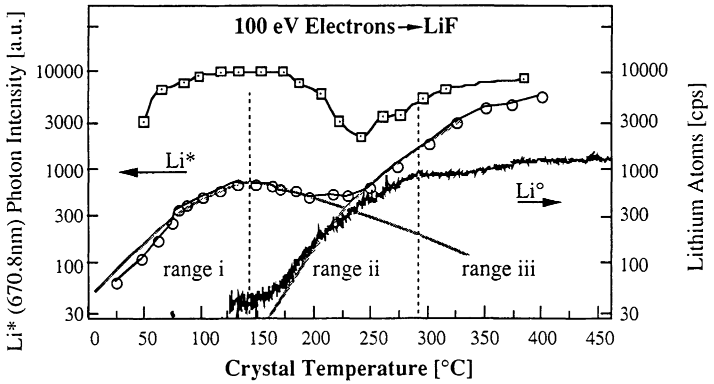

Figure 1: The dependence of the Li^{0} signal upon the crystal temperature during 100eV electron bombardment of LiF. Three temperature ranges are indicated (see text). The open symbols show the Li* yield for 100eV and 400eV, circular and rectangular symbols, respectively. Shaded lines define the domains where surface intrinsic and gas-phase excitation processes are effective.

yield is reached, if defect production limits desorption rather than evaporation. An increase of the electron flux or energy will lead to an increase in yield, but at the same time will shift range iii towards higher temperatures [5].

Comparing the temperature dependence of ground- and excited-state atoms, we note a large difference in the observed behavior. At room temperature (range i), where we have no Li^{0} desorption, there is considerable Li* desorption. This excludes a process involving gas-phase excitation of desorbed atoms in this temperature range. Furthermore, the yield of ground-state atoms increases more than two orders of magnitude, which compares to one order of magnitude for the excited-states in the same temperature range. Thus no proportionality between these two species can be extracted and we have to assume different processes of generation of either state. The yield of Li* atoms at 150°C is a factor of 10^{-3} less than the yield of Li^{0} atoms at 300°C.

For both Li^{0} and Li* desorption we observe well defined and reproducible thresholds in the energy dependence of the yield. For the excited atoms we find the onset for desorption at approximately 60eV. We performed this measurement for two different crystal temperatures: at room temperature (range i), where there is only desorption of excited atoms, and at 360°C, where we are not limited by the evaporation rate (range iii). For both temperatures we find the same energy threshold for the excited-states, as can be seen in Fig. 2a. The threshold correlates with the Li^{+} core-exciton levels of Li^{+}(1s→2s) at 60.8eV and Li^{+}(1s→2p) at 61.9eV in LiF [13]. The valence-hole level F^{-}(2p) at 14.2eV [14] (corresponding to the bandgap) or the core-hole level F^{-}(2s) at 38.2eV [13] lies far below the observed threshold.It is worthwhile to note that we do not observe any pronounced changes in the secondary electron yield for electron energies near the Li* threshold, thus the threshold cannot result from gas-phase excitation.

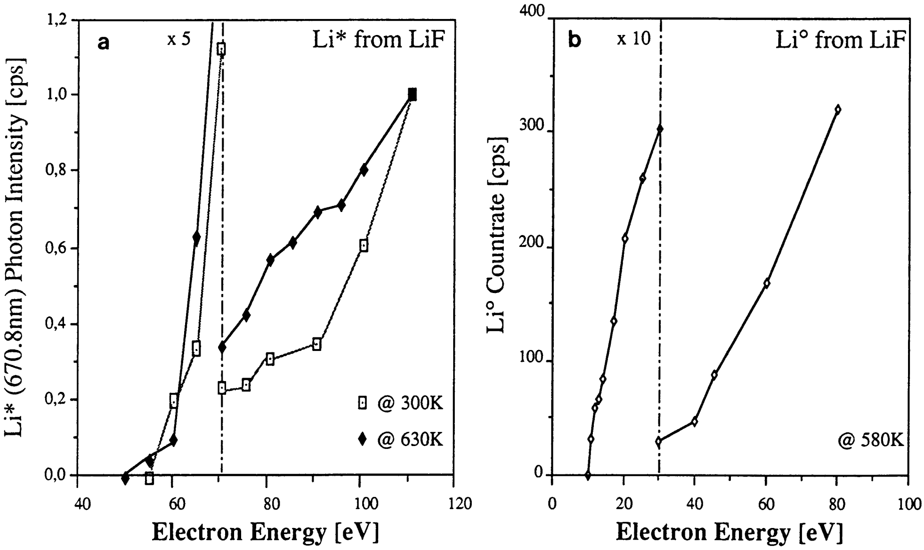

Figure 2: a) The energy threshold for Li* desorption is found at 60eV, independent of crystal temperature. b)The energy threshold for Li^0 desorption lies around 13eV. The measurement was performed at 580K (range iii) to obtain highest signal/noise ratio, but is valid for all temperatures.

For ground-state Li atoms we find an onset of the Li^0 desorption around 13eV, which is shown in Fig. 2b. This value corresponds to the energy of the valence exciton of 12.6eV [15] near the band gap energy of 14.2eV [14], thus confirming that the first step in the desorption process of ground-state alkali atoms is the excitation of a valence electron to a bound state (electron-hole pair) or into the conduction band. The total amount of Li* atoms is far less than that of Li^0 atoms, because the Li atoms originally excited and de-exciting on their way to the mass spectrometer do not add noticeably to the yield of ground-state atoms above the threshold of Li* at 60eV. However, in recent PSD measurements a small peak at 60eV in the energy dependence of Li ground-state atoms has been observed [16].

The dependence of the Li* yield on the current density helps to distinguish a surface intrinsic from a secondary excitation process [7,8]. A linear dependence of the Li* yield on the current density is expected if excitation and ejection of the Li atom is caused by the same incoming electron. A quadratic dependence of the Li* yield on the current density is expected in case of excitation in the gas-phase, because the excitation by primary or secondary electrons is not correlated with the desorption of alkali atoms as a consequence of defect generation. Fig. 3 shows our results of the dependence of the Li* yield on the current density again for two different temperatures: At room temperature (range i) we find a linear relationship, which is not surprising since in the absence of desorbing ground-state atoms only a direct process can be responsible. At 380°C (range iii), we start out with a linear dependence of the Li* yield upon the current density, which changes to quadratic behavior for high current densities.

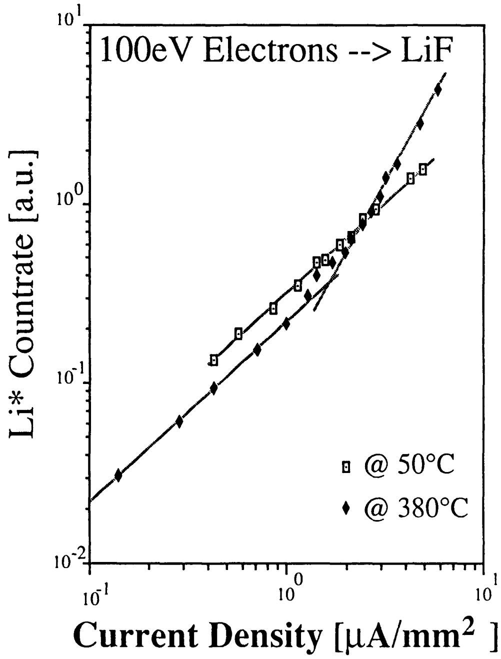

Figure 3: The dependence of the Li* yield on the current density of 100eV electron irradiation is plotted for 50°C and 380°C. Both curves are normalized, the absolute size to each other can be deduced from figure 1. The straight lines have slopes of 1 and 2 according to a linear and a quadratic dependence upon the current density, respectively.

4. Discussion

We propose a new, surface intrinsic mechanism for the generation of excited alkali atoms using concepts introduced by Tolk et al. [17]. The necessity for the new model is based on three major arguments: i) The thresholds for Li^0 and Li^* desorption differ strongly and the one for excited-states coincides well with a core-excitation of the Li ion in the crystal. ii) At room temperature no Li^0 desorption is observed, but Li^* is found in copious quantities. iii) We find a linear and a quadratic regime in the Li^* yield as a function of current density. This new mechanism consists of the following steps:

a) Provided that the primary electron has sufficient energy, the incident electron can create 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 [12,18], 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 [19,20] iii) trapped in a surface state.

c) Coulomb repulsion leads to emission of alkali ions, which is observed experimentally [9,11] and predicted by theoretical calculations [21,22].

d) While emerging from the crystal the alkali ion may capture an electron, which is localized on a nearby surface defect [19,20] or surface state, into an excited state or the ground-state. Even in the absence of Coulomb repulsion the neutral atom gains substantial kinetic energy from the reneutralization event. The sudden increase of the radius of the reneutralized ion causes a simultaneous rise of the repulsive energy. This process is referred to as Pauli shock [21].

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

Besides the surface intrinsic process also gas-phase excitation contributes to the yield of Li* atoms. In the following we will define the domains where each process is effective.

The linear current dependence of the desorption yields we found for excited Li atoms desorbed from LiF is in good agreement with some previous measurements [6,8,23] but is contradicted by others [7,8], who found a quadratic current density dependence of the yield of excited alkali atoms. The explanation for this discrepancy is that the latter authors used higher current densities and higher temperatures in their experiments. As can be seen in Fig. 3, gas-phase excitation occurs only under these experimental conditions. This is due to a high excitation probability caused by high densities of electrons and atoms in the interaction volume. Higher electron energies, which were used by these authors, result in higher desorption rates, so that the range of gas-phase excitation is reached even for current densities lower than ours. For other alkali-halides with higher alkali vapor pressure, gas-phase excitation will already occur for lower temperatures or lower current densities.

The two excitation processes can be distinguished in the Li* temperature dependence, too (Fig. 1). The surface intrinsic process is dominant in a temperature range from room temperature to 250°C, but is present also at higher temperatures as can been seen in the energy threshold of Li* at 360°C (Fig. 2a) and in the current dependence of the Li* yield (fig. 3). The increase of the Li* yield with temperature in the domain of the surface intrinsic process can be explained by decrease of the alkali metal overlayer [10] and by a higher mobility of the Li atoms on the crystal surface as the melting point of Li metal is reached [19]. This is supported by recent PSD measurements [16]. As the metal overlayer grows with electron bombardment, we observe a decrease of Li* yield with time, until an equilibrium is reached after several minutes. Beginning Li^0 desorption will decrease the amount of adatoms and eventually inhibit the surface intrinsic process. It also enables gas-phase excitation, which we believe to be responsible for the Li* yield increase after the minimum at 250°C.

The similarity between the optical emission spectrum under electron irradiation of alkali-halide crystals at elevated temperatures with an electron impact induced spectrum in an alkali vapour was used to emphasize excitations in the gas-phase in front of the crystal by primary [24] or secondary electrons [8] in this temperature range. The similarities with an electron impact spectrum are not surprising and we agree with these authors that they observe gas-phase excitation in their experiments [7,8,24].

As far as we know, there are three theoretical calculations of the possibility of ion and neutral atom ejection induced by core-electron excitation: A molecular dynamics calculation by Walkup et al. [25], molecular dynamics calculation including all interaction potentials by Elango et al. [21] and a quantum chemical calculation by Itoh et al. [22]. The two latter calculations agree with our model, whereas the first favors gas-phase excitation.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 [21,22]. 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 adatom position of an alkali atom on top of the halogen is a favorable site for desorption [21,25].

In photon-stimulated desorption experiments (PSD), a pronounced peak in the excited Li atom emission at a photon energy of 61.5eV was measured [16], suggesting excitation of a Li core-electron to a discrete level rather than excitation to the continuum of the conduction band.

5. Conclusions

We present new and conclusive experimental results to distinguish the desorption processes for ground- and excited-state atoms. The energy threshold for ground-state atoms supports the current understanding of ground-state alkali desorption from alkali-halides [1-4]. The energy threshold for excited-state atoms, found at the core-hole energy of the alkali atom, is evidence for our proposed mechanism for the desorption of excited states, which is in good agreement with theoretical calculations [21,22]. This work should end the long lasting discussion about the origin of the excited atom desorption of alkali-halides under electron and photon bombardment [6-9].

6. Acknowledgments

The authors would like to gratefully acknowledge financial support by the Österreichische Fonds zur Förderung der wissenschaftlichen Forschung (project Nrs. 5833, 5577).

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