

Neutralization of hyperthermal Ne^+ on metal surfaces

A. Kutana, M.J. Gordon, K.P. Giapis *

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, United States

Received 11 February 2006; received in revised form 6 March 2006

Available online 24 May 2006

Abstract

Relative ion yields of low energy (320 eV) Ne^+ ions scattered off a number of elemental surfaces are compared. Ion survival probabilities are seen to change significantly from one element to another depending on the surface work function, suggesting that resonant charge exchange between the metal conduction band and Ne 3s atomic level may be just as important as Auger neutralization processes. The observed yield dependence on work function is qualitatively explained using a description of resonant neutralization (RN) based on the Anderson model of an atomic level near a surface. Auger processes are found to be important in determining the final charge state of outgoing ions, while quasi-resonant interactions between the core atomic levels are seen to be nonexistent.

© 2006 Elsevier B.V. All rights reserved.

PACS: 68.49.Sf; 68.49.-h; 34.50.Dy

Keywords: Low energy ion scattering; Resonant charge transfer; Metal work function

Charge exchange in low energy ion–surface collisions has been a subject of experimental and theoretical studies for many years [1]. Interactions of alkali ions with metal surfaces involving one-electron resonant transitions between the conduction band and the ion s-level have been investigated most extensively [2–4] and these processes are now well understood. Identical resonant processes are potentially operative during neutralization of Ne^+ , which has an unoccupied 3s level close to the Fermi energy of many metals, as is the case for alkali ions. However, the added possibility of Auger neutralization (AN) into the empty 2p orbital of Ne^+ (Fig. 1) makes the problem of Ne^+ –metal charge exchange significantly more complex than the one-electron resonant transitions involving alkali projectiles. In discussions of Ne^+ charge exchange with metals, AN is usually given priority over resonant neutralization (RN), which is mentioned only as a minor neutralization pathway [5]. However, the influence of metal work

function on neutralization of noble gas ions has been recently demonstrated [6], suggesting that resonant charge exchange may be much more important than initially thought. It was shown that the positive ion yield of 2–5 keV Ne^+ scattered off Ba on W(1 1 0) decreased exponentially as the macroscopic work function was lowered below a certain threshold value. Work function variations were induced by adsorbing sub-monolayer quantities of Ba on the W surface. Displacement of the Ba valence electron towards the W surface creates an electric double-layer polarized opposite to the metal surface dipole – effectively lowering the overall work function. The observed decrease in ion yield was explained as RN of Ne^+ by electrons from the conduction band of tungsten. In the current work, low energy (100–1000 eV) Ne^+ ions were scattered off a variety of metal surfaces to evaluate how the ion yield depends on work function (ϕ). The overall Ne^+ survival rate was seen to increase by over four orders of magnitude as the work function was varied from 3 to 5 eV. Such behavior cannot be explained if AN is the only neutralization mechanism for Ne^+ on these surfaces. Instead, it is likely that RN plays a considerable role in Ne^+ neutralization, and that RN

* Corresponding author. Tel.: +1 626 3954180; fax: +1 626 5688743.
E-mail address: giapis@cheme.caltech.edu (K.P. Giapis).

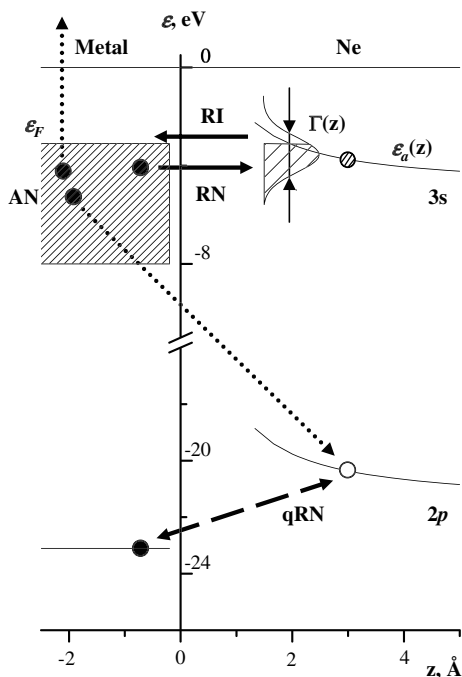


Fig. 1. Neutralization pathways for Ne^+ near a metal surface. Resonant neutralization (RN) and resonant ionization (RI) occur as a result of electron tunneling between the Ne 3s level with energy $\varepsilon_a = \varepsilon_a(z)$, width $\Gamma = \Gamma(z)$, and the metal conduction band. Auger neutralization (AN) involves two electrons from the conduction band – one hopping into the 2p level of Ne^+ , and the other gaining the excess energy to be promoted into vacuum. In quasi-RN (qRN), the electron transition occurs as a result of interaction between the core p-levels of the two atoms.

processes may be comparable to or greater than that of AN for surfaces with sufficiently low work function.

A low-energy ion beamline scattering apparatus [7] has been used in these experiments. Ne^+ ions were extracted from a floating inductively coupled plasma source, and passed through a small beam accelerator with magnetic mass-filtering. Upon exiting the deceleration stage consisting of an Einzel triplet and quadrupole, the beam was directed onto a grounded target through a 2 mm diameter aperture with a current of $\sim 100 \mu\text{A}/\text{cm}^2$. The beam energy was tuned by changing the plasma floating potential and the beam energy spread at the target was $\pm 5 \text{ eV}$ FWHM around the centerline. Specular scattering of $^{20}\text{Ne}^+$ with a 45° incident angle and 90° lab angle was used for all experiments. All metal samples were polycrystalline (except Si(100)) and cleaned using standard surface preparation techniques (sputtering + annealing). After scattering off the surface, positive ions were energy and mass filtered using an electrostatic sector followed by quadrupole mass filter. Fig. 2(a) shows a typical exit energy spectrum for 320 eV $^{20}\text{Ne}^+$ scattered off aluminum, along with a Marlowe [8] simulation of 320 eV Ne off Al(100). Several peaks resulting from different scattering trajectories are presented; however, only a single-scattered peak and a trace of double scattering are present in the experimental data due to effective neutralization by the surface. The actual trajectories of Ne atoms on the Al(100) surface corre-

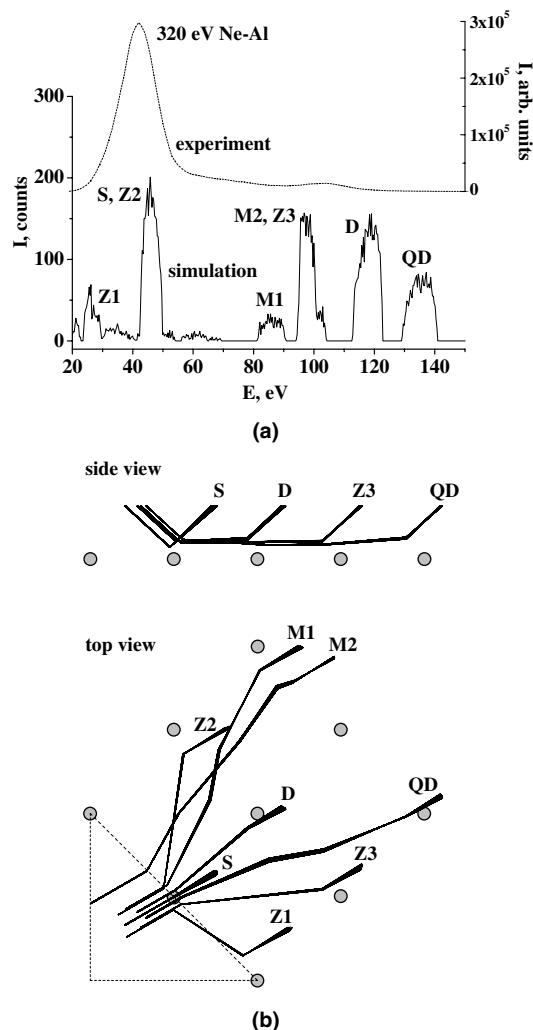


Fig. 2. (a) Experimental and Marlowe-simulated energy spectrum of Ne scattered at 45° from an Al(100) surface for 320 eV Ne beam incident at 45° . The peak resulting from a single collision (S) of Ne^+ ion with one target atom and a small doubly-scattered peak (D) are present in the experimental curve. Peaks from quasi-double (QD), zigzag (Z1–Z3), and multiple (M1–M2) collisions predicted by simulations are not observed due to effective neutralization on the surface. (b) Side view and top view of the (100) Al surface illustrating the trajectories that result in the formation of each of the Marlowe-simulated peaks. The positions of the atoms in the first layer are designated by shaded circles, and the initial bombardment area is shown by a dashed triangle. Only four trajectories are shown in the top view to avoid clutter.

sponding to the simulated peaks in the energy spectrum are shown in Fig. 2(b). The variation of length of these trajectories helps understand the correlation between the time spent by an ion in contact with the surface and its survival probability after scattering.

The area of the experimental peak, divided by the ion beam current, was taken as a measure of the survival probability of the ion. Subsequently, relative ion yields were normalized by the corresponding Ne–metal scattering cross-sections using the Molière fitting formula of the Thomas–Fermi potential and the atomic density of the (100) surface of each metal. Surface rather than bulk atomic densities were used in normalization because lattice penetra-

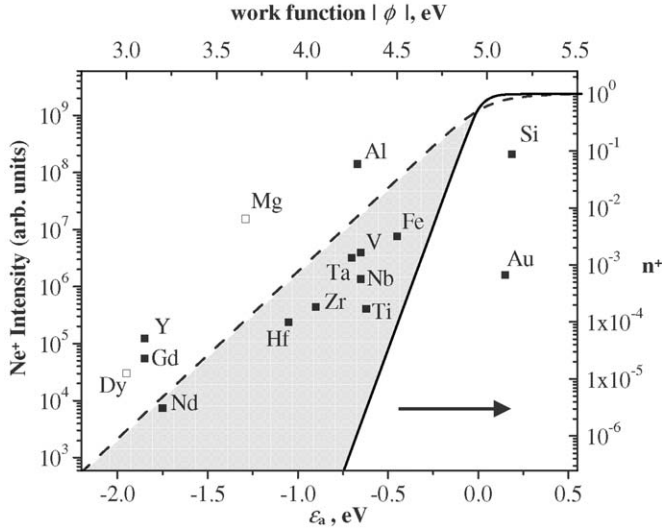
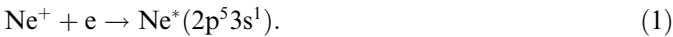


Fig. 3. (left axis) Symbols show the experimental scattering intensities measured for 320 eV Ne^+ ions off various targets versus their respective work function. A relative error of $\pm 30\%$ applies to all data points. Open symbols indicate elements for which values of $|\phi|$ are not well substantiated (Mg), or not known (Dy, for which the value of 3.0 eV for the neighboring Tb was used). (right axis) Fraction of ions surviving neutralization according to the one-level RN model as a function of the atomic level position (ϵ_a) with respect to the surface Fermi energy. Shaded region indicates the prediction of Eq. (6) for two limiting cases, corresponding to exit velocities $v_z = 0.35 \text{ \AA/fs}$ (dashed line), and $v_z = 0.12 \text{ \AA/fs}$ (solid line).

tion is rather insignificant at low projectile energy and furthermore, neutralization is very efficient for projectile ions penetrating beyond the topmost layer of the surface.

Fig. 3 shows the experimentally measured Ne^+ scattering yields for different metals versus work function (as reported for polycrystalline specimens [9]; for the heavily B-doped Si sample, the Fermi level position of 5.14 eV was used). It is seen that the survival probability grows dramatically with increasing work function of the target. Such a trend suggests that Ne^+ is neutralized via resonant interaction with the conduction band of the metal by capturing an electron into the 3s orbital to form a metastable Ne^* atom:



In resonant exchange, the final charge state of the Ne atom is determined on the exit path by the relative position of the first excited level (3s) with respect to the Fermi level of the surface (Fig. 1). The electron tunneling rate from the solid to projectile is represented as Γ/\hbar , where $\Gamma = \Gamma(z)$ is the distance-dependent width of the 3s atomic level. If the energy level of the receding ion is above the Fermi level most of the time (where many empty states are available for electron accommodation), the projectile is likely to leave the surface as an ion; in the opposite case, it will be neutralized. Neglecting the small fraction of negative ions, the interaction of a single atomic level ($|a\rangle$) with the states in the conduction band of a metal ($|k\rangle$) may be described in one dimension by the time-dependent Anderson Hamiltonian [3]:

$$H(t) = \sum_k \epsilon_k n_k + \epsilon_a(t) n_a + \sum_k [V_k(t) c_a^\dagger c_k^\dagger + \text{h.c.}], \quad (2)$$

where ϵ_k , n_k , are the energies and populations of the levels in the conduction band, ϵ_a , n_a are the same quantities for the atom, c_a^\dagger , c_k^\dagger are Fermion creation operators, $V_k(t)$ is the perturbation matrix element describing the coupling between the atom and the surface, i.e. $V_k = \langle a|V(t)|k\rangle$, and h.c. is the Hermitian conjugate. The time t and distance z variables can be used interchangeably in V , since the incoming projectile is assumed to follow a classical trajectory $z = z(t)$. The average population of the atomic level,

$$\langle n_a(t) \rangle = \langle c_a^\dagger(t) c_a(t) \rangle \quad (3)$$

can be found by solving the Heisenberg equation of motion for c_a :

$$\partial c_a(t)/\partial t = i[H, c_a(t)]. \quad (4)$$

In the case that the level width (Γ) depends exponentially on the ion–surface distance with some decay constant (α) and atomic energy level (ϵ_a),

$$\Gamma = \Gamma_0 \exp(-\alpha z), \quad (5a)$$

$$\epsilon_a = \text{const.} \quad (5b)$$

Eqs. (3) and (4) can be integrated analytically [3] to give the ion survival fraction

$$n^+ = 1 - \langle n_a(\infty) \rangle = \frac{1}{\pi} \cot^{-1} \sinh \left(-\frac{\pi \epsilon_a}{\alpha v_z \hbar} \right). \quad (6)$$

Here, ϵ_a is measured from the Fermi level of the surface, and v_z is the projectile velocity normal to the surface on the outgoing part of the trajectory. Several rather complicated methods exist for calculating the width (Γ) and atomic level position (ϵ_a) as functions of the normal distance to the surface [1,4]. The calculation of Nordlander and Tully [4] for the Na 3s level near the Al surface has been used in this work to evaluate the width of the first excited level of Ne, represented in the first approximation by Eq. (5a) using $\alpha = 2.0 \text{ \AA}^{-1}$ (extracted from Fig. 6b of [4]). The resulting exit charge fraction (Eq. (6)) is plotted in Fig. 3 using this α value, and two normal exit velocities: $v_z = 0.35 \text{ \AA/fs}$, corresponding to 320 eV Ne scattered at 90° off Au, and $v_z = 0.12 \text{ \AA/fs}$ for Ne off Mg. Exit velocities for the other metals fall between these two limiting values (shaded region). Since the measured Ne^+ survival probability is only known to within a constant factor, an absolute ion fraction must be assigned to at least one experimental point in order to perform the comparison with theory. The surviving ion fraction of 320 eV Ne^+ off Si was assumed to be $\sim 10\%$, a reasonable estimate considering high survival probability ($\sim 36\text{--}44\%$) of 4 keV Ne^+ on p-doped Si(100) [10]. It is seen that these solutions capture the general trend in intensity variations with work function. Deviations from the model are likely caused by the rather crude approximations mentioned above (especially ϵ_a being independent of projectile–surface distance) as well as the unknown contribution of AN to neutralization. By assuming ϵ_a constant

and equal to its asymptotic value, Eq. (6) underestimates n^+ , since the upward level shift results in lower occupation probability for the level. The large discrepancy between the measured intensities on the third row elements (Al, Mg) and prediction (Eq. (6)) may stem from the closeness of the interaction region to the surface (i.e. Al and Mg being considerably smaller in size than the transition metals). Since the magnitude of the shift increases with decreasing projectile–surface distance, Al and Mg will necessarily have the most upward deviation from the prediction when using a constant level model. It is worth noting that a simplistic RN model, in which the instantaneous atomic level population is calculated from a convolution of the Fermi distribution in the conduction band with a Lorentzian distribution representing the widening of the atomic level due to the ion–surface interaction [2], does not correctly reflect the observed range of intensity variations for any reasonable values of α and Γ_0 . Specifically, the prediction of the simplistic RN model [2] for n^+ is

$$n^+ = 0.5 + \pi^{-1} \arctan(2\varepsilon_a/\Gamma(z^*)), \quad (7)$$

where

$$z^* = \frac{1}{\alpha} \ln \frac{\Gamma_0}{\hbar \alpha v_z} \quad (8)$$

which approaches zero too slowly to account for the decrease in ion fraction for negative ε_a . In contrast, Eq. (6) has an asymptotic form

$$n^+ = 2\pi^{-1} \exp\left(\frac{\pi\varepsilon_a}{\alpha v_z \hbar}\right) \quad (9)$$

which echoes the observed exponential decrease.

The significant amounts of surviving Ne^+ at $|\phi| > 4.25$ eV bear similarities to the high ionization probabilities of alkali atoms, such as hyperthermal Na^+ on W(110) [2] ($|\phi| = 5.25$ eV [9]), considering the closeness in energy (4.95 and 5.14 eV) of the 3s levels of the $\text{Ne}^*(2p^3 3s^1)$ and $\text{Na}(2p^6 3s^1)$ atoms. In addition, the main difference between Na^+ and Ne^+ neutralization is the possibility of Auger processes for the latter, which may be the dominant mechanism on metals with high work functions such as gold ($|\phi| = 5.1$ eV). As AN is operative on all metals, the total fraction of surviving ions will always be less than that obtained by considering the RN process alone, shifting the intensities in Fig. 3 below the RN line.

Metals that neutralize Ne^+ most effectively also happen to have their p-levels closer to the p-level of Ne than those where the scattered ion yield is higher. Due to this correlation between the level separation and neutralization efficiency, the possibility of electron capture by Ne^+ via the quasi-resonant p-level interaction should be examined. In quasi-RN (qRN) charge exchange [11–13], the electron transition occurs as a result of interaction between the core p-levels of the two colliding atoms. Since no other manifestations of qRN were present, this correlation was concluded to be accidental, as shown by the following arguments. First, it is unlikely for qRN to occur in this

low energy regime, since this type of interaction requires significant overlap of the low-lying core level atomic orbitals of the colliding partners, which only occurs at small apses ($R_{\min} < 0.5$ Å). The apses attained in the 90° scattering of 320 eV Ne studied here are in the 0.72–0.91 Å range (as calculated for the Molière potential) – significantly above that needed for sufficient orbital overlaps. Additionally, the spread of the p-levels of the elements studied here is much larger than the resonance defects permitting the interaction with the Ne 2p level. Based on these positions, one would have to assume that the half-width of the resonance to be ~ 10 – 15 eV, which is much greater than ~ 0.5 eV predicted by theory [12]. Finally, no characteristic oscillations in the energy dependence of ion yields were observed; instead, ion yields were found to increase steadily with energy for most metals. According to various theoretical descriptions of qRN [12,13], the survival probability should be an oscillating function with amplitude that *decreases* with increasing projectile velocity. On a few metals (Mg, V), the initially increasing intensity was seen to go through a maximum and then decrease with energy. While this behavior is not believed to be related to qRN, a more detailed study of neutralization on these metals is needed to explain the observed dependencies.

In conclusion, relative ion yields of low energy (320 eV) Ne^+ scattered off different polycrystalline metals and Si(100) were measured. The observed variations in ion survival probability and its correlation with the material work function were explained in terms of resonant interactions between the Ne^+ 3s orbital and the metal conduction band. A model of RN by Brako and Newns [3] based on the one-level Anderson Hamiltonian has been used to assess the dependence of the exiting ion fraction on the position of the Fermi level in the solid. Due to the model limitations, as well as unknown contribution from AN, only qualitative agreement between the experiment and theory could be reached. It is sure that AN makes a considerable contribution to the total outgoing neutral flux for single scattering collisions; however, the work function dependence of the ion yield suggests that RN processes cannot be neglected in a discussion of surface neutralization with Ne^+ . Finally, we saw no manifestation of quasi-resonant interactions between core levels.

Acknowledgements

This work was based on research funded by the National Science Foundation (CTS-0317397).

References

- [1] J. Los, J.J.C. Geerlings, Phys. Rep. 190 (1990) 133.
- [2] E.G. Overbosch, B. Rasser, A.D. Tenner, J. Los, Surf. Sci. 92 (1980) 310.
- [3] R. Brako, D.M. Newns, Surf. Sci. 108 (1981) 253.
- [4] P. Nordlander, J.C. Tully, Phys. Rev. B 42 (1990) 5564.
- [5] H.D. Hagstrum, Phys. Rev. 96 (1954) 336;
D.P. Woodruff, Nucl. Instr. and Meth. B 194 (1982) 639;

- R. Kumar, M.H. Mintz, J.A. Schultz, J.W. Rabalais, Surf. Sci. 130 (1983) L311.
- [6] R. Cortenraad, A.W.D. van der Gon, H.H. Brongersma, S.N. Ermolov, V.G. Glebovsky, Phys. Rev. B 65 (2002) 195414.
- [7] M.J. Gordon, K.P. Giapis, Rev. Sci. Instr. 76 (2005) 083302.
- [8] M.T. Robinson, I.M. Torrens, Phys. Rev. B 9 (1974) 5008.
- [9] H.B. Michaelson, J. Appl. Phys. 48 (1977) 4729.
- [10] I. Vaquila, J.W. Rabalais, J. Wolfgang, P. Nordlander, Surf. Sci. 489 (2001) L561.
- [11] F.P. Ziemba, E. Everhart, Phys. Rev. Lett. 2 (1959) 299; R.L. Erickson, D.P. Smith, Phys. Rev. Lett. 34 (1975) 297.
- [12] Y.N. Demkov, Sov. Phys. JETP 18 (1964) 138.
- [13] W. Lichten, Phys. Rev. 131 (1963) 229; W. Lichten, Phys. Rev. 139 (1965) A27.