Energy loss of slow ions in a nonuniform electron gas

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The energy loss of slow ions scattered off an Al(111) surface is explained using a theoretical description based on scattering theory. The explicit inclusion of gradient corrections to account for a nonuniform electron density at the surface provides good agreement with the measured data over a wide range of distances (electron densities) for different ions with atomic number $Z_1 \leqslant 20$.

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I. INTRODUCTION

Stopping phenomena of energetic atomic particles in matter are of paramount importance in many scientific and technological applications and a subject of active research. An important aspect of this topic is the slowing down of ions at low energy/velocity, i.e., projectile velocities $v < v_0$ (v_0 is the Bohr velocity$=1$ atomic unit$=1$ a.u.). In this velocity regime, the energy loss of projectiles is generally dominated by interactions with electrons of the target. The stopping process can be considered to be due to scattering of conduction electrons by the screened potential of the projectile. In recent years, this intricate problem has been treated by deriving electronic stopping powers from quantum-mechanical scattering theory based on scattering potentials deduced from density functional calculations for ions embedded in a (uniform) electron gas of density n.[1]

It turns out that this nonlinear approach shows a substantial improvement in the description of electronic stopping power in comparison to theories based on linear response[2] as, e.g., demonstrated by experimental data for the passage of protons through solid targets with atomic numbers $4 \leqslant Z_2 \leqslant 83$.[3] Furthermore, this approach allows one to understand in a straightforward manner the so-called Z_1 oscillations, an experimentally observed oscillatory behavior of stopping power with increasing projectile atomic number Z_1.[4–6] Aside from considerable success of the theoretical approach to describe electronic stopping power of slow ions, comparison with experiments on a quantitative level was lacking defined conditions. For penetration of thin monocrystalline foils under channeling conditions,[4,6] elastic scattering (''nuclear energy loss'') is negligible; however, the electron density in a crystal channel is not uniform and is generally approximated by a mean value.[7,8] Furthermore, it is an open question: What effect does the gradient of electron density in a *nonuniform* electron gas have on projectile energy loss? This particular aspect on energy dissipation of atomic projectiles traversing solid matter has not been addressed so far. Since in general ''realistic'' targets are characterized by pronounced gradients in the spatial distribution of electrons, this specific problem turns out to be of considerable relevance concerning a general understanding of stopping phenomena for energetic atomic projectiles.

In this paper we report on quantitative experimental as well as theoretical investigations on this problem. We have studied the energy loss of ions in the density profile of the electron selvage in front of a metal surface. A sketch of this profile is displayed for an Al(111) surface by the solid curve with solid circles[9] in Fig. 1, showing the well-established feature of a saturation to bulk densities close to the surface and an exponential spill out towards vacuum (z axis). In a simple picture, the assumption of an interaction interval Δz at a given distance from the surface reveals an almost uniform density close to the topmost layer, whereas with an increase in distance (for smaller electron densities) considerable gradients are present. In the studies presented here, we will outline the effects on electronic stopping of ions in these two different regimes of the electron gas, i.e., the region in close vicinity of the surface plane of uniform electron density with bulk values and larger distances (some a.u.) with

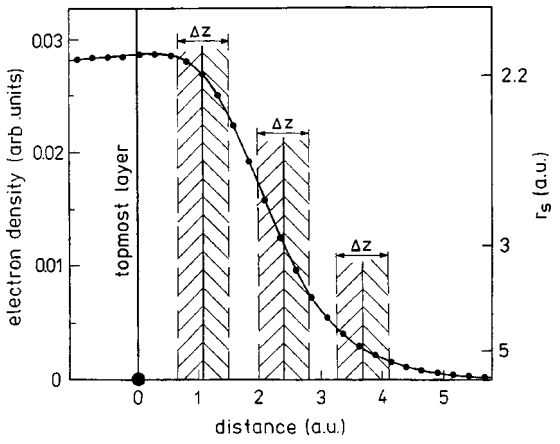

FIG. 1. Schematic representation of electron density profile $n(z)$ at Al(111) surface (Ref. 9). Origin of distance from surface z is chosen at topmost layer of surface atoms, where $n(z)=n_0$. We denote three different characteristic distances as short (1.2 a.u.), intermediate (2.4 a.u.), and long ($z=3.7$ a.u.) and typical uncertainties of Δz in determination of z, originating from trajectory and density profile calculations.

reduced electron densities and considerable gradients of these densities.

II. EXPERIMENT AND EVALUATION OF DATA

In order to derive position-dependent stopping powers, we made use of a concept proposed by Kimura, Hasegawa, and Mannami[10] for grazing incidence scattering of ions from a clean and flat surface. In this collision regime, projectiles are steered on well-defined trajectories by lattice atoms of the topmost surface layer in a sequence of small angle scattering events, i.e., (surface) ''channeling.'' [11] Then the total projectile energy loss ΔE results from the integration of a position-dependent stopping power $dE/dx(z)$ over complete trajectories (coordinates x and z are chosen parallel and normal with respect to surface plane):

$$\Delta E = \int_{\text{trajectory}} \frac{dE}{dx}(z) \quad dx. \tag{1}$$

Since projectile trajectories can be changed in a well-defined manner by varying the glancing angle of incidence Φ_{in}, $(dE/dx)(z)$ can be derived from the resulting variation of $\Delta E(\Phi_{\text{in}})$. Recently, we have reported on measurements of the energy loss ΔE for projectiles with atomic number $1 \leqslant Z_1 \leqslant 20$ and velocity $v = 0.5 v_0$ scattered off an Al(111) surface as a function of Φ_{in}.[12] The data obtained in these studies were evaluated in terms of Eq. (1) by making use of an analytical approximation for the projectile trajectory.[10] Assuming a functional dependence of the stopping power in terms of a simple exponential decay $(dE/dx)(z) = (dE/dx)(0)\exp(-z/z_0)$, the integral in Eq. (1) can be solved analytically, and the parameters $(dE/dx)(0)$ and z_0 are obtained from a best fit to the experimental energy loss as function of angle of incidence $\Delta E(\Phi_{\text{in}})$. The position-dependent stopping powers derived by this procedure[12] showed agreement with the predictions of the uniform electron density stopping power calculations[13] on a qualitative level.

In the present work we performed a more elaborate numerical analysis of our experimental data with trajectories derived for different approximations of the scattering potentials including image charge effects.[14] Position-dependent stopping powers $(dE/dx)(z)$ are described by different functional forms [single exponential, combination of exponentials that merges to the dependence of the electron density $n(z)$]. This type of analysis of data was performed for all sorts of projectiles with $Z_1 \leqslant 20$ at $v = 0.5 v_0$, and from a critical judgement of results $(dE/dx)(z)$ is obtained with an estimated absolute uncertainty of less than 20%.

As a first representative example we display in Fig. 2 the energy loss of 54-keV Be^+ ions ($v = 0.5$ a.u.) scattered from an atomically clean and flat Al(111) target as function of the grazing angle of incidence Φ_{in}. The data show a slight decrease with increasing angle. The curves represent best fits to the data comprising different assumptions of the interactions' potentials for the projectile trajectories and the functional form of $(dE/dx)(z)$. We reveal for the angular range of available data an excellent description which holds for the

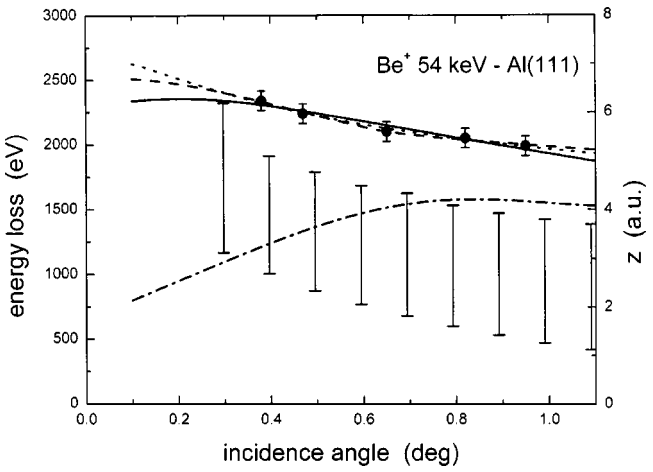

FIG. 2. Energy loss of 54-keV Be^+ ions scattered from Al(111) as function of angle of incidence. The curves represent results of best fits to trajectory calculations for different assumptions on the scattering potentials and the functional form of the position-dependent stopping power (solid curve: ZBL potential and exponential decay; dotted curve: modified Moliere potential and exponential decay; dashed curve: ZBL potential and different exponential decays referred to distance z_d). The vertical bars represent intervals between distances of closest approach to surface plane and distance where 90% of total energy loss is accumulated. Dashed-dotted curve: Energy loss derived from theoretical stopping powers (full circles in Fig. 3).

different approximations for the scattering potentials and $(dE/dx)(z)$. The solid curve represents a best fit using the ''universal'' potential proposed by Ziegler, Biersack, and Littmark (ZBL potential)[15] and a simple exponential decay of $(dE/dx)(z)$. The dotted curve is obtained in a similar manner with the Moliere potential using a screening function proposed by O'Connor and Biersack[16] and the dashed curve represents an analysis with the ZBL potential and $dE/dx(z)$ described by two single exponential functions with different decay constants below and above a distance z_d. The vertical bars in Fig. 2 represent intervals of distances z starting from distances of closest approach to the surface plane z_{min} and extending to distances where 90% of the total energy loss is accumulated. This plot of intervals illustrates the spatial sensitivity of our analysis with respect to position dependent stopping powers.

In Fig. 3 we show the resulting stopping powers as function of distance z from the topmost layer of the surface plane. Within the uncertainties inherent in the experimental data and their evaluation we find no significant deviation among the different approaches. The analysis of projectile trajectories reveals that the projectiles reach distances of closest approach between about 1 and 3 a.u. so that $(dE/dx)(z)$ is probed by our method within an interval of distances ranging from about 1 to 4 a.u. (cf. Fig. 2). The solid circles represent calculations using a scattering approach for an electron gas of uniform density as outlined in the following section. We find good agreement between these calculations and the experimental analysis for distances $z \leqslant 2$ a.u., whereas for larger z the calculations yield smaller values than the experiment. In order to demonstrate the effect of this deviation on the energy loss, we fit the theoretical $(dE/dx)(z)$ by a func-

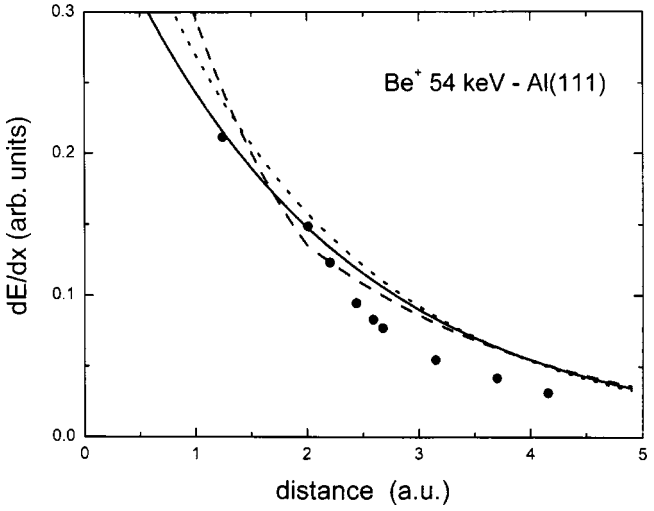

FIG. 3. Position-dependent stopping powers for 54-keV Be^+ ions in front of Al(111) surface as obtained from fit to data in Fig. 2. Solid curve, single exponential decay for scattering in planar potential with ZBL screening; dotted curve, single exponential decay for Moliere screening; short dashed curve, decay with different exponential sections for ZBL screening; full Circles, calculations with scattering approach for electron gas with uniform electron density; long dashed curve, fit to calculations with function describing electron density in front of the free electron gas metal.

tion that approximates the functional dependence of the electron density in front of a free-electron metal surface.[17] The plot of the resulting energy loss as function of angle in Fig. 2 (dashed dotted curve) shows a substantial difference in the measurements and demonstrates good resolution of our data with respect to the analysis of position-dependent stopping powers. The discrepancy between theory and experiment at larger distances is attributed to the gradient of conduction electron densities in front of the metal surface and will be discussed in detail below.

In Figs. 4 and 5 we show similar results and analysis of data for the scattering of 72-keV C^+ ions ($v=0.5$ a.u.). The experimental energy loss as function of angle of incidence is

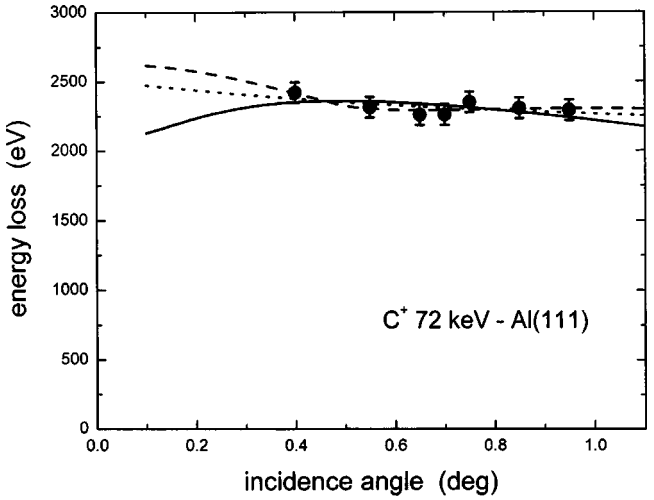

FIG. 4. Same as Fig. 2, but for 72-keV C^+ ions.

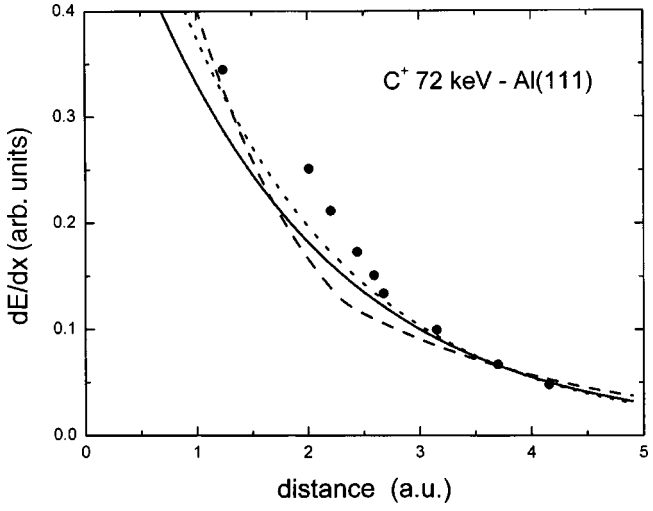

FIG. 5. Same as Fig. 3, but for 72-keV C^+ ions.

well fitted by the approaches discussed already for Be projectiles (Fig. 4). The resulting stopping powers agree quite well with calculations using the scattering approach for an electron gas of uniform density. This agreement holds in particular also for larger distances z.

As a further example we display in Figs. 6 and 7 data obtained with 240-keV Ar^{2+} ions ($v=0.5$ a.u.). Here the agreement of the position-dependent stopping powers with theory is good for small distances, i.e., for $z \leqslant 2$ a.u.; however, for larger distances we reveal a sheer discrepancy between theory and experiment. In the analysis of data performed in this work for the first 20 elements of the periodic table, we found partially good agreement between theory for a uniform electron gas and experiment as demonstrated for C. However, for noble gas ions and in particular for ions with atomic numbers $Z_1 \geqslant 15$ we find substantial differences for larger z between theory and experiment. From the analysis of the experimental data we deduce the stopping powers for distances $z=1.2$, 2.4, and 3.7 a.u. Corresponding plots of those stopping powers as function of Z_1 will be presented below and compared with theory. We will show that overall

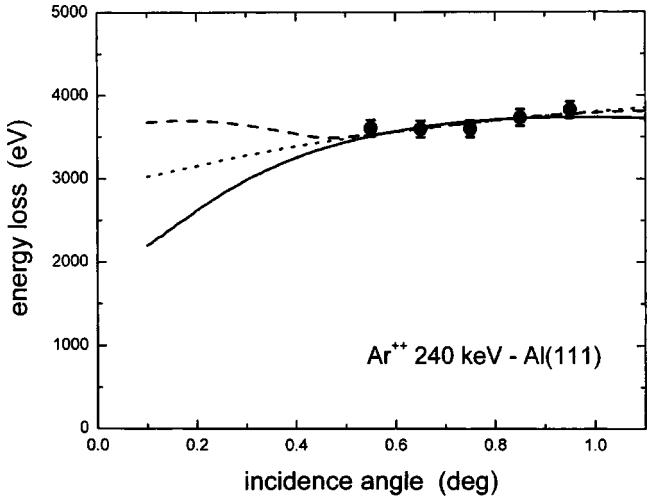

FIG. 6. Same as Fig. 2, but for 240-keV Ar^{2+} ions.

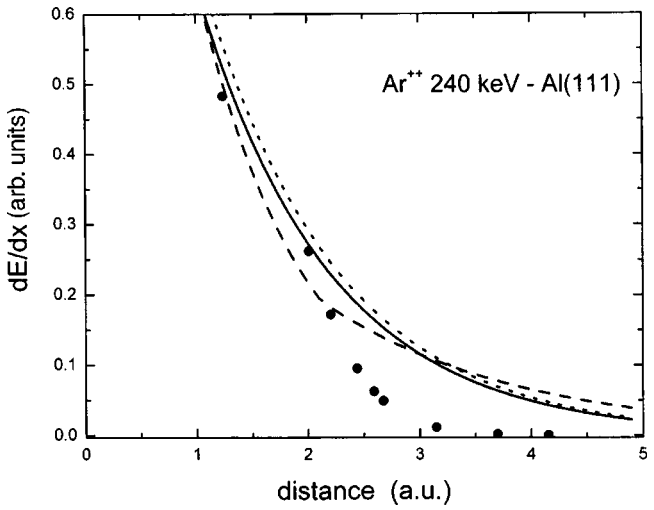

FIG. 7. Same as Fig. 3, but for 240-keV Ar^{2+} ions.

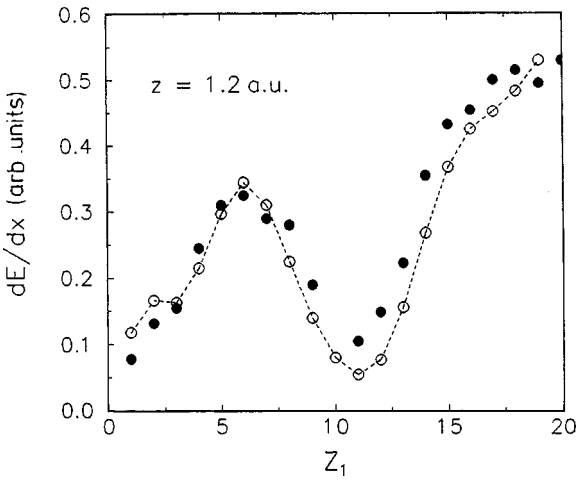

FIG. 8. Stopping power of ions with $v=0.5$ a.u. as function of atomic number Z_1 at distance $z=1.2$ a.u. from an Al(111) surface. The full circles denote experimental data and open circles results obtained for $r_s=2.2$ a.u. with Eq. (2).

good agreement of these data with theory is achieved if the gradient of the electron density in the selvage of the Al surface is taken into account in the theoretical treatment of projectile stopping.

III. THEORETICAL DESCRIPTION OF STOPPING IN A NONUNIFORM ELECTRON GAS

In our theoretical studies, a scattering approach has been used for the calculations of stopping powers for slow ions in metals with scattering potentials obtained from density functional theory for a static ion embedded in a free electron gas.[18,19] The dependence of the energy loss on the projectile charge is weak for ions of low charge[20] and will affect the energy loss only for periods of time t short compared to the total interaction time (L/v), where t is a characteristic neutralization time (typically a few femtoseconds). More specifically, the stopping power is given by[2,13]

$$\frac{dE}{dx}=n_0 v \quad v_F \sigma_{\mathrm{tr}}(v_F), \tag{2}$$

where n_0 is the electronic density, v_F the Fermi velocity, and $\sigma_{\mathrm{tr}}(v_F)$ the momentum transfer cross section at the Fermi level. The product $v_F\sigma_{\mathrm{tr}}(v_F)$ is the integrated scattering rate for momentum transfer, which governs the dissipative processes. Therefore, one can interpret the stopping power described by this formula as the result of the momentum transfer per unit time to a uniform current of independent electrons $(n_0 v)$, scattered by a fixed screened potential. For a *uniform* electron gas, there is a one-to-one correspondence between the density n_0 and the Fermi velocity $v_F=\sqrt[3]{3\pi^2 n_0}=\sqrt[3]{9\pi}/4/r_s\sim 1.92/r_s$ with r_s being the one-electron radius.

In case of a *nonuniform* electronic density $n_0(z)$, as, e.g., in front of a metal surface (see Fig. 1), one would proceed to define a local Fermi velocity in order to derive position-dependent stopping powers from Eq. (2) and then $\Delta E(\Phi_{\mathrm{in}})$ from Eq. (1). In the electronic density profile of a metal surface, we distinguish three different ranges (cf. Fig. 1): (i) short distances where the density saturates to bulk values (about n_0) and is rather uniform, (ii) regions of intermediate densities around $n_0/2$, and (iii) regions of low densities $<n_0/8$. In the latter two cases, there are significant gradients in the density profile. For specifically chosen values, $z=1.2$ a.u., $z=2.4$ a.u., and $z=3.7$ a.u. from the topmost atomic layer, the corresponding $r_s(z)=\sqrt[3]{3/4\pi n_0(z)}$ for an Al surface are $r_s=2.2$, 3, and 5, respectively.[9] A conservative estimate on the uncertainty in the determination of z of the order of 0.25 a.u. for the short and intermediate distances and 0.5 a.u. for the large distance gives a range of r_s values of the order of $2.1<r_s<2.3$, $2.7<r_s<3.3$, and $4<r_s<6$ for each distance, respectively.

In Fig. 8 we show a comparison of stopping powers calculated for $z=1.2$ a.u. $(r_s=2.2)$ (open circles) with those derived from the energy loss measurements (full circles) as a function of the projectile atomic number Z_1. We find for this case excellent quantitative agreement with the experiments for our theoretical treatment free from adjustable parameters. This shows the adequacy of the local density picture for high electron densities and small gradients. Therefore it can be considered the most detailed and stringent test of this theory so far.

However, when we compare the experimental data with the results obtained from Eq. (2) for the stopping power at an intermediate distance $(z=2.4$ a.u.) and large distance $(z=3.7$ a.u.), the agreement is poor (open circles and dashed curves in Figs. 9 and 10). A deviation in amplitude and phase of the Z_1 oscillations appears as the density decreases, particularly evident by the pronounced minima at $Z_1=2$ and $Z_1=18$ for $r_s=5$ predicted by theory. Furthermore, we cannot invoke the uncertainty in the determination of $r_s(z)$ mentioned above, since there is no r_s value that reproduces the amplitude and phase of the data.

This indicates the nontrivial role of gradient corrections in the kinetic energy functional for *nonuniform* electron densities. Therefore, the stopping power given by Eq. (2) requires that it be modified to account for this effect. We define two density parameters r_{s1} and r_{s2} related to the current density

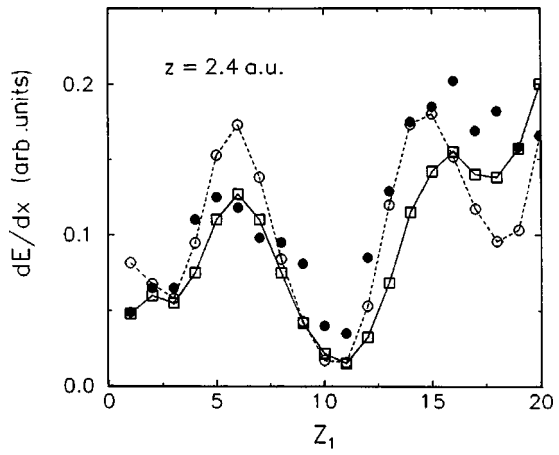

FIG. 9. Stopping power of ions with $v=0.5$ a.u. as function of atomic number Z_1 at $z=2.4$ a.u. Full circles are experimental data; dashed lines connect results obtained with Eq. (2) for $r_s=3$ a.u. (open circles); solid lines and open squares are results obtained using Eq. (4) with $r_{s1}=3.1$ a.u. and $r_{s2}=2.5$ a.u.

$n_{01}v=3v/(4\pi r_{s1}^3)$ and the effective scattering impulses $v_{F1}=1.92/r_{s1}$ and $v_{F2}=1.92/r_{s2}$. The latter is approximately given by the modification of the kinetic energy density for nonuniform systems, i.e., the so-called von Weizsäcker term,[21,22] which, for an exponential decay $\exp(-\beta z)$ of the density, leads to an increase from $v_{F1}^2/2$ to[23]

$$\frac{v_{F2}^2}{2}\cong\frac{v_{F1}^2}{2}+\frac{\beta^2}{8}. \tag{3}$$

The von Weizsäcker term accounts for the increase in kinetic energy due to gradients in the electron density. Therefore, a proper modification of Eq. (2) for the case of nonuniform density, based on the previous statements, is given by

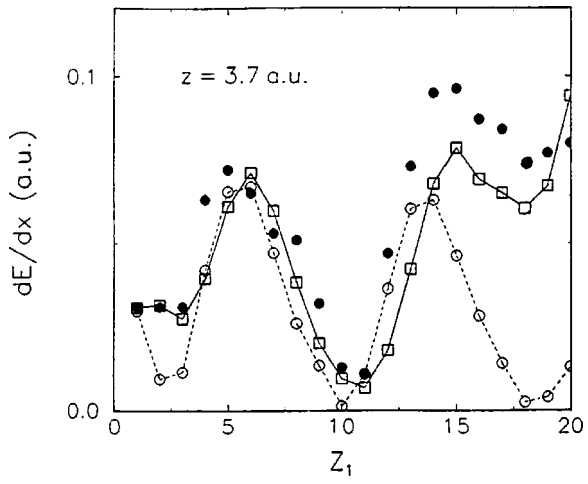

FIG. 10. Stopping power of ions with $v=0.5$ a.u. as function of atomic number Z_1 at $z=3.7$ a.u. Full circles are experimental data; dashed lines connect results obtained with Eq. (2) for $r_s=5$ a.u. (open circles); solid lines and open squares are results obtained using Eq. (4) with $r_1=4$ a.u. and $r_{s2}=2.7$ a.u.

$$\frac{dE}{dx}=[n_{01}v][v_{F2}\ \ \sigma_{\rm tr}\ (v_{F2})], \tag{4}$$

where $v_{F2}\ \sigma_{\rm tr}\ (v_{F2})$ is the scattering rate and $n_{01}v$ has already been defined as current density.

In Figs. 9 and 10 we show results for the stopping powers obtained using Eq. (3) for $z=2.4$ a.u. and $z=3.7$ a.u. with $r_{s1}=3.1$ a.u., $r_{s2}=2.5$ a.u. and $r_{s1}=4$ a.u., $r_{s2}=2.7$ a.u., respectively. The values of the parameter r_{s1} used for each distance are within the range of acceptable r_s values given above in Fig. 1. The values of r_{s2} are justified from the values of r_{s1} using Eq. (3) with $\beta=2\sqrt{2\Phi}$, where Φ is the Al(111) surface work function. β is the inverse decay length of the electron density profile at the surface. As shown in Figs. 9 and 10, we find a significant improvement in the overall quantitative description of the experimental data using Eq. (4) as compared to Eq. (2). The Z_1 oscillations of the stopping powers obtained from Eq. (4) are determined by $\sigma_{\rm tr}(v_{F2})$. As v_{F2} varies weakly with the distance from the surface (from 0.87 a.u. at $z=1.2$ a.u. to 0.71 a.u. at $z=3.7$ a.u.) the amplitude and position (shape) of the Z_1 oscillations show only a moderate change with increasing distance. However, we note that the change in magnitude of the stopping power with distance to the surface is mainly given by the factor $n_{01}(z)$, i.e., the effective number of scattering centers.

We mention that the stronger effects for the energy loss of ions in nonuniform systems around $Z_1=18$ is caused by the stronger r_s dependence of the transport cross section. At high r_s the screening cloud approaches the free atom electronic structure with minima around $Z_1=2$, 10, and 18, while at low r_s the $3p$ and $3d$ scattering resonances overlap around $Z_1=18$ and the minimum disappears.[24]

IV. CONCLUSIONS

In summary, the description of the stopping power of ions in the electron selvage of a metal surface based on scattering theory gives a remarkable quantitative agreement with experiments for $z=1.2$ a.u., where the projectile interacts in good approximation with an uniform electron gas with $r_s=2.2$. At larger distances from the surface, we clearly reveal the important role played by the *nonuniform* electron density. This nonuniformity implies an enhancement of the effective scattering energy as compared to the uniform case and makes necessary specific modifications in the scattering approach in order to find agreement with the experiments. We hope that these studies on the new aspect concerning the energy loss of ions will stimulate first principle treatments of this problem, which are of substantial relevance for a general understanding of stopping phenomena in solid matter. In this respect, other systems as, e.g., alkali-covered metal surfaces (low work function) and ionic crystals as, e.g., LiF (high ''work function'') could provide deeper insights into the mechanisms of gradient corrections for *nonuniform* distributions of target electrons.

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