Complete negative-ion conversion of halogen atoms and positive ions in surface scattering from KI(100)

H. Winter, A. Mertens, and C. Auth
Institut für Physik der Humboldt Universität zu Berlin, Invalidenstrasse 110, D-10115 Berlin, Germany

A. G. Borisov
Laboratoire des Collisions Atomiques et Moléculaires, Université de Paris–Sud, Bâtiment 351, 91405 Orsay Cedex, France
(Received 1 February 1996)

Fast positive ions and atoms with energies ranging from some 100 eV to 100 keV are scattered under a grazing angle of incidence from a clean and flat (100) surface of a monocrystalline KI sample. We observe for halogen projectiles an almost complete negative-ion conversion, i.e., negative-ion fractions up to 98.5%. Our data show a characteristic dependence on the projectile velocity, which provides important additional information on the mechanisms of formation of negative ions in the scattering from the surface of an insulator. [S1050-2947(96)02208-1]

PACS number(s): 79.20.Rf, 34.70.+e

In a recent paper published in this journal [1] we reported on the observation of high fractions of negative oxygen ions in the grazing scattering of fast oxygen atoms and positive ions from the surface of an insulator, in those studies a LiF(100) surface. Based on concepts of charge exchange developed for the interaction between atoms or ions and metal surfaces [2], this finding was at first glance very surprising, since the insulator LiF is characterized by a broadband gap that extends from the binding energies of valence-band electrons ($|E_v|>12$ eV) to vacuum energies [3,4]; i.e., over a broad energy range no electrons of the solid are available for electronic transitions to the affinity levels of negative ions.

Despite this electronic structure, we observed under specific kinematic conditions fractions of O^- ions of up to 60% [1] and up to 80% of F^- ions [5] for the scattering from a LiF(100) surface. For a first interpretation of our data we proposed a model where the population of affinity levels of negative ions proceeds via local capture in a binary type of collision between a negative ion bound in the lattice and the neutral projectile. The subsequent pronounced suppression of electron loss due to the wide band gap of an insulator will then result in high negative-ion fractions for the scattered projectiles.

The issue of this paper is the description of experiments where we have used instead of LiF(100) a KI(100) surface. The electronic structures of the valence and conduction bands of the two insulators are clearly different (see below) [3,4,6], so that we expect from these studies important additional information on charge-exchange phenomena in the still relatively unexplored field of atom-insulator interactions. Of particular interest here is a test of our predictions based on a simple model for the formation of negative ions in grazing scattering from insulators [1,5]. From this model, we expect for an insulator with lower binding energies of valence electrons than for LiF a characteristic shift of the dependence of negative-ion fractions on projectile velocity, and, in particular, an almost complete conversion for halogen projectiles to negative ions (high affinities).

The work reported here is in agreement with these concepts and has two important consequences: (1) it supports our simple model of charge exchange and can be considered as a profound basis for detailed theoretical treatments of charge exchange between atoms and insulators, and (2) it opens the way for new concepts in negative-ion sources, where instead of scattering, sputtering, etc. from low-work-function metal surfaces [8,9] the scattering from surfaces of insulators will be applied.

In brief, F^+ ions and fluorine atoms with energies ranging from 200 eV to about 100 keV are scattered from a clean and flat KI(100) surface under a glancing angle of incidence between 1° and 2°. In order to avoid a macroscopic charging up of the insulator during the bombardment with the fast beams, the target was kept at a temperature between 210 and 250 °C. In detailed studies on the deflection of charged beams as a function of target temperature and current density of the incoming beams, we found negligible effects above 210 °C and well-defined angular distributions of the scattered beams [10]. The experiments were performed at a pressure in the upper 10^{-11} mbar regime. The scattered particles are detected about 60 cm behind the target by means of a channeltron with a 0.5 mm aperture. A pair of electric-field plates between target and detector allows us to analyze the charge fractions of the scattered beams.

In Fig. 1 we show negative-ion fractions for fluorine projectiles scattered from a LiF(100) (open circles) and a KI(100) surface (full circles). The data for a LiF surface have been presented by us recently [5] and are characterized by a peaked structure as a function of projectile velocity v with a maximum of about 80% at $v\approx 0.2$ which corresponds to a projectile energy of about 20 keV.

The full circles in Fig. 1 represent our data for the scattering of F^+ ions and fluorine atoms from KI. These measurements reveal a clear shift of the peaked structure of the negative-ion fractions toward lower velocities in comparison to the data obtained for a LiF surface. For velocities $v<0.2$ a.u. we observe a pronounced enhancement of the negative fractions up to 98.5% with a broad maximum around $v=0.1$ a.u. (projectile energies of some keV). The low intensity of the projectile beams and the low response of the detector did not allow us to perform measurements below 200 eV.

The important aspects of our studies performed with the KI target are the following.

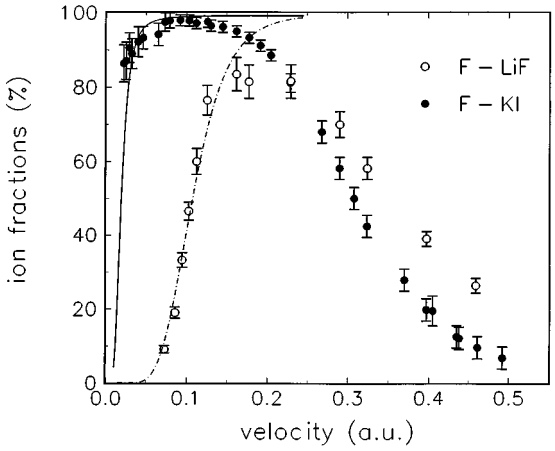

FIG. 1. Negative-ion fractions as a function of projectile velocity for fluorine atoms or positive ions scattered from a LiF(100) surface (open circles) and a KI(100) surface (full circles). The data obtained with LiF(100) stem from Ref. [5]. The glancing angle of incidence is about 1°, and the targets are kept on a temperature of about 300 °C (LiF) and 210–250 °C (KI) in order to avoid a macroscopic charging up of the target. The solid and dashed-dotted lines represent a description of the data by the model outlined in the text.

(i) Negative-ion conversion for the scattering of fast ions from an insulator is shown to be highly efficient. Similar large negative-ion fractions are observed in our measurements also for Br, S, and Cl. Since the yields for reflected projectiles are high for grazing surface scattering, overall yields of negative ions larger than 50% should be achieved via this new scheme. In this way, formation of some negative ions at the surface of an insulator is at least as efficient as established methods in the field of negative-ion sources and conversion [9].

(ii) The data presented here provide important additional information on the mechanisms of formation of negative ions in the interaction of atoms with insulators. A simple model for a first interpretation of the data is presented below.

In Figs. 2 and 3 we have sketched essential features of our model. In the scattering of fast atoms or ions from a solid surface under grazing incidence the trajectories of projectiles are described by concepts of surface channeling, i.e., the scattering process with the surface proceeds in a major number of collision events with surface atoms under relatively large impact parameters. The distance of closest approach to the topmost layer of surface atoms deduced from screened interatomic potentials amounts to typically 2–3 a.u. here.

For alkali halides electrons with the lowest binding energies forming the valence band are well localized at the sites

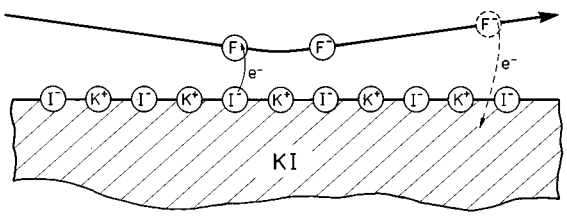

FIG. 2. Sketch of a trajectory of fluorine atoms scattered from a KI monocrystalline surface. Electron capture proceeds from I^- bound to lattice sites of the alkali halide crystal.

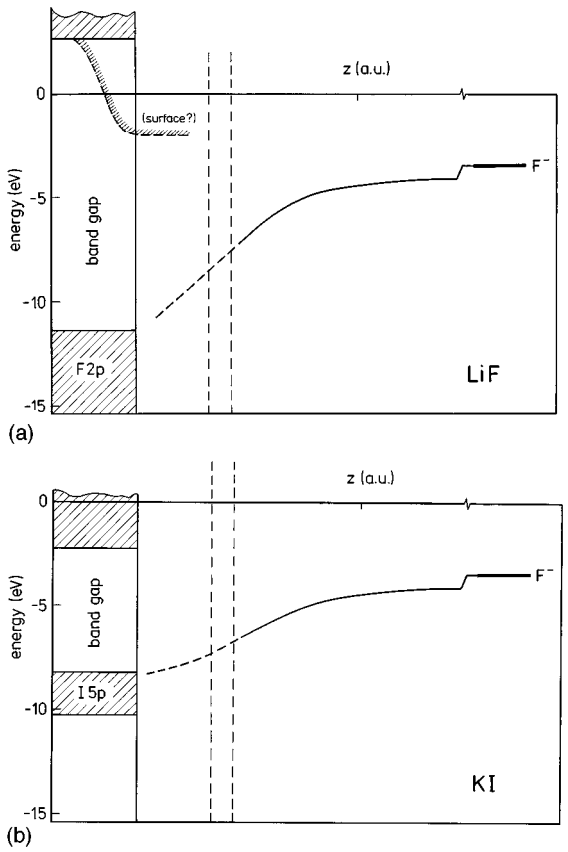

FIG. 3. (a) Energy diagram for the affinity level of a F^- ion in front of a LiF surface. The vertical dashed lines indicate a typical range of distances of closest approach of the projectiles to the surface. (b) Energy diagram for the affinity level of a F^- ion in front of a KI surface.

of the negatively charged halogen atoms (see Figs. 2 and 3). Since the electron affinity of free F^- ions is $E_{F^-} = -3.40$ eV, these electrons are expected to dominate electron capture completely. Then electron transfer to the projectile will take place in one local capture event in a sequence of spatially well separated collisions with lattice atoms as sketched in Fig. 2.

We have estimated the electron-capture probabilities P for a single binary collision of the projectiles with an atom bound at a lattice site [1,5] with the ''Demkov model'' [11]. Here we make use of a simple analytic expression that incorporates the effect of a frame transformation due to the fast projectile motion (''translational factor'') with a relative velocity v of the collision partners [12,13]

$$P(v,\Delta E) = \tfrac{1}{2}\,\mathrm{sech}^2\left(\frac{\pi}{2}\,\frac{\Delta E + v^2/2}{\gamma v}\right) \qquad (1)$$

with $\gamma = (\sqrt{2E_t} + \sqrt{2E_p})/2$ where E_t and E_p are the ionization potentials of target and projectile. The energy defect ΔE in the collision is the energy difference of the initial target and final projectile states. ΔE shows a pronounced dependence on distance (impact parameter) and can be estimated here from the Madelung potential for an electron originally bound at the site of a negative ion embedded in the ionic crystal.

In summarizing our model, we assume a summation of capture probabilities over the complete trajectory of scattered projectiles and obtain the total capture probability via the iteration $P_{i+1}=(1-P_i)P(v,\Delta E)+P_i$ with $P_1=P(v,\Delta E)$. The second essential feature for the large negative-ion fractions observed with surfaces of insulators is the broad electronic band gap. This gap strongly suppresses the ''ionization'' or detachment of negative ions, since no open electronic states of the solid are in resonance with the affinity levels. Then we assume that an electron loss can basically be induced only by kinematic effects that bring the affinity levels into resonance with the conduction band. Those processes, however, are beyond the scope of the present model.

The solid and dashed-dotted lines in Fig. 1 represent a description of the data by our model obtained with the KI and LiF surfaces, respectively. Instead of a calculation of the capture probabilities P via Eq. (1) with a complex variation of ΔE over a complete trajectory, we consider a number i of collisions, where ΔE is estimated for the region around the turning point of the trajectory. In this region we will have the smallest ΔE and consequently the largest capture probabilities for small velocities. The parameters chosen to reproduce the data are $\Delta E=0.5$ eV and $i=10$ for KI and $\Delta E=3.5$ eV and $i=20$ for LiF [14]. We have calculated a reduction of the Madelung potential from a lattice site to a position 2.5 a.u. on top of it (about the distance of closest approach of the projectiles) that is close to our choice of ΔE. The clearly different ΔE and binding energies of valence electrons are primarily due to the different lattice constants of the two insulators: 3.81 a.u. for LiF and 6.68 a.u. for KI [15]. This difference in the constants can also explain the different number of collisions, i, in our description by simple geometrical arguments.

The effect of the different ΔE on the F^- fractions is striking as shown in Fig. 1. For smaller ΔE the dependence of the negative-ion fractions on projectile velocity is shifted toward smaller v with a clear enhancement of the peak fractions. In fact, the small ΔE observed by us for KI (0.5 eV) results in low velocities needed to compensate the energy defect in the collision and practically in a saturation of the F^- fractions. This saturation is reached at comparatively low velocities where kinematically induced electron loss processes seem to play a negligible role. This situation is different for the scattering from a LiF target, where a clearly larger ΔE (3.5 eV) leads to the onset of capture probabilities at higher velocities v. Since at those v kinematic loss processes seem to be effective, the F^- fractions do not saturate.

In conclusion, from studies on the formation of negative ions via the scattering from surfaces of insulators we obtain significant support for the interpretation of the charge-exchange mechanisms and a different concept of negative-ion conversion. By a direct comparison of F^- formation via scattering from a LiF and a KI surface the following interaction mechanisms can be deduced: (1) capture of electrons in local processes from lattice atoms, and (2) suppression of subsequent electron loss due to the band gap of the insulator. The decrease of the negative-ion fractions with increasing velocity is not described by our simple model. In a recent paper [5] we have ascribed this decrease to a kinematically induced resonance with conduction-band states; however, a detailed theoretical study on this aspect has not been performed so far.

Finally we note that we observed for protons and hydrogen atoms scattered from a KI surface very low H^- fractions of some 10^{-3} (whereas 5% for LiF). This result can be understood by the position of the KI conduction band ($E_c \geqslant -2$ eV) relative to the H^- affinity level ($E_B=-1.5$ eV), so that a reionization of H^--ions on the receding trajectory is very likely. As a consequence of the findings in our scattering experiments with insulators we conclude that an insulator with a binding energy of valence electrons of some eV and a band gap extending to vacuum energies is an ideal tool for the highly efficient conversion to any type of negative-ion species.

We thank J. Sölle for the preparation of the KI sample, T. Hecht for his assistance in the preparation of the experiments, and Dr. P. Varga (Wien) for helpful discussions. This work is supported by the Deutsche Forschungsgemeinschaft (DFG) under Contract No. Wi 1336/1-1. One of us (A.G.B.) acknowledges generous support from the Alexander von Humboldt Foundation.

[1] C. Auth, A. G. Borisov, and H. Winter, Phys. Rev. Lett. **75**, 2292 (1995).

[2] J. Los and J. J. C. Geerlings, Phys. Rep. **190**, 133 (1990).

[3] M. Piancentini and J. Anderegg, Solid State Commun. **38**, 191 (1981).

[4] D. A. Lapiano-Smith, E. A. Eklund, and F. J. Himpsel, Appl. Phys. Lett. **59**, 2174 (1991).

[5] H. Winter, C. Auth, and A. G. Borisov, Nucl. Instrum. Methods Phys. Res. Sect. A (to be published).

[6] W. H. Strehlow and E. L. Cook, J. Phys. Chem. Ref. Data **2**, 163 (1973).

[7] W. P. O'Brien, Jr., and J. P. Hernandez, Phys. Rev. B **9**, 3560 (1974).

[8] C. F. A. van Os, C. Lequijt, A. W. Kleyn, and J. Los, Fusion Technol. **1**, 598 (1988).

[9] *Handbook on Ion Sources*, edited by B. Wolf (CRC Press, Boca Raton, 1995), p. 289.

[10] A. Mertens, C. Auth, and H. Winter (unpublished).

[11] V. N. Ostrowski, in *Proceedings of the XVII International Conference on the Physics of Electronic and Atomic Collisions, Brisbane, 1991*, edited by W. R. MacGillivray *et al.* (Adam Hilger, Bristol, 1992), p. 435.

[12] E. W. McDaniel, J. B. A. Mitchell, and M. E. Rudd, *Atomic Collisions, Heavy Particle Projectiles* (Wiley, New York, 1993), p. 381.

[13] S. J. Pfeifer and J. D. Garcia, Phys. Rev. A **23**, 2267 (1981).

[14] Due to the inclusion of the frame transformation in Eq. (1) the parameters for LiF are different from those reported in Ref. [5].

[15] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986), p. 71.