Positive-ion production by electron bombardment of alkali halides

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We present an experimental investigation of positive-ion production by electron bombardment of alkali halides. Measurements of the mass distributions and yields of both positive ions and neutral species indicate that the positive ions are formed by gas-phase ionization of ground-state neutral atoms and molecules. The gas-phase mechanism is shown to account for the ion mass distributions, the magnitude of the ion yields, and the dependence of ion yield on incident electron current.

The ejection of particles from solid surfaces by bombardment with electron or photon beams is of substantial current interest. The ejection mechanism generally involves excitation to electronic states that are repulsive, followed by the competing processes of nuclear motion and deexcitation.[1] For positive-ion desorption from ionic insulators such as alkali halides, there is an interesting class of transitions which lead to repulsive states.[2,3] In NaCl, for example, Cl^+ can be formed by core ionization of Cl^-, followed by Auger decay. The Cl^+ ion can be regarded as a localized two-hole state, which is expected to be sufficiently long lived for desorption to be possible.[4-7] The repulsive forces which drive the desorption process arise from the reversal of the Madelung potential. This mechanism, referred to as the Knotek-Feibelman mechanism, has been invoked in all previous studies of positive-ion desorption from alkali-halides.[8-14] However, there are a number of experimental observations which are difficult to explain by this mechanism. For example, the yield of positive alkali ions is generally greater than that of positive halogen ions, and the mass distributions often contain clusters[8,10] such as $NaCl^+$ and Na_2Cl^+. It is not understood how such clusters could be ejected from the surface by a reversal of the Madelung potential. Difficulties have also been suggested by theoretical investigations.[15] Trajectory calculations indicate that the Coulomb repulsion mechanism *fails* to expel positive ions from normal lattice sites of alkali halides. That is, even if reneutralization does *not* occur, positive ions are *not* expected to be expelled from the surface of a perfect crystal. Instead they become trapped, and the repulsive potential energy goes into defect formation and heat.[15] Thus there are substantial difficulties in understanding the origin of the experimentally observed positive ions. This is particularly disturbing because the alkali halides are regarded as comparatively simple and well-understood materials, and thus they should serve as useful prototypes for understanding the behavior of ionic insulators in general.

In this Rapid Communication, we present experimental results on positive-ion production by electron bombardment of alkali halides; the objective is to identify the ion production mechanism(s). In addition to the Knotek-Feibelman mechanism, other mechanisms must be considered. We will show that the experimental data indicate that the positive ions are formed by gas-phase ionization of neutral atoms and molecules.

The experimental apparatus is outlined below. A 200–2000-eV electron beam with currents of 0.1–10 μA was used to bombard NaCl crystals in ultrahigh vacuum (UHV) ($\approx 5 \times 10^{-10}$ Torr). The crystals were cleaved in air and then cleaned by pumping in UHV at room temperature overnight, followed by heating to the desired temperature.[16] The electron beam was incident at 45° from the normal to the (100) surface. The bombarded region had dimensions of $\approx 1 \times 2$ mm^2. Sample temperatures from 290 to 700 K were studied. Neutral species and positive ions were monitored with a quadrupole mass spectrometer (QMS). The axis of the QMS was along the surface normal, with direct line of sight to the bombarded region. For neutral detection, the ionizer of the QMS was turned on (with an electron energy of 50 eV), and for ion detection, the ionizer was turned off and biases were applied to collect the positive ions.

The surfaces of alkali halide crystals can be altered by electron bombardment, thus the experimental conditions should be chosen to minimize such effects. There is a very efficient mechanism for desorption of neutral halogen atoms due to a bulk defect-mediated process.[17] For NaCl bombarded by $\sim$1-keV electrons at $T \approx 570$ K, the yield of neutral Cl is $\sim$5 atoms per incident electron.[18] The desorption of alkali atoms is controlled by additional factors, such as F-center diffusion to the surface;[19] thus the alkali and halogen loss rates can differ. At low temperatures, the bombarded material is observed to develop an alkali-enriched stoichiometry.[18] However, for NaCl, it has been shown that at sufficiently high temperatures ($T > 570$ K), the material remains stoichiometric even for very large doses.[18] Thus there are two possible methods of minimizing effects due to radiation damage. (1) Use very small electron doses, $\ll 10^{13}$ e cm^{-2}. (2) Use temperatures which are high enough to prevent modification of the stoichiometry. Because of limitations in experimental sensitivity, the first method is impractical; thus we must resort to the second technique. As an additional measure, we restrict the bombardment time to a few minutes, and we make comparisons with results obtained by translating the sample to bring unexposed material under the beam.

The mass distribution of neutral atoms and molecules desorbed by bombardment of NaCl with 1-keV electron
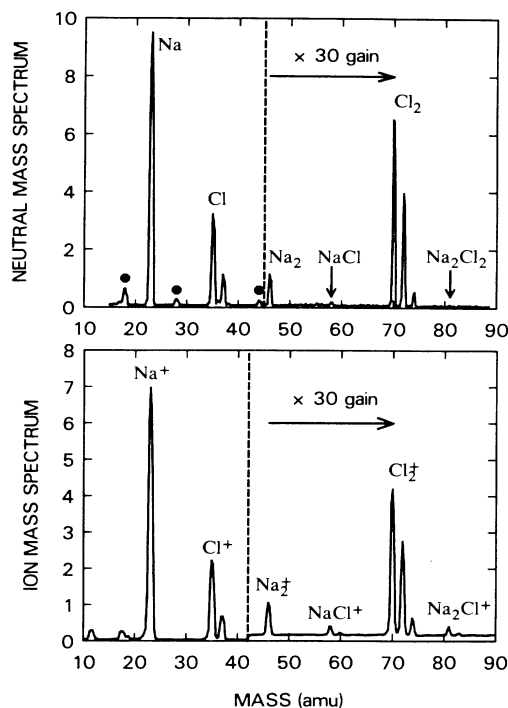
FIG. 1. The upper curve shows the mass distribution of neutral species for bombardment of NaCl by 1-keV electrons at 570 K and $I_e = 5$ μA. Peaks at mass 18, 28, and 44 are due to H_2O, CO, and CO_2 in the residual gas. The lower curve shows the mass distribution of positive ions under identical conditions, except $I_e = 1$ μA. The positive ions are labeled except for the peaks at m/q of 11.5, 17.5, and 18.5, which are due to Na^{2+} and Cl^{2+}.

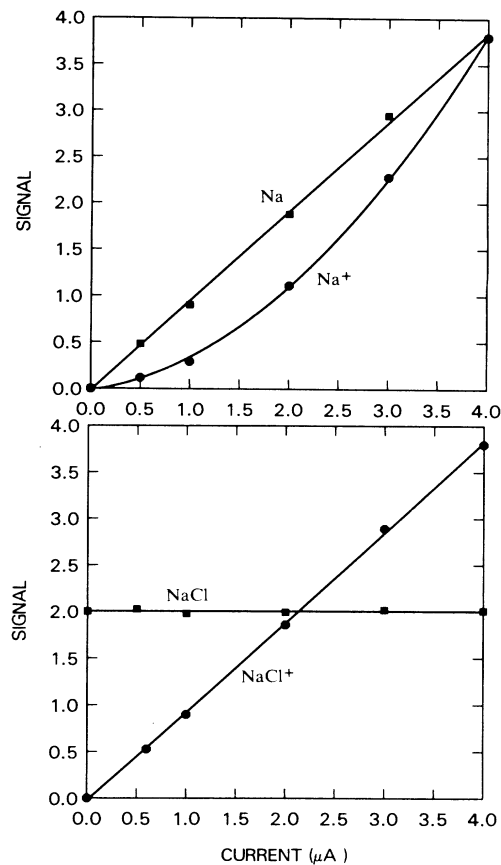

FIG. 2. The upper panel shows the Na neutral yield (squares) and Na^+ ion yield (dots) vs incident electron current at $T = 570$ K. The lower panel shows the NaCl neutral yield (squares) and $NaCl^+$ ion yield (dots) vs current at $T = 570$ K. The signal is given in arbitrary units.

(5 μA) at $T = 570$ K is shown in Fig. 1 (upper curve). The neutral species which are *stimulated* to desorb are Na, Cl, Na_2, and Cl_2. The yield of each of these neutrals was observed to be approximately *linear* in incident current over the experimentally available range, 0.1–10 μA, as shown in Fig. 2 (upper curve) for neutral Na. In addition to the neutrals listed above, mass peaks due to residual gas, i.e., H_2O, CO, and CO_2, were detected. The neutral molecules NaCl and Na_2Cl_2 were also present in the residual gas, and there were trace amounts of organic contaminants. The observed signals from NaCl and Na_2Cl_2 are consistent with the equilibrium vapor pressures[20] at 570 K, i.e., $\sim 1 \times 10^{-12}$ Torr for NaCl, and $\sim 3 \times 10^{-14}$ Torr for Na_2Cl_2. Electron ionization of NaCl primarily results in Na^+ and $NaCl^+$ ions, and ionization of Na_2Cl_2 yields Na_2Cl^+ ions.[21] The yields of NaCl and Na_2Cl_2 neutrals were observed to be independent of incident-electron current, as expected for molecules which thermally desorb from the surface. The neutral NaCl signal versus incident electron current is shown in Fig. 2 (lower curve).

The mass distribution of positive ions produced by bombardment of NaCl with 1-keV electrons (1 μA) at $T = 570$ K is shown in Fig. 1 (lower curve) The ions include Na^+, Na^{2+}, Cl^+, Cl^{2+}, Na_2^+, Cl_2^+, $NaCl^+$, and Na_2Cl^+. The ion mass distribution closely parallels the neutral mass distribution. The yields of Na^+, Na^{2+}, Cl^+,

Cl^{2+}, Na_2^+, and Cl_2^+ were each observed to be approximately proportional to the *square* of the incident electron current. The Na^+ signal versus current at $T = 570$ K is shown in Fig. 2 as an example. For these data, the ion yield is $\propto I_e^{1.80 \pm 0.05}$. Small deviations from purely quadratic behavior were observed, due to mild radiation damage of the sample. For larger temperatures ($T > 570$ K) such deviations were quite small, but for lower temperatures ($T < 470$ K) the yield versus current measurements are affected by the formation of an alkaki-enriched layer.[18] This results in a weaker dependence of ion yield on current, and a greater fraction of alkali ions in the mass distribution. These effects are minimized by limiting the exposure time, translating the sample to bring unexposed material under the beam, and operating at elevated temperatures. In contrast to the other ionic species, the yields of $NaCl^+$ and Na_2Cl^+ were observed to be approximately *linear* in incident electron current, as shown in Fig. 2 for $NaCl^+$ at $T = 570$ K.

Order-of-magnitude estimates of the ratio of ion to neutral flux were made, based on the ratio of the experimental signals combined with estimates of the ionization efficiency of the QMS. For incident electron currents of $\simeq 1$ μA, the estimated Na^+ ion to Na neutral flux is

$\sim 10^{-6}$. Taking into account the differences in incident electron current, this estimate is in good agreement with similar estimates by Friedenberg and Shapira[8] and Pian et al.[10]

The similarity of the neutral and ion mass distributions, and the dependence of neutral and ion yields on current suggest that the positive ions are produced by gas-phase ionization of neutral atoms and molecules. In particular, we suggest that Na^+, Cl^+, Na_2^+, and Cl_2^+ are formed by single ionization of the corresponding neutral species; Na^{2+} and Cl^{2+} are formed by double ionization of neutral Na and Cl atoms; and $NaCl^+$ and Na_2Cl^+ are formed by ionization of neutral NaCl and Na_2Cl_2 molecules. This accounts for the quadratic yield observed for Na^+, Na^{2+}, Cl^+, Cl^{2+}, Na_2^+, and Cl_2^+, and it accounts for the linear yield observed for $NaCl^+$ and Na_2Cl^+. Ions in the first group are produced by gas-phase ionization of neutrals which were *stimulated* by the electron beam to desorb from the surface, whereas ions in the second group are formed by ionization of neutrals which *thermally* desorb from the surface. Of course, a linear yield is also consistent with direct desorption of $NaCl^+$ and Na_2Cl^+. However, we will show that the gas-phase ionization mechanism accounts for the magnitude of the experimental signal.

The probability that a given neutral atom (or molecule) will be ionized is $\sim n_e \sigma_i v_e \tau$, where n_e is the electron density, σ_i is the ionization cross section, v_e is the electron velocity, and τ is the interaction time. An integration over the electron energy distribution is implied, including both the incident beam and secondary electrons. The interaction time is $\tau \simeq L/v$ where L is a path length and v is the velocity of the neutral atom (or molecule); L is approximately equal to the radius of the electron beam. Uncertainties in the secondary-electron yields and energy distributions prevent accurate quantitative predictions of the ionization probability. Nevertheless, rough estimates can be made using literature values for the ionization cross sections[22,23] and the secondary yield[24] and energy distribution,[25] by numerical integration of the ionization rate over electron energy. For Na atoms, ionization by secondary electrons is predicted to dominate over the primary beam by a factor of ~ 10. For a 1 μA incident beam in a 1×2 mm^2 area, the net probability that a Na atom will be ionized is estimated to be $\sim 5 \times 10^{-7}$. This agrees with the experimental estimate of $\sim 10^{-6}$ to within error (a factor of ~ 10). Similar estimates for Cl atoms, using the known ionization cross section,[23] indicate that $\sim \frac{1}{2}$ of the ionization is due to secondary electrons, with the remainder due to the primary beam. The probability that a Cl atom will be ionized is estimated to be $\sim 2 \times 10^{-7}$ for the conditions listed above. The other neutral species Na_2, Cl_2, NaCl, and Na_2Cl_2 are expected to be ionized to a similar extent.[26] Although there are uncertainties in these estimates, two important points are clear. (1) Gas-phase ionization accounts for the order of magnitude of the ion signals. (2) Secondary electrons can produce a substantial fraction of the ionization observed.

Qualitative trends in the ion mass distribution can be understood in terms of the gas-phase ionization mechanism. For example, consider the relative abundances of

Na^+ and Cl^+. The flux of neutral Na and Cl are equal (for our conditions), and the velocity distributions are primarily thermal.[27] The yield of Na^+ is somewhat larger than the yield of Cl^+ because Na is more efficiently ionized due to its low ionization potential and large cross section. Doubly charged ions are also observed. For 1-keV incident electrons, Na^{2+} and Cl^{2+} are detected with ratios of $I(Na^{2+})/I(Na^+) \sim 0.04$ and $I(Cl^{2+})/I(Cl^+)$ ~ 0.1 (uncorrected for QMS transmission). To within a factor of 2, these ratios agree with estimates using cross sections for double ionization of neutral atoms by the incident electrons.[28] The gas-phase mechanism also accounts for the presence of $NaCl^+$ and Na_2Cl^+. The neutral precursors are present in the gas phase, with densities sufficient to account for the ion yields observed. In addition, the experimental yields versus temperature are consistent with neutral production by thermal vaporization.[20]

Our results are consistent with the data on ion production by electron bombardment of alkali halides obtained by previous workers.[8,10] In some of the earlier studies, however, measurements of the ion yields as a function of current were affected by beam-induced changes in stoichiometry. The formation of an alkali-enriched region results in a weaker dependence of ion yield on incident current, and a greater fraction of alkali ions in the mass distribution. These effects can be understood in terms of neutral desorption from the modified layer, and ionization in the gas phase. However, such effects are dose dependent, and are not characteristic of desorption from stoichiometric alkali halides. We have reproduced these earlier observations and shown that for higher temperatures and lower doses, where the substrate remains stoichiometric, the dependences of ion and neutral yields on incident current clearly indicate a gas-phase ionization mechanism, as described above. Measurements of the ion energy distributions could, in principle, critically test the gas-phase mechanism because the energy distributions for the neutral species are known.[27] However, the published ion energy distributions[10] are inconclusive because of surface charging.[29] In addition to electron bombardment, gas-phase ionization is also likely to be important in experiments on positive-ion production by *photon*-stimulated desorption (PSD) of alkali halides.[9-13] Parks et al.[11] showed that the ion yields versus incident photon energy were very similar to the secondary electron yield, in qualitative agreement with a gas-phase ionization mechanism. However, it is important to realize that for a gas-phase ionization mechanism, the dependences of ion and secondary-electron yields may not be identical because the neutral yields, the secondary electron energy distributions, and the extent of surface charging may also depend on incident photon energy. Experimental estimates of the absolute ion yield in PSD experiments[30] agree with order-of-magnitude estimates of ion production by gas-phase ionization of neutral atoms. Thus, the available data on PSD are consistent with a gas-phase ionization mechanism. However, at the present time one cannot exclude the possibility of some additional contributions to the ion flux due, for example, to ion desorption from certain defect sites, or more complicated mechanisms involving short-range repulsive forces.[15]

In conclusion, we have presented experimental data which indicate that the positive ions produced by electron bombardment of alkali halides are formed by gas-phase ionization of neutral atoms and molecules. The gas-phase mechanism accounts for the ion mass distribution, the magnitude of the ion yields, and the dependences of ion yield on incident electron current. Recent experiments on alkali halides have shown that gas-phase electron-impact excitation of neutrals produces the electronically excited atoms observed.[31] Thus a unified picture of desorption from alkali halides is now obtained. Ground-state neutral atoms and molecules are stimulated to desorb via bulk defect mediated processes, with very large yields. Because of the large ground-state neutral yields, excited atoms and positive ions can be formed by gas-phase excitation and ionization of the ground-state species. Both secondary electrons and the incident electron beam contribute to the excitation and ionization processes.

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