Charge State Dependence of the Energy Loss of Slow Ions in Metals

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It is shown that the energy loss of multicharged ions in an electron gas has a strong dependence on target electronic screening and the occupation of projectile levels. In our calculations, an enhancement (or decrease) of the energy loss as it depends on the number of vacancies in the inner shells is found for L (or K) shells. Experiments on the charge state dependence of the energy loss of multicharged N ions scattered under grazing incidence condition off an Al(111) surface are explained consistently by our model. [S0031-9007(98)08368-9]

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When ions traverse solid matter they lose kinetic energy by electronic excitations and by collisions with lattice atoms ("electronic" and "nuclear" energy loss, respectively). In recent years, the availability of powerful ion sources for highly charged ions resulted in an increasing number of experimental studies on the energy loss of slow multicharged ions ($v \leq v_0 =$ Bohr velocity) in solid matter. One is faced with the interesting question, how preequilibrium of charge states does affect the energy loss of multicharged projectiles, which is closely related to the charge transfer dynamics.

Several experimental studies on the energy loss of multicharged ions in solid targets have been devoted to seek the effect caused by the projectile charge state. Different conclusions have been revealed from experiments via transmission through thin foils [1] or specular reflection from surfaces under grazing incidence [2–4], but no conclusive explanation of the effect in the energy loss due to the presence of inner-shell vacancies has been given. In the case of transmission experiments the preequilibrium length is too short compared to the target thickness [1], while in ion-surface scattering either the authors have concentrated on the final charge state dependence [2] or only two initial charge states have been used [3,4]. Very recently Schenkel *et al.* [5] reported on energy loss of O^{q+}, Ar^{q+}, Kr^{q+}, Xe^{q+}, and Au^{q+} projectiles with velocity $v = 0.3v_0$ transmitted through thin carbon foils, where an enhancement of the energy loss with the initial charge is observed for O^{q+}, Xe^{q+}, and Au^{q+} ions. The authors extract from these data the presence of preequilibrium contributions to the stopping of ions in conducting solids.

In a simple intuitive picture, preequilibrium effects have been described by an enhanced effective charge resulting in a higher energy loss as compared to projectiles in low charge states [1,6]. However, screening effects by conduction electrons make the electronic stopping of atomic projectiles a complex problem that cannot be described by making use of a simple picture as an effective charge model [7]. In this respect, information is needed about the effect produced on the electronic stopping by the presence of inner-shell vacancies in the projectile ions [8]. The aim of this paper is to demonstrate that the combined projectile and target electron screening affects the energy loss of multicharged projectiles in a nontrivial manner: The stopping shows a specific dependence on the occupation numbers of the projectile bound states. We discuss the energy loss of slow N^{q+} ions scattered from an Al(111) surface under a grazing angle of incidence. Under these conditions, the scattering angles in individual projectile target atom collisions are very small, so that the nuclear energy loss is negligible.

The measured energy loss ΔE enables us to estimate the order of magnitude of the distances and time scales involved in the experiment and its interpretation according to model calculations of the stopping power dE/dx [9]. Atomic units (a.u.) will be used unless otherwise stated. We define an effective interaction length (L) by the relation

$$\Delta E = \left(\frac{dE}{dx}\right) L \tag{1}$$

and obtain $L \approx 200$ a.u. for 140 keV N^+ ions scattered off an Al(111) surface under 0.7° angle of incidence. One can interpret this length as the part of the trajectory in which the ion passes through a dense electron gas exciting electron-hole pairs. Furthermore, assuming a turning point about $z_0 \approx 0.8$ a.u. from the topmost layer [10], we find that the perpendicular distance that corresponds to this length $[\Delta z \approx \Phi_i(L/2)]$ is about 1.2 a.u. and is localized at the jellium edge $z_{\text{edge}} \approx z_0 + \Delta z$. The corresponding effective interaction time for the energy loss ($L \approx v\tau$) is $\tau \approx 10$ fs. This value compares well with other estimates based on trajectory calculations by Folkerts *et al.* [11]. In Fig. 1 we show a schematic picture of the trajectory of the projectile illustrating the relevant distances.

The electronic stopping power for N^{q+} ions in different charge states is obtained from the self-consistent screened

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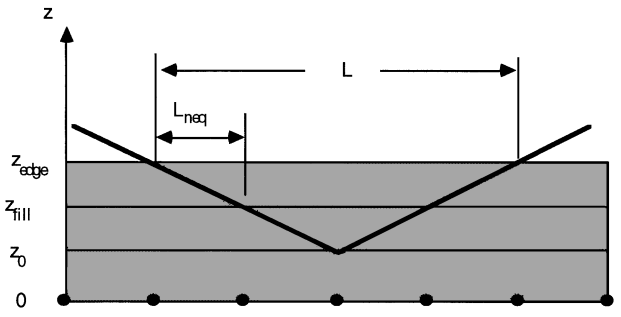

FIG. 1. Schematic representation of the interaction region, where the energy loss is significant. $L_{\rm neq}$ is the distance the ion travels until it reaches equilibrium, and L is the total length for the energy loss [see Eq. (1)]. z_0 is the distance of closest approach, $z_{\rm fill}$ is the distance for complete relaxation, and $z_{\rm edge}$ corresponds to the jellium edge position. $z = 0$ is the position of the topmost layer of Al atoms. See text for values of the different quantities.

potential calculated in density functional theory,

$$\frac{dE}{dx} = v n_0 v_{\rm F} \sigma_{\rm tr}(v_{\rm F}) = v Q(v_{\rm F}), \qquad (2)$$

where n_0 is the electronic density of the target, and $v_{\rm F}$ is the Fermi velocity. $\sigma_{\rm tr}(v_{\rm F})$ is the transport cross section at the Fermi level that is obtained from a full phase-shift calculation of electron scattering [12]. We take the density parameter $r_s = 2$ a.u. for aluminum ($r_s = \sqrt[3]{3/4\pi n_0}$). We have not taken into account the energy loss suffered by the projectile in charge exchange processes: Resonant capture does not imply an energy loss, and Auger capture is not expected to significantly contribute to the stopping at low velocities [13]. The different projectile charge and excitation states are considered to give rise to different configurations, specified by occupation numbers of the $1s$, $2s$, and $2p$ states [14], that we approximate by Kohn-Sham orbitals [15], for a given number of holes (N_h) in K and L shells. It is not trivial to define a charge state for different N^{q+} ions immersed in the electron gas using the number of bound electrons only, as for a free ion in vacuum. The many-body character of screening, which is mainly reflected in the screening by continuum electrons, can be expressed by the generalization of the Friedel sum rule (charge neutrality) [16,17].

If one separates the bound and scattering contributions to the induced charge density and their corresponding integrated values (N_b) and (N_ε), one always finds $Z_1 = N_b + N_\varepsilon$. However, it is not straightforward to interpret N_ε as the charge state of the ion in all cases, due to the fact that the existence of weakly bound states (like the $2p$ level in the N case) is strongly dependent on the occupation number of the projectile levels, as well as on the electronic density of the target. For example, the ground state of the N ion in an electron gas with $r_s = 2$ has $N_b = 4$ ($1s^2 2s^2$ core) and $N_\varepsilon = 3$ (essentially a p-wave resonance [14]), but is completely screened within a distance of 2 a.u. Consequently, one should not consider it as a N^{3+}. Therefore, we use N_h to describe the different configurations.

In Fig. 2 we plot the dependence of the friction coefficient Q on N_h. For comparison we also show the friction coefficients for the ground state ($N_h = 0$) configurations of different Z_1 ions. For a given K-shell occupancy the stopping is affected in an appreciable manner by the number of L-shell electrons: Q increases as the number of holes in the L shell increases for $N_h > 3$, while it is essentially constant for $N_h \leq 3$. The L-subshell distribution of electrons has practically no influence on Q. However, Q decreases as the number of holes in the K shell increases when N_h is low and is almost constant when N_h is high. The above mentioned opposite behavior of Q as a function of the number of holes in the K and L shells is related to the degree of spatial localization of the different orbitals: While the K shell is strongly localized (within a distance $d_k \sim 1/Z_1$), L-shell orbitals are much more extended in a distance $d_L > 4d_k$, which also depends on the occupation of the levels. As a consequence, the main effect of increasing the number of K-shell holes (N_K) is that Fermi energy electrons see an increased charge $Z_1 + N_K$ in the core of the potential, since the wavelength of the electrons at the Fermi level is much larger than d_k. However, holes in the L shell have a different effect on the screened potential from which electrons with Fermi velocity are scattered: It basically changes its range in a scale comparable to the electron wavelength.

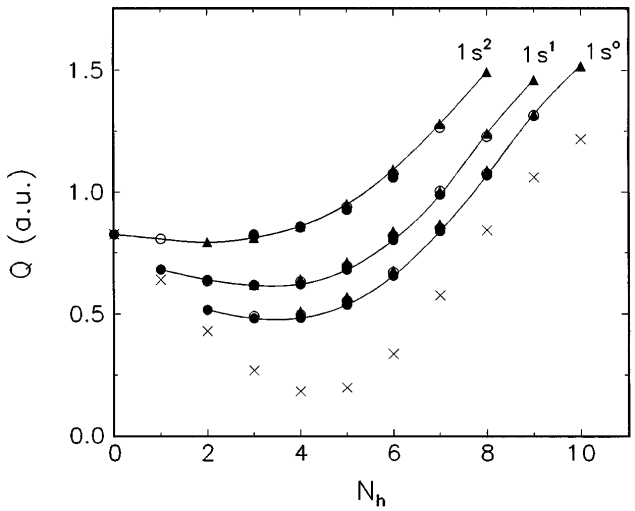

FIG. 2. Friction coefficient Q as a function of the total number of inner-shell holes (N_h) for $Z_1 = 7$ in an electron gas with $r_s = 2$ a.u. The curve $1s^2$ is obtained for a filled K shell, $1s^1$ for one electron in the K shell, and $1s^0$ for an empty K shell. The solid circles represent the $2s^2$, the open circles represent $2s^1$, and the solid triangles $2s^0$ are configurations of the L shell. The solid lines are drawn to guide the eye. The crosses indicate Q for the ground state configuration (without inner-shell vacancies) of projectiles with different Z_1 (Z_1 oscillations) using the notation $N_h = Z_1 - 7$.

TABLE I. Example of neutralization/relaxation sequence for a N^{5+} ion in jellium. The different configurations are denoted by the occupation number of the $1s$, $2s$, and $2p$ states. The asterisk means that the $2p$ level is not bound. N_b, N_ε, and N_h denote the number of bound electrons, the amount of charge induced in the continuum, and the number of holes, respectively. Q is the value of the friction coefficient, and E is the energy of the configuration [14].

$(1s, 2s, 2p)$	N_b	N_ε	N_h	Q (a.u.)	E (eV)
$(2,0,0)$	2	5	8	1.49	−1328
$(2,0,1)$	3	4	7	1.28	−1358
$(2,1,1)$	4	3	6	1.08	−1393
$(2,1,2)$	5	2	5	0.94	−1411
$(2,2,2)$	6	1	4	0.86	−1435
$(2,2,*)$	4	3	0	0.825	−1448

The three different sets of data in Fig. 2 can be used to understand the neutralization/relaxation sequences for incident N^{5+}, N^{6+}, and N^{7+} ions. In Table I we show a possible neutralization sequence for N^{5+} that has reached the jellium edge. It is worthwhile to mention that the total energy released in the relaxation/neutralization sequence ($\approx$120 eV) is much lower than the total energy loss, and it is essentially absorbed by electrons in Auger processes. The capture of electrons in the incoming part of the trajectory can be interpreted as an increase of the initial L-shell population. For N^{6+} and N^{7+} ions the main difference is a longer neutralization sequence due to the presence of K-shell holes. The filling of the K-shell vacancy is interpreted as a transition to the adjacent curve in the figure towards a smaller N_h value for a KVV process and towards a larger value of N_h value for a KLL process.

In our experimental studies we have scattered N^{q+} ions with energies of 70 and 140 keV ($v = 0.45v_0$ and $0.63v_0$) from a clean and flat Al(111) surface under a grazing angle of incidence $\Phi_{\text{in}} \approx 0.7°$. The surface was prepared by cycles of grazing sputtering with 25 keV Ar^+ ions and subsequent annealing at 500 °C for about 10 min. The base pressure in our UHV chamber was in the upper 10^{-11} mbar regime, and the energy spectra of the well collimated beams were recorded by means of an electrostatic analyzer with cylindrical electrodes of 0.5 m radius and a resolution of $\delta E/E < 10^{-3}$.

In Fig. 3 we plot the mean energy loss ΔE for 70 and 140 keV N^{q+} as a function of the charge q of the incident ions. The data show a monotonic increase of the energy loss with an increasing charge state. For N^{q+} ions the energy loss is constant for a variation of the angle of incidence [18], which simplifies the analysis of the energy loss data. More precisely, the constancy of ΔE with variations of Φ_{in} implies $\Delta E \sim v\, dE/dx$ [19] and allows one to neglect effects on the energy loss by changing the trajectory. This observation excludes, in this case, the explanation given in Ref. [4] for the observed enhancement of the energy loss with charge q for Ar^{q+} ions scattered from a graphite surface: The attractive

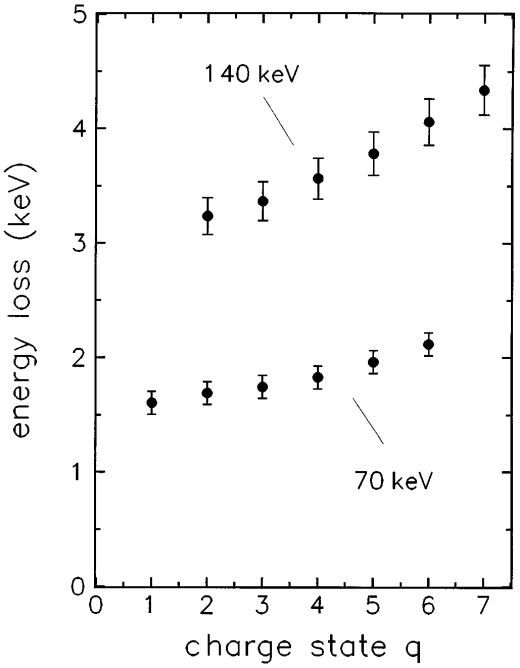

FIG. 3. Energy loss for 70 and 140 keV N^{q+} ions as a function of the incident charge state of the projectiles after scattering from an Al(111) surface under a grazing angle of incidence $\Phi_{\text{in}} \approx 0.7°$.

image force increases the effective angle of incidence for high q in such a way that ΔE has the same angular dependence as for low charge incident ions. The authors of Ref. [4] find no charge state effect in the stopping power. Inspection of our data reveals that the energy losses for 70 and 140 keV scale with projectile energy, which is consistent with a velocity proportional stopping power at low velocities.

The enhanced energy loss for higher charge states of the incident ions can be attributed to the enhanced friction coefficients Q obtained in our calculations for ions with several L-shell vacancies. Whereas the calculation shows an enhancement of electronic stopping for projectiles with empty L shells (N^{5+}, N^{6+}, and N^{7+} ions) over ground state ions by a factor of 2, the experimental energy loss increases with charge only by up to 35%. This finding can be considered as an indication of the fact that the lifetime of L-shell vacancies (τ_L) is shorter than the interaction time of the ions with the surface. ($\tau_L \approx 2$ fs is consistent with the calculations by Díez Muiño *et al.* [20,21] and Vaeck and Hansen [22].) Therefore, only on the initial part of the (incoming) trajectory a large number of L-shell vacancies can be present and lead to an enhanced stopping of projectiles.

The following conclusions on the interaction of multicharged ions with surfaces can be derived from our combined theoretical and experimental studies on the energy loss:

(1) In the experiment we observe an increase of the energy loss with increasing charge state, no matter

whether K-shell holes are present or not, which is explained by the theoretically found increase of the stopping power as a function of the number of vacancies in the L shell for $q \leq 5$ (curve $1s^2$ of Fig. 2) and a longer lifetime of the L-shell holes when K-shell vacancies are present for $q > 5$ [20,21].

(2) The measured enhancement of the energy loss for N^{6+} and N^{7+} ions also implies that the K shell will be predominantly filled before the L shell is completely filled. This is consistent with the opening of the KLL Auger channel when two L-shell electrons are present. Furthermore, the KLL Auger rate is higher for a higher number of L-shell electrons [23].

(3) By comparing the measured energy loss of N^{+} and N^{6+} ions and using the calculated values of the stopping for the different charge states, we can estimate an effective distance from the surface (z_{fill}) at which the ion is fully neutralized and relaxed ($N_h = 0$) along a given trajectory. We obtain $z_{\mathrm{fill}} \approx 1.3$ a.u. from the measured enhancement of the energy loss of about 35% instead of a factor of 2. This means that the N^{6+} ions have inner-shell holes during only approximately a quarter of its total effective length of energy loss L, but nothing can be concluded about the distance of first electron capture.

In conclusion, the charge state dependence of the energy loss of slow multicharged ions traveling through the electron gas of a metal is the outcome of a complex situation, where both the different screening (and the resulting different stopping powers) and the lifetimes of the excitation states of the ions play a role. As an example, for N^{q+} ions we find (i) an opposite behavior of the dependence of the stopping power on the number of vacancies in K and L shells, and (ii) that the experimentally observed increase of the energy loss with the charge state of the ion can be explained by a larger stopping power of ions with vacancies in the L shell and by a longer lifetime of the configurations with K-shell holes. Finally, we point out that theoretical studies such as the one presented here provide a basis for an analysis of previous and future experiments on this subject.

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