

Stopping power of fluorides for low-velocity protons

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A combined experimental and theoretical study of the energy loss of protons in fluorides is presented. The measurements were performed in fresh AlF_3 evaporated *in situ* on self-supported C foils, extending the low-energy range from 25 down to 0.7 keV. The transmission method is used in combination with time-of-flight spectrometry. The experimental stopping power increases almost linearly with the mean projectile velocity, showing a velocity threshold at about 0.1 a.u. These features are well reproduced by a model based on quantum scattering theory that takes into account the velocity distribution and the excitation of the active $2p$ electrons in the F^- anions, and the properties of the electronic bands of the insulators. The model also reproduces the threshold behavior measured previously on LiF.

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The stopping of ions in matter has been a subject of investigation for many years and is the basis of many applications in materials science, radiation physics, and other areas. More recently, with the development of faster electronics, which require semiconductor devices produced by shallow ion implantation, its knowledge at low ion velocities has become critical.

In the case of metals, where the valence electrons can be modeled as a free electron gas (for instance, Al), the stopping power has been found to be proportional to the ion velocity in the low-energy range [1,2]. However, for the transition metals Cu, Ag, and Au, a departure from this velocity proportionality has been measured [3,4]. In these metals the number of target electrons contributing to the energy loss increases when the projectile velocities reach values large enough to excite the d electrons, thus generating a steeper dependence at ion velocities larger than some apparent threshold.

In the case of solid insulators, a departure from the linear dependence of the stopping power with the ion velocity (referred to also as the *threshold effect* [5]) was observed in grazing scattering of protons from flat LiF surfaces [6] and in backscattering of protons from LiF films evaporated on Au substrates [7]. The case of insulator materials is interesting because in this case it is expected that the large binding energy of the active electrons should produce a behavior similar to that measured in noble gases like He and Ne [5,8]. Surprisingly, the stopping power values measured for LiF showed an apparent threshold effect more similar to that of Au than to the noble gases. This effect was interpreted in terms of a reduced gap resulting from electron promotion effects [9].

In the present work, we provide experimental values for the stopping power of another fluoride, AlF_3 , which is important for technological applications [10]. The observed behavior of the energy loss of protons in AlF_3 is interpreted by means of a recent theoretical model based on calculations of the momentum transfer cross sections for the electron-ion

collisions using quantum scattering methods, which incorporates the energy gap of the insulator and the velocity distribution of the active $\text{F}^- 2p$ electrons. A similar theoretical approach has been very recently used to explain the experimental trends of d -electron metals [4].

The measurements of the energy loss were performed by combining the transmission method with time-of-flight (TOF) analysis through very thin AlF_3 layers evaporated *in situ* under ultrahigh-vacuum (UHV) conditions on self-supported carbon foils. Although the TOF method has a lower energy resolution than measurements performed with an electrostatic analyzer, its sensitivity is higher because it is a multichannel technique where both neutrals and ions can be collected. Ions and neutrals can also be measured separately for charge fraction experiments [11]. The approach allows measurements of stopping powers with fluences as low as 10^{10} ions/cm² per spectrum, thus producing only undetectable damage on the insulating films. This was corroborated by the concordant results obtained on the same target at the beginning and the end of extended measurement series.

The UHV chamber is connected to an ion accelerator working from 0.5 to 100 keV [12]. H^+ and H_2^+ ion beams were produced in a radio-frequency source, mass-analyzed by a magnet, and finally collimated to a typical angular divergence below 0.1° with several movable slits to areas ranging from 0.1 to 2 mm². For TOF measurements, the ion beam was pulsed with pairs of parallel plates at frequencies of about 40 kHz, resulting in resolution times of ~ 30 –200 ns for proton energies from 1 to 20 keV, respectively. The current densities for the continuous and the chopped beams were below 500 and 1 pA/mm², respectively. The detection is performed by a channeltron electron multiplier located at the end of a 1.586-m-length drift tube fixed at a scattering angle of 0° with an angular acceptance of $\sim 0.2^\circ$.

The C foils of nominally $4 \mu\text{g}/\text{cm}^2$ thickness were bought from ACF Metals [13]. We used two C foils of the same lot, obtaining very similar results. The thickness of the C foils was measured with a calibrated Autoprobe CP atomic force microscope (AFM) from Park Scientific Instruments, and also by normalizing the energy loss results taken at

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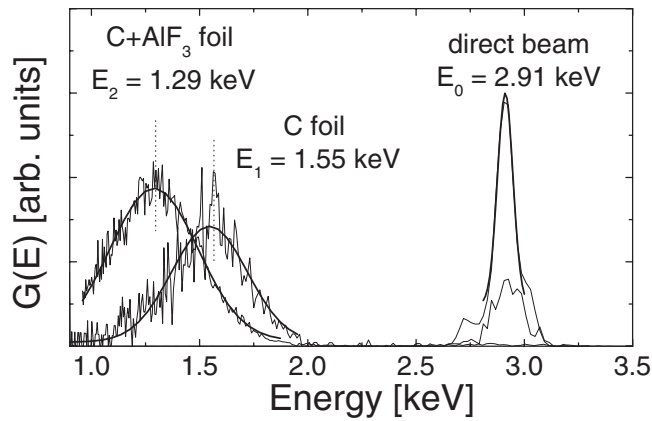


FIG. 1. Energy spectra for 2.9 keV H^+ passing through a 280 Å C foil and through a 280 Å C+230 Å AlF_3 foil. The energy spectra for the corresponding direct beams are also shown.

9 keV with the stopping power values obtained with the SRIM 2003 program [14]. The result was 280 ± 50 Å.

Fluoride depositions were performed from a Knudsen cell charged with anhydrous AlF_3 [15] on one of the C foils. The cell was carefully degassed and shuttered to avoid sample contamination. Pressures in the 10^{-9} Torr range were kept throughout the evaporation and the measurements. The deposition speed and the evaporated mass were monitored *in situ* by a quartz crystal balance of a known aperture placed on the sample holder. The thickness of the AlF_3 film was measured with the AFM, giving a thickness of 230 ± 50 Å. This allowed us to check that the film density was similar to that of the bulk material (within an error of 15%). The stoichiometry and the dielectric properties of the evaporated film were checked by TOF direct recoil spectroscopy, Auger electron spectroscopy, and electron energy loss spectroscopy [11,15].

TOF spectra were measured for the direct beam, for the beam transmitted through C self-supporting foils, and for the beam transmitted through the C foil with a layer of AlF_3 . The projectile energies ranged from 0.7 to 28 keV. The TOF spectra were converted into energy distributions and corrected by the energy dependence of the channeltron efficiency fitted from Ref. [16]. As an example, Fig. 1 shows the energy spectra for 2.9 keV protons transmitted through a 280 Å C foil, and after evaporating 230 Å of AlF_3 on the back of the C foil. For this case, the energy losses are 1.34 keV (4.8 eV/Å) in the C foil and 0.26 keV (1.2 eV/Å) in the AlF_3 film. As can be seen from the beam profile, also included in the figure, the experimental resolution does not introduce significant uncertainties in the energy loss determinations.

The summary of the measured energy loss as a function of the incoming energy for C and C+ AlF_3 is presented in Fig. 2 together with the results obtained for the AlF_3 film. The data were obtained in the following way. (1) A set of measurements for the pure C foil was obtained and the data fitted with a polynomial. (2) A similar data set after evaporation of the AlF_3 was measured, with frequent measurements on the other pure C foil used as reference. The difference between the data points measured for C+ AlF_3 and the polynomial provided the energy loss data in the fluoride. Each data set is

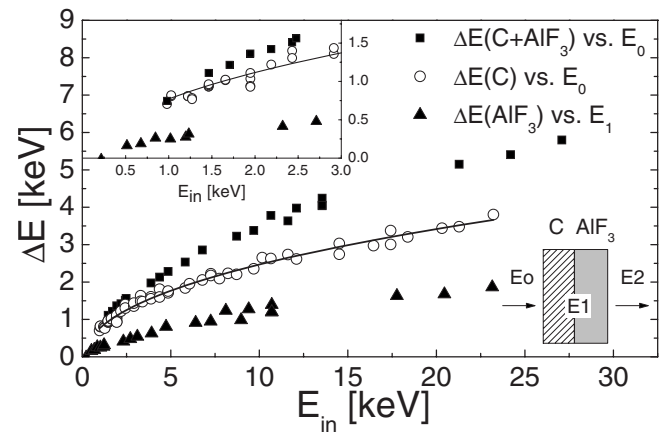


FIG. 2. Energy loss measured in C and C+ AlF_3 thin foils. The line corresponds to a polynomial fit of the energy loss in C. The energy loss in AlF_3 has been obtained by subtracting the C polynomial fit from the C+ AlF_3 values. Inset: Span of the very low-energy region.

then plotted in Fig. 2 versus the incoming proton energy in each layer (E_0 for the pure C foil and E_1 in the fluoride).

The results for pure C were in very good agreement with those presented previously by other authors [17], and show the well-known proportionality of the stopping with the mean ion velocity in the foil [$\langle v \rangle = (v_{out} + v_{in})/2$], without any apparent threshold. These data together with a detailed description of the setup and charge fraction measurements for C and Au foils will be reported in a forthcoming presentation.

With the aim of comparing stopping values for different materials, we evaluate the stopping cross sections per atom (SCS) obtained for C, AlF_3 , and LiF (from Ref. [7]), using target atomic densities equal to 1.13×10^{23} , 0.89×10^{23} , and 1.22×10^{23} atoms/cm³, respectively. The stopping cross section values for the fluoride samples are very similar, as one would expect for ionic insulators where the behavior of the stopping at low energies is dominated by the 2*p* electrons [18] provided by the F^- anions. The stopping values of these insulators are about one-third lower than those of the C sample.

The dependence of the stopping power for AlF_3 and LiF (taken from Refs. [7,19]) as a function of the mean projectile velocity are shown in Fig. 3. The experimental method used in the present work allowed us to extend the measurement of the stopping on fluorides down to ~ 0.1 a.u., showing a clear threshold around this velocity, and a linear dependence of the stopping power.

The effects of deviations of the experimental stopping power results from the velocity proportionality have been commented on by several authors, but, as stressed in Ref. [19], there is not, up to now, a model that could describe the velocity threshold, nor the stopping power behavior in insulators at low projectile energies. In this work, an approach is made at taking account of these characteristics.

The theoretical analysis of the energy loss of slow ions in solids considers the energy loss in collisions with target nuclei and the excitation of the valence electrons by the moving ion with velocity v . Under the present experimental condi-

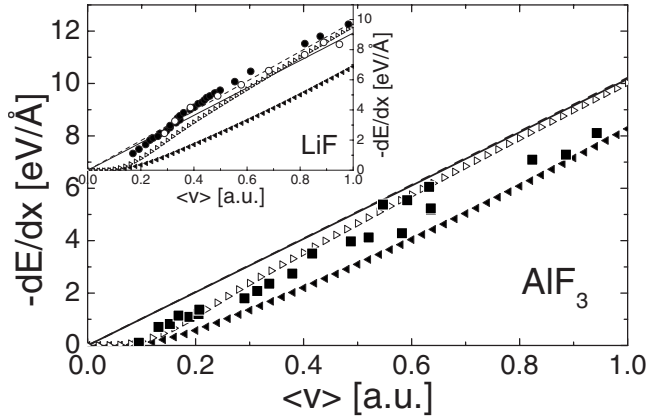


FIG. 3. Stopping power values for AlF_3 measured (■) as a function of the mean projectile velocity. The lines show the calculations of the stopping power using the phase shifts taken from the DFT model (---), and those calculated here from the nonlinear approach (—) with $U=0$ eV. The open and solid triangles show the corresponding calculation for $U=10.8$ eV. Inset: Similar calculations performed for LiF with $U=0$ and 14 eV, compared to experimental values of proton projectiles taken from Refs. [7] (●) and [19] (○).

tions, zero exit angle with very low angular acceptance, the trajectories of the particles traversing the foils should be almost rectilinear; strong interactions with target nucleus will cause the particles to be emitted at larger angles, out of the detector acceptance. So, the contribution of nuclear (elastic) energy loss can be neglected as compared to electronic excitations, and only the latter will be considered here.

The interaction of the moving ion with target electrons produces a stopping force which, for $v < v_0$ (with v_0 the Bohr velocity) may be expressed as

$$-\frac{dE}{dx} = Qv, \quad (1)$$

where Q is the value of the stopping coefficient. A more general expression for a slow ion moving in a system of electrons described by a velocity distribution $F(v_e)$ is given by [20,21]

$$-\frac{dE}{dx} = \frac{4\pi}{3}nv \int_0^\infty v_e^4 \sigma_{\text{tr}}(v_e) \left(-\frac{dF(v_e)}{dv_e} \right) dv_e, \quad (2)$$

where n is the electron density and σ_{tr} is the transport or momentum-transfer cross section (TCS), calculated, according to the scattering theory, as

$$\sigma_{\text{tr}} = 2\pi \int_0^\pi |f(\theta)|^2 (1 - \cos \theta) \sin \theta d\theta, \quad (3)$$

where $f(\theta)$ is the scattering amplitude given by

$$f(\theta) = \frac{\hbar}{mv_r} \sum_l (2l+1) e^{i\delta_l} \sin(\delta_l) P_l(\cos \theta). \quad (4)$$

Here v_r and θ are the relative ion-electron velocity and the scattering angle in the center of mass system, and δ_l is the

phase shift corresponding to the scattering of waves with angular momentum l .

The described TCS method may be modified in order to take into account a possible energy threshold U in the electronic excitations. For this purpose, and following Ref. [3], we define a *restricted* transport cross section σ_{tr}^* by

$$\sigma_{\text{tr}}^* = \sigma_{\text{tr}}^*(v, v_r, U) = 2\pi \int_{\theta_{\min}(v, v_r, U)}^\pi |f(\theta)|^2 (1 - \cos \theta) \sin \theta d\theta, \quad (5)$$

where we have introduced a minimum scattering angle θ_{\min} , which in the usual model for zero-gap materials (metals) is taken as zero ($U=0$).

In the case of materials with a finite energy gap U , we must reconsider the calculation to take into account only those processes that provide energy transfers $\Delta E \geq U$. The connection between θ_{\min} and U may be obtained by considering that a scattering angle θ is associated with an energy transfer ΔE in the laboratory system given by [20,21]

$$\Delta E(\theta) = mv_r(1 - \cos \theta). \quad (6)$$

Therefore, the minimum scattering angle θ_{\min} , corresponding to energy transfers larger than U , is determined by the condition $\Delta E(\theta_{\min}) = U$, which yields $\cos \theta_{\min} = 1 - U/mv_r$. Then, in the case of insulators, or other materials with significant band gaps, the energy loss expression of Eq. (1) contains a velocity-dependent stopping coefficient given by

$$Q = \frac{4\pi}{3}n \int_0^\infty v_e^4 \sigma_{\text{tr}}^*(v, v_e, U) \left(-\frac{dF(v_e)}{dv_e} \right) dv_e. \quad (7)$$

For the case of ionic compounds like AlF_3 and LiF, the valence band is formed by the $2p$ orbitals of the F^- anion. Taking into account the atomiclike character of these orbitals, the electron velocity distribution $F(v_e)$ has been calculated using the method described by Ponce in Ref. [22].

For the phase shifts δ_l , we have considered two different approaches. On one hand, we used a model that considers the stopping medium as a homogeneous electron gas, and calculates the values of δ_l for each ion atomic number Z_1 using the density functional theory (DFT) [23]; this model has shown good agreement with experiments in the case of ideal metals (like aluminum) and transition metals with localized d electrons (Cu, Ag, and Au) [3,4]. The use of this approach has been extended to semiconductors [2] and compounds [24] with surprisingly good results, although for the moment no clear proof of the conditions of applicability is available. Following this approximation, we used the tabulated results for the phase shifts obtained by Puska and Nieminen [23] using the r_s values of both fluorides (1.446 a.u. for AlF_3 , and 1.5 a.u. for LiF). On the other hand, we used an alternative method to calculate the phase shifts, which does not assume the free electron picture. In this case, we determined the phase shifts by direct numerical integration of the radial Schrödinger equation [25] using the mean velocity of the F^- $2p$ electrons (2 a.u.). This provides a more atomistic ap-

proach which may be considered more adequate to describe the localized atomiclike behavior of the $F^- 2p$ ions in our fluorides.

The comparison of the stopping power calculated using both phase shift methods with the experimental data of AlF_3 and LiF is presented in Fig. 3. Calculations for both compounds were made assuming zero energy gaps as well as using their respective gap values (10.8 eV for AlF_3 and 14 eV for LiF).

Within the present model the threshold velocity value, i.e., the ion velocity where the theoretical curve crosses the x axis, is given by the equation $\cos \theta_{\min} = 1 - U/mv_m$ with $\theta_{\min} = \pi$. Therefore, by taking into account the corresponding gap, the threshold ion velocity for the AlF_3 case becomes 0.1 a.u., in good agreement with our experimental data. In the case of LiF , the experimental energy threshold is not so well determined but the trend of the points appears to indicate a fair agreement with the theoretical value (0.13 a.u.).

The comparison between the experimental results and the present model shows that not only are the velocity thresholds well explained, but also the general behavior of the stopping power versus projectile velocity is fairly well reproduced.

This is compatible with the simple picture where the valence electrons in large-band-gap insulators behave like free electrons once the minimum excitation energy transferred by the incoming projectile is larger than the band gap energy.

In summary, the present energy loss measurements of low-velocity protons in AlF_3 show a well-defined threshold at $v \approx 0.1$ a.u., and, starting from there, an almost linear increase with the mean projectile velocity $\langle v \rangle$. A model that explains the threshold behavior and the main features of the stopping curve in high-band-gap insulators is presented. It considers the $F^- 2p$ electrons present in both fluorides as responsible for the low-energy behavior and the magnitudes of the band gap for each compound as the determining quantities. The model, which contains no free parameters, yields a good description of the experimental results for both AlF_3 and LiF .

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