



## Charge state dependence of the energy loss of slow nitrogen ions reflected from an aluminum surface under grazing incidence

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### Abstract

The experimentally observed monotonic increase of the energy loss with charge  $q$  for  $N^{q+}$  ions impinging on an Al(111) surface under grazing angle of incidence is explained by a model that accounts for the effect of K- and L-shell vacancies in the stopping power. Our model allows us to estimate the characteristic time scales (and distances from the surface) for the neutralization and relaxation of multicharged ions. We use a transport cross section formulation of the electronic stopping of ions in an electron gas, as well as a self-consistent calculation of the scattering potential within density functional theory. © 1999 Elsevier Science B.V. All rights reserved.

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The charge state dependence of the energy loss of ions through matter has been investigated since the early years of this century both theoretically and experimentally. In the weak coupling limit ( $Z_1/v \ll 1$ , where  $Z_1$  is the ion nuclear charge and  $v$  the ion speed measured in atomic units), first order perturbative approaches give a dependence on the square of the charge. However, when  $Z_1/v \geq 1$  nonlinear effects start to be important

and first order treatments are no longer valid. Measured data are explained by an effective charge concept [1], which is defined artificially as the square root of the stopping ratio to equal velocity protons for the same target. This approach is particularly inadequate for slow ions in solid matter, as recent experiments [2] that follow the so-called  $Z_1$ -oscillation in stopping show. In this respect it is worth to mention that in the case of slow ions in metals one cannot interpret the effective charge in stopping as the nuclear charge minus the number of bound electrons. At low velocities, the magnitude of the stopping cross section is determined by the strength of the scattering

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of Fermi energy electrons, which is an oscillatory function of the range of the scattering potential due to the quantum mechanical wave nature of the electrons. Furthermore, the equilibrium charge state of slow ions in metals is always low (mostly neutral or singly charged ion).

The challenge of studying pre-equilibrium effects that appear for slow multicharged ions introduces another source of unknowns in the description of the problem, i.e. the time scale for neutralization and relaxation of the ions. The availability of powerful ion sources to produce this type of ions has stimulated an increasing number of experimental studies on ion–surface interactions, not always completely understood, like electron emission, X-ray emission, energy loss or sputtering [3]. Although the time scales for neutralization and relaxation of slow multicharged ions interacting with solid surfaces are not precisely known, the analysis of several experiments by different groups has established order of magnitude estimates that are consistent with recent calculations [4]. Therefore, one can use this information to design new experiments with the purpose of investigating specific effects, like the charge state dependence of the energy loss of slow multicharged ions interacting with solid matter. In the case of transmission experiments charge state equilibrium is reached too fast to observe any significant charge effect in the measured energy loss [5], which is expected to be more significant in ion–surface collisions. The difficulty in designing an experiment to show that the initial charge of slow ions has an effect on the energy loss arises when choosing the relevant impact energy and angle of incidence: the ions must be reflected (not too large incident angle) after interacting strongly enough with the surface in a time scale comparable with that of neutralization and relaxation and, at the same time, the ion speed should be below the Fermi velocity of the target electrons. In our combined theoretical and experimental study we address the question of the dependence of the energy loss of several keV/amu N ions on incident charge. The results of our study show that the expectation of a higher energy loss for higher charge is far from being trivial and, in principle, not applicable to every system.

In the experiments  $N^{q+}$  ions ( $q \leq 7$ ) were scattered from a clean and flat Al(111) surface under a grazing angle of incidence of  $\phi_{in} \cong 0.7^\circ$ . The preparation of the surface consisted in cycles of grazing sputtering with 25 keV  $Ar^+$  ions and subsequent annealing at  $500^\circ C$  for about 10 min. The base pressure in the UHV chamber was in the upper  $10^{-11}$  mbar regime. Typical energy spectra for 140 keV  $N^{q+}$  ions are shown in Fig. 1 for  $q=2$  and  $q=6$ . They were obtained using well-collimated beams by means of an electrostatic analyzer with cylindrical electrodes of 0.5 m radius and an energy resolution of  $\delta E/E < 10^{-3}$ . Most of the scattered projectiles are neutral after reflection at the surface, but only singly charged nitrogen ions were detected by the energy analyzer.

In Fig. 2 we plot the mean energy loss  $\Delta E$  as a function of the incident charge  $q$  for 140 keV N ions (and 300 keV). The corresponding ion velocities are  $v = 0.63v_0$  and  $v = 0.93v_0$ , respectively. The data show a monotonic increase of  $\Delta E$  with  $q$  of about 1.2 keV when  $q$  varies from 2 to 7 for 140 keV impact energy, and of about 3.5 keV when  $q$  varies from 3 to 7 for 300 keV impact energy.

In Fig. 3 it is shown that the measured energy loss  $\Delta E$  for  $N^+$  ions does not depend on the angle of incidence. This suggests that effects of the energy loss on changes of the trajectory can be dis-

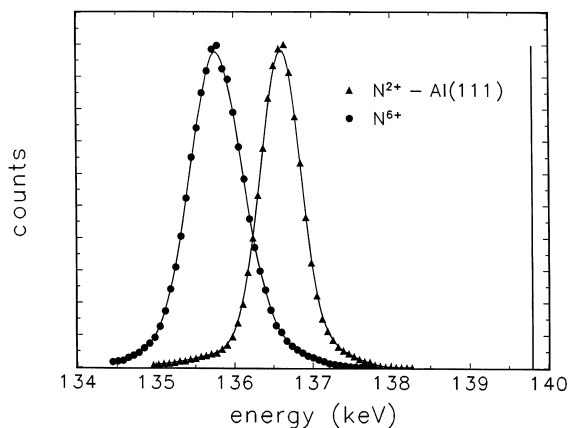


Fig. 1. Energy spectra of the direct and scattered beams after interaction of 140 keV  $N^{2+}$  and  $N^{6+}$  ions with an Al(111) under an angle of incidence  $\phi_{in} \cong 0.7^\circ$ .

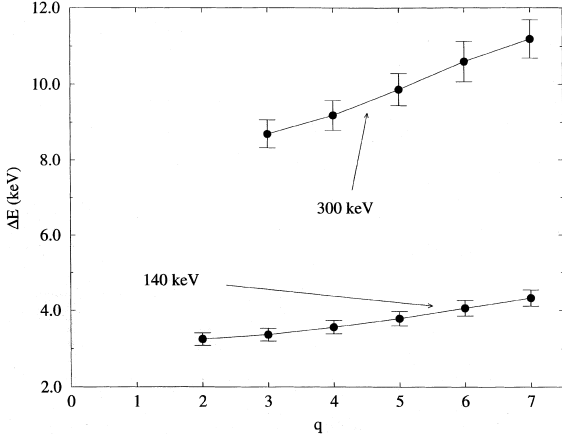


Fig. 2. Energy loss for 140 and 300 keV  $N^{q+}$  ions as a function of the incident charge state of the projectiles after scattering from an Al(111) surface under a grazing angle of incidence  $\phi_{in} \cong 0.7^\circ$ .

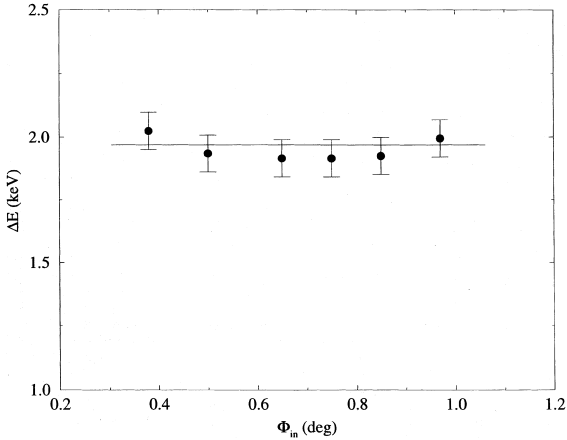


Fig. 3. Most probable energy loss as a function of the angle of incidence for 100 keV  $N^+$  ions scattered from Al(111).

regarded and allows us to analyze the experimental data using the relation:

$$\Delta E = \frac{dE}{dx} L, \quad (1)$$

where  $L$  is an effective interaction length and  $dE/dx$  the stopping power of the ion. For 140 keV  $N^+$  we obtain  $L \approx 200$  a.u. which implies an effective perpendicular distance of interaction  $\Delta z$  about 1.3 a.u. From calculations of the trajectory performed by

using an averaged surface planar potential constructed from the atomic ZBL universal potential, we obtain a turning point of the trajectory  $z_0$  at around 1.3 a.u. from the topmost layer. This implies that the part of the trajectory in which the ion excites efficiently the conduction band of the metal extends up to  $z_{eff} = z_0 + \Delta z \approx 2.6$  a.u. from the topmost layer. This distance is around 0.4 a.u. outside the jellium edge, which is consistent with the approximation introduced in Eq. (1) that neglects the exponential tails of the dependence of the stopping power on the distance from the surface.

For higher charge states, the attractive image force produces both an increase of the effective angle of incidence (a few tens of degree for the higher charges) and of the distance of penetration of the projectile. As a result of the combined action of these two effects appears an approximate compensation: the effective interaction length  $L$ , i.e. the length of the part of the trajectory within the distance  $z_{eff}$ , remains essentially constant (see Fig. 4). This is a further justification for neglecting the trajectory effect and implies that the enhanced energy loss for higher charge states should be explained by the dependence of the stopping power on the charge state of the ion.

The electronic stopping power for  $N^{q+}$  ions in different charge states is obtained from the self-consistent screened potential calculated within density functional theory [6]:

$$\frac{dE}{dx} = vn_0v_F\sigma_{tr}(v_F) = vQ(v_F), \quad (2)$$

where  $Q$  is the friction coefficient, which is proportional to the density of conduction band electrons of the metal ( $n_0$ ) and to the transport cross section at the Fermi level ( $\sigma_{tr}$ ) of the corresponding screened potential. We neglect any contribution to the energy loss from charge exchange processes since in the resonant capture there is no energy change and in the Auger capture at low velocities the transition energy is absorbed by the excited electron. The different charge and excitation states are considered to give rise to different configurations, specified by the occupation numbers of the 1s, 2s and 2p states for a given number of holes ( $N_h$ ) in K- and L-shells [7]. In Table 1 the values of the friction coefficient  $Q$  of an electron gas with

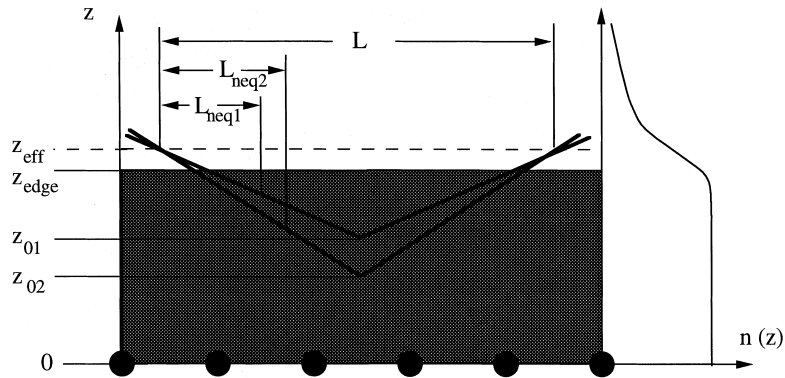


Fig. 4. Schematic representation of the trajectory of two different charge states of N reflected under grazing angle of incidence from Al(111).  $L_{\text{neq1}}$  and  $L_{\text{neq2}}$  are the distances the ions travel until they reach the equilibrium for the lower and higher charge states, respectively.  $z_{01}$  is the distance of closest approach for the lower charge state,  $z_{02}$  the distance of closest approach for the higher charge state,  $z_{\text{edge}}$  corresponds to the jellium edge position,  $z_{\text{eff}}$  the outermost border of the region where the ions lose energy in an effective way and  $z = 0$  is the position of the topmost layer of Al atoms.  $L$  is the total length for the energy loss [see Eq. (1)]. Note, that despite of the changes in the trajectory due to the image force,  $L$  does not depend on the charge state.  $n(z)$  represents the electronic density profile at the surface.

Table 1  
Values of the friction coefficient  $Q$  for different configurations characterized by the number of holes in the inner-shells ( $N_h$ )<sup>a</sup>

| $N_h$ | $q_{\text{min}}$ | $Q(1s^2)$ | $Q(1s^1)$ | $Q(1s^0)$ |
|-------|------------------|-----------|-----------|-----------|
| 10    | 7                |           |           | 1.52      |
| 9     | 6                |           | 1.46      | 1.32      |
| 8     | 5                | 1.49      | 1.24      | 1.08      |
| 7     | 4                | 1.28      | 1.0       | 0.85      |
| 6     | 3                | 1.07      | 0.82      | 0.67      |
| 5     | 2                | 0.94      | 0.7       | 0.55      |
| 4     | 1                | 0.86      | 0.63      | 0.5       |
| 3     |                  | 0.82      | 0.62      | 0.49      |
| 2     |                  | 0.79      | 0.63      | 0.52      |
| 1     |                  | 0.81      | 0.68      |           |
| 0     |                  | 0.825     |           |           |

<sup>a</sup> For a given number of holes three different configurations are considered which correspond to different distributions of holes between the K- and L-shells. In the column  $Q(1s^x)$  the values of  $Q$  when  $x$  electrons are present in the K-shell are shown. In the column labelled  $q_{\text{min}}$  we give the minimum initial charge of the ion that during the neutralization/relaxation process can give raise to configurations with  $N_h$  holes.

density parameter  $r_s = 2$  (corresponding to aluminum) for N ions are listed for different number of inner-shell holes  $N_h$ . We note that  $N_h$  can be larger than  $q$  or  $Z_1$ , due to the existence of excited states. For example, for  $q = 6$  the configuration  $(1s^1, 2s^0,$

$2p^0)$  has  $N_h = 9$ , and for  $q = 1$  the configuration  $(1s^2, 2s^1, 2p^3)$  has  $N_h = 4$ .  $q_{\text{min}}$  is the minimum value of the charge state of the incident ion needed to achieve an electronic configuration inside the solid with a given number of holes ( $N_h$ ). The data show an increase of  $Q$  with the number of holes in the L-shell when  $N_h > 3$  and  $Q$  is essentially constant when  $N_h \leq 3$ . On the other hand,  $Q$  decreases as the number of holes in the K-shell increases for low  $N_h$  and is almost constant when  $N_h$  is high. This opposite behaviour of  $Q$  as a function of the number of holes in the K- and L-shells is related to the different degree of localization of the K- and L-shell orbitals [7].

Thus, the enhanced energy loss for higher charge states is attributed to the enhanced friction coefficient  $Q$  for ions with several L-shell vacancies. The calculations show an enhancement of the stopping for projectiles with empty L-shells ( $N^{5+}$ ,  $N^{6+}$  and  $N^{7+}$ ) over the ground state ( $N_h = 0$ ) value by a factor of 2 whereas the experimental energy loss increases with charge by only up to 35%. This indicates that the lifetime of the L-shell vacancies ( $\tau_L$ ) is shorter than the interaction time of the ion,  $\tau_L \cong (L/v)/4$ . This is consistent with the theoretical calculations [4,8]. Therefore, only on the initial part of the trajectory a large number of holes can be present and lead to an enhanced stopping

power. For  $N^{6+}$  and  $N^{7+}$  ions the main difference, as compared to  $N^{5+}$  ions, is a longer time for the full neutralization and relaxation sequence (larger  $\tau_L$ ) due to the presence of K-shell holes [7], that implies a further enhancement of the energy loss.

The study of other systems, i.e. projectile and target combinations, requires specific calculations due to the complexity of nonlinear screening. For a given projectile there will be always inner shells which are localized in a distance shorter than the Fermi wavelength playing the role of the K-shell for N ions, and more extended outer shells playing the role of the L-shell for N ions. For example, for Ar projectiles the L-shell is localised and the M-shell is more extended. Furthermore, as the lifetime of the outer vacancies is also playing a role in determining the energy loss and the effects due to changes in the trajectory can be significant for other systems, one cannot predict a priori an enhancement of the energy loss with increasing charge for a given system, in the same way as the  $Z_1$ -oscillations in stopping could not be explained by any first order calculation or effective charge theory.

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