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Dynamic Halogen Desorption Stimulated by Electron Bombardment of Alkali Halides

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 holes). Lack of fast electronic relaxation implies that these excited states can interact with a lattice to form localized defects which subsequently can decay leading to desorption. In the particular case of an impinging electron the elastic part of the interaction can be neglected due to a highly unfavourable mass ratio between the projectile and the target atom. Thus, the electron-stimulated desorption provides a unique opportunity to study the electronic processes responsible for transfer of the energy deposited primarily in the electronic system of the solid into the energy of atomic motion causing the desorption. As a result, high desorption yields (of the order of 1–10) have been observed experimentally in various laboratories [1–3]. A flux of desorbing particles consists of atoms of both solid components (alkalis and halogens) and neutral molecules. A small fraction of positive ions has also been observed but interpreted as due to secondary process of electron impact ionization of desorbing neutrals in the gas phase [4]. Most of the above listed particles are emitted with thermal energies. For several alkali halides, however, a considerable fraction of halogen atoms is ejected with non-thermal energies, i.e. of the order of 01. eV [2,3].

The purpose of the present paper is to summarize the selected experimental data obtained recently in my laboratory and to sketch current views on the mechanism responsible for this dynamic ejection of halogen atoms due to electron bombardment of alkali halides.

TIME-OF-FLIGHT DISTRIBUTIONS OF DESORBED ATOMS

Electron-stimulated desorption of alkali halides has been studied already for over 2 decades but only very recently sufficiently sophisticated experimental techniques became available yielding accurate data necessary for comparison with the existing models. In particular, it has been shown that angular-resolved kinetic-energy distributions of desorbed particles can provide a direct verification of the mechanisms involved in the desorption [6,5]. For the first time such measurements for alkali halide single crystals have been performed in my laboratory [5–7] using the time-of-flight spectrometric technique.

The time-of-flight spectrometer used in these experiments was described previously [3]. The base pressure in the system was below 5×10^{-7} Pa. A VG LEG-62 electron gun supplied a beam of 1–10 μA, 0.2–5 keV electrons onto a spot of 2–3 mm in diameter. Neutral particles leaving the sample along the surface normal were ionized in an electron-impact ionizer and mass selected in a quadrupole mass spectrometer. Time-of-flight distributions were measured with a correlation technique [3]. The samples were high-purity (100) single crystals of KCl, KBr, and KI cleaned by heating to 650 K in vacuum for several hours. This procedure is known to produce well-ordered, single-crystal surfaces of alkali halides as examined by LEED and Auger-electron spectroscopy [8,9]. Since the surface composition for potassium halides remained stoichiometric for temperatures above 90°C [9], all experimental data reported here were taken above this temperature.

Time-of-flight (TOF) spectra of halogen neutral atoms desorbed from surfaces of KBr, KCl and KI single crystals are characterized by a two-component velocity distribution. This type of distribution is indicative of two distinct kinetic energy components. Temperature-dependent TOF spectra taken along the surface normal for (100) KBr [10] are shown in Fig. 1; similar spectra have also been measured for (100) KCl and KI. These spectra of halogen neutral atoms 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 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 Fig. 2), suggests that these hyperthermal atoms do not originate in the bulk of the crystal. Had they migrated from inside the crystal, then their distribution would have included energy loss processes involved in getting to the surface; no such loss processes are observed suggesting that hyperthermal halogen atoms are emitted from the surface directly.

Angular-dependent 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 characteristic of isotropic emission; in contrast, the nonthermal halogen atoms have a strikingly more peaked angular dependence. In Fig. 3a and b the angular distributions of the nonthermal Br signal

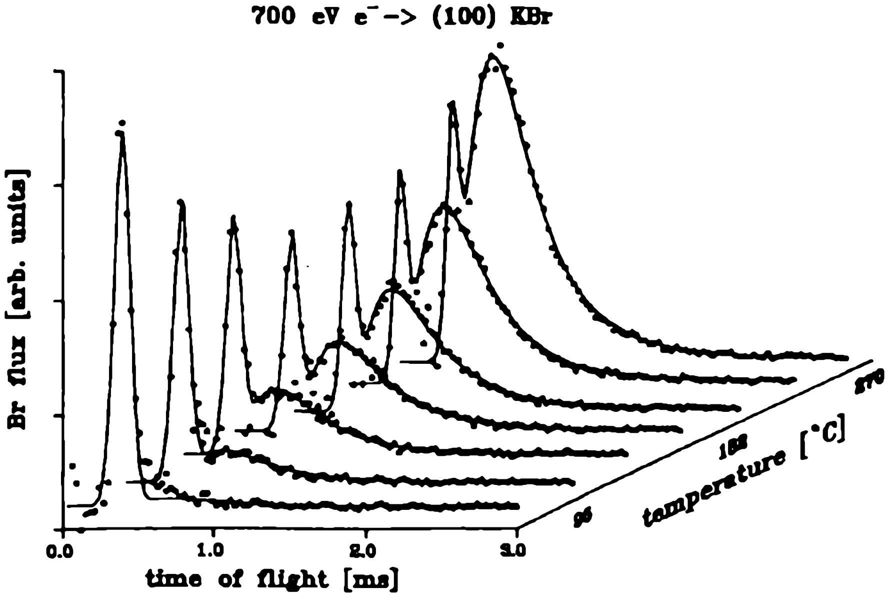

Fig. 1. A set of angular-resolved time-of-flight distributions of Br atoms leaving a (100) surface of KBr at temperatures from 95 to 270°C. The observation angle was 0°C. The distributions were normalized to reproduce the temperature dependence of the total intensity. Due to Kolodziej *et al.*, ref. [10]

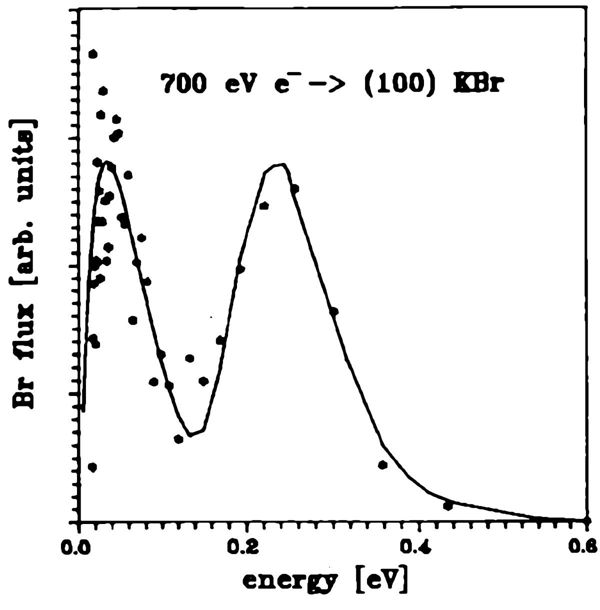

Fig. 2. The energy distribution of Br atoms desorbed from a (100) KBr crystal at 95°C. The observation angle was 0°C. The solid curve was drawn to guide the eye

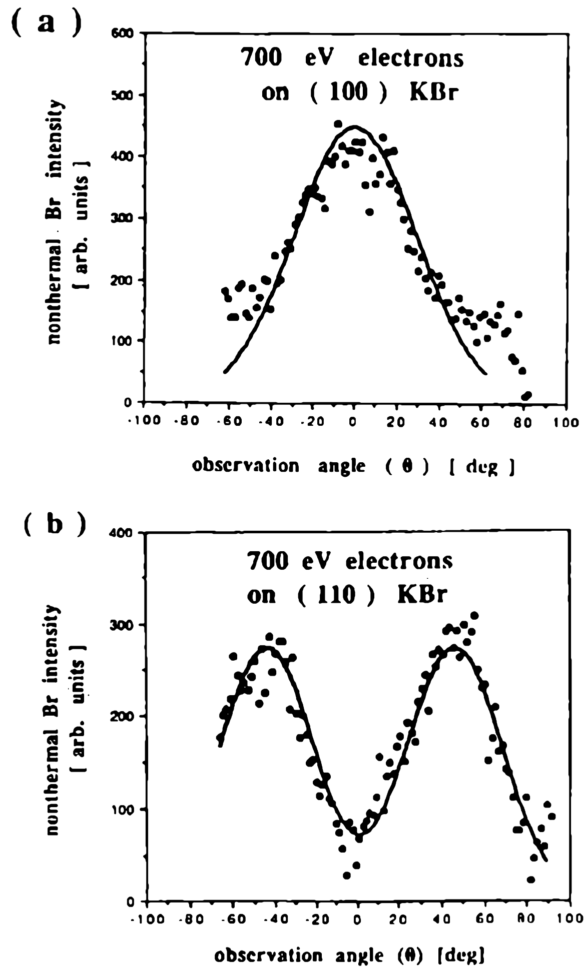

Fig. 3. Angular distributions of the nonthermal Br atoms desorbed from a KBr crystal at 140°C. a) The distribution measured in a (010) plane of the (100) KBr crystal. b) The distribution measured in a (001) plane of the (110) KBr crystal. Due to Szymonski *et al.*, ref. [6]

are shown taken 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. 3b, centered at +45° and −45° with respect to the surface normal. From the above data, it is clear that desorption of nonthermal halogen atoms from alkali halide surfaces is strongly collimated along the < 100 > axis of the crystal.

CURRENT VIEWS OF ESD MECHANISMS

As the author has already mentioned, electrons incident on crystalline alkali halides create excitons and holes. In fact, the most important electronic transitions leading to these excitations are from the valence band (formed by p-type valence halogen electrons) to the conduction band of the crystal. The transitions to so-called excitonic states within the band gap are also possible. The resulting electrons and holes are able to move in the crystal; they also can form a Coulombically bound pair, equivalent to the primary excited exciton. Excitons in alkali halides interact very fast with the lattice and form localized defects. Such self-trapping occurs in picosecond times [11]. In alkali halide crystals, the valence excitons activate a halogen sublattice only since the binding energy of the outermost electron in the halogen negative ion is much lower than that of the alkali positive ion. Ax exciton ($e^- + h^+$) localized on a halogen negative ion (X^-) can become self-trapped when this excited halogen ion covalently bonds with its nearest-neighbor halogen ion:

$$X^{-\bullet} + X^- \rightarrow X_2^{-2\bullet}.$$

This self-trapped exciton (STE) is essentially an electron bound to the site of a halogen-molecule negative ion (X^-) where the inter-atomic spacing of the two negative ions is reduced by the screening of the trapped hole. The STEs can decay with emission of polarized light. This decay scheme appears to dominate at low temperatures [12]. Alternatively, they can undergo a non-radiative decay, to form a pair of separated Frenkel defects (vacancy-interstitial pairs). According to Pooley [13] and Hersh [14] the lowest state of the STE can decay nonradiatively forming 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 > axis of the crystal:

$$X_2^{-2\bullet} \rightarrow F + H.$$

Townsend [1] suggested that this Pooley-Hersh (PH) model could be used to describe ESD processes in alkali halides. Should the STE decay within the range of the replacement collision sequence from the surface, then hyperthermal halogen atom could be ejected as a consequence of the energy stored in the STE. Since then many modifications to the original Pooley model have been made. Perhaps the most significant alteration suggests that the energy for dynamic $F - H$ formation, and separation by the < 110 > focused replacement sequence, was derived from stored energy of higher excitonic states of the STE [15]. 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 PH model would predict that hyperthermal halogen species should be preferentially ejected from the surface along this < 110 > direction (see Fig. 4).

Nonradiative decay of the STE from deeper in the crystal would require thermal diffusion for an H center to reach the surface where it could desorb thermally as proposed by the present author [16]. Halogens that diffuse to the surface and evaporate would come off with a cosine-form of angular distribution. Since these electronic transitions lead to selective desorption of halogen atoms, the alkali component would simply evaporate thermally from the halogen deficient surface, providing that its vapor pressure at the sample temperature is sufficiently high. The expected angular distribution in this case is cosine-form too.

The experimental findings described in the previous subsection clearly contradict the predictions of the PH model and indicate need for a new theoretical

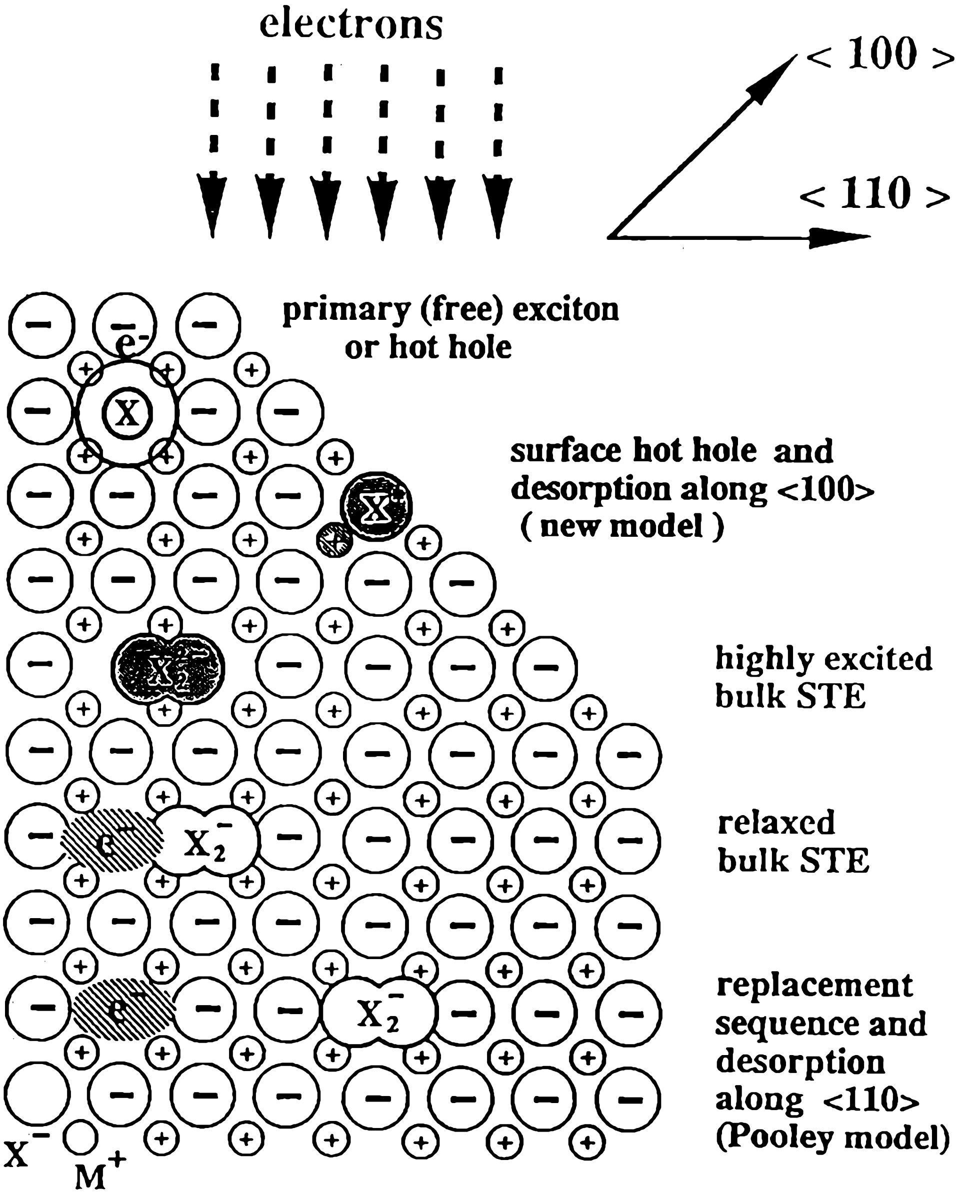

Fig. 4. A schematic view of the lattice excitations in alkali halides leading to desorption via the focused replacement sequences (Pooley model) and repulsion of the hole neutralized at the surface halogen ion (new model). X denotes a halogen and M alkali atoms

approach to explain the nonthermal emission in ESD of alkali halides. Any new model should address the following observations: 1) nonthermal halogen atoms are emitted with a well-defined energy spectrum between 0.1–0.5 eV (no low-energy tail seen), 2) emission is strongly collimated along the $< 100 >$ direction of the crystal, and 3) the yield of hyperthermal atoms is relatively large suggesting that electronic excitation from considerable depths of the solid must be contributing to this emission.

In recent publications we have proposed a model which is based on the concept of excited, "hot" electron-hole pairs created within the penetration range of the incident electrons [5,9,10]. Hot holes could be created in a valence band of alkali halides which has a width of about 3 eV. Thus, on the average, the hole could have as much as 1.5 eV excess energy which might be used for migration. That means that the hot holes can migrate to the surface from the depth of several hundred Å providing a very efficient transport of the energy deposited in the bulk of the crystal to the surface.

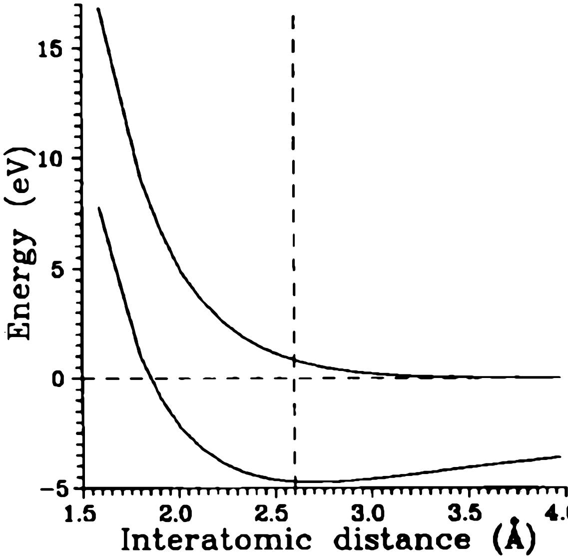

Fig. 5. Interaction potential between K^+ and Br^- ions (lower curve) compared with the repulsive Born-Mayer part of the interaction (upper curve). Plotted from the tabulated data of the ref. [18]

The new model of ESD in alkali halides assumes that thermalized hole arriving at the surface can be transiently localized at the halogen surface ion due to its intrinsic surface states. A surface halogen ion neutralized by the halogen hole would find itself in a repulsive electrostatic potential. In order to understand a nature of this repulsive interaction we will make the following consideration. The most commonly used potential for halides is the one due to Rittner [18] who, basing on classical arguments, proposed that the interaction energy between the ions M^+ and X^- of and alkali halide is given by (all in atomic units):

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

where the 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 the adjustable parameters A and a. The second term is the Coulomb attraction between the two ionic charges. The third term gives the interaction between the charge of an ion and 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. In Fig. 5 such potential is plotted for a K^+ and Br^- ions and compared with a repulsive term of the potential (Born-Mayer type) alone. Neutralization of a surface halogen ion by a suddenly arriving hole would result in cancellation of the attractive term $-1/R$ and a possible reduction of the higher order terms. Subsequently, the surface should further assist the emission of neutral halogen with nonthermal energies. For ionic NaCl-type surfaces, the surface halogen five nearest alkali neighbors (four in the plane of the surface and one below the surface halogen) are all positive ions. The net repulsive force would be directed between the sub-surface alkali ion and the surface-halogen + hole complex; this direction is along the $< 110 >$ axis and is consistent with the hyperthermal emission observed.

CONCLUDING REMARKS

I have presented what seems to be a consistent explanation of the ESD process leading to dynamic ejection of nonthermal halogen atoms from alkali halide surfaces. This process consists of the following steps: (1) creation of highly excited (hot) electron-hole pairs within the penetration range of the primary electrons, (2) fast hot-hole diffusion to the surface (the mean diffusion range is comparable to the penetration depth of the primary electrons), and (3) hot-hole localization at the surface resulting in directional emission of the nonthermal halogen atoms due to its repulsive interaction with a subsurface alkali ion along the $< 100 >$ axis of the crystal.

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