## New Mechanism for Electron-Stimulated Desorption of Nonthermal Halogen Atoms from Alkali-Halide Surfaces

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Fully angular-resolved kinetic-energy distributions of alkali and halogen atoms emitted due to electron-stimulated desorption have been measured for (100) and (110) alkali-halide surfaces. An unexpected strong directional emission of nonthermal halogen atoms along the (100) axis of the investigated crystals has been found which is in contradiction to the predictions of the previously proposed "Pooley model." We propose a new model involving diffusion of hot holes to the surface, and sudden localization of the excited hole at the surface of the crystal.

PACS numbers: 79.20.Kz, 71.35.+z, 78.55.Fv, 82.65.My

Since the early work of Townsend and Kelly [1] and Palmberg and Rhodin [2], it is known that electron irradiation of alkali-halide surfaces results in the efficient desorption of alkali and halogen atoms. Several attempts have been made to construct a model of electron-stimulated desorption (ESD) in alkali halides [3-8]. In particular, the "Pooley model" has been applied as an explanation of ESD from alkali halides by Townsend [3,6]. The main idea of this model is that nonradiative decay of the bulk self-trapped exciton followed by a focused replacement sequence along the closely packed (110) chains of the halogen atoms is responsible for halogen desorption. Thus, this bulk-exciton model predicts strong directional emission of halogen atoms along the (110) directions of the crystal. Despite a rather wide acceptance of the Pooley model, we believed that a comprehensive experimental test of its predictions had not yet been performed. Early attempts to measure angular dependence of emitted species were done by means of a collector method [3,6,9]. Unfortunately this technique does not provide any information about either mass or charge of the different desorbing species that arrive at the collected deposit and stick with various probabilities. In addition, resputtering of the collector deposit by reflected primary electrons, strongly focused along surface crystallographic directions [10], is likely to influence such results.

The first time-of-flight measurements for ESD of alkali halides were performed by Overeijnder *et al.* [11] for compressed powder samples. The only published energy distributions for halogen atoms desorbed from singlecrystal material were obtained by Postawa and coworkers [12,13]. In the work we report here, for the first time a direct correlation has been measured among the direction of ejection, the mass and translational energy of a desorbed particle, and the crystallographic structure of a well-characterized insulator surface. In particular, we present a direct comparison between angle-resolved energy spectra of bromine atoms taken for (100) and (110) surfaces of KBr. The data demonstrate that independent of the surface orientation the directional ejection of nonthermal halogen atoms takes place along the  $\langle 100 \rangle$  axis of the bombarded crystals rather than along the  $\langle 110 \rangle$  direction as predicted by the Pooley model. Our data strongly indicate the need for a new theoretical approach to explain the ESD of alkali halides.

The time-of-flight spectrometer used in these experiments was described previously [13,14]. The base pressure in the system was  $5 \times 10^{-7}$  Pa. A 0.7-keV electron gun supplying a beam of 5-10  $\mu$ A onto a spot of 3-4 mm was mounted on the same manipulator as the sample holder. Thus, variation of the observation angle during the angular distribution measurements could be achieved with a fixed bombardment angle (45° with respect to the surface normal). In addition, the manipulator allowed independent rotation of the sample in the horizontal plane, so that the angular scans could be made in various, arbitrarily chosen planes of the crystal. Neutral particles leaving the sample within a solid angle of  $1.4 \times 10^{-4}$  sr were ionized in an electron-impact ionizer and mass selected in a quadrupole mass spectrometer. Time-offlight distributions were measured with a correlation technique [15].

The samples were high-purity (100) and (110) single crystals of KBr and a (100) crystal of KCl, cleaned by heating to 700 K in vacuum for several hours. This procedure is shown to produce well-ordered, single-crystal surfaces of alkali halides as examined by LEED and Auger-electron spectroscopy [10,16]. The composition of the electron-bombarded surface was monitored in this experiment by means of Auger-electron spectroscopy. We found using this technique that the surface composition for KCl and KBr remained stoichiometric for temperatures above 90 °C. Consequently, all experimental data were taken above this temperature.

Time-of-flight spectra of Br atoms desorbed from a (100) surface of a KBr crystal for several observation angles are shown in Fig. 1(a). The scans were taken in the (010) plane of the crystal. The spectra were normalized so that the total area under each time-of-flight distribution corresponds to the respective data point of the measured angular dependence of the total Br yield. Two velocity distributions can be distinguished in the time-of-flight spectra in the range of observation angles measured from 0° to 45°. The broad peak with a maximum at 1 ms may be attributed to a Maxwellian distribution of thermal atoms, while the second, sharp peak with a maximum at 0.4 ms and a sharp cutoff below 0.2 ms (1.2 eV),



FIG. 1. Time-of-flight spectra of Br atoms desorbed from a KBr crystal at 140 °C. The distributions were normalized so that the total area under each distribution corresponds to the respective data point of the measured angular dependence of the total Br yield. The solid lines represent best fits of the superposition of a Maxwellian distribution with temperature T = 140 °C and an arbitrarily chosen Gaussian function. For better visual presentation the time-of-flight distributions were not corrected for varying ionization efficiency of our electron-impact ionizer which is inversely proportional to the velocity of the detected atoms. (a) Distributions measured for four different observation angles in the (010) plane of the (100) KBr crystal. (b) Distributions measured for four different observation angles in the (110) KBr crystal.

corresponds to a faster, nonthermal distribution of Br atoms.

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 cosinelike function characteristic of isotropic emission; in contrast, the nonthermal bromine atoms have a strikingly more peaked angular dependence as shown in Fig. 2(a). From the above analysis, it is clear that desorption of nonthermal halogen atoms from a KBr (100) sample is strongly directed along the  $\langle 100 \rangle$ axis of the crystal.

Our time-of-flight measurements indicate that for tar-



FIG. 2. Angular distributions of the nonthermal Br atoms desorbed from a KBr crystal at 140 °C. The data points were obtained by subtracting the cosine angular distribution observed for thermal halogen atoms from the experimentally measured dependence for total Br intensity. The solid curves are drawn to guide the eye. (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.

get temperatures below  $100 \,^{\circ}$ C, practically only nonthermal Br atoms are emitted along the  $\langle 100 \rangle$  axis as shown in Fig. 3. The time-of-flight distribution of the nonthermal Br atoms is found to be very narrow (halfwidth of 0.12 ms); its position and width were observed to be independent of temperature. If the nonthermal atoms would originate in the bulk of the sample, subsequent energy-loss processes, for example, phonon decay occurring during transport to the surface, would result in broadening of the low-velocity side of the time-of-flight spectrum. Such broadening is definitely not observed and this would indicate that the nonthermal halogen atoms are emitted from the surface.

The time-of-flight distributions measured for a (100) surface of KCl show the same behavior as the ones described for KBr. The ratio of nonthermal-to-thermal halogen yield for KCl, however, for the same observation angle and target temperature, is smaller than that for KBr. For example, at  $\Theta = 0^{\circ}$  and  $T = 140 \,^{\circ}$ C, this ratio equals 0.29 for KCl and 1.88 for KBr.

In order to learn more about the nature of the directional emission of nonthermal halogen atoms, we measured the angle-resolved time-of-flight spectra for a specially polished (110) surface of KBr. In this case the  $\langle 100 \rangle$  axis forms an angle of  $\pm 45^{\circ}$  with the surface normal in the (001) plane. The time-of-flight spectra for this case are shown in Fig. 1(b). The angular distribution of the nonthermal Br signal, taken in this plane, is shown in Fig. 2(b). In contrast to the distribution from Fig.



FIG. 3. Time-of-flight distribution of Br atoms desorbed from a (100) KBr crystal at 95 °C. As in Fig. 1 the distribution was not corrected for the velocity-dependent ionization efficiency. The observation angle was  $0^{\circ}$ . The solid curve is drawn to guide the eye.

2(a), two peaks are seen, centered at  $+45^{\circ}$  and  $-45^{\circ}$  with respect to the surface normal. It has been found, however, that the cosine distribution with respect to the surface normal for the (110) surface still describes the thermal emission of Br atoms and the total emission of K atoms at all temperatures. Thus, indeed only the non-thermal Br atoms are ejected directionally within the narrow cone around the  $\langle 100 \rangle$  axis of the crystal which, in this case, does not coincide with a surface normal.

As we have mentioned above, the Pooley model of ESD of alkali halides predicts that a  $\langle 110 \rangle$  direction of the crystal [i.e.,  $\Theta = \pm 45^{\circ}$  for the (100) sample] should be the preferred one for halogen emission. Our experimental results clearly contradict this expectation which was based on bulk exciton decay. In order to explain our results, we propose a new model which invokes a sudden localization of the excited ("hot") hole at the surface of the crystal. Recently, it became evident that hot holes in the valence band and free electrons are created with high probability by ionizing radiation [8,17-20]. The initial kinetic-energy distribution of hot holes could be described by the valence-band density of states [18,21]. It follows from the photoemission measurements that in KBr this energy can be as high as 2.6 eV with the average value of 1.3 eV [22]. Furthermore, due to this high initial energy acquired in primary excitation, hot holes can migrate over considerable distances in alkali halides [17-20], thus providing a necessary transport mechanism for the excitation energy to go from the bulk to the surface. The excited halogen hole  $X^*$  arriving nonadiabatically at the surface would likely experience a repulsive potential due to breaking of the bulk symmetry. Simple electrostatic considerations for the ionic, NaCl-type surface indicate that the repulsion would be directed preferentially along the axis between a subsurface alkali ion  $(M^+)$  and the surface halogen site occupied by  $X^*$  as seen in Fig. 4. Note that the  $M^+$ -X<sup>\*</sup> axis coincides with the (100) direction for both (100) and (110) surfaces of the NaCl-type crystals; this ejection direction is consistent with our angular-resolved measurements. An alternate possibility of hot-hole localization at the surface would be via a halogen molecular complex  $(X_2^{2^{-}})^*$  (in analogy with the bulk decay of a self-trapped exciton), but as pointed out by Williams [8], it would more likely lead to the ejection of a halogen negative ion  $X^-$  along  $\langle 110 \rangle$ .

Although negative ions could not be measured with our time-of-flight spectrometer, significant negative halogen emission has been observed previously [1,9]. Since the collector technique is not able to distinguish between negative-ion and neutral-atom emission, some of the directional  $\langle 110 \rangle$  and  $\langle 211 \rangle$  spots observed by Townsend *et al.* [3] and by Schmid, Braunlich, and Rol [9], ascribed so far to directional emission of neutrals, could have been due to the negative ions. Note that in the laser experiment of Schmid, Braunlich, and Rol only *the lowest excitonic states* could be excited with the available photon en-



FIG. 4. A schematic view of the lattice excitations in alkali halides leading to desorption via the focused replacement sequence (Pooley model) and repulsion of the hot hole localized at the surface (new model). X denotes a hologen and M an alkali atom.

ergy and the central  $\langle 100 \rangle$  spot was not observed. In our experiment, however, as well as in the collector experiment by Townsend *et al.* [3], the energy of primary electrons used for desorption was sufficient to create highly excited holes and indeed the central  $\langle 100 \rangle$  emission was observed.

In conclusion, we can distinguish the following steps in the proposed model to explain ESD of nonthermal halogen atoms: (a) creation of highly excited (hot) electronhole pairs within the penetration range of the primary electrons, (b) fast hot-hole diffusion to the surface within a time range of picoseconds (the mean diffusion range is comparable to the penetration depth of the primary electrons), and (c) 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  $\langle 100 \rangle$  axis of the crystal.

The authors wish to thank Dr. Hideo Sambe and Dr. David Ramaker for their helpful suggestion concerning the  $M^+$ - $X^0$  complex. Fruitful discussions with Dr. C. S. Ewig are gratefully acknowledged. This work is part of the Joint Collaboration Project No. MEN/NIST-89-6, sponsored by the Polish-American Maria Sklodowska-Curie Fund II and additionally supported by the Polish Ministry of National Education, Grant No. P/04/238.

Two of us (N.H.T. and J.F.) express grateful appreciation to the Institute of Physics of the Jagellonian University for its kind hospitality during their stay as visiting scientists.

- [1] P. D. Townsend and J. C. Kelly, Phys. Lett. 26A, 138 (1968).
- [2] P. W. Palmberg and T. N. Rhodin, J. Phys. Chem. Solids 29, 1917 (1968).
- [3] P. D. Townsend, R. Browning, D. J. Garlant, J. C. Kelly, A. Mahjoobi, A. J. Michael, and M. Saidoh, Radiat. Eff. 30, 55 (1976).
- [4] N. Itoh, Nucl. Instrum. Methods 132, 201 (1976).
- [5] M. Szymonski, Radiat. Eff. 52, 9 (1980).
- [6] P. D. Townsend, in Sputtering by Particle Bombardment, edited by R. Behrish (Springer-Verlag, Berlin, 1983), Vol. 2, p. 147.
- [7] R. F. Haglund, Jr., R. G. Albridge, D. W. Cherry, R. K. Cole, M. H. Mendenhall, W. C. B. Peatman, N. H. Tolk, D. Niles, G. Margaritondo, N. G. Stoffel, and E. Ta-glauer, Nucl. Instrum. Methods Phys. Res., Sect. B 13, 525 (1986).
- [8] R. T. Williams, Radiat. Eff. Defects Solids 109, 175 (1989).
- [9] A. Schmid, P. Braunlich, and P. K. Rol, Phys. Rev. Lett. 35, 1382 (1975).
- [10] I. Marklund and S. Andersson, Surf. Sci. 5, 197 (1966).
- [11] H. Overeijnder, M. Szymonski, A. Haring, and A. E. de Vries, Radiat. Eff. 36, 63 (1978); 38, 21 (1978).
- [12] Z. Postawa and M. Szymonski, Phys. Rev. B 39, 12950 (1989).
- [13] Z. Postawa, P. Czuba, A. Poradzisz, and M. Szymonski, Radiat. Eff. Defects Solids 109, 189 (1989).
- [14] M. Szymonski, A. Poradzisz, P. Czuba, J. Kolodziej, P. Piatkowski, and N. H. Tolk, Nucl. Instrum. Methods Phys. Res., Sect. B (to be published).
- [15] G. Comsa, R. David, and B. J. Schumacher, Rev. Sci. Instrum. 52, 789 (1981).
- [16] L. S. Cota Araiza and B. D. Powell, Surf. Sci. 51, 504 (1975).
- [17] C. T. Reimann, W. L. Brown, and R. E. Johnson, Phys. Rev. B 37, 1455 (1988).
- [18] V. N. Kadchenko and M. Elango, Phys. Status Solidi (a) 46, 315 (1978).
- [19] M. A. Elango, V. N. Kadchenko, A. M. E. Saar, and A. P. Zharakovski, J. Lumin. 14, 375 (1976).
- [20] T. A. Green, G. M. Loubriel, P. M. Richards, L. T. Hudson, P. M. Savundararaj, R. G. Albridge, A. V. Barnes, and N. H. Tolk, in *Desorption Induced by Electronic Transitions*, edited by G. Beta and P. Varga, Springer Series in Surface Science Vol. 19 (Springer-Verlag, Berlin, 1990), p. 281.
- [21] E. O. Kane, Phys. Rev. 159, 624 (1967).
- [22] S. P. Kowalczyk, F. R. McFeely, L. Ley, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 3573 (1974).