

Scattering of alkali atoms and ions from alkali-halide surfaces: No evidence found for electronic surface states within the band gap of the insulator

A. Mertens, C. Auth, and H. Winter

Institut für Physik der Humboldt-Universität zu Berlin, Invalidenstrasse 110, D-10115 Berlin, Germany

A. G. Borisov

Laboratoire des Collisions Atomiques et Moléculaires, Université Paris-Sud, Bâtiment 351, F-91405 Orsay Cedex, France

(Received 21 October 1996)

Fast alkali atoms and ions are scattered with keV energies under grazing incidence from the surface of the alkali halides LiF(100), KCl(100), KI(100), and the scattered beams are analyzed with respect to their charge fractions. From our experiments we find no evidence for occupied or unoccupied electronic surface states within the band gap of the insulator. [S1050-2947(97)50602-0]

PACS number(s): 34.50.Dy

In a recent paper we reported on the observation of high fractions of negative ions after the scattering of fast oxygen ions under a grazing incidence from the surface of an insulator [in this case LiF(100)] [1]. Since the LiF target is electronically characterized by a very broad band gap [extending from binding energies of valence-band electrons ($E \leq -12$ eV) to vacuum energies] and negative ions have affinity energies up to some eV, our experimental results came as rather surprising. In understanding this process of the efficient formation of negative ions, it was evident that, in front of an insulator, electron loss from an affinity level was widely suppressed due to the electronic band gap of the target. However, the first step—the population of the affinity levels of the negative ions via capture of electrons from the target surface—could not simply be understood by available concepts of charge transfer between atoms and solid surfaces.

The relevance and broad interest of these studies come from the fundamental aspect of understanding an alternative type of atom-surface interaction and the potential applications of this conversion scheme in ion sources or neutral particle detection, where, e.g., this simple technique may provide detection of oxygen atoms in space [2].

In order to understand the formation of substantial negative-ion fractions in the scattering from LiF, we propose a model of the local capture of $2p$ valence electrons from a halogen site of the crystal in the topmost layer during the sequence of collisions with the insulator [1,3]. This model—based on the Demkov approach [4] for describing the capture probability—reproduces two essential features of the experiment: a sharp onset of the negative-ion fractions with increasing velocity and high ion conversion efficiencies. From this model we expect a full saturation of ion fractions for insulating materials with binding energies of valence electrons that are clearly less than for LiF. And indeed, in experiments on the formation of F^- ions in the scattering from a KI(100) surface we observed ion fractions up to $(98.5 \pm 1)\%$ [5].

A key issue of our model is the energy-level confluence in the collision with the solid. In a recent paper we discussed the mechanism that brings atomic and valence electron-energy levels in near resonance, in order to mediate electron

transfer from an alkali-halide site to an atom [6]. With respect to the discussions here it is sufficient to approximate the results of *ab initio* calculations by a simple analytical expression for the energy defect in the collision ($R \gg a$; a is the lattice constant)

$$\Delta E(R) \approx \Delta E_\infty - (1-q)/R + \Delta E_{\text{im}}, \quad (1)$$

where ΔE_∞ is the energy difference between the unperturbed affinity level of the atom and the valence-band level of the crystal, and R is the distance between a halogen site and the atomic core of charge q . ΔE_{im} is the energy shift due to the image charge interaction, which is smaller than about 1 eV for the conditions of the scattering process with the insulator surface.

In order to obtain a sufficient probability for charge exchange, ΔE has to be reduced from the generally large ΔE_∞ by an appreciable amount. This is achieved for the formation of a negative ion ($q=0$) by the direct Coulomb interaction of the electron hole at the halogen site with the electron forming the affinity level. On the other hand, for the formation of a neutral atom ($q=1$) this direct interaction is cancelled, and the energy shift ΔE is even slightly increased from ΔE_∞ by image charge interactions. In Fig. 1 we give a very simplified sketch of the position of the affinity level of a negative ion and of the ground-term level of an (neutral) alkali atom as a function of the distance from the surface of an insulator. The clearly different behavior of the two levels in front of the surface is of crucial importance to the discussion of the work presented here.

An alternative interpretation of our experiments on negative-ion formation in front of the surface of an insulator is based on the assumption of the presence of occupied electronic surface states with binding energies of about -4 eV. The existence of surface states within the band gap of LiF has been speculated on already in the interpretation of electron stimulated desorption experiments by Wurz *et al.* [7]. Those states (indicated by a hatched area in the energy diagram in Fig. 1) would result in an efficient population of

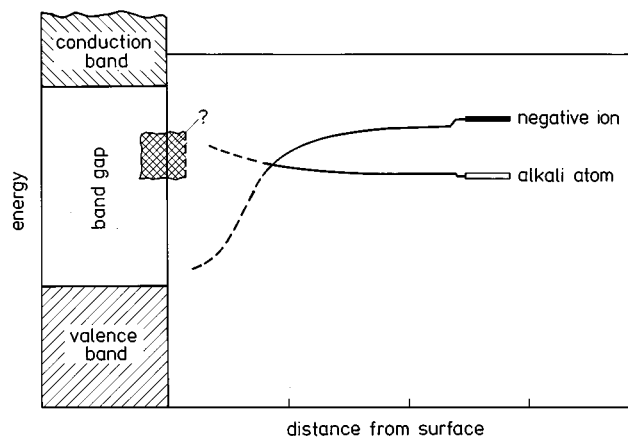


FIG. 1. Sketch of the electronic energies of a negative ion and an alkali atom in front of an alkali-halide surface. The crosshatched area in the band gap illustrates surface states.

affinity levels via resonant one-electron transfer and could explain the experiments in a more conventional manner.

An important test of this alternative interpretation can be provided by studies on charge exchange of alkali atoms under the same conditions as for the experiments on negative-ion formation. Since ground terms of alkali atoms have binding energies of typically 4–5 eV (slightly shifted by ΔE_{im}), one would expect for occupied surface states substantial fractions of neutralized atoms in the scattered beams. In the experiments reported here we have performed detailed tests on this problem [8].

Fast singly charged alkali ions and also neutral Na atoms in the keV domain with velocities ranging from $v \approx 0.1$ a.u. to about 0.4 a.u. are scattered under grazing angles of incidence of typically $\Phi_{in} \approx 1^\circ$ from a LiF(100), a KCl(100), and a KI(100) surface, respectively. All these crystal surfaces are prepared by cleaving in air and mechanical polishing before mounting on a precision manipulator and bringing into a UHV-scattering chamber. *In situ* preparation of the targets is performed by grazing sputtering with 25-keV Ar^+ ions and simultaneous and subsequent annealing of the samples. The target is generally kept on a temperature of typically 200 °C–300 °C, where alkali halides show sufficient conductivity in order to avoid a macroscopic charging up that affects ionized beams. The charge fractions of the scattered beams are analyzed with a pair of electric-field plates, and the fast particles are detected with a channeltron, where a thin carbon foil covering the entrance aperture of the detector provides an equal response for projectiles in different charge states. In the analysis of the data, image charge effects on the trajectories of charged projectiles have to be taken into account.

In Fig. 2 we show the neutral fractions as a function of the projectile velocity for Li^+ , Na^+ , and K^+ ions scattered from LiF(100). We observe neutral fractions of about 5% at lower velocities and an increase with velocities $v > 0.3$ a.u., i.e., the projectile ions leave the surface predominantly as ions. In Fig. 3 we show similar data for the scattering of Na^+ ions from LiF(100), KCl(100), and KI(100), respectively. Here it is even more evident than from the data for LiF(100) in Fig. 2 that the neutral fractions are very small at low velocities. From these ion-scattering experiments we can

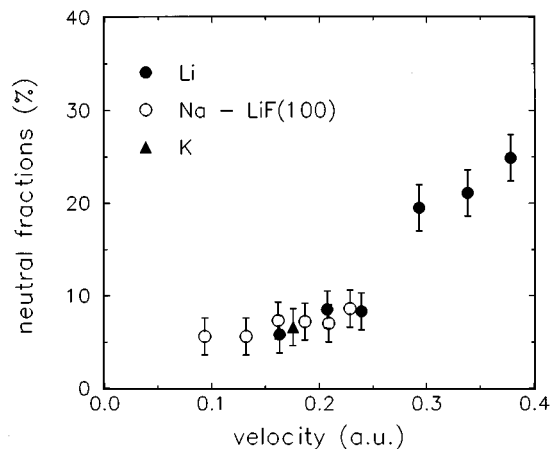


FIG. 2. Neutral fractions of Li^+ , Na^+ , and K^+ ions scattered from a LiF(100) surface under $\Phi_{in} \approx 1^\circ$ as a function of projectile velocity.

conclude that electron capture has to be negligible here, because either electron-capture rates are small or the interaction is dominated by ionization processes.

In order to obtain more specific information in this respect, we also performed experiments with neutral incident projectiles produced in a Na-vapor target mounted in the beamline between the ion source and the UHV chamber. The data obtained for the scattering of Na^+ ions as well as Na atoms from KCl(100) are displayed in Fig. 4. Within the experimental uncertainties we observe for $v > 0.15$ comparable small neutral fractions in both cases. However, at smaller velocities a pronounced effect of the incident charge state is evident. For the lowest velocities of our studies $v \approx 0.07$ a.u. (projectiles with lower velocities could not be handled with our setup), we find that the charge state of the incident projectile tends to be preserved, i.e., no charge transfer seems to be effective.

In summarizing our experiments, we can conclude that the small fractions of neutral atoms observed with ionized projectiles are not consistent with a substantial occupation of surface states within the band gap of the insulator. Such an

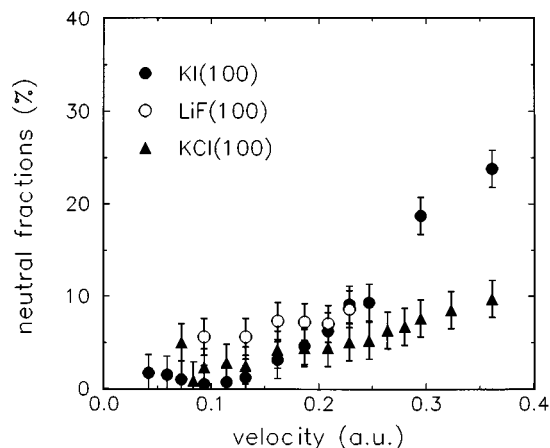


FIG. 3. Neutral fractions of Na^+ ions scattered from a LiF(100), KCl(100), and KI(100) surface, respectively, under $\Phi_{in} \approx 1^\circ$ as a function of projectile velocity.

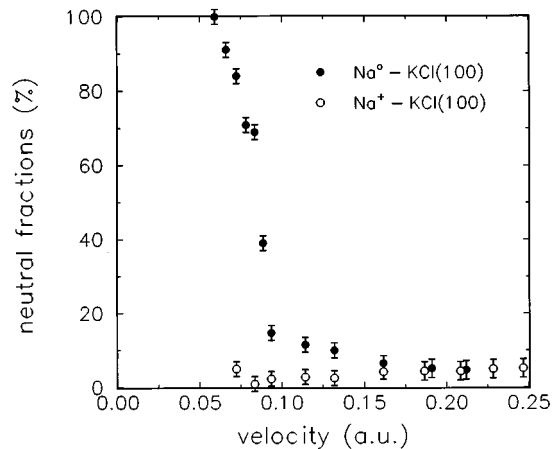


FIG. 4. Neutral fractions of Na atoms (full circles) and Na⁺ ions (open circles) scattered from a KCl(100) surface under $\Phi_{in} \approx 1^\circ$ as a function of projectile velocity.

occupation, however, has to be assumed, in order to interpret the high negative-ion fractions in an alternative manner. From the data with the neutral projectiles we can state, in addition, that charge transfer between alkali atoms and alkali halides is obviously not affected by surface states at all.

We attribute the pronounced dependence observed for the data displayed in Fig. 4 to kinematic effects, which bring the atomic levels into resonance with the conduction band of the solid or with vacuum states. A rough estimate on the kinematic threshold for this ionization process can be obtained from a frame transformation (Galilei transformation; for details see [3]) $v_{\parallel} > -(E_{atom}^* - E_{CB})/|\vec{g}_{\parallel}|$, where

E_{atom}^* is the shifted atomic binding energy, E_{CB} the energy of the bottom of the conduction band, and \vec{g}_{\parallel} a two-dimensional reciprocal vector of the halide lattice. From $E_{atom}^* \approx -4$ eV and $E_{CB} \approx -2$ eV, $g_{\parallel} \approx 0.75$ a.u. for KCl(100), we get $v_{\parallel} > 0.1$ a.u., which is of the correct size of the experimental observations. It is clear that higher-order and other processes will contribute, but a more detailed discussion on this aspect is beyond the scope of this work.

Finally, we note that the low fractions of neutral atoms in the scattered beams indicate also that the densities of defects in the surface plane are obviously too small to affect the charge-transfer processes. In a test, where we generated surface defects and alkali-metal enrichment via low-energy electron bombardment [9], we observed clear effects on the charge fractions in the scattered beams.

Aside from these studies with alkali atoms we observed for the scattering of noble-gas ions from LiF(100) a suppression of Auger neutralization for He⁺ and, in particular, Ne⁺ ions [10]. This suppression is also not consistent with the presence of surface states within the band gap. Further evidence for our conclusions comes from recent deexcitation studies of thermal metastable He beams by Kempter *et al.* [11]. Similar to charge exchange in grazing surface scattering, this method is also extremely sensitive to the region above the topmost surface layer and gives no indication of surface states in the band gap of LiF.

This work is supported by the Deutsche Forschungsgemeinschaft (DFG) under Contract No. Wi1336/1-1. We thank J. Sölle for the preparation of the targets used in the studies reported here.

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