Threshold in the Stopping of Slow Protons Scattered from the Surface of a Wide-Band-Gap Insulator

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We have measured the energy loss of slow protons scattered with energies from 300 eV to 28 keV from a clean and flat LiF(001) surface under a grazing angle of incidence. Our data reveal a threshold behavior of stopping at low projectile energies. The effect on the outgoing charge state indicates that electron capture and loss are dominant mechanisms for the stopping of slow protons interacting with a wide-band-gap insulator. Our data allow one also to deduce information on charge transfer in front of the surface of an insulator. [S0031-9007(98)07770-9]

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Stopping of atomic projectiles in matter is an important subject in fundamental and, in particular, applied research. An interesting problem in this field, that has been paid increasing attention to recently, is the (electronic) stopping of light ions with low velocities ($v < v_0$, v_0 is the Bohr velocity) in insulators. From simple intuitive arguments one would expect that the band gap of insulators will suppress electronic excitation phenomena by the projectiles. Then stopping of slow light ions in insulators should clearly differ from stopping in metals, where excitations of conduction electrons close to the Fermi energy play a decisive role [1]. Similar as for the stopping by noble gas atoms, where substantial electronic excitation energies give rise to threshold effects for projectile stopping [2], one should observe similar effects also with insulator targets.

In a recent paper Eder *et al.* [3] reported on the energy loss of slow protons traversing thin foils made from large-band-gap insulators. No threshold effects for projectile stopping in insulators (Al_2O_3, SiO_2, or LiF) are observed down to energies of about 2 keV. Instead, the stopping power shows the linear dependence $-dE/dx \sim v$. The authors interpret their data in terms of excitations owing to a local reduction of the band gap of the target in collisions of the projectiles with target atoms.

Motivated by these studies, we investigated the stopping of slow protons by an insulator for projectile energies down to 300 eV. We observe a threshold behavior in the stopping by the wide-band-gap insulator LiF ($E_g \approx 14$ eV). Since defined energy losses of atomic projectiles at those low energies with solids can hardly be measured via transmission through solid matter, we have scattered the incident ions (protons) from the surface of a crystal target under a grazing angle of incidence. Under this condition the projectiles do not penetrate the solid but are reflected specularly from the surface with a distance of closest approach of typically 2–3 a.u. The overall energy loss of scattered projectiles is generally much lower than the initial energy (typically some percent). Data on projectile stopping obtained via bulk transmission or surface scattering can be compared to some extent, since (1) at low velocities small impact parameters resulting in larger angular deflections play a negligible role, and (2) the electronic structure of the LiF target is practically identical in the bulk and at the surface (no surface states [4–6], reduction of band gap by a lowering of the Madelung potential at the surface is small [7]).

In the experiments we have scattered protons with energies ranging from 300 eV to 28 keV from a LiF(001) surface under a grazing angle of incidence $\Phi_{in} \approx 0.6°$ to 2°. The clean and flat target is kept at a base pressure of 10^{-10} mbar. In order to avoid a macroscopic charging-up by incident ions, the target is kept at $T \approx 300\,°C$. The energy loss of incident protons is measured by (1) an electrostatic energy analyzer and (2) a time-of-flight (TOF) setup with an overall energy resolution of typically 10 to 50 eV.

In grazing scattering from surfaces one has well-defined trajectories in the regime of (planar) channeling [8]. Then, in contrast to transmission experiments, projectiles are less affected by multiple scattering, resulting in a limited range, a considerable angular spread, and nuclear energy loss. An analytical expression for trajectories can be derived from a collective interatomic scattering potential approximated by the exponential dependence on the distance z from the surface plane $U(z) = a_1 \exp(-a_2 z)$ [9]. For the interaction potential of hydrogen in front of a LiF(001) lattice we deduce from a fit to a potential based on the sophisticated Ziegler-Biersack-Littmark screening [10]: $a_1 = 13.85$ eV and $a_2 = 0.88$ a.u.

A position dependent stopping power $S(z) = -dE/dx$ can be derived from measured energy losses ΔE [9] where

one approximates $S(z)$ at a fixed energy E by

$$S(z) = S_0(E)\exp(-\alpha z) = S_0(E)\exp\left[-\frac{1}{2}a_2(1+\beta)z\right], \quad (1)$$

with α and β as parameters. Integration over the trajectory for a given angle of incidence leads to the energy loss [11] (Γ represents the "gamma function")

$$\Delta E = \frac{4}{a_2}S_0(E)\left(\frac{E}{a_1}\right)^{(1+\beta)/2}\frac{\sqrt{\pi}}{2}\frac{\Gamma[(1+\beta)/2]}{\Gamma(1+\beta/2)}\Phi_{\text{in}}^{\beta}. \quad (2)$$

The free parameters $S_0(E)$ and β are obtained from experimental studies on the dependence of ΔE on Φ_{in} at a fixed energy E. Here we observe a poor variation of ΔE with angle, i.e., $\beta \approx 0$. From, e.g., $\Delta E = 350$ eV at 6 keV we deduce from Eq. (2) $S_0(6\text{ keV}) \approx 2.5$ eV/a.u. [12].

For a variable energy Eq. (2) leads with $\beta = 0$ to

$$\Delta E = \frac{2\pi}{a_2 a_1^{1/2}}S_0(E)E^{1/2}. \quad (3)$$

In Fig. 1 we present data for the (most probable) energy loss as a function of the projectile energy E at $\Phi_{\text{in}} = 0.6°$. ΔE shows a linear dependence with energy (dashed line) below about 15 keV ($v \leq 0.8$ a.u.). Note the deviation below some keV (see below). According to Eq. (3) such a linear behavior is observed for $S_0(E) \sim E^{1/2}$, the well-established linear v-dependence of stopping power or stopping cross section for metallic and atomic targets at low projectile velocities ($v \leq v_0$) [13,14]. This finding is in accord with the transmission experiments through thin foils by Eder *et al.* [3]. An extrapolation of our stopping powers to the bulk region yields $S_0(E)$ of the same size as presented in Ref. [3] and as obtained from the TRIM code [10]. The linear v-dependence was observed in the previous studies [3] down to about $E = 2.5$ keV for a LiF target. A threshold behavior, presumably present at lower velocities (energies), could not be cleared up.

For grazing scattering of protons from LiF at low energies ($E < 2$ keV) the neutral charge fraction dominates, whereas the H^- fractions amount to some percent and the H^+ fractions to less than 10^{-3}. As a consequence, only projectiles emerging as negative ions from the surface could be investigated with the electrostatic analyzer, and TOF techniques are needed to study the energy loss of projectiles emerging as neutral atoms. In our setup we used a drift length of about 1 m.

In Fig. 2 we show data for $E \leq 2$ keV and $\Phi_{\text{in}} = 0.8°$. Open circles represent data for emerging neutral atoms, full circles data for emerging H^- ions. Neutral atoms and H^- ions are separated in these TOF measurements by a pair of electric field plates. The energy losses for both charge states coincide and show a linear dependence with energy down to energies of about 1.3–1.4 keV,

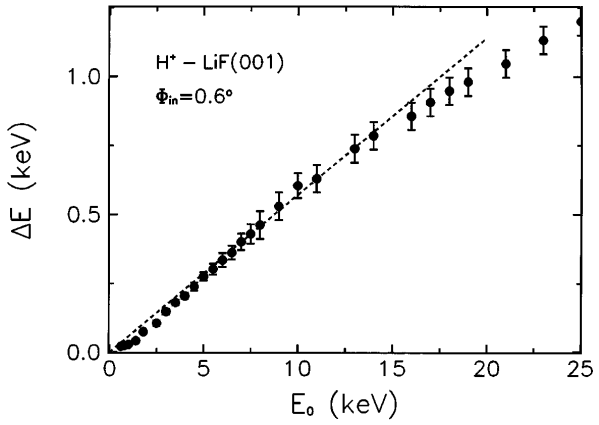


FIG. 1. Energy loss as a function of projectile energy for protons scattered under $\Phi_{\text{in}} = 0.6°$ and specular reflection from LiF(001). After scattering H^- ions are analyzed with the electrostatic analyzer. The dashed line represents a linear dependence with energy.

however, clearly below the linear E-dependence revealed in Fig. 1 (dashed line). Then the energy losses split and reach constant values of about (3 ± 1.5) eV for neutrals and about (18 ± 3) eV for H^- ions. These data give evidence for a threshold behavior for entering a linear v-dependence of stopping power of slow protons in an insulator.

For a detailed discussion on the data we display in Fig. 3 TOF spectra for incident protons with $E = 600$ eV. The spectra are transformed to energies and fitted by Gaussian line shapes. The overall energy

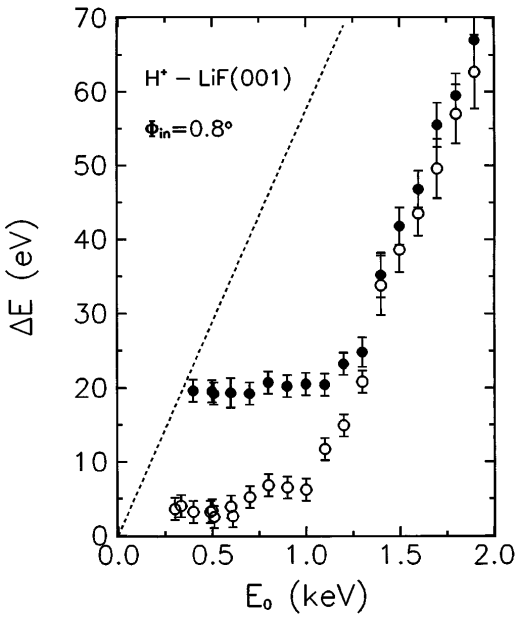


FIG. 2. Energy loss as function of projectile energy for protons scattered under $\Phi_{\text{in}} = 0.8°$ from LiF(001). The data are recorded with the TOF setup for emerging H^0 atoms (open circles) and H^- ions (full circles). The dashed line represents the linear dependence with energy shown in Fig. 1.

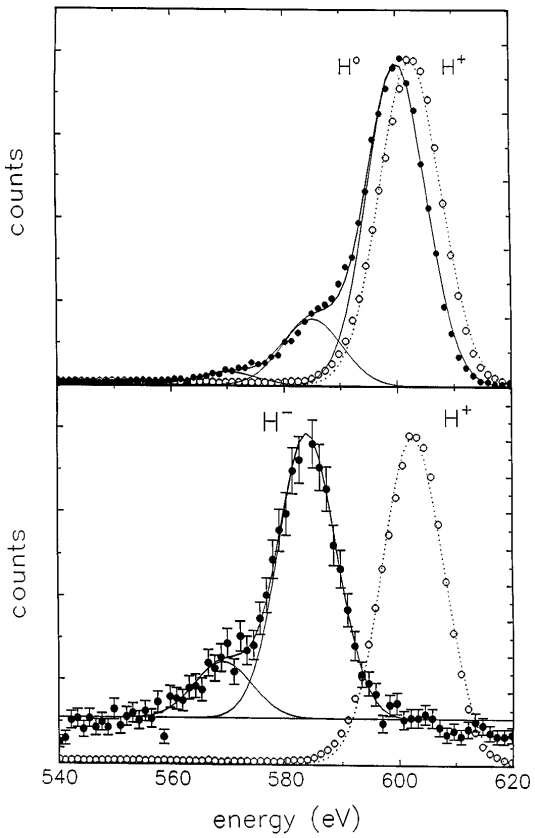


FIG. 3. Upper panel: TOF spectrum (transformed to energy) for 600 eV protons scattered under $\Phi_{in} = 0.8°$ from LiF(001). Open circles: incident H^+ ions; full circles: scattered projectiles emerging as H^0 atoms. The curves represent fits to a Gaussian line shape. Lower panel: Scattered projectiles emerging as H^- ions.

resolution for the incident H^+ beam has a FWHM $\approx$ 12 eV (open circles). The scattered neutral particles (full circles, upper panel) show a peak of comparable width with an energy shift of about 3 eV. Furthermore, a smaller peak shifted by about an additional 15 eV can be identified in the low energy tail of the spectrum.

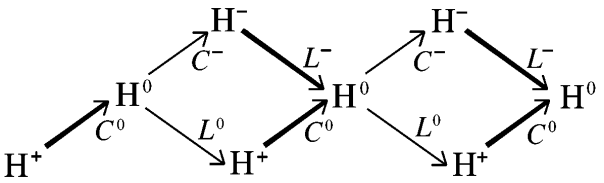
For scattered particles emerging as negative ions (lower panel) the spectra are shifted by a clearly larger energy loss of about 18 eV. Note that the background and the poorer statistics for these data are owing to the reduced intensities of H^- ions. Also here an additional peak shifted by about 15 eV can be identified.

For a qualitative discussion of our data we consider the electronic structure of the wide-band-gap insulator LiF. The occupied valence band formed by $F\ 2p$ electrons has a maximum in binding energy of -12 eV and a width of about 5 eV [15,16]. The band gap is about 14 eV and extends to vacuum energies. Direct excitations of valence/conduction band electrons the dominant mechanism for stopping of slow ions in metals [1], can be excluded owing to the presence of the band gap. We explore here the role of the charge exchange as a mechanism for stopping by considering the energies of the initial and final states in the collision system [17].

Incident protons will be neutralized via (near) resonant capture of valence band electrons with a final energy of the hydrogen $1s$ state $E_{H^0} = -13.6$ eV. Note that an atomic level shift via image charge interaction is compensated by the energy gained in the image charge acceleration on the incident trajectory [18] (typically 1 eV [19]). Thus the projectile energy is affected by energy defects in the collision ranging from about $+1.5$ to -3.5 eV with an unweighted average for the energy loss of about 1 eV. The measured data at low energies are slightly higher, which might be ascribed to slight shifts of valence band levels at the surface or by dissipation of energy in the eV range by, e.g., excitation of phonons [20] (38 meV [21]). For receding negative ions, the final state energy is the binding energy for the H^- $1s1s'$ level of $E_{H^-} = -0.75$ eV. So for capture of a further electron from the $F\ 2p$-valence band [19] the energy difference amounts from about 11 to 16 eV. This explains the larger energy loss for projectiles converted to negative ions, measured here to be about 15 eV larger than for neutral atoms. An energy loss of comparable size associated with H^- formation has been observed also in backscattering of 100 eV H^+ projectiles from LiCl [22].

Important information on the atom-surface interactions can be deduced from the energy spectra in Fig. 3. In both spectra an additional peak can be identified at an energy loss of about 15 eV and an intensity of about 20% with respect to the prominent peak. We ascribe the additional peak to a further cycle of electron loss and capture. In contrast to measurements of charge fractions only, we can identify those cycles via the energy loss related to charge exchange. In this respect our measurements can be considered as an interesting variant of "translational energy spectroscopy," a well-established method to study atomic collisions in the gas phase [23].

From the comparable peak ratios for the H^0 and H^- data in Fig. 3, respectively, we conclude that both charge states have to be closely related in the charge exchange sequence. Then single electron capture and loss events will dominate and may proceed according to the following scheme:



For energies $E \leq 1$ keV we can conclude from the very small fraction of H^+ in the scattered beams that the probability for near resonant capture (C^0) of valence band electrons is large. In additional experiments with H^- projectiles we find no evidence for survival of these ions so that also the probability of electron loss from H^- (L^-) is large. From the spectra shown in Fig. 3 it follows from

the intensities of the second peaks that about 20% of the projectiles have undergone a further cycle of charge exchange.

On the basis of the present data it is not possible to deduce information on the relative weight of the two different capture/loss channels sketched above. However, it is likely from the observed H^- fractions of some percent and the high probability for loss (L^-) that the formation of negative ions plays an important role here. Our conclusion is supported by previous model calculations on negative ion formation via local capture from F^- sites, where we estimate probabilities in the range of about 10% [17,19,24]. On the other hand, electron spectra induced by slow protons scattered from LiF are interpreted by the ionization of H^0 to H^+ via an electron promotion mechanism [25]. Our data indicate that formation and subsequent electron loss of H^- ions might be also a source in that electron emission.

Returning to the primary subject of the paper we identify charge exchange as a dominant mechanism for (electronic) stopping of slow protons by LiF. Energy loss results from electron capture to form neutral atoms or, to a much lesser extent, negative ions with about 2 to 3 eV for H^0 atoms and about 18 to 20 eV for H^- ions, respectively. With increasing energy ($E \geq 1$ keV) enhanced probabilities for capture and loss lead to additional cycles accompanied by larger energy losses, and the clear-cut separation of the H^0 and H^- data disappears. At higher energies stopping by ionization of H^0 via electron promotion mechanisms as proposed in Refs. [3] and [25] may be important. From the similarity of available data on stopping in transmission and surface scattering it is likely that the mechanisms for electronic stopping are comparable.

In conclusion, in a study on stopping of slow protons by a wide-band-gap material (LiF), performed via grazing ion-surface scattering, we find evidence for a threshold behavior. We have shown that charge exchange is the dominant mechanism for stopping. In this respect, we consider our work as an important contribution to the field of atomic collisions in solids, where a microscopic understanding of the stopping of atomic projectiles in insulators has been paid increasing attention to recently.

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