Simultaneous laser-induced fluorescence and quadrupole-mass-spectroscopy studies of electron-stimulated desorption of ground-state lithium atoms from lithium fluoride crystals

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Under certain experimental circumstances, a number of authors have observed an unexpected increase in the yield of desorbed lithium atoms (a "delayed maximum") following the cessation of electron bombardment. The origin of this delayed maximum remains uncertain and continues to be a subject of active study. In all previous experiments that monitored delayed emission, a quadrupole mass spectrometer (QMS), which is relatively insensitive to the kinetic energy of the desorbing particles, was used for the detection of the desorbed lithium atoms. An important question is whether the delayed maximum arises from lithium atoms rather than dimers (which would appear as atoms following the ionization state of the QMS), and whether their velocity distribution is thermal as is the case for alkali-metal atoms desorbed *during* electron bombardment. To address these issues, we performed simultaneous laser-induced fluorescence (which is sensitive to the velocity of the desorbed atoms) and quadrupole-mass-spectrometry experiments, under experimental conditions where a delayed maximum could be observed. Our results prove that the occurrence of the delayed maximum is caused by the desorption of lithium monomers, not dimers, and indicate that the velocity distribution of the lithium atoms contributing to the delayed maximum does not appear to correspond to a Maxwell-Boltzmann velocity distribution. In addition, we observed an unexpected shift of the velocity distribution of the emitted atoms during bombardment as measured by laser-induced fluorescence that cannot be explained by any reasonable change in the surface temperature of the crystal during electron impact. Further, our data show that the substrate temperature dependence of the lithium desorption yield is the same for both experimental measurement techniques.

INTRODUCTION

It is well known that ionizing radiation incident on alkali halide crystals leads to the formation of F and H centers.[1] Both species agglomerate at temperatures where they are mobile.[2-6] When an F center reaches the surface of the crystal, it neutralizes an alkali-metal ion. The process of neutralization is well accepted, but not understood in detail.[7] If the temperature of the crystal is high enough, the neutral alkali-metal atoms may desorb thermally from the surface.[7,8] Several authors investigated the desorption of alkali-metal atoms induced by electron or photon bombardment by means of laser-induced-fluorescence spectroscopy (LIFS).[8] The data strongly support a model in which ground-state neutral alkali-metal atoms are desorbed thermally from the crystal surface during irradiation.

Betz *et al.*[9,10] investigated delayed emission of lithium from lithium fluoride by means of quadrupole-mass spectroscopy (QMS). After the electron gun is turned off at temperatures in the range above 250 °C, they observed a prompt decay, which was faster than their detector time resolution of 70 ms, and a delayed decay, whose time constant (in the range of seconds to minutes) was found to depend on several parameters, including temperature, dose rate, and integrated dose. Under certain conditions, within the temperature range 380–440 °C, the signal following the prompt decay was observed to increase again long after the electron gun was turned off (a matter of seconds). This is referred to as a "delayed maximum." The authors interpreted this surprising result to be due to the disintegration of F clusters, which were formed during electron bombardment. The model used to explain this effect was based on a homogeneous nucleation pic-

ture, which mathematically described the phenomena by a series of rate equations. In this model it was assumed that (a) effects due to diffusion could be neglected (i.e., diffusion time is much shorter than the lifetime of clusters) and (b) larger centers are thermally more stable than smaller ones. The authors did not specify whether the observed behavior was due to the disintegration of very large clusters (colloids), or due to small F-center clusters. Recently, Seifert *et al.*[11] investigated lithium desorption from LiF using crystals doped with divalent cations. Their results indicated that small clusters consisting of a small number of F centers (rather than hundreds of F centers) must be involved in the occurrence of the delayed maximum. Loubriel *et al.*[7] performed laser-induced fluorescence spectroscopy (LIFS) investigations of the delayed lithium desorption from LiF crystals under similar conditions, but smaller irradiation times (m rather than s). They did not observe the occurrence of a delayed maximum. It was therefore not clear if the delayed maximum was not observed because experimental conditions were different, or because the occurrence of the delayed maximum is not due to thermally emitted lithium atoms which consequently cannot be characterized by a Maxwell-Boltzmann distribution as is the case for alkali-metal atoms desorbing during electron bombardment.[8] QMS, in contrast to LIFS, is quite insensitive to the kinetic energy of the desorbing alkali-metal atoms, and also to the original spatial distribution of the alkali-metal atoms on the surface of the bombarded crystals. It is further possible that the delayed maximum originates from small lithium agglomerates such as dimers which disintegrate in the post-ionization section of a quadrupole. The Li agglomerates would arrive later than single Li atoms at the quadrupole, since the average velocity of the agglomerates is smaller than that of single Li atoms. Our goal was therefore to clarify the origin of the desorbed particles which contribute to the observed delayed maxima.

Our temperature-dependent LIF and QMS measurements of the delayed emission of Li from LiF performed simultaneously under electron bombardment show that both experimental methods give qualitatively identical results. We further show that the occurrence of the delayed maximum is not consistent with the assumption of a Maxwell-Boltzmann velocity distribution. We also observed that the fluorescence spectrum shifts during electron bombardment. We show that this cannot be explained by a local heating effect.

EXPERIMENTAL SETUP

We bombarded (100) single-crystal surfaces with electrons at different target temperatures (533–710 K). The energy of the electrons was 160 eV and the electron current density about 4 μA/mm^2. The experimental set-up is shown schematically in Fig. 1. The angle of incidence of the electron beam was along the target normal. Ground-state Li atoms were detected simultaneously with a quadrupole-mass analyzer after electron beam post ionization and by means of LIFS. The laser beam originates from a single mode cw dye laser, with a linewidth
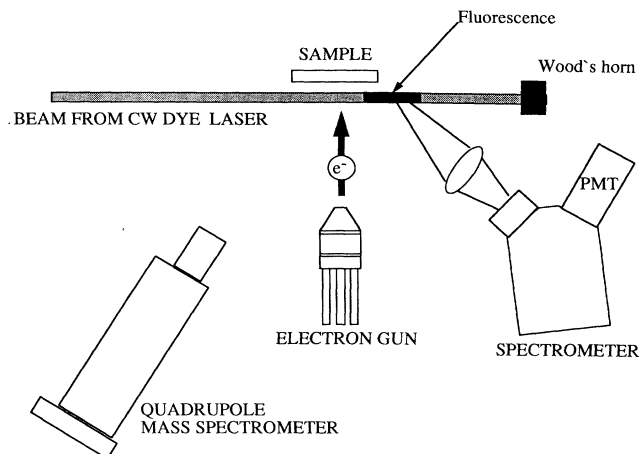

FIG. 1. In a typical experimental setup the laser beam was injected parallel and the electron beam normal to the crystal surface. Noise was reduced by trapping the laser light by means of a Wood's horn. Different regions along the laser beam could be viewed by moving the spectrometer-PMT system.

less than 2 MHz, pumped by an argon ion laser. The beam is transported to the chamber by an approximately 20-m-long optical fiber. The maximal intensity was about 10–50 μW/cm^2. The laser beam with a diameter of about 1 mm passed the target parallel to the surface at a distance of approximately 0.2 cm. The electron beam spot size was about 14 mm.

For measurements of ground-state neutral desorption yields by means of LIFS, the wavelength region around 6709 nm (in air) was investigated with a spectrometer-photomultiplier (PMT) combination arranged to view a small region (200 μm diameter) in front of the surface. The $(2p)\,^2P_{1/2}\rightarrow(2s)\,^2S_{1/2}$ transition of Li(7) atoms (lithium with atomic mass 7) and the $(2p)\,^2P_{3/2}\rightarrow(2s)\,^2S_{1/2}$ transition from Li(6) atoms fall into this region. The wavelengths given by the wavemeter have not been corrected. Different small regions of the fluorescing volume could be viewed by moving the spectrometer-PMT system. Since in the case of Li the fluorescence signal has the same frequency as the laser beam, background effects had to be removed by using a Wood's horn to trap the laser beam.

We did not choose the alignment used by previous authors where the laser goes through the crystal along the surface normal,[8] since the surface darkens during bombardment in the visible range and the laser light is hindered to penetrate the crystal.[12,13]

The UHV system maintained a base pressure of less than 10^{-9} Torr. The crystals were cleaved in air and cleaned in the vacuum system by prolonged heating at 400 °C. The temperature was measured with a thermocouple, which was clamped onto the front surface of the crystal.

RESULTS AND DISCUSSION

Figure 2 shows the QMS and LIF data recorded simultaneously. In this figure, the QMS data were normalized

to the LIF data. The electron beam-on time was approximately 5 s. About 1 s after the cessation of the electron beam, delayed maxima were observed using both methods. This implies that the delayed maxima are not related to desorbed lithium agglomerates which could disintegrate due to electron bombardment in the ionization stage of the quadrupole-mass analyzer. The delayed maximum clearly arises from the desorption of *individual* ground-state Li atoms. We have recorded a frequency scan over a spectral region which includes the $(2p)\,^2P_{1/2} \rightarrow (2s)\,^2S_{1/2}$ transition, which is shown in Fig. 3. Figure 3 also shows that these data can be fitted with a Maxwell-Boltzmann (MB) velocity distribution with parameters corresponding to the crystal surface temperature. The frequency scans of Fig. 3 or Fig. 1 inset (thin line) were taken after a couple of minutes of continuous electron bombardment and took about 1 min. They represent steady-state conditions. We have plotted the LIF signals as a function of wavelength for three different time slices in the inset of Fig. 2. The thin solid line represents a frequency scan performed under steady-state conditions and fits the experimental data of Fig. 1 (time slice $t2$). The filled rectangles represent the experimental data for time slice $t1$ (wavelength dependence immediately after the bombardment commences). The data can be fitted by the shifted frequency scan spectrum. It was not possible to perform a frequency scan for conditions similar to time slice 1 or 3 since scanning the frequency took too long. The reason for the shift will be discussed in the next paragraph. However, it is interesting to note that in
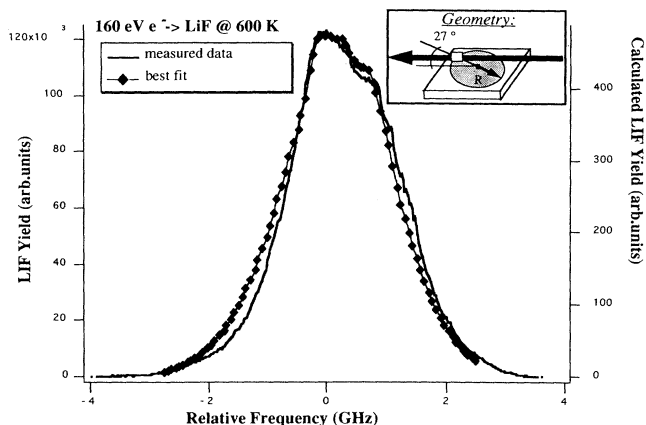

FIG. 3. Best fit of the shape of the fluorescence spectrum for electron bombardment at 600 K taking into account all hyperfine contributions for the measured $(2p)\,^2P_{1/2} \rightarrow (2s)\,^2S_{1/2}$ transition and the isotope shift. The fit gave a laser surface distance of 2 mm and an angle between the surface and the viewing spot direction (see inset) of about 27°. The radius of the electron spot R was about 7 mm.

the case of time slice 3 (diamonds, delayed desorption) the observed frequency spectrum cannot be fitted any more by a shifted spectrum which was recorded at steady state (inset of Fig. 2). This provides strong evidence that the lithium atoms which desorb after the electron beam is turned off cannot be characterized any longer by a
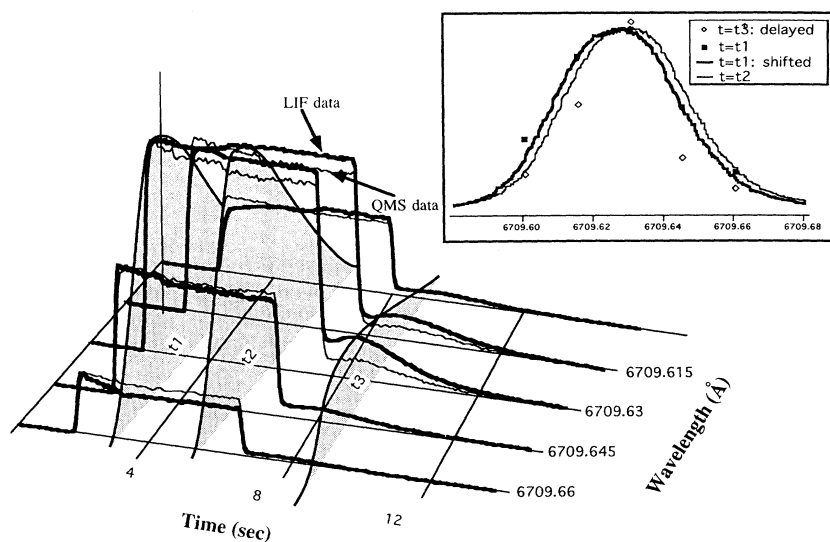

FIG. 2. In a geometry where the spectrometer viewed a small region at the edge of the electron spot (see Fig. 3 inset), one can clearly see the laser wavelength dependence of the LIF signal. The QMS signal is normalized to the LIF signal for comparison. For small wavelengths, the LIF signal increases slowly as the QMS signal is more or less constant as a function of the bombardment time, whereas for large wavelengths, the LIF signal decreases until it saturates. The delayed maximum can be observed by QMS and LIFS. For frequencies close to resonance, the LIF yield of the delayed maximum is clearly more pronounced than the QMS yield. The inset shows the wavelength dependence of the LIF yield for three different time slices. The thin line represents the measured data for a scan under steady-state conditions. The thick line represents the same scan, but we shifted it to show that a shift of the spectrum explains the observed decrease and increase of the LIF data (filled rectangles) as a function of wavelength. Clearly the shape of the fluorescence spectrum changes after the cessation of the electron beam (diamonds). The stated laser wavelengths have not been calibrated.

Maxwell-Boltzmann velocity distribution of a three-dimensional gas. The QMS and the LIF data coincide for wavelengths at the tails of the frequency spectrum, but clearly deviate close to the resonance frequency (Fig. 2). Following the cessation of the electron beam, the velocity distribution narrows but does not appear to shift. A temperature change after the bombardment corresponding to sample cooling cannot explain the measurements, since this would require a shift of the spectrum which was not observed. One possibility could be that the angular dependence of the desorbed Li atoms changed after bombardment due perhaps to the formation of Li islands on the surface of the crystal. This could be described in the following way. *During* electron bombardment lithium atoms and lithium islands are formed on the surface. Since the vapor pressure of the single lithium atoms is much higher than that of the lithium islands (the former are only bound by Van der Waals forces to the substrate), the major contribution of the lithium desorption rate is due to the evaporation of single lithium atoms. The velocity distribution of these desorbing atoms can be described by a MB velocity distribution with the crystal surface temperature. This explains that during electron bombardment we and other authors observe that the alkali-metal atoms desorb thermally. But *after* electron bombardment the relatively slow, delayed emission dominates, since most of the single atoms desorb very fast immediately after the cessation of the electron beam. The angular distribution of the emission directions of lithium atoms desorbing from lithium islands cannot be characterized anymore by a cosine distribution. This is because the lithium atoms at the edge of the islands are less tightly bound (due to the substrate) compared to lithium atoms in the center of the lithium islands. It is not reasonable to assume because of the high lithium vapor pressure at these temperatures that Li islands desorb for 5–10 s at 400 °C.[14] One possible model is to assume that small lithium islands nucleate near impurity sites and are responsible for the observed effect. They are probably more stable than normal lithium islands on the surface, which are bound only to the substrate. This is supported by the fact that it is known that the delayed emission can be enhanced by doping the crystals.[11] We would like to emphasize that this model assumes that lithium islands stabilized on the *surface* at impurity sites are responsible for the occurrence of the delayed maximum rather than F center clusters *in* the crystal as previous authors proposed.[9–11] However, this model is clearly only a tentative explanation of the origin of the delayed maxima, and further investigations are obviously needed. We plan to continue our studies of the delayed emission with LIF under a variety of experimental conditions and will correlate our measurements with calculations of the effect of small lithium islands at impurity sites on angular distributions. Clearly Loubriel *et al.*[17] did not observe the delayed maximum because their irradiation times were too short.[9–11]

One can clearly see that the fluorescence spectrum shifts during bombardment as shown in the increase and decrease of the LIF signal with respect to the QMS signal at the tails of the fluorescence spectrum (Fig. 2). The

magnitude of the shift is about 100 MHz. The spectrometer-PMT system viewed the surface at an angle of approximately 27° (see inset of Fig. 3), which was verified by fitting the fluorescence spectrum (Fig. 3). The geometry of the alignment (electron spot diameter, laser distance from surface, etc.) was roughly known, but accurate values were obtained by fitting the measured fluorescence spectrum. The spot size of the electron spot had to be quite large (14 mm diameter) in order to observe the delayed maximum clearly. We would like to emphasize that we were only able to fit the spectrum for the electron beam-on situation. Not enough data were available to fit the delayed spectrum (the scanning took much longer than the occurrence of the delayed maximum). The previous discussion has shown, however, that the delayed emission cannot simply be described by a MB velocity distribution where the average velocity corresponds to the surface temperature of the crystal. We therefore had not only to integrate over the MB velocity distribution

$$\frac{dn}{dv} = Cv^2 \exp\left[-\frac{mv^2}{2kT}\right] ,$$

where n is the number of atoms with mass m per velocity interval dv, but also spatially over the two-dimensional electron spot. C denotes a normalization constant. The detected fluorescence yield Y is given by

$$Y \propto \int d\mathbf{r} \left[\int dv \left[G(\theta,R,d)L(w,v)\frac{\partial n}{\partial v}(T,m)\right]\right] ,$$

where $G(q, R, d)$ takes into account the geometry of the alignment, i.e., it depends on the size of the electron spot R, on the distance of the laser from crystal surace d, and on the region where the spectrometer looks at q. The Lorentzian resonance line for the transition with frequency w_0 is given by

$$L(w,v) = \frac{\gamma/2\pi}{(\omega'-\omega_0)^2} + (\gamma/2)^2 ,$$

g denotes the natural half width of the transition. We actually integrated over six Lorentzians corresponding to all the hyperfine transition contributions and the isotope shift.[15] w' is the Doppler-shifted laser wavelength w_L given by

$$\omega' = \omega_L \left[1 - \frac{v_x(\mathbf{r})}{c}\right] ,$$

where v_x denotes the velocity component in the laser direction. Therefore, v_x depends on the spatial distribution of the electrons.

We also fitted the spectrum for different target temperatures and found good agreement which indicates that during the beam-on period, the lithium atoms desorb with a temperature close to that of the surface before bombardment. The fit is surprisingly good, considering we assumed that the electron distribution was uniform over the irradiated spot. In the case when the spectrometer-PMT system viewed an area located above the middle of the electron spot, we did not observe a shift

of the fluorescence spectrum. A shift can only be caused by a change in the velocity distribution dn/dt either by a change of surface temperature or a change of the electron distribution, perhaps due to charging.

The maximum change of the crystal surface temperature due to electron bombardment is about 2 K under our experimental conditions (Fig. 4). This result is based on the solution of the one-dimensional heat conduction equation

$$\nabla^2 u - \frac{1}{\kappa^2} \frac{\partial u}{\partial t} = -\frac{\eta}{l} \ ,$$

where u denotes the temperature, k the diffusivity, η the heat produced per unit time and unit volume, and l the thermal conductivity. Since the physical situation actually corresponds to a three-dimensional problem, the computed temperature changes are somewhat too large and can be regarded as upper limits. However, the one-dimensional diffusion equation can be regarded as a reasonably good approximation to the real physical situation, since the electron spot diameter is much smaller than the average diffusion length of the heat for a typical bombarding time of 5 s. Therefore only the diffusion of heat in the direction normal to the surface is relevant, since the heat energy is produced in a 50 Å thin region. We computed the fluorescence spectrum shift for a 50 K temperature increase, which is much higher than the temperature change due to the electron impact. The results show that the spectrum broadens slightly, but does not shift at all. The reason that a temperature increase barely affects the shape of the fluorescence spectrum is due to the large electron spot size as compared to the distance of the laser beam to the surface. The computed width of the spectrum caused by Doppler broadening in the case of lithium atoms desorbing from a very small spot on the surface of the crystal is much smaller than the observed width. The large electron spot contributes to a substantial broadening of the fluorescence spectrum.

To summarize, we can say that fitting the shape of the fluorescence spectrum obtained using LIF for different target temperatures indicates that during electron bombardment the lithium atoms desorb with thermal energies corresponding to the surface temperature as has been observed already by other authors.[7,8] But the shift of the spectrum cannot be explained by a reasonable temperature change caused by electron bombardment. Our calculations have shown that we need a temperature change of the order of 300° in order to account for the observed shift.

One possibility which could cause the fluorescence spectrum to shift is that the integrand angular distribution of the emitted lithium atoms changes *during* bombardment. This could be caused, for example, by local charging of the surface which will change the spatial location of the irradiated area. Since the QMS is much less sensitive to a change of the initial lithium distribution on the surface perhaps caused by a change in electron and therefore defect distribution, this change can only be seen by means of LIF spectroscopy.

Figure 5 shows the LIF and QMS lithium desorption yields for different bombarding temperatures during electron bombardment. Under steady-state bombardment conditions (after a couple of seconds of bombardment) there was only a small shift in the measured distribution with temperature for the 27° geometry throughout the entire temperature range (533–710 K). However, the velocity spectrum broadened for higher temperatures. A pronounced shift (~ 100 MHz) was observed between the distribution immediately following the onset of electron bombardment and the distribution a few seconds later characteristic of steady-state conditions. Our data indicate that this shift is caused by charging as previously discussed and not by a temperature change of the crystal surface during electron bombardment.

In the case of the LIF data, the laser was set to the maximum of the fluorescence spectrum for each temperature. We clearly did not observe any significant difference between LIF and QMS data in this experiment. The alignment which we used for this experiment was such that the spectrometer viewed the area above the middle of the electron spot. The results indicate that the temperature dependence of the LIF and QMS signal is
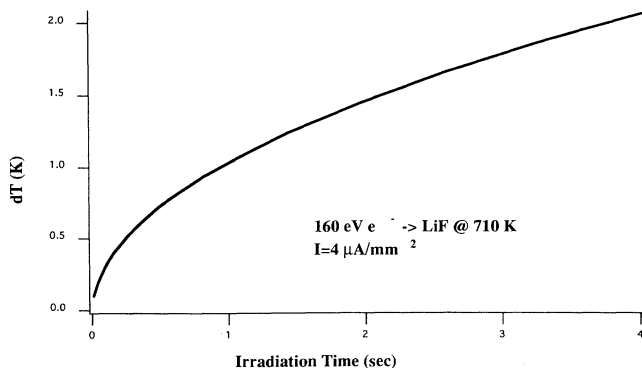

FIG. 4. Computed increase of the surface temperature for low-energy electron bombardment of a LiF crystal under typical conditions at 710 K. The model used was the one-dimensional heat conduction equation. Losses due to radiation have been neglected.
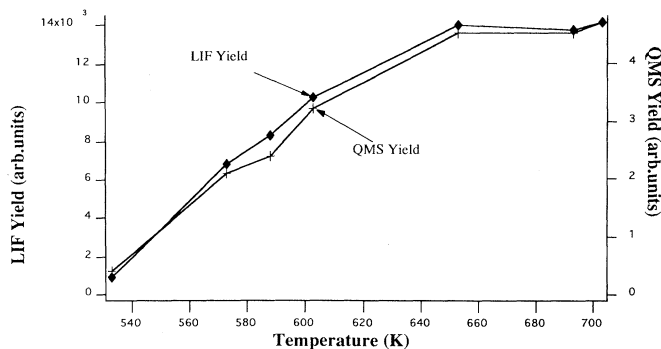

FIG. 5. LIF and QMS lithium signals are plotted as a function of crystal surface temperature. One clearly sees that the temperature dependences of LIF and QMS yields are the same. The laser frequency has been set to the maximum of the fluorescence spectrum for each temperature.

the same for the investigated temperature regime (533–710 K) if the laser frequency is tuned to the maximum of the resonance line for each temperature. We also investigated the temperature difference in the case of the off-center geometry. Also in this geometry we did not observe any discrepancy between QMS and LIF data in contrast to previous investigations.[8,16] The observed discrepancy between results described in Ref. 8 (LIF) and Ref. 16 (QMS) arises probably because of differences in measured experimental parameters, for example, surface temperature and electron-beam energies.

CONCLUSION

We have performed simultaneous LIF and QMS measurements of the electronically stimulated desorption (ESD) of lithium atoms from LiF during and after electron bombardment. The results indicate strongly that the velocity distribution of lithium atoms emitted during electron bombardment is described by a Maxwell-Boltzmann velocity distribution and therefore desorbs

with thermal energies, whereas the atoms emitted during delayed desorption cannot be described by a Maxwell-Boltzmann velocity distribution. The temperature dependence of ESD of alkali-metal atoms is in agreement for both methods. The unexpected shift of the velocity distribution of the emitted atoms *during* bombardment as measured by laser-induced fluorescence may be explained by changes in the incident beam density due to surface charging rather than by a change of the surface temperature of the crystal caused by electron impact.

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