Charge Exchange and Energy Dissipation of Particles Interacting with Metal Surfaces

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(Received 21 December 1988)

Theoretical and experimental results for the charge state and energy loss of low-energy He scattered off a Ni(110) surface are compared. A first-principles theory is used to analyze both the charge state and the energy loss. Charge-exchange processes are of primordial importance to explain the energy-loss spectra. Energy straggling plays an important role in the system under study.

PACS numbers: 79.20.Rf

The interaction of energetic particles with metal surfaces is of great interest in many areas of physics such as thin-film growth, sputtering, plasma wall interaction in fusion devices, space shuttle glow, etc. Two important aspects of the particle-solid-interaction phenomena are the charge state of the particle during its passage through a metal and the energy losses that it experiences. The interaction of swift particles with bulk metals can be considered reasonably well understood and a classical field of physics.[1] Experimental and theoretical work on the interaction of particles with surfaces has been focused mainly on the charge-state problem[2-4] due to its importance for analytical techniques like ion scattering or secondary-ion mass spectrometry. Little work has been done on energy losses. In the present Letter, we present energy-loss and charge-state experimental results, and explain them with a comprehensive and unified theory based on first principles. For the first time, charge states and energy losses are calculated quantitatively from the same physical model.

We have obtained experimental data for the scattering of incident He^+ at 2, 3, and 5 keV at grazing incidence (glancing angle 5°) off a clean Ni(110) surface. With a time-of-flight (TOF) system,[5] energy spectra for both neutral and charged particles have been measured. The TOF detector is at a fixed laboratory scattering angle of 10° with an aperture of 1.2° (full width).

In this Letter we shall be concerned with charge exchange and energy loss for random directions. Along these directions, the ion charge-state fraction, $He^+/(He^+ + He^0)$ is around 0.67×10^{-2}, 2.3×10^{-2}, and 3.5×10^{-2} for 2, 3, and 5 keV, respectively.[6]

For slow He^+ ions, charge-exchange processes are controlled mainly by Auger capture and by dynamic resonance loss[7] with the $1s$ level.[6-8] In the Auger-capture process, an electron is captured to a bound state of the ion via the excitation of a third body, namely, an electron-hole pair. Condensed-matter effects are important here, since electrons in valence-band states are involved. In the resonant-loss case an electron in the $1s$ state is lost in a process induced by the time-dependent crystal potential as seen from a reference system fixed to the moving ion. For the ion energies considered in this Letter, the Auger-capture cross section is much larger than the resonant-loss one, and it can be calculated using the approach of Ref. 6. We obtain an Auger lifetime of 1.7×10^{-15} s for τ^A; the corresponding mean free paths ($\lambda = v\tau^A$) for $E = 2$, 3, and 5 keV are 5.2, 6.3, and 8.2 Å, respectively. The quantity d_s is an e^- 1 decay length and it is the distance, measured perpendicularly from the first Ni layer of ion cores, beyond which no Auger-capture process due to the Ni s electrons would occur. $d_s = 1.3$ Å is obtained following Ref. 6. From the same reference we also know that the effect of the d electrons, due to the strong localization of the d orbitals, is negligible.

Further input into the theoretical analysis is obtained from a MARLOWE[9] calculation. As a result, the ion trajectories near the metal surface are obtained and are shown in Fig. 1. The calculations include thermal vibrations using a surface Debye temperature of 200 K. As indicated we define by means of d_s an average trajectory length L. The trajectories shown are a randomly chosen subset of a total of 20000 trajectories calculated by tak-

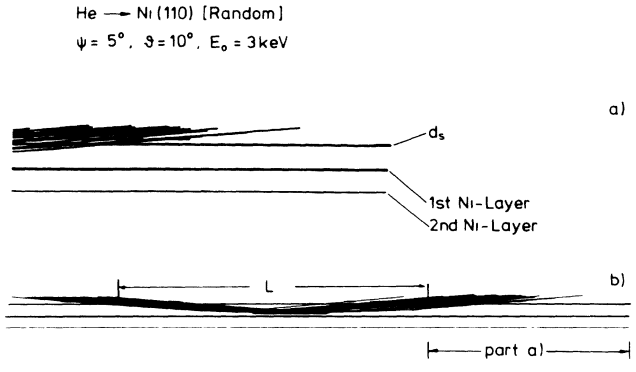

FIG. 1. Calculated trajectories for He on Ni, glancing angle 5°, scattering angle 10°, and acceptance angle 1.2°. The total trajectory distribution showing the definition of the average trajectory length L (for 3 keV: $L = 25$ Å).

ing into account the experimental details of, e.g., the energy, the impact angle, scattering angle, and the angle of acceptance of the detector of 1.2° (full width). It should be noted that the elastic energy loss for all trajectories is essentially zero; hence the inelastic loss is randomly distributed over all trajectories.

The energy loss experienced by the ions before entering (and after emerging) the length L, i.e., the energy loss before (and after) penetrating the solid due to the long-range coupling[10] to electron-hole excitations,[11] scales linearly with the ion velocity and is a small contribution to the total energy loss.[10] We estimate such a contribution to the loss to be 3 eV for an incident energy of 5 keV.

The fraction of He^+ leaving the surface can be obtained in terms of the Auger capture τ^A and resonant-loss lifetime τ^R:

$$\frac{dn(He^+)}{dt} = -\frac{1}{\tau^A} n(He^+) + \frac{1}{\tau^R}[1 - n(He^+)] . \quad (1)$$

This has the following solution:

$$n(He^+) \approx \tau^A/\tau^R + e^{-t/\tau^A} , \quad (2)$$

where $\tau^R \gg \tau^A$, as mentioned above.[7] The term e^{-t/τ^A} of Eq. (2) represents the fraction of initial He^+ still present in the beam. This contribution can be calculated if we know the time t, or the trajectory length L, that the ion is in contact with the surface. We find this contribution negligible, showing that the ion fraction is mainly due to the reionization processes, τ^A/τ^R, appearing at the exit part of the trajectory. From the point of view of the energy spectra, to be discussed below, this result shows that ions and neutrals should yield the same energy spectra, a point which is confirmed experimentally.

We proceed now to analyze the results for the energy loss. In Fig. 2 we show the energy spectra of He^0 scattered from Ni(110) in a random direction for primary energies of 2, 3, and 5 keV. The characteristic of these curves is that they are appreciably more asymmetrical than expected in energy-loss experiments.

In this Letter we show that the asymmetry is due to charge-exchange processes between the ion and the metal. The main point to notice is that the friction coefficient Υ is different for He^+ and He^0: The ion loses more energy than the neutral.

Our analysis is based on Eq. (2); now we neglect resonant-loss processes which have a small contribution to the stopping power. Thus, we find

$$\frac{dn(He^+)}{dt} \simeq -\frac{1}{\tau^A} n(He^+) , \quad (3a)$$

and, equivalently,

$$\frac{dn(He^0)}{dt} \simeq \frac{1}{\tau^A} n(He^+) . \quad (3b)$$

A neutral atom reaching the detector has lost energy in two different processes: Before neutralization, it loses energy, dQ_S^+ per unit length given by (Υ_S^+ is the surface friction coefficient, v is the particle velocity)

$$dQ_S^+ = \Upsilon_S^+ v\, dl , \quad (4a)$$

while after neutralization it loses

$$dQ_S^0 = \Upsilon_S^0 v\, dl . \quad (4b)$$

Combining Eqs. (3) and (4) we get the following energy-loss spectra:

$$\frac{dn(He^0)}{dQ} \propto \exp\left[\frac{-(Q-Q_0)}{(\Upsilon_S^+ - \Upsilon_S^0) v^2 \tau^A}\right] \theta(Q-Q_0) , \quad (5)$$

where Q is the energy loss, $Q_0 = \Upsilon_S^0 v L$, and θ is the step function. The results (Fig. 2) are indeed asymmetric [due to the presence of the step function $\theta(Q-Q_0)$] but the position of the maximum is shifted with respect to the experiment.

In Eq. (5) the straggling of the energy loss[12] has been neglected. The straggling can be included in the calculation by convoluting Eq. (5) with $\exp[-(Q-Q')^2/2\Omega^2]$. This yields

$$\frac{dn(He^0)}{dQ} \propto \exp\left[\frac{-(Q-Q_0)}{(\Upsilon_S^+ - \Upsilon_S^0) v^2 \tau^A}\right] \times \left[1 + \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt\right] , \quad (6)$$

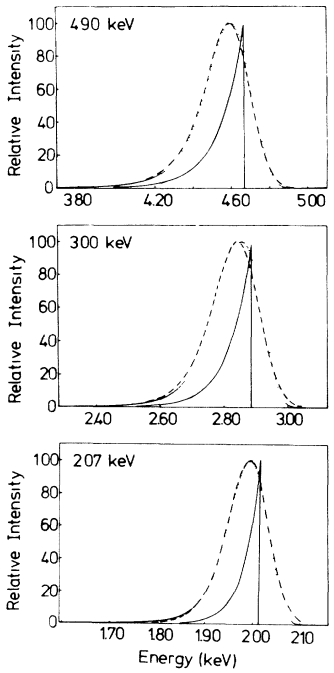

FIG. 2. Energy-loss spectra for emerging He^0 with incident He^+ scattered off Ni(110) for three primary incident energies, 4.90, 3.00, and 2.07 keV. The scattering geometry is shown schematically in Fig. 1. The dotted line is the experimental result, the dashed line is the theoretical result including straggling [Eq. (6)], and the solid line is the theoretical result excluding straggling [Eq. (5)].

TABLE I. Experimental and theoretical peak shifts ΔE and parameters used in Eqs. (5) and (6) to fit the energy-loss spectra (a) and the corresponding values calculated from a local-density approximation (b) [Eq. (7)].

Energy (keV)	ΔE (eV) Expt. ($\pm 10\%$)	Theor.	Q_0 (eV) (a)	(b)	Ω (eV) (a)	(b)	γ_S^0 (a.u.) (a)
2.07	75	80	49	57.6	38	25.3	0.26
3.00	136	150	102	96.7	54	39.6	0.37
4.90	287	280	217	199.4	84	83.6	0.44

where

$$x=\frac{\Omega}{\sqrt{2}}\left(\frac{Q-Q_0}{\Omega^2}-\frac{1}{(\gamma_S^+-\gamma_S^0)v^2\tau^A}\right).$$

Notice that $dn(\mathrm{He}^0)/dQ$ depends on the parameters τ^A, γ_S^+, γ_S^0 and the straggling parameter Ω^2; τ^A has been calculated above. γ_S^+/γ_S^0 has been calculated in linear theory[13] for an electron gas as a function of the electron density. We find that a good fit to the experimental data can be obtained by taking $\gamma_S^+/\gamma_S^0=3.7$, corresponding to r_s between 1.5 and 2, a density parameter appropriate for Ni.

Finally, γ_S^0 and Ω^2 have been chosen for each energy in such a way that Eq. (6) gives the best fit to our experimental data. Figure 2 shows our theoretical results, Eq. (5) as well as Eq. (6), and Table I shows the values for Q_0, Ω, and γ_S^0. The inclusion of the straggling of the energy loss leads to good agreement between the theoretical and experimental curves. Only for 2 keV do we find a slight disagreement for energies close to the primary energy.

We have also calculated Q_0 and Ω using a local-density approach by means of

$$Q_0=\int_{-\infty}^{+\infty}\gamma_S^0(l)v\,dl\,, \tag{7a}$$

$$\Omega^2=\int_{-\infty}^{+\infty}W(l)dl\,, \tag{7b}$$

where γ_S^0 and W are obtained locally[14,15] assuming that they take in each point the values associated with the corresponding electronic local density. The results are listed in Table I.

We should mention that another source of straggling is the change in the particle trajectory length, e.g., due to the detector aperture. This effect can also be taken into account as a Gaussian broadening of the energy spectra; notice that this effect is more important for shorter trajectory lengths, L; this fact explains why in Table I the fitted Ω values are larger than the theoretical ones for smaller energies.

It is also worth mentioning that $Q_0=\gamma_S^0 vL$ changes with the ion energy due not only to v but to γ_S^0 and L, too. Our results show that γ_s^0 and L are roughly linear in v; this suggests a v^3 dependence of Q_0 with the velocity, a behavior that seems to be followed by the experimental data of ΔE (Table I).

In the previous discussion, we have followed a simplified mean statistical theory, introducing straggling effects by means of a Gaussian function. It might be argued that this approach is inappropriate since it allows particles to gain energy from the target: In order to prove the validity of the previous method to describe the experimental energy spectra we have evaluated such spectra for $E=5$ keV using the so-called "convolution method."[16,17]

In this method, the complete energy-loss spectrum, $P(\omega)$, for a particle interacting with a metal is given by the probability density function for n collisions combined with the Poisson distribution of n collisions. Thus,

$$P(\omega)=\sum_n\frac{P_0^n}{n!}e^{-P_0}f_n(\omega)\,, \tag{8}$$

where $P_0=L/\lambda_0$; λ_0 being the mean free path for collisions and f_n the probability density distribution around the mean energy $n\bar{\omega}$ ($\bar{\omega}$ being the mean energy loss for a single collision). f_n should be calculated by a n-fold convolution of a single probability density spectrum.[16] In our present case, for low-velocity particles, this single spectrum does not present strong asymmetries since, on the one hand, plasmons cannot be excited and, on the other, tails in the spectrum going like $1/\omega^2$ do not appear.[10] Because of this we can replace f_n, with good accuracy, by

$$f_n\sim\exp[-(\omega-n\bar{\omega})^2/2n\omega_0^2]\,, \tag{9}$$

where $n\omega_0^2$ defines the intrinsic straggling of the probability density function for n collisions. We should comment that λ_0, $\bar{\omega}$, and ω_0 can be obtained from the mean lifetime for collisions τ_0, the stopping power S, and the straggling per unit length W:[12]

$$\lambda_0=v\tau_0\,, \tag{10a}$$

$$S=\hbar\bar{\omega}/\lambda_0\,, \tag{10b}$$

$$W=[(\hbar\bar{\omega})^2+(\hbar\omega_0)^2]/\lambda_0\,. \tag{10c}$$

Equations (8), (9), and (10) yield the energy spectrum for the case of a slow particle interacting with a metal. In our case, with exchange of charge between the ion and the metal, Eq. (8) has to be generalized taking into

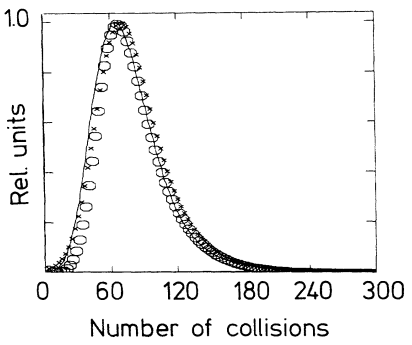

FIG. 3. Energy-loss spectra for 5-keV incident He^+ on Ni(110) in nonsymmetric direction. Solid curve: experiment; circles: "convolution method" as explained in the text; crosses: mean statistical theory.

account the ion neutralization probability: This is done by splitting the total length L into two parts, x and $L-x$. The ion is assumed to interact with the metal along the length x, while the neutral does it along the distance $L-x$. Then, probabilities of having the two particles colliding with the metal quasiparticles have to be combined; finally, the total energy-loss spectrum is obtained by an integration in x along the length L, after we have introduced the neutralization probability, $(dx/\lambda_A)\exp(-x/\lambda_A)$ (details will be published elsewhere).

Figure 3 shows the case of 5 keV; different curves correspond to the experiments, to the one evaluated using mean statistical theory, and to the one calculated via the "convolution method" using for S and W [Eqs. (10b) and (10c)] the fitted values of Table I, and for τ_0 the results of Ref. 18 for $r_s=1.5$. The agreement between different curves is excellent, showing that the mean statistical method discussed above is quite appropriate in the limit of low velocities discussed in this paper. Moreover, it is also important to notice that a calculation, taking a single charge state, along the lines of the "convolution method" yields a Gaussian energy-loss distribution.

In conclusion, our results show that energy losses are intimately related to the charge-exchange processes. In particular, the large asymmetry of the energy spectra is due to the neutralization process that He^+ suffers in its interaction with the metal surface, and to the different friction coefficients calculated for He^+ and He^0.

Financial support by the Deutsche Forschungsgemeinschaft (DFG), the Deutscher Akademischer Austauschdienst (DAAD) as part of the Acciones Integradas Hispano-Alemanas, and the Comisión Asesora de Investigación Científica y Técnica (Contract No. 0388-84) is gratefully acknowledged. One of us (A.N.) gratefully acknowledges the hospitality of the Departamento de la Materia Condensada which made this work possible. P.M.E. thanks Gipuzkoako Foru Aldundia, Eusko Jaurlaritza, and Euskal Herriko Unibertsitatea and P.M.E. and F. F. thank Iberduero S.A. for help and support.

[1]N. Bohr, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **18**, No. 8 (1948); M. Inokuti, Rev. Mod. Phys. **43**, 297 (1976); S. P. Ahlen, Rev. Mod. Phys. **52**, 121 (1980); Y. H. Ohtsuki, *Charged Beam Interactions with Solids* (Taylor and Francis, London, 1983).

[2]H. D. Hagstrum, in *Electron and Ion Spectroscopy of Solids,* edited by L. Fiermans, J. Vennik, and W. Dekeyzer (Plenum, New York, 1978), p. 178.

[3]M. Aono and R. Souda, Nucl. Instrum. Methods Phys. Res., Sect. B **27**, 55 (1987).

[4]D. M. Newns, Phys. Rev. **178**, 1123 (1969); R. Brako and D. M. Newns, Solid State Commun. **33**, 713 (1980); Surf. Sci. **108**, 253 (1981).

[5]B. Willerding, H. Steininger, K. J. Snowdon, and W. Heiland, Nucl. Instrum. Methods Phys. Res., Sect. B **230**, 453 (1984); D. Rathmann, N. Exeler, and B. Willerding, J. Phys. E **18**, 17 (1985).

[6]R. Monreal, E. C. Goldberg, F. Flores, A. Närmann, H. Derks, and W. Heiland, in Proceedings of Ecoss X, 1988 [Surf. Sci. **211/212**, 271 (1989)].

[7]F. Sols and F. Flores, Phys. Rev. B **30**, 4878 (1984).

[8]F. Guinea, F. Flores, and P. M. Echenique, Phys. Rev. Lett. **47**, 604 (1981); P. M. Echenique, F. Flores, and R. H. Ritchie, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1989), Vol. 43.

[9]M. T. Robinson and I. M. Torrens, Phys. Rev. B **9**, 5008 (1974); H. Derks, A. Närmann, and W. Heiland, Nucl. Instrum. Methods Phys. Res., Sect. B **44**, 125 (1989).

[10]F. García-Moliner and F. Flores, *Introduction of the Theory of Solid Surfaces* (Cambridge Univ. Press, New York, 1979).

[11]T. L. Ferrell, P. M. Echenique, and R. H. Ritchie, Solid State Commun. **32**, 419 (1979); R. Núñez, P. M. Echenique, and R. H. Ritchie, J. Phys. C **13**, 4229 (1980).

[12]M. A. Kumakhow and F. F. Komarov, *Energy Loss and Ion Ranges in Solids* (Gordon and Breach, New York, 1981), p. 116.

[13]T. L. Ferrell and R. H. Ritchie, Phys. Rev. B **16**, 115 (1977).

[14]P. M. Echenique, R. M. Nieminen, J. C. Ashley, and R. H. Ritchie, Phys. Rev. A **33**, 897 (1986).

[15]J. C. Ashley, A. Gras-Marti, and P. M. Echenique, Phys. Rev. A **34**, 2495 (1986).

[16]H. Bichsel, Rev. Mod. Phys. **60**, 663 (1988).

[17]M. Kato, J. Phys. Soc. Jpn. **55**, 1011 (1986).

[18]I. Nagy, A. Arnau, and P. M. Echenique, Phys. Rev. B **38**, 9191 (1988).