Apparent Velocity Threshold in the Electronic Stopping of Slow Hydrogen Ions in LiF

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The electronic energy loss of hydrogen ions (protons and deuterons) in thin supported films of LiF has been studied in backscattering geometry for specific energies from 700 eV/u to 700 keV/u, using Rutherford backscattering spectroscopy and time-of-flight low-energy ion scattering spectroscopy. For specific energies below 8 keV/u, our data confirm velocity proportionality for the stopping cross section ε (like in a metal) down to 3.8 keV/u, as observed previously for protons and antiprotons despite the large band gap (14 eV) of LiF. Below 3.8 keV/u, the present results indicate an apparent velocity threshold at about 0.1 a.u. for the onset of electronic stopping.

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The interaction of slow ions with electronic systems that have a large minimum excitation energy $T_{\min}$ (noble gas atoms or large band gap insulators) revealed very interesting and puzzling aspects, ever since Golser and Semrad found a strong dependence of the stopping cross section ε on the ion velocity ν for protons in He gas [1]. ε is closely related to the energy loss per path length, i.e., the stopping power, $-dE/dx$. The results of Ref. [1] were in contrast to the scaling $\varepsilon \propto \nu$ theoretically predicted for ions in a free electron gas at low velocities [2] and experimentally found to hold for many materials [3]. Numerous models have been developed for proton stopping in noble gases [see [4] and references therein]—all based on binary collisions—which essentially trace the observed velocity dependence of ε back to finite excitation energies and to charge exchange. Recently, for Si a velocity threshold of 5×10^{-2} a.u. (1.1×10^5 m/s) was deduced from energy loss measurements using various ion species at velocities >0.1 a.u. [5]. The threshold reported in [5] is considerably larger than the theoretical value (2×10^{-2} a.u.) obtained from collision kinematics for the known values for the gap energy E_{gap} and the maximum valence electron energy. This discrepancy was explained by the low probability to excite an electron-hole pair just across the band gap in a binary collision. Also in noble metals, there is a gap effect due to the finite binding energy of the d electrons with respect to the Fermi level. Thus, the electronic stopping of Au for protons exhibits a more complex velocity dependence below 6 keV [6,7], which was explained on the basis of binary proton-electron collisions.

The situation is more complex for large band gap insulators. For Al_2O_3, SiO_2 (band gap energy $E_{\text{gap}} = 8$ eV), and LiF ($E_{\text{gap}} = 14$ eV), the electronic stopping cross section was found to be proportional to velocity, $\varepsilon \propto \nu$, for light ions [8] down to a velocity of 0.31 a.u., corresponding to a proton energy of about 2.5 keV. Consequently, electron promotion processes instead of binary collisions were assumed to be responsible for the efficient electronic stopping. Surprisingly, the results could be described by a nonlinear free electron gas stopping theory [9]. The electronic stopping of slow antiprotons in LiF yields fascinating complementary information, due to the absence of the charge exchange channel in this case. Recently, this experiment was performed for energies down to 2.5 keV, and again ε proportional to velocity was observed [10]. These results have been compared to the classical binary encounter theory including a "shell correction" to account for the velocity distribution of the valence electrons in LiF [11]. Thus, two theories (free electron gas and binary encounter) describe the experimentally observed velocity proportionality, but without *a priori* justification. A quantum mechanical close-coupled calculation shows that the ionization energy of an atom (H, He) vanishes if the antiproton approaches sufficiently close [12], as predicted by Fermi and Teller [13]. Analogously, one can qualitatively understand how antiprotons can efficiently raise target electrons across the band gap in collisions with F^- in LiF.

In grazing surface scattering, a thresholdlike behavior was observed for the energy loss of slow hydrogen ions from LiF(001), with charge exchange cycles (e.g., $H^0 - H^-$) as dominating energy loss mechanism [14]. Electron emission studies showed the relevance of surface exciton excitation and the existence of H^- at the surface for 600 eV protons and LiF [15]. For LiF, the electron emission threshold was explained by the fact that electron promotion ($H^0 + F^- \rightarrow H^- + F^0$) requires a sufficiently close collision [16], while for Al the threshold can be described by classical projectile-electron binary encounters [17].

To summarize, the electronic interaction of slow ions with large band gap insulators is described by creation of negative ions and charge exchange via electron promotion, while for the interaction with metals binary ion-electron collisions are dominant.

The aim of the present work is to investigate the electronic stopping cross section of hydrogen ions in LiF down to very low projectile energies (~700 eV) and to explore its velocity dependence at velocities well below the kinematic threshold $\nu_{\text{th}} \approx 0.2$ a.u., corresponding to a proton

energy of 1 keV. Since for proton stopping in LiF the data in [10] differ considerably from those in Ref. [8], we extended the energy range of the current experiment up to 700 keV and fix the absolute value of ε at higher energies [18,19].

It is not feasible to produce self-supported foils of these insulators of appropriate thickness for the low energies of interest; therefore, the energy loss was measured in backscattering geometry. For this purpose, multilayered samples were produced: a set of Si substrates was covered with a boron layer of 10 μg/cm^2, onto which a thin gold film (4.1 μg/cm^2) was deposited, which served as a marker [20]. Finally, these samples were partly covered with an evaporated layer of lithium fluoride, with a thickness in the range from 0.74 to 8 μg/cm^2. During evaporation, the thickness of the deposited layers was monitored by a quartz microbalance. The surface topography of the layers was characterized by atomic force microscopy (Veeco Instruments Dimension 3100) in the tapping mode, and a rms surface roughness of 0.29, 0.51, and 0.97 nm was obtained for the B/Si, Au/B/Si, and LiF(1.4 μg/cm^2)/Au/B/Si samples, respectively, indicating good quality of the layers.

Two different setups were used to measure the stopping cross section of protons and deuterons in LiF in the specific energy range from 700 eV/u to 700 keV/u (u denotes the atomic mass unit). The high energy data (35–700 keV) were obtained by Rutherford backscattering spectrometry (RBS) using the Van de Graaff accelerator AN-700 of the University of Linz. Three thin-film samples (400 nm Cu/Si, Au/B/Si, and LiF/Au/B/Si) were simultaneously placed in the RBS chamber and consecutively analyzed at a given primary energy. The copper film was used for tuning of the experimental parameters at each energy. Then, spectra for Au/B/Si and LiF/Au/B/Si were taken. Since ionic crystals like LiF are very delicate under particle bombardment due to electronic sputtering, the electronic stopping information was obtained at a primary fluence of $\sim 10^{13}$ ions/cm^2 per spectrum. Typically, one spectrum was taken per spot on the LiF sample, although it was proven that the LiF film did not deteriorate even for successive acquisition of several spectra at one spot. In this respect, the high energy RBS data are the most crucial ones.

Figure 1(a) shows spectra of 150 keV protons backscattered from Au/B/Si and LiF (2.6 μg/cm^2)Au/B/Si samples. For LiF/Au/B/Si, the Au peak is noticeably shifted to lower energies as compared to that for Au/B/Si. For LiF/Au/B/Si, also a peak corresponding to backscattering from fluorine can be seen [see the peak at 120 keV in Fig. 1(a)]. From the difference in the position of the Au peaks $\Delta E = kE_0 - E_1$ due to the energy loss of the projectiles in the LiF layer, the stopping cross section for LiF is obtained by standard procedures [21]. The LiF thickness was fixed by the requirement that at $E >$

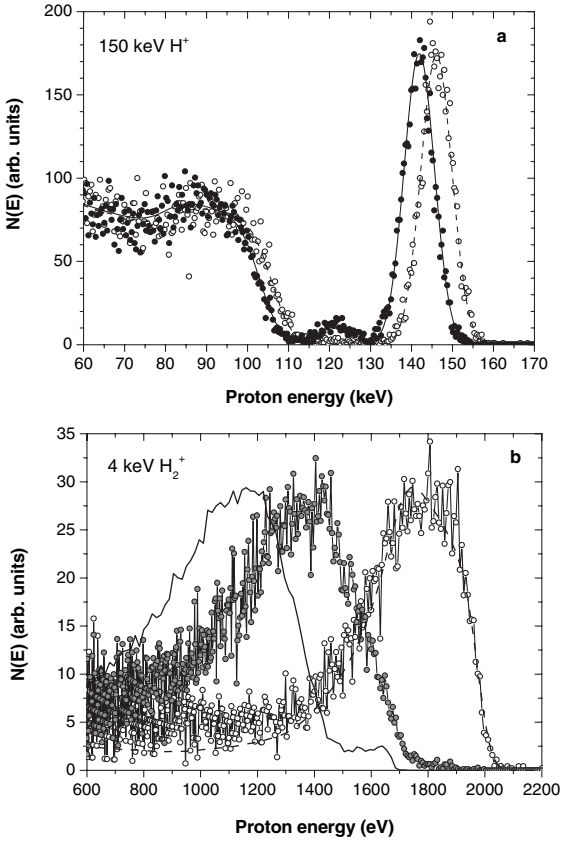

FIG. 1. (a) Experimental RBS spectra for 150 keV protons scattered from Au/B/Si (open circles) and LiF/Au/B/Si (filled circles). The corresponding simulated spectra (SIMNRA) are also shown as dashed lines and full lines, respectively. For details, see text. (b) As (a) for 4 keV H_2^+ ions and TRBS simulations.

100 keV the absolute value of ε coincides with the data from Refs. [18,19]. This procedure is accurate within 5% and revealed that the data of [8] which were based on the reading of a quartz microbalance are high by a factor of 1.63. In Fig. 1(a), also simulated spectra are shown, obtained using the binary collision program SIMNRA [22] with proper stopping powers [23] and realistic thickness values.

The low-energy data (primary energy $E_0 \leq 10$ keV) were measured by time-of-flight low-energy ion scattering (TOF-LEIS) in the UHV setup ACOLISSA [24], which permits us to record TOF spectra of projectiles backscattered into a stop detector situated at an angle of 129°, irrespective of the charge state of the projectiles. Again, two samples (Au/B/Si and LiF/Au/B/Si) were simultaneously loaded into the target chamber and studied analogously as in the RBS regime. LiF layer thicknesses in the range from 0.74 to 1.4 μg/cm^2 were used. As projectiles, mass-separated atomic and molecular ions H^+, H_2^+, H_3^+, D^+, D_2^+, and D_3^+ with energies in the range 2–10 keV were used. At each energy, TOF spectra were recorded for the two samples. The total ion fluence during spectrum acquisition did not exceed $\sim 1 \times 10^{13}$ ions/cm^2. Figure 1(b) shows energy spectra (converted from TOF

spectra applying standard procedures) of 4 keV H_2^+ ions backscattered from Au/B/Si and 1.4 μg/cm^2 LiF/Au/B/Si. These beam parameters are (almost) equivalent to scattering of 2 keV protons. In these spectra, the main peak is again due to scattering from Au atoms. Note that the finite width of the Au peak due to the finite thickness of the Au layer (11 monolayers) is easily resolved. For LiF/Au/B/Si, the Au peak is appreciably shifted towards lower energies by ΔE, due to energy loss of the projectiles in the LiF layer. Because of the high scattering probability at low energies, this energy shift ΔE may be influenced by multiple scattering. Therefore, the electronic stopping cross section in LiF was obtained from a comparison of the experimental spectra to Monte Carlo simulations [TRBS [25]] using proper input data for stopping powers and thickness values. The influence of multiple scattering was found to be small. In Fig. 1(b), also TRBS spectra are shown for Au/B/Si and LiF/Au/B/Si. Note that in the TRBS spectrum of the LiF/Au/B/Si sample the energy shift of the Au peak due to the energy loss in LiF results too large, if just velocity proportional stopping is used with parameters that are appropriate for proton energies above 4 keV/u.

In Fig. 2(a) we present the resulting stopping cross section per LiF molecule for hydrogen ions as a function of specific energy in the range 0.7–700 keV/u. At specific energies above 2.5 keV/u, our results are in very good agreement with the corrected transmission data from Ref. [8] (reduced by a factor of 1.63). For energies $\geq$4 keV/u, our data are concordant with tabulated data [PSTAR [26] and TRIM [27]]. The scatter of the data corresponds to a standard deviation of 5%–10%, respectively, and no systematic difference in stopping of protons and deuterons is observed. At specific energies below 3.8 keV/u, the data are no longer proportional to velocity, but exhibit steeper velocity dependence (roughly $\propto \nu^{1.6}$). In Fig. 2(b) the data are presented as a function of the ion velocity, exhibiting an apparent velocity threshold at $\sim$0.1 a.u., corresponding to a proton energy of $\sim$250 eV. From Fig. 2(b) it becomes clear that the vicinage effect at low energies is weak, as expected [6], leading to about 5% lower stopping cross section data obtained in backscattering geometry for molecular ions with respect to that obtained for atomic projectiles.

The most important feature of the present results is that we observe a transition from $\varepsilon \propto \nu$ to a $\varepsilon \propto (\nu - \nu_{\mathrm{th}})$ dependence at a velocity $\nu_{\mathrm{kink}} \approx 0.39$ a.u. (3.8 keV for protons), with an apparent velocity threshold $\nu_{\mathrm{th}} \approx 0.1$ a.u., which has not been perceived at energies $\geq$2.5 keV—neither for protons (deuterons) nor for antiprotons [8,10]. For comparison, the proton results from Ref. [10] are shown in Fig. 2(b), which also demonstrate the incipient departure from velocity proportionality below 4 keV.

Compared to the results presented here, the situation in grazing surface scattering is different, since the threshold

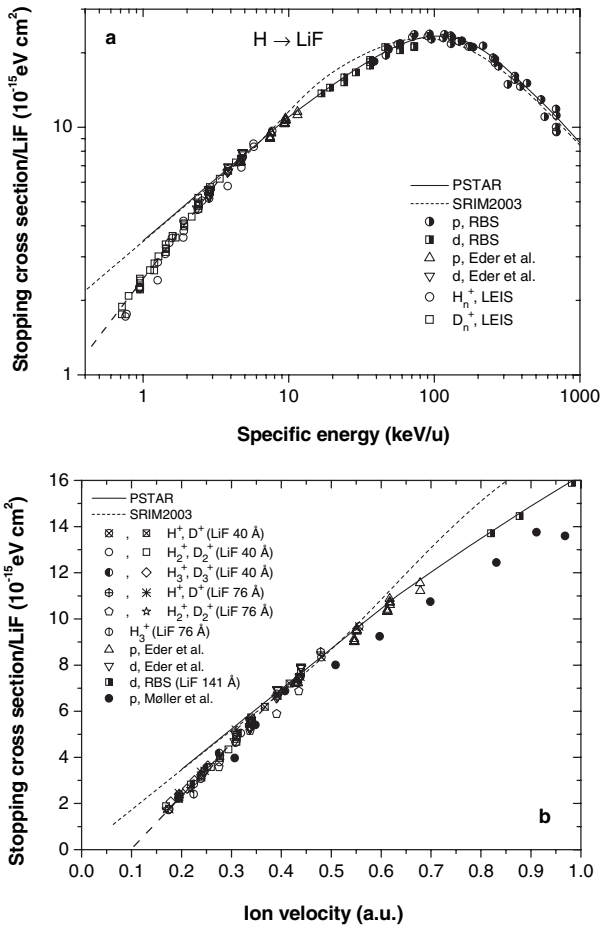

FIG. 2. (a) Stopping cross section per molecule for hydrogen ions in LiF, obtained for protons, H_2^+, H_3^+, deuterons, D_2^+ and D_3^+, as a function of the specific energy (keV/u). Also shown are the corrected data from Ref. [8] (triangles), and data from tabulations: SRIM2003 [27] (dashed line), PSTAR [26] (full line). For details, see text. (b) As (a) for energies below 25 keV/u, as a function of the ion velocity in a.u. Also shown are the data from Ref. [10] (filled circles).

observed there [14] depends on both, ion energy and scattering geometry, and represents an impact parameter threshold at 2 a.u. [16]. Note that in transmission of 1 keV deuterons through LiF impact parameters $\geq$1 a.u. contribute to multiple scattering [28,29], explaining the high efficiency in electron-hole pair excitation.

Comparing our results for LiF to those for Au and Si, the main difference is that the observed velocity threshold for LiF (0.1 a.u.) is far *below* the kinematic limit (0.2 a.u.), in clear contrast to the findings for Au and Si. From the explanation of electronic sputtering [30] it is clear that also in LiF excitation of electron-hole pairs is the dominant electronic excitation mechanism, but most probably via promotion of diabatic levels due to interaction of target electrons with projectile electrons along the trajectory [31]. A detailed theoretical analysis is required to elucidate the

physical processes dominating the electronic stopping of slow ions in insulators.

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