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COLLISIONAL AND ELECTRONIC PROCESSES UNDER ION, ELECTRON AND PHOTON BOMBARDMENT OF ALKALI AND ALKALINE-EARTH HALIDES

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The interaction of energetic ions or electrons with alkali halides and alkaline-earth halides results in elastic and inelastic energy transfer to the near surface region. The emission of secondary sputtered and desorbed particles has been studied to identify these processes. In particular, we have compared the emission of neutral ground state and excited alkali and alkaline-earth atoms from NaCl, LiF and CaF_2. The intensity of the sputtered and desorbed particles and their velocity distributions have been measured as a function of the target temperature between room temperature and 400 ° C. For NaCl under ion bombardment neutral ground state Na atoms desorb predominantly (*ion-beam-induced*) thermally, even at room temperature, while Ca atoms from CaF_2 desorb mainly thermally above 300 ° C and purely collisional below 250 ° C. For 400 eV electron bombardment desorption of thermal neutral ground state atoms is observed whenever a thermal contribution is present under ion bombardment. Excited Na and Ca atoms with energies in the eV range have been observed for ion bombardment. For electron bombardment excited Na has been identified with thermal velocities at all target temperatures. Contrary, excited Ca was not found even at target temperatures where substantial ground state Ca is desorbed. For NaCl as well as CaF_2 and electron as well as ion bombardment inelastic processes play an important role for particle ejection above a certain target temperature.

1. Introduction

Ion bombardment of solids has been investigated to a large extent for a long time. Various aspects of the collision process and resulting secondary events have been studied due to the interesting associated physical questions and also because of the many practical applications. The emission of secondary particles due to ion bombardment is one important and much studied aspects. Most of the experimental results and the best theoretical models are available for metal targets and ion beams with medium energies. Even this relatively simple case (collisional sputtering), however, is far from being fully understood. The emission of excited atoms and of charged particles can serve as an illustrative example [1,2]. Inelastic processes are of minor importance with metal targets [3]. However, electronic processes can be very efficient with insulators [3].

In this paper we will describe experiments on ionic materials. The desorption of neutral ground state and excited atoms is one important feature by which electronic excitations in the solid manifest themselves [4,5]. Therefore, investigations of desorbed particles can yield information about electronic excitations due to particle irradiation, or, if we put in the other way round, desorption phenomena of ionic materials can be explained by electronic excitations. In ionic materials (alkali halides and alkali earth halides will be treated as prototypes within the context of this paper) the formation of *excitons* by photon or electrons, but also by ions is well known [5,6]. The exciton state is the initial step in the formation of a self-trapped exciton in the crystal leading to point defects, which are believed to be responsible for desorption.

The measurements presented here can be classified in four different groups, each emphasizing a different aspect of the desorption process. *Velocity distributions of desorbed particles* can be used to distinguish between elastic and inelastic processes. In general, particles desorbed via inelastic processes have a velocity distribution clearly different from the characteristic velocity distribution of elastically sputtered particles. *The yield of ground state and excited alkali atoms as a function of the target temperature* for alkali and alkali earth halides with different bulk composition and bulk geometry provides information about the general features of the desorption process initiated by electronic excitations. The different phenomena observed have to be distinguished in those which can be attributed to the physical properties of the bulk components and those which are believed to be general features of ionic materials. *Transient effects of the desorption yields.* Desorption of particles can continue after the irradiation beam is switched off for a considerable amount of time, or even made possible only after irradiation by increasing the target temperature. *Measurements of the dependence of the desorption yield on the energy of the irradiating photon beam* can give us an indication of core hole excitations, which also leads to desorption.

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2. Experimental

A duoplasmatron ion source was used for ion bombardment. Mass separated argon ion beam currents were typically 6 μA cm^{-2} and ion energies of 15 keV were used. A low energy electron gun was operated at 400 eV with electron currents of 200 μA cm^{-1}. The pressure in the target chamber was in the 10^{-9} mbar region.

The photon experiments were performed on the Grasshopper Mark V beam line of the Synchrotron Radiation Center facility of the University of Wisconsin. The Mark V monochromator has a low energy limit of 32 eV and was used in the region from this limit up to 100 eV. The typical electron energy of the storage ring was 800 MeV, the beam current dropped from a starting value of approximately 200 mA down to about 40 mA during one measurement cycle of 6 h. In the vacuum chamber attached to the beam line a base pressure in the low 10^{-10} mbar region was easily obtained so that even at low desorption rates the surface of the sample remained clean over the entire run.

Neutral ground state atoms were measured by Laser Induced Fluorescence (LIF), their velocity distributions were obtained by Doppler Shift Laser Fluorescence Spectroscopy (DSLFS). Both methods have been described in detail previously [7–9]. Excited atoms were detected via Bombardment Induced Light Emission (BLE) and their velocity distribution could be obtained by measuring the Doppler Broadening of the fluorescence line [12,16].

3. Experimental results

3.1. Velocity distributions

We studied the temperature dependence of the velocity distribution of alkali atoms in the electronic ground state as well as in excited states for several alkali halides and alkali earth halides for electron, photon and ion bombardment. The most complete set of data has so far been obtained for NaCl, CaF_2 and LiF due to the fact that the Na, Ca and Li could be measured by LIF.

The velocity distribution of desorbed Na ground state atoms was measured for electron and ion bombardment of a NaCl single crystal. The target was held at room temperature for these measurements. Within the accuracy of our measurements both velocity distributions were identical and could be fitted with a Maxwell–Boltzmann distribution at the target temperature. This result is astonishing as the presence of particles with higher energies is expected for ion bombardment where elastic collisional sputtering should contribute to te emission of neutral Na atoms in the electronic ground state. The corresponding velocity distribution is well known [10] and should peak at about 1 eV. On the other hand, it should be a good assumption to neglect collisional sputtering in the case of electron bombardment. From these results and considerations we can conclude that inelastic, electronic excitations are the dominant desorption mechanism in the case of a NaCl target even for ion bombardment. For NaCl this has been verified for target temperatures ranging from room temperature up to 500 ° C.

The velocity distribution of sputtered excited Na atoms ($3p^2P^0$ level), however, clearly exhibit a different velocity distribution for electron and ion bombardment. This has been obtained from measuring the Doppler profile of the emission line ($3p^2P^0$–$3s^2S$ resonance transition, 588.9 nm). These Doppler profiles can be fitted with theoretical distributions and we obtain a thermal velocity distribution for the electron case and an velocity distribution with a maximum at 2 eV for the ion case. This energy maximum is typical for excited sputtered particles whenever elastic collision sequences cause particle emission [1,3,15,16].

Results, differing substantially at first sight from those just described, have been obtained for CaF_2 (single crystals.) At room temperature no emission of excited or ground state Ca is observed for electron bombardment, indicating the absence of the relevant inelastic desorption mechanism in this temperature regime. This, indeed, is also verified by the velocity distribution of neutral Ca ground state atoms desorbed by ion bombardment. The corresponding velocity distribution shown in fig. 1 can be fitted with a Thompson distribution [10] typical for elastic sputtering. Moreover, the obtained surface binding energy (1.4 eV) (*the maximum of the Thompson distribution is a measure of the surface binding energy*) is in good agreement with previously reported values for Ca atoms [11] sputtered from metallic Ca. We have also determined the velocity distribution of excited Ca atoms desorbed from CaF_2 by ions via the Doppler broadening of the resonance line and found a maximum of 6.5 eV which, again, is the same value we have previously found for metastable Ca sputtered from metallic Ca [1].

However, above 300 ° C target temperature and ion bombardment, the velocity distribution of neutral Ca ground state atoms shows an increasing thermal contribution, which dominates the spectrum above 350 ° C (fig. 1). In this temperature regime desorption of neutral Ca ground state atoms has also been observed under electron bombardment with a thermal velocity distribution. Contrary to the case of NaCl, we have not ob-

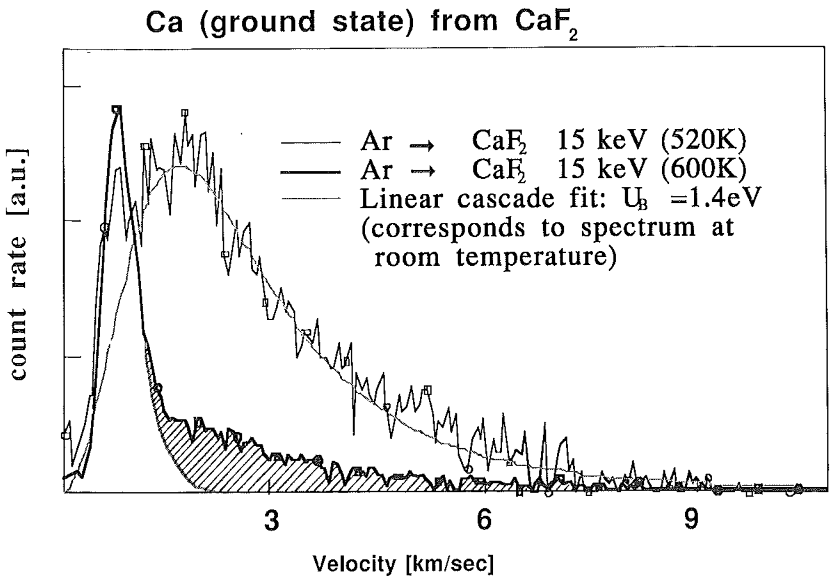

Fig. 1. Normalized velocity spectra of ground-state Ca atoms under 15 keV Ar$^+$ bombardment from CaF$_2$. At 520 K the distribution is mainly collisional and can be fitted by the linear cascade theory assuming a surface binding energy of 1.4 eV. At 600 K the spectrum is already mainly thermal and the cascade contribution is only visible in the tail of the distribution (shaded area). For even higher temperatures the cascade contribution is no longer visible due to the dominating thermal peak. The thermal part of the spectrum always corresponds to a Maxwell–Boltzmann distribution at target temperature.

served desorbed excited Ca atoms under electron bombardment in the temperature regime up to 450 ° C.

The velocity distribution of photon desorbed alkali atoms was measured for LiF targets. In good agreement with all the other cases where electronic excitations are relevant, the energy distributions were found to be thermal.

3.2. Temperature dependence of desorption yields

The target temperature is an important physical parameter which allows us to control the effectiveness of electronically initiated desorption processes. This is easily understood for two reasons: (a) The important final step in the desorption process of neutral alkali atoms is their thermal desorption from the surface. In this case the target temperature controls the vapor pressure of the alkali atoms on the surface. (b) The migration of point defects created in the near surface region is another important step in the desorption process and is temperature dependent. For these reasons it is important to study the desorption yields as a function of the target temperature.

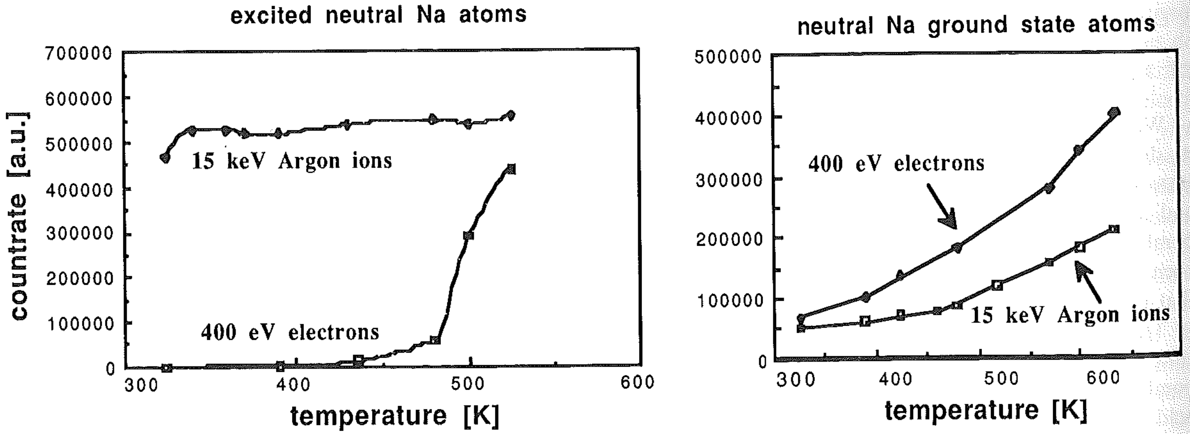

Fig. 2. Temperature dependence of Na ground- and excited-state (Na I, 588,9 nm) atom yields under 15 keV Ar$^+$ or 400 eV electron bombardment of NaCl measured by LIF or BLE, respectively.

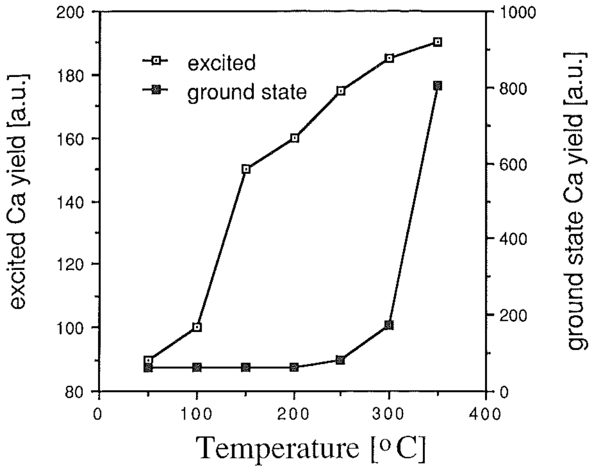

Fig. 3. Temperature dependence of the Ca ground- and excited-state (Ca I, 426 nm) yield under 15 keV Ar$^+$ bombardment of CaF$_2$ measured by LIF or BLE, respectively.

In fig. 2 the yield-temperature function of the Na ground state and excited state atoms is shown for argon ion and electron bombardment of NaCl. The yield of ground state atoms increases with target temperature, both for ion and electron bombardment. The yield of excited Na atoms under electron bombardment sharply increases above 180 ° C while the yield under ion bombardment essentially is constant in the room temperature to 300 ° C regime.

Also, the corresponding Ca yields from CaF$_2$ as a function of the target temperature were measured. Electron bombardment of CaF$_2$ results in desorption of neutral Ca atoms only above 250 ° C and then only neutral Ca ground state atoms are observed. For ion bombardment (fig. 3) neutral Ca ground state desorption also starts to increase dramatically in this temperature region, due to a strong ion beam induced thermal contribution (see also fig. 1). Excited Ca under ion bombardment showed a steady but much weaker increase from room temperature up to 400 ° C. The absence of excited Ca desorption for electron bombardment in a temperature regime where neutral ground state Ca is desorbed by electrons has consequences for the explanation of the excitation mechanism.

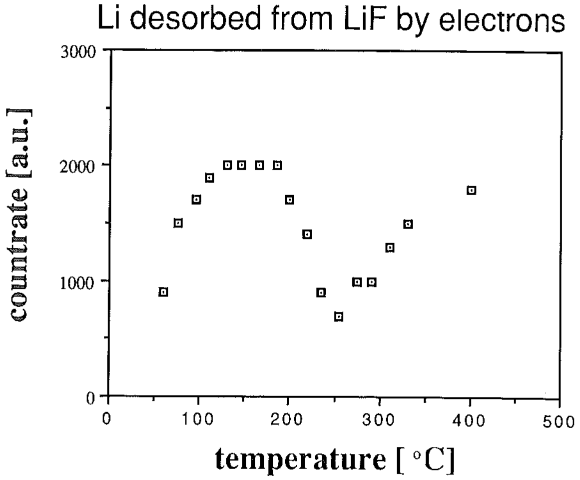

Fig. 4. Temperature dependence of the Li excited state (Li I, 670,7 nm) yield under 400 eV electron bombardment of LiF measured by BLE.

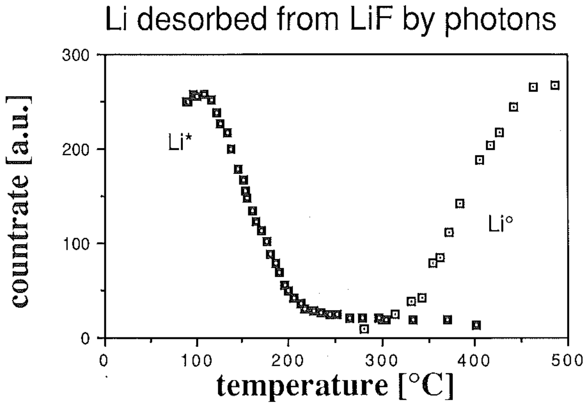

Fig. 5. Temperature dependence of the Li ground- and excited-state (Li I, 670.7 nm) yield under synchrotron photon bombardment (white synchrotron light) of LiF measured by LIF or BLE, respectively.

In fig. 4 and fig. 5 we present the temperature dependent yields for electron and photon induced desorption of Li from LiF. For electron bombardment the yield of excited Li exhibits a peculiar minimum around 200 ° C. For photon irradiation (white synchrotron light) the yield of excited Li drops to zero in this temperature range and the yield of ground state Li starts to increase.

3.3. Transient effects

When CaF$_2$ is bombarded with ions or electrons at target temperatures above 300 ° C where desorption induced by electronic transitions is observed and the bombarding beam is switched off, the desorption yield of ground state Ca decreases within less than 0.1 s to a value approximately 30% of the original value. Within the next several minutes a further decrease is observed until the value of desorption due to regular thermal evaporation is reached (fig. 6).

A similar effect is observed for photon desorption of Li from LiF. Fig. 7 shows the neutral Li ground state yield for photon irradiation at a temperature where a moderate Li signal is observed (see fig. 5). Then the photon beam is turned off and the yield nearly disappears. When the target is heated above 400 ° C (where as shown in fig. 5 a high Li yield is observed), Li desorption starts again and lasts for several minutes until all the stored energy has been released.

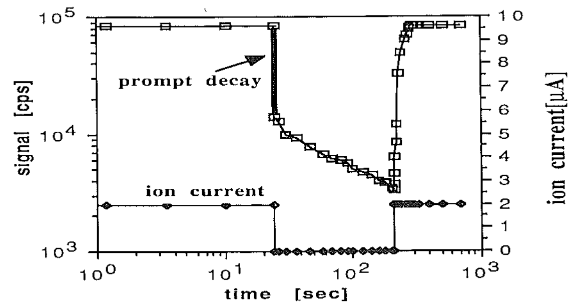

Fig. 6. Time dependence of the Ca ground-state signal from a CaF2 target at 600 K if ion bombardment is interrupted. The fully part of the curve, labelled "prompt decay", corresponds to a signal decrease within less than 0.1 s.

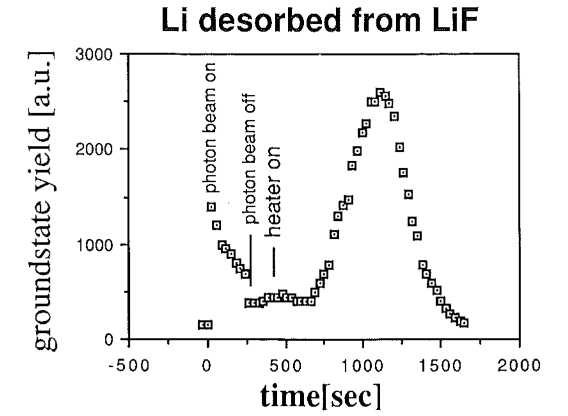

Fig. 7. A LiF single crystal target is bombarded with synchrotron radiation at a target temperature of approximately 300 ° C (negative times in the figure). At time zero the photon beam is turned off and after some time the target is heated above 400 ° C. The yield of desorbed ground state Li is monitored by LIF.

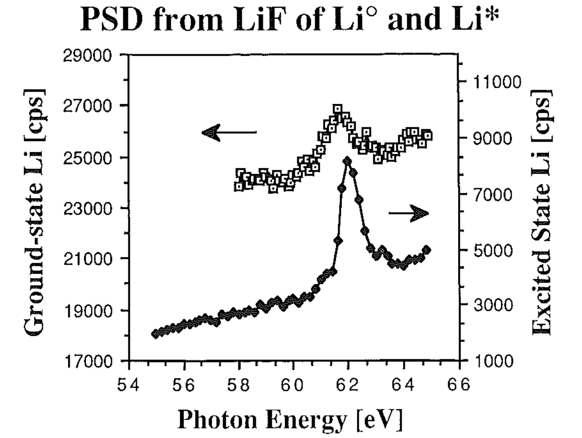

Fig. 8. Dependence of the ground- and excited-Li yield on the energy of the photon beam.

3.4. Energy dependence of the desorption yield

The photon desorption yield of ground state and excited Li has been measured as a function of the energy of the irradiating photon beam. Both, excited and ground state atoms show an enhanced desorption yield around 62 eV. But, while the enhancement of excited desorbed atoms is very pronounced, for ground state atoms only a few percent enhancement is observed. Furthermore, the maximum is shifted 0.5 eV to lower energies, as can be seen in fig. 8.

4. Discussion

Defect formation initiated by the creation of self-trapped excitons is believed to be responsible for the desorption in alkali halides and alkaline-earth halides [5,6]. The creation of these excitons can be achieved by ions, electrons, synchrotron photons and in some cases even by UV-laser photons [12–14]. In the literature two types of excitons are distinguished: valence excitons and core–hole excitons [5]. The desorption of neutral atoms is widely believed to be initiated by valence excitons. The steps leading to the ejection of particles following the excitation have been discussed by several authors [4,5,6] and seem to be a good basis also for the experimental results presented in this paper. The resonant enhancement of neutral ground state Li around 61.5 eV, however, indicates that also core excitations contribute to some extent to the desorption mechanism.

The desorption of excited atoms (and also of ions) has been attributed by Itoh [5] to core excitations. He proposed a mechanism for the desorption of excited Na from NaCl in which a Cl^+ is created in the near surface region by core-hole excitation. This Cl^+ is neighbored by Na^+ ions, a configuration which is highly non adiabatic and, therefore, results in ejection of Na ions which may capture an electron close to the surface into an excited state. The crucial point for this model, however, is that the velocity of the desorbed excited alkali atoms must be higher than for thermal particles. This velocity distribution also results from a similar model proposed by Walkup et al. [17]. In [5] it is argued that such higher velocities have been observed by Haglund et al. [4], but all the data we have obtained for electron beam desorbed excited alkali atoms (Na^* from NaCl and Ca^* from CaF_2) give thermal velocity distributions. For Na^* the same result has also been obtained by Walkup et al. [15] using a different method.

Non-thermal velocity distributions for Na^* from NaCl and Ca^* from CaF_2, however, were obtained for ion bombardment. The shape and the energy range of the measured distributions agrees very well with the energy distribution reported for excited atoms from metal targets. The interpretation of the spectra (see fig. 1) in the light of elastic collision cascades, therefore, seems to be reasonable. On the other hand, we should remember the fact, that desorption of neutral ground state atoms is dominated by inelastic processes, even for ion bombardment, provided the target temperature is high enough to allow sufficient evaporation of the excess alkali metal (for Na already at room temperature, for Ca above 250 ° C). If the target temperature is lower than this critical temperature, electronic desorption will stop shortly after the irradiation is started, because a metallic overlayer will develop, preventing further electronic desorption. This overlayer, however, can be sputtered by ion bombardment, as we have shown for CaF_2. For NaCl we believe that the same situation can be achieved, if the target temperature would be sufficiently low to prevent Na evaporation. If one still attributes the emission of excited alkali atoms for ion bombardment in the regime where electronic processes dominate elastic collision cascades an efficiency of excited state production by collision cascade by two to three orders of magnitudes higher than the efficiency by inelastic excitations follows, which is the case for electron or photon bombardment. In addition, we would like to suggest an alternative explanation based on the model by Itoh [5]. The energy distribution of excited alkali atoms as shown in fig. 1 would follow from Itoh's model straightforward. But it has to be modified in so far, as the Cl^+ needed for the Ca^* ejection cannot develop with high efficiency for electron bombardment because of the high concentration of negative charges in the near surface region, but can be produced for positive ion bombardment.

The existence of desorbed excited atoms for electron or photon bombardment can be caused by an intrinsic excitation process [4,18] or could be attributed to excitation of desorbed neutral ground state atoms by secondary electrons or the primary electron (photon) beam. The results for photon desorbed Li from LiF clearly favours an intrinsic excitation, as can be clearly seen from fig. 5. At temperatures where excited Li is desorbed, no ground state Li atoms are desorbed. At higher temperatures a high ground state desorption yield is observed, but no excited Li atoms. Furthermore, the yield of secondary electrons also increases sharply in this temperature range. Electron bombardment, shown in fig. 4, exhibits a minimum in the excited desorption yield around 250 ° C. The increase above 250 ° C, not found for photon desorption, might be attributed to excitation by the primary electron beam.

The energy dependence shown in fig. 8 is an indication, that excited Li and ground state Li production originate to a large extent from different excitations, i.e. core–hole excitations are more important for Li^* production than for ground state production. The shift in energy by about half an eV can be interpreted by a sort of chemical shift and indicating that the excitations occur at different lattice sites.

Initial studies of transient effects have shown that at least two different lifetimes of the excitations involved can be observed. Lifetimes of the V_k centers are believed to be in the order of 10^{-3} to 10^{-5} s [6] and, indeed for NaCl the observed desorption can be correlated to the irradiating beam in this time scale. However, for CaF_2 and LiF desorption has been observed after turning off the irradiating beam for times much longer than the V_K center lifetime (see figs. 8 and 9). In addition, processes with at least two different time constants can be identified for CaF_2 representing themselves by a prompt signal decrease and a slow one. Furthermore, we have found that electron bombardment generally provokes longer time constants which may be due to a deeper penetration depth of the electrons.

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