Electronic Excitations of Slow Ions in a Free Electron Gas Metal: Evidence for Charge Exchange Effects

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Electronic energy loss of light ions transmitted through nanometer films of Al has been studied at very low ion velocities. For hydrogen, the electronic stopping power S is found to be perfectly proportional to velocity, as expected for a free electron gas. For He, the same is anticipated, but S shows a transition between two distinct regimes, in both of which S is velocity proportional—however, with remarkably different slopes. This finding can be explained as a consequence of charge exchange in close encounters between He and Al atoms, which represents an additional energy loss channel.

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Electronic interactions of slow light ions in solids are of importance for many fields of research like astrophysics, plasma physics, or material science [1–3]. Slow ions are of special interest, since two distinct processes significantly contribute to the energy transfer between ion and solid [4]. First, electronic stopping accounts for the excitation of electrons by Coulomb interaction with the ion. This process exclusively dominates the energy loss of fast light ions (with energies larger than a few hundred keV) along their trajectory. Second, nuclear stopping accounts for the energy transfer to nuclei in collisions with the impinging ion. With decreasing energy, the cross section for large angle scattering increases. Consequently, a more significant part of the ion's kinetic energy is dissipated via this mechanism [5]. This nuclear energy loss channel strongly depends on the atomic numbers of projectile and target atoms. Nevertheless, for H and He ions, electronic stopping still dominates, even at energies of several keV.

The stopping power S is the retardation force acting on an ion that moves with velocity v in a medium. To get rid of the trivial density dependence of S, the electronic energy loss can be characterized by the stopping cross section (SCS) ε, that is closely related to S, via $\varepsilon = (1/n)S$ with the atomic number density n.

For fast ions, electronic stopping can be predicted by first principles theories [6]. Here, the deceleration process is mainly due to excitation of core shell electrons, and chemical effects do not play a significant role. At intermediate velocities, charge state effects in electronic stopping have been studied theoretically [7,8]. The electronic loss is known to exhibit a noticeable dependence on the impact parameter [9]. At high energies, the impact parameters relevant for these electronic processes are much larger than those leading to significant elastic energy losses in atomic scattering. Therefore, in this regime electronic and nuclear losses can be regarded as disentangled. It is in the regime of medium energy ion scattering (~ 100 keV), where backscattering collisions are correlated with an increased probability of inner shell ionization [10,11]. When the ion energy is further reduced, core electrons cannot be excited efficiently and details of the density of states in the valence and conduction band of the solid become important. Even if in this regime the projectiles interact only with the delocalized electrons, correlation between elastic and inelastic processes was suggested by Oen and Robinson in an empirical model [12]. In contrast, comprehensive comparison of experimental energy spectra to Monte Carlo simulations revealed that the origin of the surface peak (single scattering peak), which is the most pronounced feature in charge integrated spectra in low energy ion scattering (LEIS), can only be explained by applying a nonlocal energy loss model [13].

A model system with respect to the electronic energy loss of slow ions is a free electron gas (FEG). Fermi and Teller [14] and consecutive studies [15–17] showed that in this case ε is expected to be proportional to the ion velocity v. This has been experimentally observed for many materials at $v < v_0 \equiv c/137$ [18].

Materials, which exhibit a velocity threshold for electron-hole pair excitations, have been of special interest from the early days of ion-solid interaction [19]. Noble gases and large band gap insulators are the most prominent systems that have been investigated to learn about electronic excitations by slow ions. In He, strong nonlinear effects in the velocity dependence of ε were observed for protons. This could be quantitatively explained by the electronic properties of the system [20]. Large band gap insulators feature similar minimum excitation energies like noble gases, however, in the band structure of a solid. Very recent experiments demonstrated that below a certain velocity threshold no energy can be transferred to the electronic system of such an insulator. This occurs, however, at much lower ion velocity than expected [21–23]. Theoretical approaches by time-dependent density functional theory (DFT) are about to explain qualitatively the origin of the observed effect [24].

In the present study we investigate the interaction of very slow light ions with a FEG-like metal, i.e., Al [25]. It is a question of major interest, if in this case the electronic processes can indeed be described as interaction of the ion charge with a FEG. To follow this aim, electronic excitations in polycrystalline ultrathin Al films by very slow hydrogen (H^+, D^+) and He^+ ions were studied in transmission using a heavy substrate as backscatterer.

Samples were produced in the following way [26]. A Ta substrate was prepared in a UHV chamber at a base pressure of 5×10^{-10} mbar. Al was deposited *in situ* on the substrate; two sets of samples were investigated with thicknesses of 2.1 and 4.2 nm (0.565 and 1.13 $\mu g/cm^2$). Thicknesses of Al layers were obtained using reference stopping power values for protons at sufficiently large ion velocities ($v > 0.4$ a.u., i.e., at proton energies >5 keV) [27]. Note that at these energies nuclear energy losses hardly contribute to the energy loss and, therefore, do not influence the results presented below [5]. Spectra of backscattered projectiles were recorded by time-of-flight (TOF) LEIS in the UHV setup ACOLISSA [28], which permits one to record TOF spectra of projectiles backscattered from the sample by 129° into a stop detector. Charge states were not discriminated. Two samples (Ta and Al/Ta) were simultaneously loaded into the main chamber and consecutively exposed to the ion beam at a given primary energy. To avoid irradiation damage, the primary fluence was kept below $\sim 10^{10}$ ions/cm^2 per spectrum, and it was checked that the Al layer did not deteriorate due to ion bombardment induced damage. Auger electron spectroscopy before and after exposure to the ion beam proved the high quality of the investigated Al surfaces.

As projectiles, mass-separated atomic and molecular ions of H and He with primary energies E_0 in the range 0.7–10 keV were used. Deuterons yield equivalent stopping information as protons with equal velocity, i.e., with half kinetic energy, as long as velocity scaling of electronic stopping holds. The use of molecular projectiles (H_n^+, D_n^+, $n = 2$ or 3) extends the range of accessible energies further to E_0/n. The projectile velocity is related to the reduced energy $E_r = E_0(M_p/M_1)$, where M_p and M_1 denote the proton mass and the mass of the projectile, respectively.

In the energy spectra, the main feature is due to projectiles backscattered from Ta atoms [26]. This continuum has a well-defined high-energy cutoff due to collision kinematics [29]. In the spectrum obtained for the Al/Ta sample, the onset of the spectrum is shifted towards lower energies, due to energy loss in the Al film.

The contributions from electronic energy loss and atomic collisions to this energy shift were disentangled by means of Monte Carlo simulations (TRBS [30]) using an adequate scattering potential [31]. In the simulations, energy spectra of backscattered ions are calculated, allowing for both multiple scattering and electronic energy loss along the path; the SCS in the Al layer is the only adjustable parameter. Each data point is represented by the ε value used in the simulation at the primary velocity. In the present investigation, the accessible energy range is limited by the increasing contribution of backscattering by Al atoms. Consequently, at $v < 0.1$ a.u. no precise analysis of ε is possible, due to blurring of the high-energy onset of the spectra.

In Fig. 1 experimental spectra (converted to energy) and results from TRBS simulations are shown for 8 keV He^+ ions ($v = 0.283$ a.u.) scattered from the Ta reference sample and from Al/Ta. For the proper choice of ε in Al, the spectrum for Al/Ta is perfectly reproduced by the simulation. In order to demonstrate the sensitivity of the evaluation procedure, two additional simulations are presented, with ε values increased and decreased by ±20%, respectively. From the resulting shifts in the position of the high-energy onset, we estimate the maximum statistical error in ε to be well below 10%. Systematic errors in ε are possibly inferred by inaccuracies in the reference SCS used for thickness calibration (± 5% standard deviation) and in the scattering potential used in the evaluation [32] (± 8% at most).

In Fig. 2, the resulting electronic SCS values are shown for H and He ions in the range of reduced energies $E_r =$ 350 eV–8 keV and $E_r = 250$ eV–2.5 keV, respectively. For H^+ and D^+, $\varepsilon \propto v$ is observed in the whole energy range. Isotope effects are absent within experimental uncertainties. Additionally, significant vicinage effects [33] on ε can be ruled out in the present investigation. Our results are in very good agreement with earlier measurements [27] (open squares) and at the same time extend the range, where $\varepsilon \propto v$ is observed, by a factor of 2 towards lower energies. For H projectiles, our data are in perfect agreement with theoretical calculations for a FEG [34,35] with a density parameter r_s of 2.13, appropriate for Al [36] (gray dotted line). From this, it can be concluded that excitation of electron-hole pairs in binary collisions along the ion trajectory is the only relevant energy dissipation

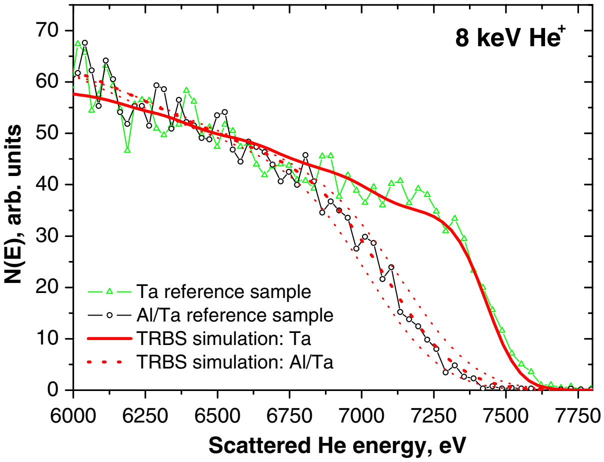

FIG. 1 (color online). Experimental energy spectra $N(E)$ for 8 keV He^+ projectiles backscattered from Ta (triangles) and Al/Ta (circles). Simulated spectra (TRBS) are shown as full and dotted lines, respectively. For details, see text.

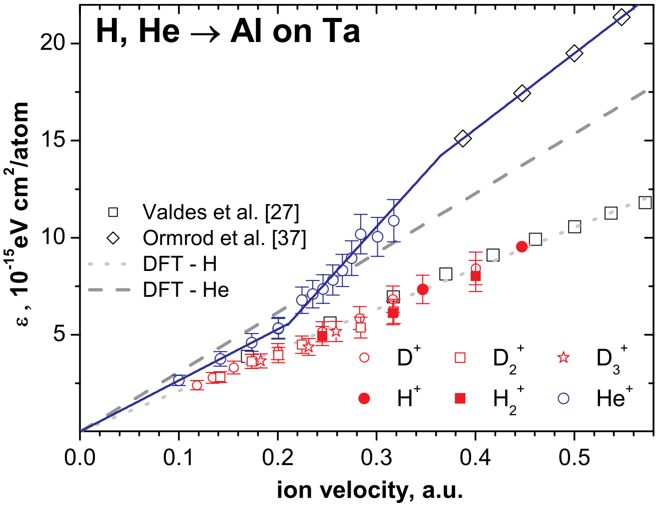

FIG. 2 (color online). Electronic SCS of H, D, and He ions in Al as a function of velocity. Also shown are data from [27,37]. Predictions from DFT for slow H and He in a FEG are shown as dotted and dashed gray lines, respectively [34,35].

mechanism active when slow H ions move in Al. Note that for H, a possible systematic error due to nuclear stopping would amount to at most 0.2×10^{-15} eV cm^2/atom, i.e., <8% of the obtained SCS at lowest energies. At higher energies, this possible source of uncertainties diminishes quickly (< 2% at $v = 0.2$ a.u.).

For He ions, a strong deviation from $\varepsilon \propto v$ is observed. At higher energies, our data are consistent with earlier experiments [37] (diamonds in Fig. 2) and $\varepsilon \propto v$. At velocities between 0.2 and 0.28 a.u. corresponding to 4–8 keV He$^+$ ions, ε exhibits a different velocity dependence, pointing towards an apparent velocity threshold of ~0.12 a.u.. At velocities below 0.2 a.u. corresponding to 4 keV, $\varepsilon \propto v$ holds again, however, with a slope that differs by ~40%. This complex velocity dependence can be attributed to an energy dissipation mechanism, which is visible only at ion energies above 4 keV. DFT predictions (gray dashed line) slightly overestimate the observed ε at low velocities (+ 13%); energy loss at energies above 8 keV is clearly underestimated (− 26%).

In the following, we trace back the observed velocity dependence of He stopping power to charge exchange between He and Al atoms. When He is scattered from Al, the He 1s level is known to exhibit very strong promotion. At an interaction distance of 0.75 a.u., He 1s is known to be shifted above the Fermi level E_F of Al [38,39]. This leads to very effective neutralization of He$^+$ ions within 1–2 monolayers [40]. The same promotion mechanism also enables ionization of He atoms: at sufficiently close distance neutral He can lose an electron and thus become (re)ionized. These processes change the charge state of the projectiles recurring along their trajectories. In reionization, the kinetic energy of the ion is decreased due to promotion of the electronic state above E_F [41]. This can occur below a He-Al distance, which for 10 keV He leads to scattering angles ≥ 1.8°, with a nuclear energy loss of 1.5 eV, i.e., 1.5×10^{-4} of E_0. In consequence, ions lose energy by charge exchange processes along a rather straight trajectory, in addition to electron-hole pair excitation. At 1 keV, the same interaction distance corresponds to a scattering angle of 16° with an elastic energy loss of 11 eV, i.e., 1.1% of E_0. Thus, at low ion velocities, coupling exists between elastic and inelastic energy losses, i.e., between atomic scattering and charge exchange. At low energies charge exchange for He in Al occurs along trajectories, which exhibit multiple large angle collisions and, consequently, a massive nuclear energy loss. In this regime, electronic energy loss cannot be treated in a straightforward way by a stopping power approach $\Delta E \propto dE/dx$. In contrast, electronic stopping includes an impact parameter dependent contribution, which exhibits a strong energy dependence. As a consequence, only projectiles which have not undergone charge exchange contribute to the low velocity data in Fig. 2 ($v < 0.2$). Thus, only at very low energies DFT results are expected to adequately describe the observed energy loss, which then exclusively is due to electron-hole pair excitation.

The observed effect is expected to be relevant whenever an impact parameter dependent energy dispersive charge exchange process is active at low ion energies. For Cu, Ag, and Au, reionization processes occur at higher energies only. Therefore, effects of correlated electronic and elastic energy loss will start to contribute at larger energies, where they can hardly be separated from the increasing contribution due to electron-hole pair excitation.

In light of the present findings, some interesting open points in electronic interaction of slow ions can be understood. For instance, for a dilute FEG, DFT predicts that He ions should be less efficiently decelerated than H ions, in contrast to experimental findings [34,35,42]. For Mg, H and He ions were predicted to experience the same deceleration force, while much stronger stopping was observed for He ions. This excessive stopping can be traced back to the contribution of charge exchange processes, since Mg is known to exhibit reionization at similarly large distances in a He-Mg collision [43].

Also, the SCS of slow H and He in SiO$_2$ [21] can now be explained. For H projectiles, ε behaves similar to other insulators with comparable band gap, like LiF, AlF$_3$, or KCl [21,23]. In contrast, for He projectiles, no clear threshold in the SCS was observed. Also, Si is known to exhibit neutralization behavior similar to Al. Furthermore, O is known to very efficiently contribute to reionization [44]. Thus, a high reionization rate along the trajectories will cause an additional contribution to ε. Since electron-hole pair excitation is severely suppressed at very low velocities, energy loss due to charge exchange can dominate for He ions in insulators like SiO$_2$. Note that this line of argument would not apply to other large band gap insulators like LiF or KCl, for which the anions exhibit a much higher reionization threshold while for the cations neutralization is strongly hampered by the ionic character of the chemical bond [43,45].

To conclude, we present experimental evidence that in FEG-like metals charge exchange processes between ion and the solid significantly contribute to the electronic energy loss. Whereas for hydrogen ions $\varepsilon \propto v$ is valid in the whole range of energies investigated, distinctly different velocity dependence is observed for He ions. This finding can be traced back to energy loss in recurring charge exchange events between He and Al along the trajectories. Since these processes exhibit a strong distance dependence, a pronounced coupling between elastic collisions and inelastic energy loss results. These findings are not a peculiarity of the He-Al system, but of general relevance: on the one hand, it can be comprehended why slow He ions exhibit stronger electronic interactions in FEG metals than predicted by theory. On the other hand, the effectiveness of electronic energy loss of He ions in large band gap insulators like SiO_2 can be understood. Consequently, for a realistic description of the energy loss of ions an inclusion of a distance dependent contribution to the energy loss due to electronic excitations in charge changing collisions is important. For a more detailed understanding, a thorough theoretical analysis of the underlying processes is requested, and further experiments on appropriate systems will be elucidative.

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