Electronic Sputtering of Alkali Halides

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Synopsis

Inelastic interactions of energetic charged particles and photons with surfaces of alkali halides result in sputtering of various particles such as ions, atoms and molecules. A dominant fraction of this emission is in the form of halogen and alkali atoms characterized by a thermal (Maxwellian) spectrum of translational energies. For several alkali halides, however, a significant part of the halogen atoms is ejected with nonthermal energies, i.e. energies of the order of 0.1 eV. At first, a brief review of old experimental data is given and previously proposed mechanisms of electronic halogen sputtering, due to non-radiative decay of the self-trapped exciton in the bulk of the crystal, are critically discussed. Subsequently, recent systematic studies of angular-resolved kinetic-energy distributions of the emitted particles are presented and current views on the electronic mechanisms of sputtering are described. In particular, it is shown that the widely accepted bulk excitonic mechanism (often called 'the Pooley-Hersh mechanism') cannot explain new experimental findings about the emission of nonthermal halogen atoms. Instead, some recently proposed concepts of electronic sputtering are described and compared with the experimental data.

1 Introduction

A charged particle slowing down in an ionic insulator, in addition to displacing atoms from their lattice positions, creates electronically excited states (excitons and electron-hole pairs). These initially delocalized excitations can interact with a lattice to form localized excited states, so-called 'self-trapped holes' and 'self-trapped excitons'. Such localized excitations can subsequently decay nonradiatively leading to defect production in the bulk of the crystal and/or particle emission from the surface. In the particular case of an impinging low-energy electron, the elastic part of the interaction can be neglected due to a highly unfavorable mass ratio between the projectile and the target atom. Similar electronic sputtering (desorption) phenomena have been observed for UV or X-ray photon irradiation. Such processes provide a unique opportunity to study the electronic transitions
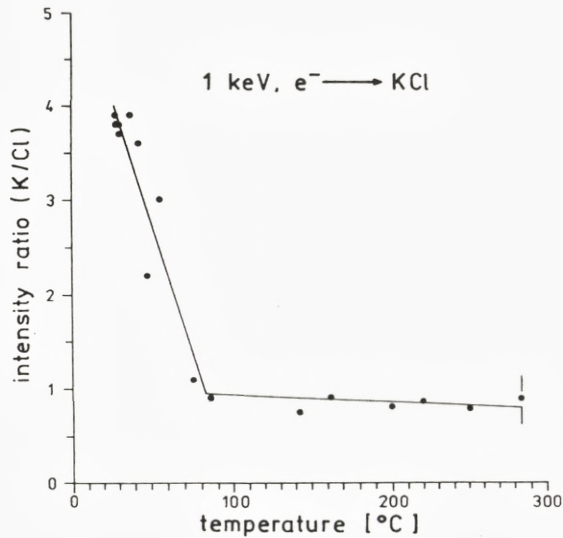
Figure 1. Composition changes in the (100) KCl surface induced by bombardment with a 1 keV electron beam. The K LMM 252 eV and Cl LMM 181 eV steady-state Auger intensity ratios are plotted as a function of the sample temperature. Due to Szymonski et al. (1992a).

responsible for transfer of the excitation energy deposited primarily in the electronic system of the solid into the energy of atomic motion leading to surface sputtering.

Interactions of charged particles and photons with alkali halides have been studied for several decades. In the early stages of these investigations a problem of defect production and radiolytic decomposition in the bulk of the crystal was observed (Crawford, 1968; Royce, 1967). Later, Palmberg & Rhodin (1968) and Townsend & Kelly (1968), reported on the efficient emission of particles from electron bombarded surfaces of alkali halides. Similar sputtering phenomena were also observed for photon irradiated surfaces (Townsend & Elliott, 1969; Brinciotti et al., 1991). In an extensive review Townsend (1983) concluded that electronic sputtering (ES) of alkali halides can be adequately understood in terms of what he called 'the Pooley-Hersh model', primarily used for explanation of Frenkel-pair formation in the bulk of alkali halides (Pooley, 1966; Hersh, 1966). Now, 10 years later, it appears that neither the primary defect structure and evolution in the bulk, nor the surface emission phenomena were sufficiently known. In this last decade, considerable theoretical development of self-trapped excitons and related defect formation in the bulk has been made (for reviews see: Williams & Song, 1990; Itoh & Tanimura, 1990; Song & Williams, 1993). But new, much more sophisticated experiments,

performed recently, have provided new insight into the basic mechanisms involved in the electronic sputtering of alkali halides. It is the purpose of this review to summarize the most important experimental findings in this field over the last two decades and to outline possible electronic processes leading to sputtering from alkali halide surfaces.

Generally, such electronic sputtering processes are of fundamental importance and, to a large extent, they should be observed for various ionic insulators such as halides, oxides and oxidized surfaces. Alkali halides can be used as model systems for studying these electronic interactions since they have simple and well-known crystallographic and electronic structures, and because electronic sputtering in these materials is very efficient.

2 First Experimental Findings on Electronic Sputtering of Alkali Halides

In the very first experimental investigations of alkali halide electronic sputtering two methods were used: (1) investigations of the surface composition cha nges induced by prolonged electron bombardment and (2) measurements of the accumulated sputtered material on the collector disc. The first experiment by Palmberg & Rhodin (1968), followed by some others (Cota Araiza & Powell, 1975; Friedenberg & Shapira, 1979) belonging to group (1), resulted in a very important observation. Alkali halide surfaces subjected to prolonged electron bombardment at room temperature showed a significant deficiency in the halogen component as measured by Auger Electron Spectroscopy. Temperature-dependent studies revealed that the apparent enrichment of the alkali component vanishes with increasing surface temperature at a rate related to its thermal evaporation properties. An example of such temperature dependence taken from recent work by Szymonski et al. (1992) is presented in fig. 1. The most significant conclusion was that the ES occurred due to the activation of the halogen sublattice only, whereas the alkali component was neutralized and evaporated thermally from the surface. This last finding is consistent with the work of Townsend et al. (1976) who measured a cosine angular distribution for Na atoms desorbed from NaCl with a 'hot-wire' detector.

In an early attempt by Elliott & Townsend (1971) to detect halogen emission, angular scans were made with a quartz crystal oscillator to measure the sputtered mass. The results for NaCl and KI samples showed a smooth cosine-like background with a superimposed maximum at 45° with respect to the <100> direction. This maximum became much more apparent when the sample temperature was raised from 250 to 350°C. Later, Townsend et al. (1976) used a silica disc to collect the particles desorbed from a (100) NaCl crystal. Despite some degradation of the
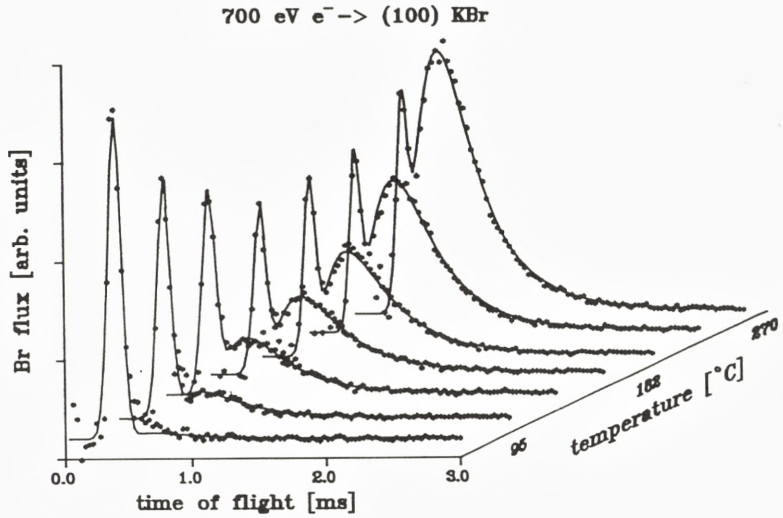
700 eV e⁻ –> (100) KBr

Figure 2. A set of angular-resolved time-of-flight distributions of Br atoms leaving a (100) surface of KBr at temperatures from 95 to 270°C. The observation angle was 0° . The distributions were normalized to reproduce the temperature dependence of the total intensity. Due to Kolodziej et al. (1992a).

deposit when it was exposed to the atmosphere for analysis, the authors were able to observe a rather complex pattern. It consisted of a central star feature with eight arms obtained on 'all occasions' and additional <011>, <112> and <133> spots found under what the authors called 'controlled conditions'. Although the appearance of the <011> spots was discussed in terms of the so called 'Pooley model' described below, the origin of the central pattern and the other spots was left unexplained. In fact, we should note at this point that the interaction of the backscattered primary electrons (Marklund & Andersson, 1966; Egelhoff 1984 & 1987; Ascolani et al. 1991) with the deposit might account for some if not all of its features observed in the work of Townsend et al. (1976). The autho rs noted that the collector plate was cooled to 77 K in order to inhibit previ ously observed resputtering by the reflected primary electrons, but even at this low temperature ES of non-thermal chlorine atoms from a thin NaCl deposit is expected to occur, leaving behind areas of higher contrast containing colloidal sodium. Furthermore, the collector technique does not provide any information about either the mass or charge of the different sputtered species that arrive at the collector plate and stick with various probabilities.

Directional features along the <110> and <112>axes with the collector tech-

nique were also measured by Schmid et al. (1975) under multiphoton laser ablation of NaCl, KBr and KCl at room temperatures and in vacuum of 10^{-6} Torr. In this laser experiment only the lowest excitonic states could be excited with the available photon energy, and in contrast to Townsend's experiments the central spots were not observed. In order to find the nature of this directional emission Schmid et al. used microchannel plate detectors and a miniature Mattauch-Herzog mass spectrometer. Well-localized emission of negative ions was observed with the microchannel detectors from KBr and KCl with a narrow angular distribution around the <110> and <112> directions. Also strong emission of neutral halogen atoms was registered but its angular distribution could not be measured with the available mass spectrometer.

The observed anisotropies in the emission patterns registered on the collector deposits were used as a major argument for the so-called 'Pooley-Hersh mechanism' proposed by Townsend for explanation of the electronic sputtering of alkali halides (Elliott & Townsend, 1971; Townsend et al., 1976). The Pooley-Hersh mechanism will be described in more detail in section 6.2. At this point it should be noted, however, that this model predicted directional emission of halogen atoms along the <110> direction of the crystal. Therefore, it would only account for some of the observed spots in the collector experiments.

3 Time - of - Flight Spectroscopy of Desorbed Halogen Atoms

The first time-of-flight (TOF) measurements for electron sputtered alkali halides were performed by Overeijnder et al. (1978a, b) for compressed powder samples. The most important result of these investigations was that the TOF spectra of halogen neutral atoms sputtered with 540 eV electrons from RbCl, KBr, RbBr, KI and RbI samples were characterized by a two-component velocity distribution. This type of distribution is indicative of two distinct mechanisms causing the emission of halogen atoms. Recently, it has been shown that the absolute sputtering yield as well as the relative ratio between the thermal and non-thermal halogen component is strongly dependent on the sample impurity content and the electron current density of the primary beam (Kolodziej et al., 1992b). Neither of these factors were controlled in the experiments by Overeijnder et al., thus we will not report further on that work.

The first published energy distributions for halogen atoms sputtered from single-crystal material were obtained by Postawa & Szymonski (1989) and Postawa et al. (1989). Later, such spectra were measured for well prepared surfaces, characterized with LEED and Auger Electron Spectroscopy (Szymonski et al., 1991a, b;
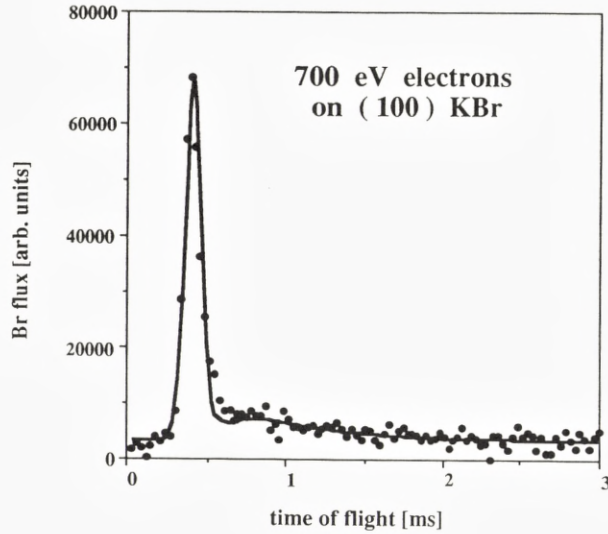
Figure 3a. Br atoms sputtered from a (100) KBr surface with 700 eV electrons. The surface temperature was 95°C and the observation angle was 0° . The solid curves were drawn to guide the eye. Time-of-flight distribution of the Br atoms. Due to Szymonski et al. (1991).

Szymonski et al., 1992). Examples of the temperature-dependent TOF spectra taken along the surface normal for (100) KBr (Kolodziej et al., 1992) are shown in fig. 2; similar spectra have also been measured for (100) KCl, RbCl, RbBr, KI, and RbI. These neutral halogen atom spectra consist of both a broad peak that has a temperature-dependent maximum and a narrow, higher velocity peak whose energy (at peak maximum) is temperature-independent. The broad peak can be fitted by a Maxwellian energy distribution that is representative of the specimen temperature and is due to thermally emitted particles. The differential flux, $\Phi(E)$, of such thermally evaporating particles can be expressed by the formula:

$$\Phi(E) \sim E e^{-E/k_\mathrm{B}T}, \tag{1}$$

where k_B is the Boltzmann constant and T is the temperature of the surface.

The narrow peak, whose maximum corresponds to a kinetic energy of 0.25 eV in KBr, is due to the ejection of hyperthermal halogen atoms. The lack of any apparent broadening of this hyperthermal peak on the low energy side of the distribution (see figs. 3a,b), suggests that these hyperthermal atoms do not originate in the bulk of the crystal. If they were emitted from inside the crystal, then their distribution should include energy loss processes involved in getting to the surface. Such loss processes were not observed suggesting that hyperthermal
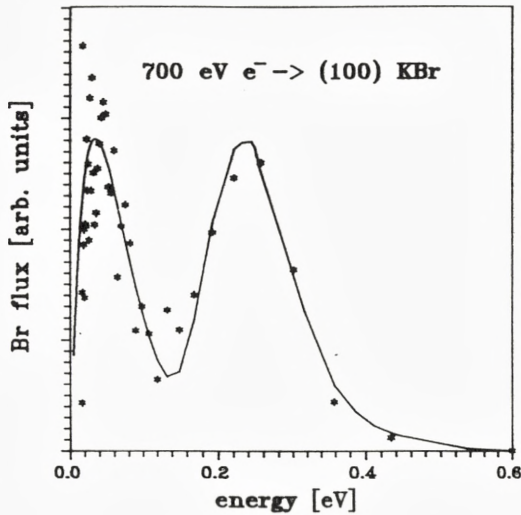
Figure 3b. Same as figure 3a. Energy distribution of Br atoms. Due to Szymonski et al. (1991).

halogen atoms were emitted from the surface directly.

Angular-resolved measurements of the thermal and nonthermal distributions show that they have markedly different angular distributions. The thermal particles can be described by a cosine-like function; in contrast, the nonthermal halogen atoms have a strikingly more peaked angular dependence. In fig. 4, the angular distributions of the nonthermal Br signal are shown for the (100) and the (110) surfaces of the KBr crystal respectively. Note that in the case of the (110) surface the <100> axis forms an angle of ± 45° with the surface normal in the (001) plane. Accordingly, two peaks are seen in fig. 4b, centered at + 45° and -45° with respect to the surface normal. From the above data, it is clear that emission of nonthermal halogen atoms from alkali halide surfaces is strongly collimated along the <100> axis of the crystal.

There is also a basic difference in the temperature dependence of these components. As is shown on the Arrhenius plot in fig. 5 (Kolodziej et al., 1992 a), the nonthermal emission decreases with an increase in the target temperature. At the same time, the yield of thermally evaporated atoms increases. It is seen, however, that the thermal Br component can not be described by a single rate equation process and a linear fit can only be made for temperatures above 160°C. There, the least squares fit gives an activation energy of 0.19 ± 0.04 eV. Accordingly, Dou & Lynch (1992) have found 2 temperature regions in the Arrhenius plots for NaCl
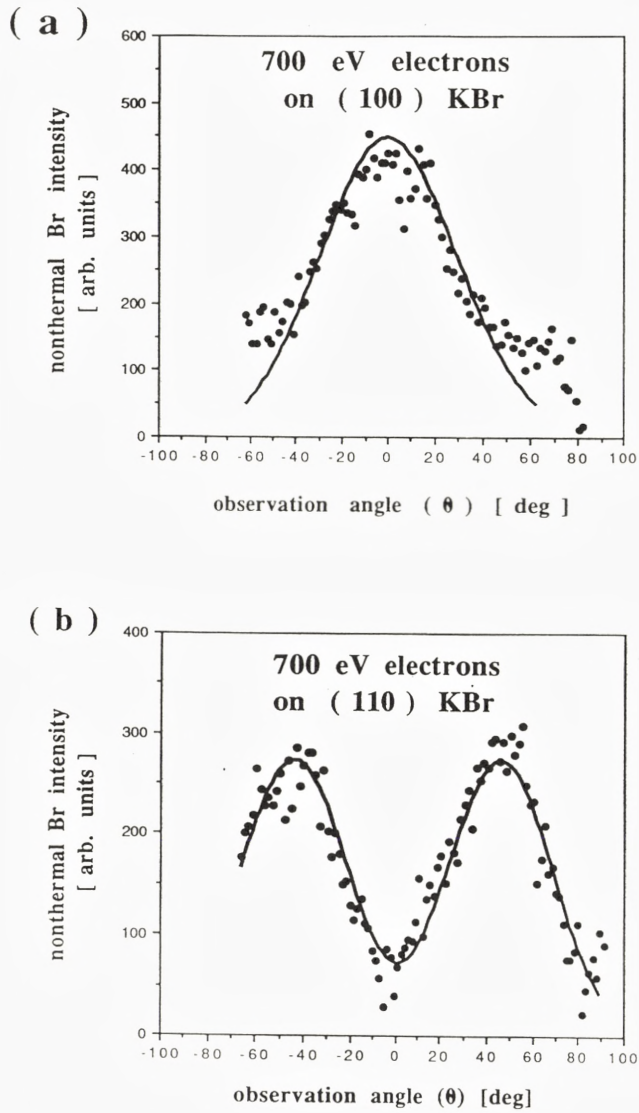
(a)

(b)

Figure 4. Angular distributions of nonthermal Br atoms sputtered from a KBr crystal at 140 °C. a) The distribution measured in a (010) plane of the (100) KBr crystal. b) The distribution measured in a (001) plane of the (110) KBr crystal. Due to Szymonski et al. (1991).
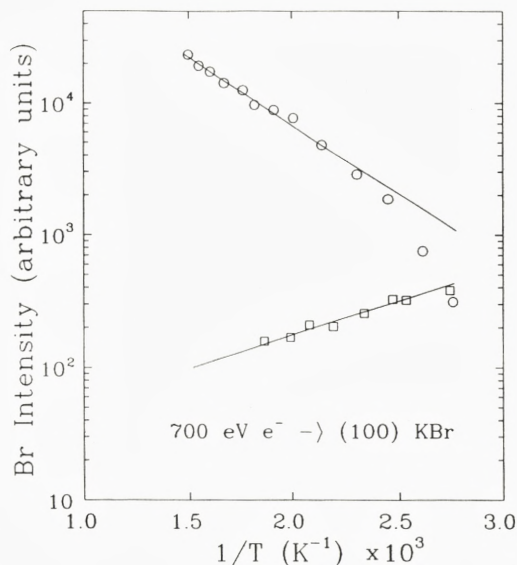
Figure 5. Arrhenius plot of the temperature dependence of the thermal (circles) and nonthermal (squares) yields of Br atom desorption from (100) KBr. The upper solid line was fitted to the experimental points above 160°C and has a slope corresponding to the activation energy of 0.19 eV. The lower line fits the nonthermal experimental points. Due to Kolodziej et al. (1992a).

and KCl crystals. The high temperature region activation energies (temperatures at which thermal sputtering dominates) were 0.07 eV and 0.12 eV for NaCl and KCl respectively. Low temperature values were much larger (0.29 and 0.27 eV, respectively) and they were interpreted as due to a partial surface metallization occurring at low temperatures. In contrast, the nonthermal component of the Br flux sputtered from KBr surface closely follows a straight line dependence on the Arrhenius plot (see fig. 5) but with a positive slope. The 'negative' activation energy in this case is 0.09 ± 0.02 eV (Kolodziej et al. 1992a).

The target temperature is not the only parameter determining the yield. In fig. 6 we present the energy dependence of the thermal and nonthermal partial yields for Br atom desorption from (100) KBr (Postawa et al., 1993a). The nonthermal signal increases steeply at low electron energies, reaches a maximum around 900 eV, and then drops. On the other hand, the thermal yield component at first decreases with the electron energy up to about 2.5 keV and then it starts to rise. A different behavior has been observed for Cl atom sputtering from a (100) NaCl sample, as presented in fig. 7. In this last case, the nonthermal component of the energy spectrum is not found and the dependence of the Cl atom yield on the electron
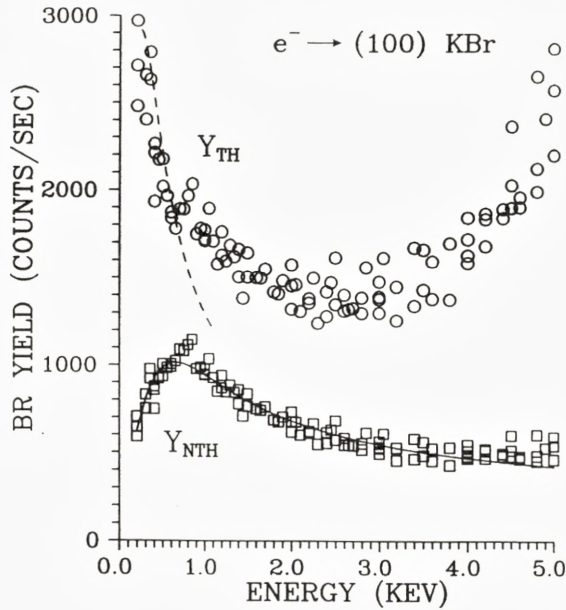
Figure 6. The dependence of thermal (circles) and nonthermal (squares) Br atoms sputtered from (100) KBr on the electron beam energy. The solid line was calculated theoretically as described in the text. Due to Postawa et al. (1993a).

beam energy is not pronounced. It is clear, however, that the character of this dependence changes with the target temperature.

Intense nonthermal emission has only been observed in some alkali halides, namely the chlorides, bromides and iodides of potassium and rubidium. In the other halides, either both the halogen and the alkali emission is thermal over the whole investigated temperature range, or a small contribution due to nonthermal halogen atoms is observed at room temperature (NaF and NaCl). A comparison of the relative yield ratio of the thermal component to the nonthermal one is shown in Table I (Kolodziej et al., 1992c). Since this ratio is strongly dependent on the sample temperature, the beam energy, and the electron current density, the numbers presented in Table I were obtained under exactly the same experimental conditions.

Recently, Kolodziej et al. (1992b) have been able to study the dependence of ES processes on the electron beam current density for the two velocity components of the sputtered flux. It appears that the yield of thermally emitted atoms decreases with an increase of electron current density, especially at low current densities (see
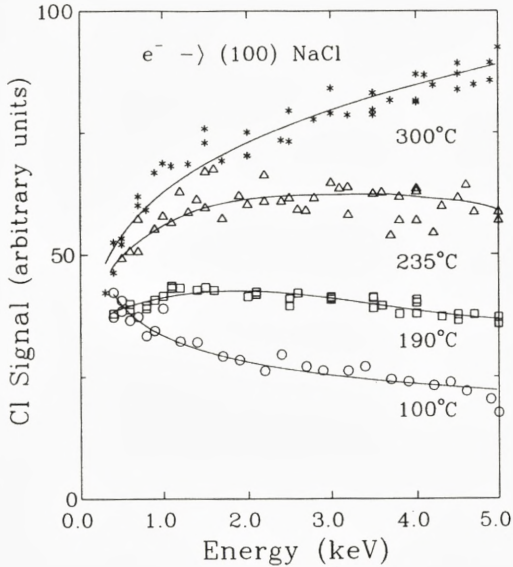
Figure 7. The dependence of the yield of Cl atoms desorbed from (100) NaCl on the primary electron energy at various surface temperature. Due to Postawa et al. (1993b).

fig. 8). The change in the nonthermal yield is negligible and within the experimental error that part can be considered as constant. The current density dependence of the thermal component indicates that electron sputtering measurements have to be performed under carefully controlled current density conditions. Unfortunately, many older experimental reports do not specify such conditions at all.

4   Thermal Desorption of the Alkali Component

The behavior of the complementary alkali component which is emitted appears to be different in character from that which has been seen for the halide. The angular distribution of K atoms for a (100) KCl at 140°C, shown in fig. 9, was easily fitted by a cosine dependence. There is no evidence of any preferential angular emission as there was for Cl. The same cosine-like angular distributions were observed for alkali atoms sputtered electronically from other alkali halides (Townsend et al., 1976; Szymonski et al., unpublished data).

The energy distributions for alkali atoms sputtered from single crystal alkali halides are always Maxwellian, eq. (1), as already reported by Szymonski et al. (1984). An example of such distributions obtained for a (100)NaCl at various

Table I. Comparison of yield ratio of nonthermal to thermal component for different alkali halides bombarded with a 1-keV electron beam at a surface temperature of 150°C.

Sample	Yield Ratio
KCl	0.37
KBr	0.67
KI	0.29
RbCl	0.49
RbBr	0.93
RbI	0.65

surface temperatures is reproduced in fig. 10 (from the work by Postawa et al. (1989)). These distributions are shown in a semi-logarithmic plot where $\Phi(E)$ is divided by E and presented as a function of E. In such a diagram, formula (1) is represented by a straight line with a slope determined by $1/T$. It can be seen that the energy distributions for sodium atoms shown in fig. 10 are purely thermal for all target temperatures. The shape of the distributions did not depend on the angle of observation. Temperatures obtained from a fit of formula (1) were equal to within 10% to the target temperature, measured with a thermocouple attached close to the sample surface. Measurements for single crystals generally agree with an earlier study for compressed powders by Overeijnder et al. (1978), except that Overeijnder had measured the thermal distribution as proportional to $\sqrt{E}$, rather than to E as in formula (1). It has been shown, however, that this observation of a $\sqrt{E}$ factor was caused by a technical problem with the slit width used in the time-of-flight spectrometer (Szymonski & de Vries, 1981). The Maxwellian energy distributions of alkali atoms emitted from electron bombarded alkali halides have also been confirmed using a Doppler-Shifted Laser-Induced Fluorescence (DSLIF) technique (Husinsky et al., 1988; Czuba et al., 1991). We would, therefore, conclude that the emission of alkali atoms must be due to thermal processes which take place after the electronic sputtering of halogen atoms occurs: the residual alkali ions left behind on the surface are neutralized and simply evaporate.

There have been several papers published in recent years reporting on alkali component emission from surfaces substantially modified by electron bombardment (Betz et al., 1990; Sarnthein et al., 1991; Seifert et al., 1991). These measurements were performed at relatively low sample temperatures, so that the alkali component could not balance the fast sputtering of halogen and accumulated in a form of islands, agglomerates and metal-like overlayers. A favorite sample for such a study was LiF since Li has the lowest vapor pressure of all alkalis. A closely related
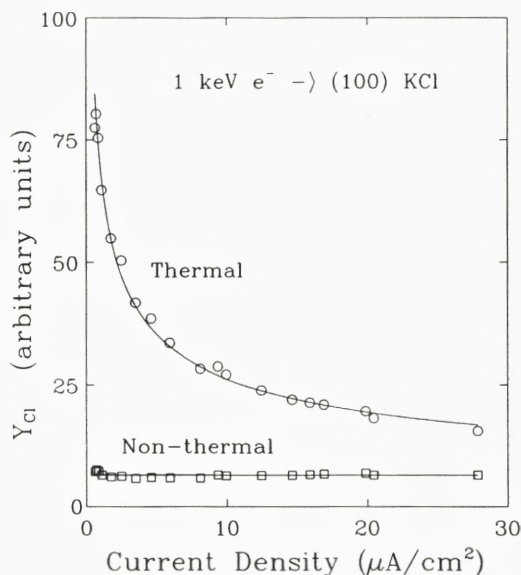
Figure 8. The dependence of thermal (circles) and nonthermal (squares) Cl atoms desorbed from (100) KCl on the electron beam current density. Due to Kolodziej et al. (1992b).

phenomenon seemed to be a delayed emission of alkali atoms from LiF (Green et al., 1987; Betz et al., 1990) and recently from KI (Brinciotti et al., 1993). Since this review is focused on the fundamental mechanisms of electronic sputtering which occur for stoichiometric, unperturbed crystals, topics related to alkali enrichment are not covered in detail.

5   Photon-Induced Sputtering of Alkali Halides

While electron-induced sputtering of alkali halides has been studied extensively over the past two decades, a review of the literature of photon-stimulated sputtering/desorption (PSD) does not reveal many experimental data. Parks and coworkers have observed desorption of positive halogen and alkali ions from a NaF crystal as the Na(1s) absorption edge was traversed in a synchrotron experiment and from LiF for photon energies near the F(2s) and Li(1s) edges (Parks et al., 1983 and 1984). The magnitudes of the positive-ion yields were rather small (3 ions per 10^8 photons absorbed) but the ion yield dependence on the X-ray energy closely resembled that of the total yield of secondary electrons generated by the same core-level excitations.
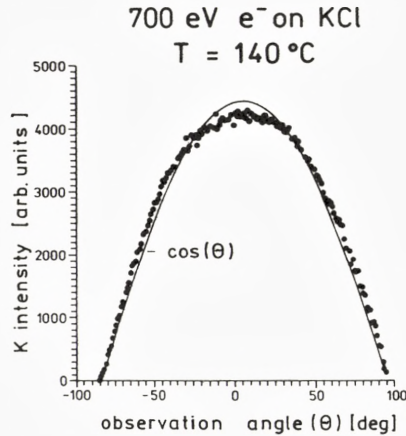
Figure 9. Angular distribution in a (010) plane of K atoms leaving a (100) surface of KCl at 140°C. The solid line represents a cosine function fitted to the experimental data.

There are only a few reports on PSD of neutrals from alkali halides, mostly due to valence excitations (Townsend & Elliott, 1969; Taglauer et al., 1986; Haglund et al., 1988). The early work on ground-state neutral sputtering yields reported that there was either no correspondence with the X-ray absorption spectrum or there was only a few percent enhancement in the yield of ground state Li atoms desorbed from LiF at the Li(1s) core excitation energy (Husinsky et al, 1988). The first systematic studies of PSD obtained by excitation of a KI single crystal in the fundamental absorption region up to 10 eV were performed by Brinciotti et al. (1991). They provided crucial information on the threshold excitation energies required for sputtering of neutral halogen atoms to occur. The results of their work are reproduced in fig. 11a,b. Al though we selected the halogen component data only, the dependences for the potassiu m component are essentially the same. We can clearly see an onset at about 5. 3 eV, followed by a band peaked at about 5.6 eV and dependent on the temperature. This structure can be related to the well-known optical absorption features of potassium iodide (Eby et al., 1959). The optical transition to the lowest excitonic state occurs at 5.6 eV at room temperature. The transition energy moves towards lower energies and broadens as the temperature increases. Thus, the band at 5.6 eV in the yield spectra of both K and I arise from the nonradiative decay of the exciton in its lowest excited state formed at those excitation energies. The subsequent slow increase in the yield spectra, starting at about 5.9 eV, can be correlated with the onset of the band-to-band fundamental absorption in potassium iodide. The photon absorption in this region produces
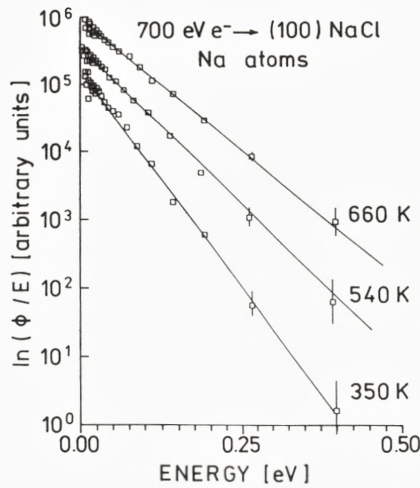
Figure 10. Energy distributions, $\Phi(E)$ divided by E, of Na atoms leaving a (100) NaCl target at three different target temperatures under bombardment of 700 eV electrons. A solid lines represent the best fits of the formula (1) to the experimental points. Temperatures measured with the thermocouple were 335 K, 525 K and 630 K respectively. Due to Postawa et al. (1989).

electron-hole pairs. Further increase of the excitation energy results in a fast rise in the desorption yield, due to transitions to higher excitonic and ionized states. The most important conclusion of this work is that the valence electronic excitation is sufficient for electronic sputtering of alkali halides. Since in the case of low energy electron bombardment these valence excitations are produced with the highest cross section, this type of energy loss process is therefore, the most important one for electron sputtering.

Sputtering of neutral sodium atoms from the (100) surface of single-crystal NaCl following Cl(1s) core-level excitation with synchrotron radiation has been observed by Szymonski et al., (1992). It was found that the bulk NaCl crystal shows significant sputtering at and above th e Cl K-edge, and that the dependence of the Na atom yield on X-ray energy has the same threshold and gross features as the total electron yield spectrum (see fig. 12). However, desorption from a 20 Å thick NaCl layer deposited on Si(100) could not be detected. This implies that accumulation of the decaying products of primary excitations over a considerable depth of bulk NaCl is required in order to account for the appreciable Na atom sputtering yield observed from the bulk crystal and the absence of any Na atom desorption from the thin film. Furthermore, the temperature dependence observed in this experiment suggests that the final steps in the Na sputtering process are
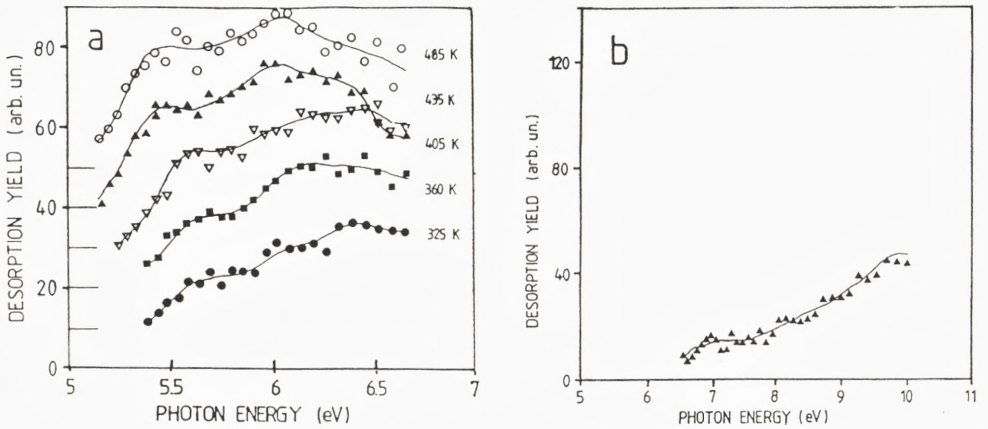
Figure 11. Desorption yield of iodine atoms emitted from (100)KI as a function of exciting photon energy. a) Measured at different sample temperatures in the 5.2 - 6.7 eV photon energy range. b) Measured at 393 K in the 6.5 - 10 photon energy range. Due to Brinciotti et al. (1991).

very similar to those occurring in electron bombarded alkali halides. It is very plausible, therefore, that even at these high photon energies the sputtering process is driven by valence electron-hole pairs created by fast secondary electrons from photoexcitation and Auger decay of the primary core-excitons.

There is still another very recent, important experiment on photon-stimulated ejection of atoms from alkali halide nanocrystals (Li et al., 1992). Interband excitation of single alkali halide nanocrystals, in the form of mass-selected $M_{n\pm1}X_n^\pm$ beams (M = K, Cs and X = Br, I), by ultraviolet radiation leads exclusively to halogen-atom emission with a large cross section. Beyond the cross section, it was significant that the halogen-emission process was certainly not the lowest energy fragmentation channel and that it could not be observed in thermally activated clusters (Hwang et al., 1990).

6   Current Views on the Mechanisms of Electronic Sputtering

6.1   Primary Excitations in Alkali Halides

As I have already mentioned, electrons incident on crystalline alkali halides create excitons and electron-hole pairs. In fact the most important electronic transitions leading to these excitations are from the valence band (formed by outermost p-
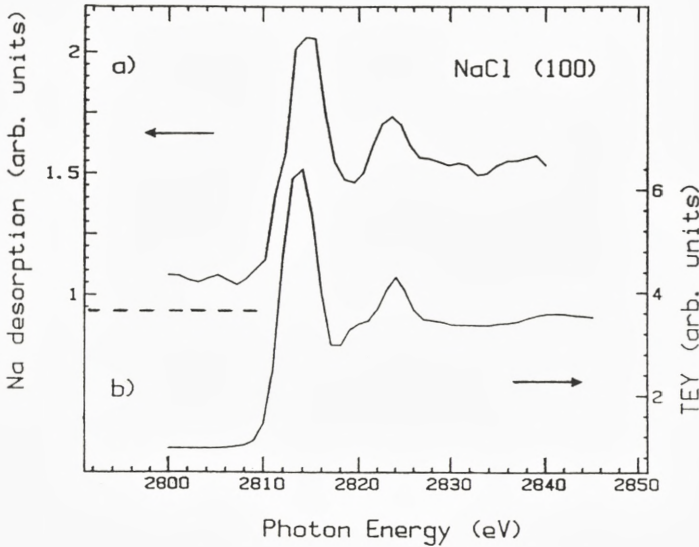
Figure 12. Synchrotron radiation in the energy region of the Cl K-edge interacting with a NaCl(100) crystal kept at 430 K. a) Na atom signal from a quadrupole mass spectrometer is plotted against photon energy. The dashed line indicates the background level of Na atom signal. b) Total electron yield spectrum. Due to Szymonski et al. (1992b).

type electrons of halogen atoms) to the conduction band of the crystal (Brinciotti et al., 1991). The resulting electrons and holes are free to move in the crystal; they also can form coulombically bound pairs, the excitons. Direct transitions to such excitonic states within the band gap are also possible.

A valence hole in an alkali halide quickly localizes (self-traps) on a covalently bonded pair of lattice halide ions, where the binding is induced by the hole's occupancy of an antibonding orbital (Williams & Song, 1990). The two bonded halide ions relax toward each other symmetrically along <110> in NaCl-type alkali halides (Kabler, 1972). A self-trapped exciton results when an electron becomes bound to the site of the self-trapped hole or so called V_k center (Song & Williams, 1993). Such self-trapping occurs on a sub-picosecond time-scale (Williams, 1989). The STEs can decay, with the emission of polarized light. This decay scheme appears to dominate at low temperatures (Kabler, 1964).

According to Pooley (1966) and Hersh (1966) the lowest state of the STE can decay nonradiatively forming a pair of separated Frenkel defects, i.e. an electron trapped in the halogen vacancy (an F-center) and an interstitial halogen atom (H-center) that is removed by a chain of replacement collisions along the <110>
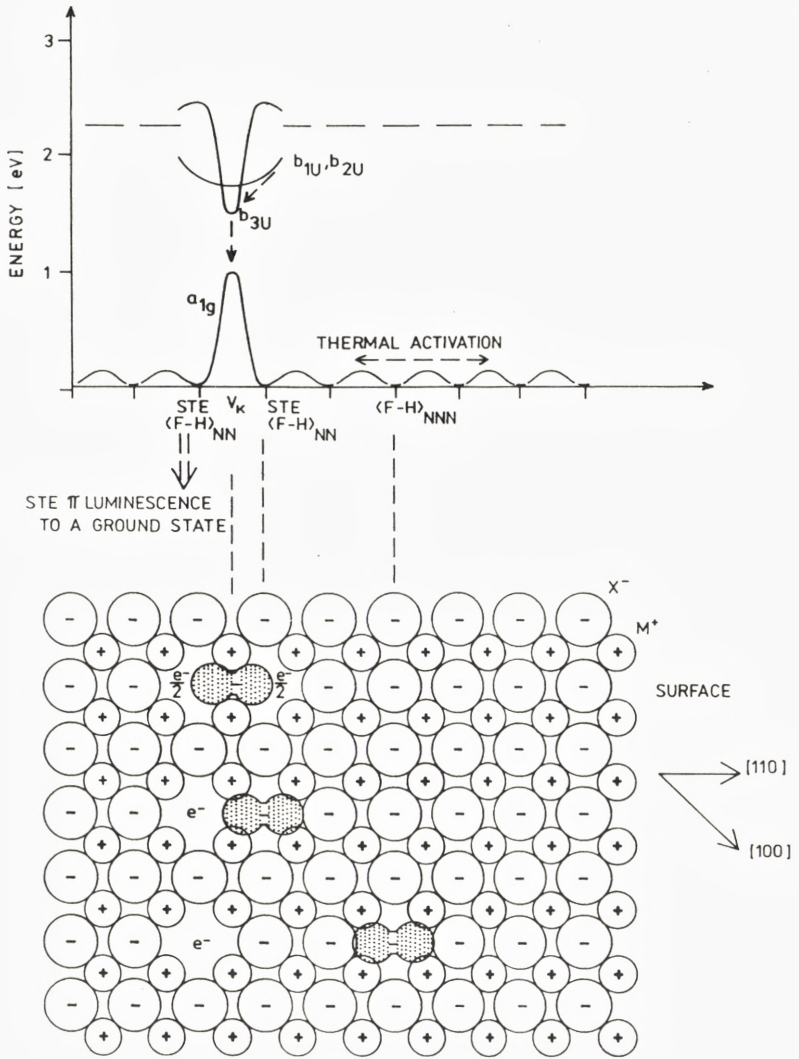
Figure 13. The change of the lattice energy relative to the perfect lattice of KCl versus the translational coordinate along the <110> axis. The STE states are designated by the electron orbitals. In the lower part of the figure, pictorial representations of lattice configurations for the 'on-center' and 'of-center' STE and F-H pair in a next nearest-neighbor position are shown. Due to Williams et al. (1986).

axis of the crystal. More recently Williams (1989) has distinguished two types of F-H pair production: a diffusive, thermally activated process and a dynamic one. The diffusive channel starts from the lowest STE electronic state which is unstable against a shift along the <110> axis to an 'off-center' equilibrium position. The adiabatic potential energy diagram (Williams et al., 1986) is shown in fig. 13. It is seen that the F- and H-center separation can occur by thermally-assisted diffusion of a halogen atom out of the relaxed STE in its lowest, π-luminescent state. Thermally activated motion of the halogen can also cause a recombination of the F-H pair into the STE with the subsequent emission of a π-luminescence photon (Szymonski, 1990). Consequently, the probability for achieving a sufficient separation of the F and H center so that they would not be able to recombine by competing processes is increasing with the sample temperature.

In the dynamic process, the energy for F-H pair formation and separation is derived from the energy of higher electronic states of the STE (Itoh & Saidoh, 1973; Williams et al., 1986). As indicated in fig. 13, the STE, relaxing through these higher levels, should cross into the lowest a_{1g} potential surface near the configuration with 'on-center' (V_k -like) symmetry. Since the a_{1g} surface at this point is unstable, the H center may be ejected at sufficient velocity to continue on for several lattice spacings along <110> direction of the crystal before thermalizing (Williams et al., 1986). The proposed mechanism of the dynamic F-H center pair formation is constrained to those specific crystals for which the energy drop associated with translation of the H-center along <110> from the 'on-center' position is relatively high allowing for stable F-H separation (Williams, 1989).

6.2 Nonthermal Emission of Halogen Atoms

Townsend et al. (Elliott & Townsend, 1971; Townsend et al., 1976) suggested that the Pooley-Hersh (PH) model could be used to describe ES processes in alkali halides. Should the STE decay within the range of the replacement collision sequence below the surface, hyperthermal halogen atoms could be ejected at the expense of the energy stored in the STE. Since then many modifications to the Pooley model have been made. Perhaps the most significant alteration suggests that the energy for dynamic F-H pair formation and for separation by the <110> focused replacement sequence is derived from the energy of higher excitonic states of the STE (Williams et al., 1986). A schematic visualization of the PH model is given in fig. 14. Because of the geometric orientation of the STE, the H center, and the direction of the halogen replacement collision sequence, all of which are oriented along the <110> direction, the hyperthermal halogen species would be preferentially ejected from the surface along this <110> direction. This is in contrast to recent observations (see section 3). For instance, it is clearly visible in
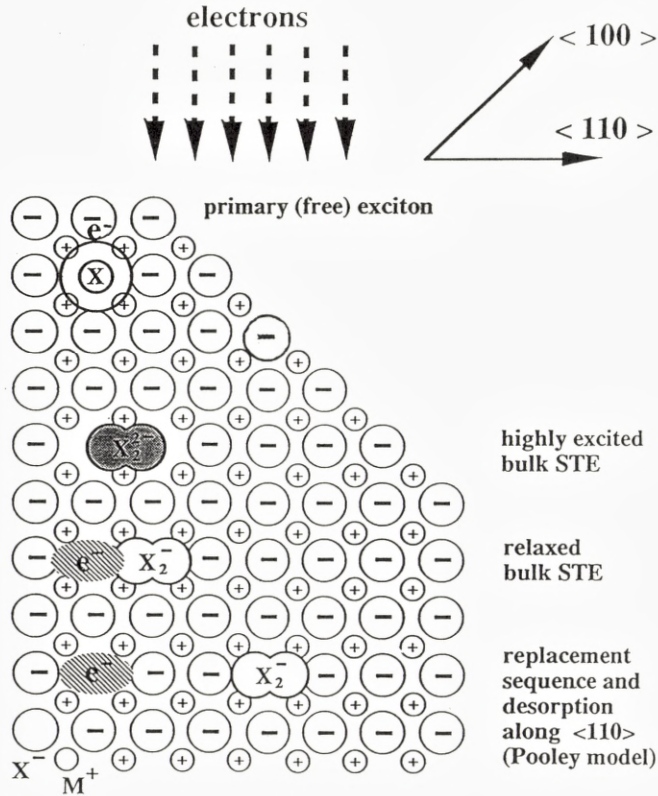
Figure 14. A schematic view of the lattice excitations in alkali halides leading to desorption via the focused replacement sequences (Pooley-Hersh model). X denotes a halogen and M an alkali atom.

fig. 4 that non-thermal Br atoms are predominantly emitted from both the (100) and the (110) surfaces of KBr crystal, along the <100> crystallographic axis.

This and other experimental findings described in the previous subsection clearly contradict the predictions of the PH model and indicate the need for a new theoretical approach to explain the nonthermal emission from alkali halides. Any new model should address the following observations:

- Nonthermal halogen atoms are emitted with a well-defined energy spectrum (not broadened at the low-energy side) in the range between 0.1 - 1 eV. The lack of broadening suggests that the nonthermal atoms are emitted from the surface directly. If they have to migrate from inside of the crystal, the energy

spectrum should reflect energy loss processes encountered in this migration.

- Emission is strongly collimated along the <100> direction of the crystal.

- The yield of hyperthermal atoms is relatively large, suggesting that electronic excitation from considerable depths of the solid must be contributing to this emission. Therefore, an efficient transport of this excitation energy from the bulk to the surface is required.

- The nonthermal halogen flux has been found to decrease slowly with increasing temperature of the sample.

- The yield of nonthermal emission has a well-defined maximum for primary electron energy equal to about 1 keV (in KBr).

In recent publications a new model has been proposed (Szymonski et al., 1991, 1992) which is based on the concept of excited, 'hot', conduction electron - valence hole pairs created within the penetration range of the incident electrons (Elango et al., 1976; Kadchenko & Elango, 1978; Green et al., 1990). Hot holes could be created in the valence band of alkali halides with a rather wide distribution of initial kinetic energies, corresponding to the valence band density of states (Elango et al., 1976). For example, in KBr the width of the valence band is about 2.6 eV (Kowalczyk et al., 1974) so that, on average, the holes could have as much as 1.3 eV excess energy. This high initial energy acquired in primary excitation makes the hot holes very mobile: they can migrate over distances of several hundred Å, thus providing very efficient transport of the energy deposited in the bulk of the crystal to the surface. The diffusion of holes has been described by Reimann et al. (1988) in relation to electronically stimulated desorption of rare gas solids. Postawa et al. (1993a) have used essentially the same formalism and solved the following diffusion equation:

$$D_+ d^2 n_+/dx^2 - n_+/\tau_+ + I_0 H_+ = 0, \qquad (2)$$

where $n_+(x)$ is the hole density radially and temporally averaged over many incident electron trajectories, D_+ is the diffusion coefficient of holes, and τ_+ is the trapping lifetime of a hole. The source function of holes, $I_0 H_+(x)$, can be approximated using the model of Al Jammal & Townsend (1973) for the depth distribution of the deposited energy, $H(x)$ (see fig. 15a). I_0 is the flux of incident electrons. The hole diffusion length is given by $L^2 = D_+ \tau_+$. With the help of the above equation one can transform the profile of the primary deposited energy, $H(x)$, into the depth distribution of the hot holes (see fig. 15b). It has been shown by Postawa et al. (1993a) that the best agreement between the experimental results for KBr and the model calculations can be obtained if $L = 100$Å. The value of L is not affected
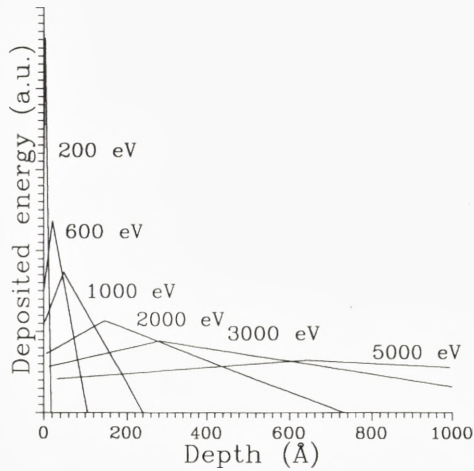
Figure 15a. The depth distribution of energy deposited in the (100) KBr crystal by different energy primary electrons. The distribution function $H(x)$ was calculated as proposed by Al Jammal & Townsend (1973) with the total electron range values taken from Bronstein & Procenko (1970).

by the state of the surface, i.e. whether the surface is reflecting or absorbing. The absolute sputtering yield, however, is strongly dependent on the surface reflectivity. The solid line in fig. 6 represents the result of the model calculations for $L = 100\text{Å}$ and a totally absorbing surface, i.e. every electron-hole pair arriving at the surface could potentially lead to emission of a nonthermal halogen atom.

The final precursor state at the surface responsible for this emission is not known yet with any certainty. Szymonski et al. (1991) postulated that the hot hole arriving at the surface can be transiently localized at a surface halogen ion (within a fraction of a vibrational period). Such a suddenly-neutralized halogen ion would find itself in the repulsive potential of neighboring alkali ions and it would perhaps be ejected with hyperthermal energy. In order to understand the nature of this repulsive interaction we make the following consideration. The most commonly used potential for halides is the one due to Rittner (1951) who, starting from classical arguments, proposed that the interaction energy between the ions M^+ and X^- of an alkali halide is given by (all in atomic units):

$$V(R) = Ae^{-aR} - \frac{1}{R} - \frac{\alpha_+ + \alpha_-}{R^4} - \frac{2\alpha_+\alpha_-}{R^7} - \frac{C_6}{R^6}, \qquad (3)$$

where α_+ and α_- are the polarizabilities of the positive and the negative ions. Here, the first term represents the short range Born-Mayer type repulsion energy, with adjustable parameters A and a. The second term is the Coulomb attraction
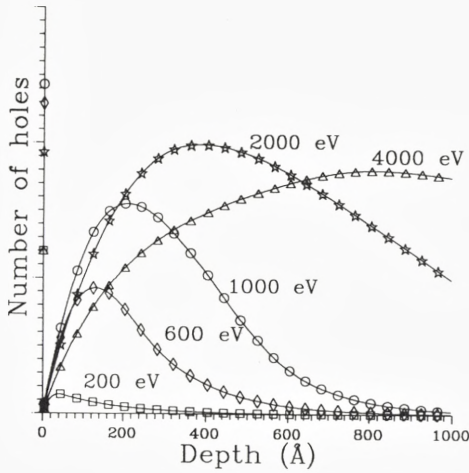
Figure 15b. Same as fig. 15a. Depth distributions of holes calculated from the solution of eq. (2) for a totally absorbing surface and with the diffusion length L = 100 Å.

between the two ionic charges. The third term gives the interaction between the charge of one ion and the induced dipole moment of the other ion, while the fourth term provides the interaction between the two induced dipoles. The last term is the dispersion force, in which the van der Waals coefficient C_6 can be obtained by standard techniques. A detailed discussion and further refinement of equation (3) is given by Patil (Patil, 1987). Neutralization of a surface halogen ion by a suddenly-arriving hole would result in cancellation of the attractive term $-1/R$. Consequently, the surface halogen ion + hole complex could experience a repulsive, short-range potential initiating the ejection. In fact, molecular-dynamics calculations by Green et al. (1989) have shown that the net potential of a neutral F atom approaching an alkali cation at the (100) NaF surface is positive for distances equal to or smaller than the anion-cation distance of the regular NaF lattice; thus the interaction is repulsive. For ionic NaCl-type surfaces, the surface halogen's five nearest alkali neighbors (four in the plane of the surface and one below the surface halogen) are all positive ions. The net initial repulsive force would then be directed between the sub-surface alkali ion and the surface halogen (see fig. 16); this direction is along the <100> axis and is consistent with the nonthermal emission observed.

At larger M^+-X^0 distances, however, the long-range forces related to multipolar polarizabilities of the halogen atom by the neighboring surface ions start to dominate over the short range repulsion. The resulting interaction is attractive and the
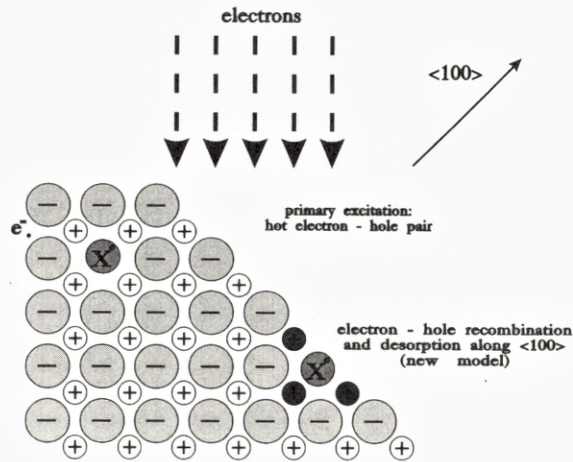
Figure 16. A schematic view of the new model proposed for explanation of ES of energetic halogen atoms. Hot electron-hole pairs created in the bulk of the crystal can diffuse and recombine at the surface. The surface halogen ejection is initiated by the repulsive interaction between the surface halogen, neutralized by the arriving hole and the neighboring alkali ions sharing an extra electron.

atom can be bound above the surface (Green et al., 1989). It has been pointed out by Itoh (Itoh, 1992) that the energy acquired due to short-range repulsion among the alkali ions and the halogen atom alone is not sufficient to overcome the long-range attraction. Also Song & Chen (Song & Chen, 1993), in a very recent theoretical work concluded that no halogen atom escape could be obtained when only the hole was present on the surface. The situation might be quite different, however, if we realize that the primary excitation process produces electron-hole pairs rather than isolated holes. It is likely, therefore, that the hole arriving at the surface halogen site is surrounded by a delocalized electron charge shared by the neighboring alkali ions. Partial neutralization of these ions should reduce the attractive forces preventing the halogen from ejection, initially driven by the short range repulsion between X^0 and M^+. Furthermore, the surrounding lattice and the electron may transform into the F-center configuration facilitating the final desorption of nonthermal X^0.

Essentially the same surface ejection mechanism has been proposed recently by Li et al. (1992) in order to explain photon-stimulated ejection of halogen atoms from alkali-halide nanocrystals. The emission process was illustrated on the calculated potential energy diagram reproduced in fig. 17. The repulsion following the vertical excitation process (due to UV-photon irradiation in that work) results in
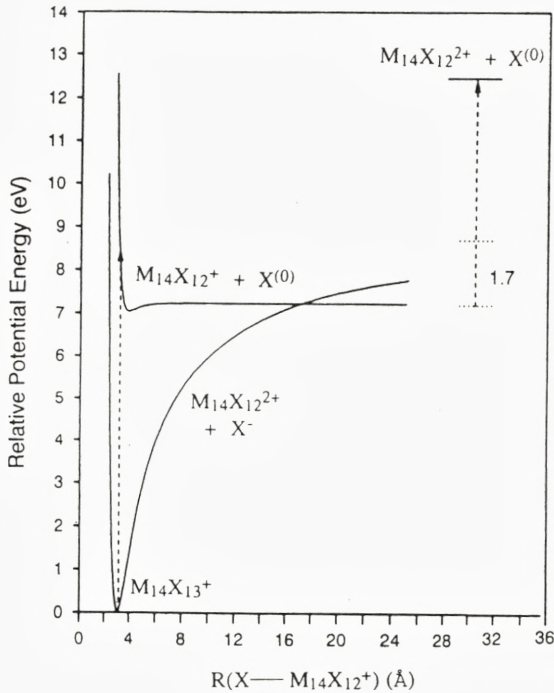
Figure 17. The relative potential energy curves for the halogen atom emission from the surface of the cubic $M_{14}X_{13}^+$ cluster. (The energy and distance axes are appropriate for the homolog M=Na, X=F and so must be scaled for KBr or other halides). The ionic curve (lower) is a Born-Mayer potential and the neutral curve for $X^{(0)}$ loss (upper) is a Lennard-Jones 6-12 potential fitted to asymptotic energies for $M_{14}X_{13}^+$, $M_{14}X_{12}^{2+}$ and $M_{14}X_{12}^+$. The asymptotic difference is 1.7 eV. Due to Li et al. (1992).

a gain in kinetic energy of about 1 eV for the neutral halogen which is sufficient to overcome the weaker attractive interactions. At long distance, where the neutral surface meets the ionic surface (see fig. 17) a (non)crossing occurs allowing for further separation along the neutral surface, if the velocity of the ejected atoms is sufficiently high (Li et al., 1992). Simultaneously, the neighboring cations and the electron relax into the F-center geometry. At reduced velocity, the trajectory may cross to the ionic surface, leading to recombination of an electron-hole pair and relaxation.

Lately, Puchin et al., (1992) have performed theoretical studies of atomic emission caused by electronic excitation at the (100) surface of NaCl. In particular, they calculated adiabatic potential energy surfaces (APES) that described the re-

laxation of the lowest triplet excited state and the ground (singlet) state of the electron-hole pair localized on the Cl site in the top surface layer. The excited state consist of a hole localized on the Cl p-orbital and an electron distributed over the nearest cations and outermost (diffuse) s-orbital of Cl. This situation is quite similar to the one treated by Li et al. and shown in fig. 17. Thus, Puchin et al. (1992) confirmed that an electron-hole pair localized on a surface halogen can lead to the prompt ejection of a nonthermal halogen atom.

It is the personal opinion of the present author that surface electron-hole recombination with direct ejection of the nonthermal halogen atom along the <100>, such as described by Li et al. (1992) and Puchin et al. (1993), represents the most plausible scenario for the final surface step in ES of nonthermal halogen.

In the same work Puchin et al. (1993) have also calculated the APES for an H-center near the surface as a function of its distance from the top surface layer. It has been shown that the H-center approaching the surface tends to be oriented along a direction which is only about 20° ±10° away from the <100> direction perpendicular to the surface. This is in contrast to the bulk orientation of the H-center which is along the <110> axis. The reoriented surface H-center can decompose into a halogen ion on the lattice site and an emitted Cl atom. However, it has been found that there is no stable relaxed atomic configuration corresponding to the self-trapped exciton located in the first two layers of the surface. Puchin et al. postulated, therefore, that the self-trapped excitons formed below the surface can decay producing H-centers which subsequently become reoriented towards the <100> and decomposed with emission of energetic halogen atoms.

Very similar results have been obtained recently by Song & Chen (1993) for the potential energy surface of the STE created on and near the (100) surface in NaBr, KBr and RbBr. In all three samples the energetic halogen desorption is described as due to the STE instability. A resulting neutral halogen atom is driven toward the surface with about 1 eV energy along <110> initially. Near the surface, the ejected atom starts to reorient along <100> axis as described above.

We note at this point very recent, important experiments by Meise et al. (1993). These authors have shown that in KBr, at 4 K, the dynamically created F-H pairs are the 4th nearest neighbours. This effectively means that the kinetic energy, derived from the STE instability, is used up after about 4 anion separations along <110>. If the maximum energy available initially is about 1 eV, the minimum energy to continue the replacement sequence is about 0.1 eV. Thus, according to Song and Chen (1993), the expected energies of dynamically emitted halogen range from 1.0 eV to 0.1 eV, depending on the place of origin of the STEs. This expectation is compatible with the experimental data (Kolodziej et al., 1992a).

6.3   Thermally Assisted Desorption of Halogens

Nonradiative decay of the STEs in near-surface layers or deeper in the crystal will form pairs of separated F and H centers as described in subsection 6.1. At temperatures of interest for this paper, H-centers can migrate inside the crystal, arrive at the surface and desorb thermally as proposed by the present author (Szymonski, 1980). The rate of the process should increase with temperature. Halogens that diffuse to the surface and evaporate would come off with a cosine-like angular distribution.

At room temperature, the H-centers are known to form interstitial aggregates, as was recently observed for iodides (Allen & Comins, 1990 and 1992). At elevated temperatures there will be a temperature-dependent competition between coagulation and free diffusion of interstitials. We believe that our observation of the thermal Br signal, which does not follow a single rate equation but sharply increases in the temperature range below 160 °C (see right hand side of fig. 5) may reflect the temperature dependent enhancement of the number of interstitial halogen atoms (H-centers) available for diffusion towards the surface. Only above 160°C does the diffusive mechanism dominate over the coagulation and the desorption of thermal Br then follows an Arrhenius dependence. At this high temperature limit, the yield of desorbing Br can be described by (Kelly, 1979):

$$S_{th} \cong \frac{E_0}{E^*} C_H^{diff}(0) \lambda_{th}, \tag{4}$$

where E is the incident electron energy, E^* is the energy consumed per created interstitial halogen atom, λ_{th} is the diffusion range and $C_H^{diff}(0)$ is the spatial distribution of the interstitial halogen atoms prior to diffusion, which is assumed to be uniform over a range much larger then λ_{th}. For thermally activated motion the diffusion range depends exponentially on $1/T$. From the least-squares fit to the upper part of such dependence in fig. 5 it appears that the activation energy for this motion equals to 0.19 eV. This value is considerably higher than the activation energies for translation and rotation of an isolated H-center in KBr which are known to be 0.09 eV and 0.037 eV (Bachman & Kanzig, 1968; Dienes & Smoluchowski, 1976).

The yield of thermally emitted halogen atoms depends not only on the diffusion range of the interstitial halogen atoms but also on the depth of deposited energy. At low electron energies, the penetration of primary projectiles is usually smaller than the mean migration range of H centers. In this limit, the number of emitted halogens should increase with the energy of the incident electrons because more and more energy is deposited in the volume of the crystal contributing to the desorption. However, once the migration range of H centers is exceeded, the fraction of the primary electron energy deposited in the 'active' subsurface region will decrease

and the desorption yield should drop. Such behavior is indeed visible in our data at low temperatures. Moreover, since the mean diffusion range increases with the target temperature, the maximum in the yield-energy dependence shifts toward higher energies. This is reflected in the the energy dependent curves taken at high surface temperatures (upper part of fig. 7).

As seen in fig. 8 the yield of thermal halogen atoms decreases with the current density, especially at low currents. It is plausible that the range of diffusing interstitial halogen can be reduced in a crystal damaged by high current density electron irradiation. The density of the created defects, such as vacancies, dislocations, etc. should increase with the current density and consequently cause a quenching of the halogen diffusion. The coagulation of the H-centers into interstitial aggregates should also be strongly current density dependent, particularly at low temperatures. This effect could further reduce the fraction of interstitial halogen atoms able to diffuse to the surface under high current density conditions. This interesting phenomenon needs further experimental investigations.

6.4   Thermal Desorption of Alkali Atoms

Since the electronic transitions lead to the selective desorption of halogen atoms, the alkali component should simply evaporate thermally from the halogen-deficient surface, provided that the remaining alkali ions will be efficiently neutralized and the alkali vapor pressure at the sample temperature is sufficiently high. The expected angular distribution in this case is cosine-like.

The problem of charge neutralization of originally positive alkali ions in the altered surface layers was discussed by Green et al. (1987). It has been suggested that the F-centers must diffuse from their place of origin to the surface, neutralizing metal atoms, which then may thermally desorb. The authors argued that this model could explain the considerable delays in emission of ground state alkali atoms as observed experimentally for LiF crystal by Loubriel et al. (1986). In general, the F-centers are rather immobile compared to H-centers, but they might be created much closer to the surface than was previously thought (see subsection 6.2). In addition, Puchin et al. (1993) in their theoretical work, calculated that a ground state F-center arriving at the surface cannot cause emission of the neighboring alkali atom. The same conclusion holds for two F-centers formed at the surface by diffusion. Instead, it is suggested that formation of the F-center clusters and/or alkali metal clusters in the near-surface layers might be required to explain the delayed alkali emission. On the other hand, it should be noted that electronic sputtering of alkali halides at sufficiently elevated temperatures and low-to-moderate electron current densities results in stoichiometric emission of both alkali and halogen components (Szymonski et al., 1992).

Until now, there has been no experimental evidence that alkali atoms could be emitted from electron bombarded alkali halide surfaces with nonthermal energies. This indicates that emission processes based on Coulomb repulsion of positive ions created by Auger de-excitation of core-level excitons (Feibelman & Knotek, 1978; Knotek & Feibelman, 1978) or alkali atom emission due to its interaction with an excited F-center at the surface (Puchin et al., 1993) does not contribute significantly to electronic sputtering from surfaces of alkali halides.

7   Concluding Remarks

Electronic sputtering of alkali halides has been studied experimentally and theoretically for several decades. A careful analysis of the experimental data accumulated over the years allows the following conclusions:

- The flux of sputtered particles consists mainly of alkali and halogen atoms in their electronic ground states. Emission of halogen neutral dimers, positive and negative ions as well as excited alkali atoms has also been reported but amounts to only a small fraction of the sputtered flux and has not been discussed in the present review.

- Photon-induced-sputtering experiments have shown that the valence electronic excitations are most important for emission of halogen and alkali neutrals.

- A significant fraction of the halogen atom emission from electron-sputtered surfaces of chlorides, bromides and iodides of potassium and rubidium has a nonthermal spectrum of translational energies (in the energy range 0.1 - 1.0 eV). A remaining part of the halogen atoms and all alkali atoms evaporate from the surface with a Maxwellian spectrum of kinetic energies characterized by the macroscopic surface temperature. The emission of neutrals from alkali halides other than those listed above was only thermal, except NaCl and NaF at the room temperature where some indications of small nonthermal emission were registered.

- The nonthermal halogen atoms are ejected from the surface preferentially along the <100> crystallographic directions.

- Electronic sputtering yields of alkali halides are of the order of 1-10 per incident electron of 1 keV energy. Since the total range of such electrons is of the order of 100 nm, an efficient, long range transport mechanism of the deposited energy from the bulk to the surface is required. It has been shown

that fast hot-hole diffusion can supply a significant fraction of the electron-hole excitations to the near-surface layers. Such a large number of surface excitations is necessary in order to explain the high sputtering yields.

- A new model has been discussed for the ejection of energetic halogen atoms. This model is based on recombination of the electron-hole pair, transiently localized on the surface halogen ion, with direct ejection of the nonthermal halogen atom along the <100> direction of the crystal. The model is supported by the results of recent cluster calculations and is consistent with current experimental observations. Alternatively, a model based on near-surface ejection of an H-center due to the STE instability, reoriented at the surface along the <100> prior to emission, has been proposed.

- The emission of thermal halogen atoms is consistent with a model in which interstitial halogen atoms and/or aggregates are produced in the bulk of the crystal from decaying self-trapped excitons. Subsequently, halogen interstitial atoms can diffuse thermally to the surface and then evaporate.

- The origin of the alkali atom component can be described by the neutralization and subsequent thermal evaporation of excess alkali atoms from the halogen deficient surface.

Acknowledgements

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