Thermally Enhanced Neutralization in Hyperthermal Energy Ion Scattering

C. E. Sosolik,* J. R. Hampton,[†] A. C. Lavery,[‡] and B. H. Cooper[§]

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501

J. B. Marston

Department of Physics, Box 1843, Brown University, Providence, Rhode Island 02912

Neutralization probabilities are presented for hyperthermal energy Na^+ ions scattered from a Cu(001) crystal as a function of surface temperature and scattered velocity. A large enhancement in neutralization is observed as the temperature is increased. Velocity-dependent charge transfer regimes are probed by varying the incident energy, with the most prominent surface temperature effects occurring at the lowest energies. The data agree well with results obtained from a model based on the Newns-Anderson Hamiltonian, where the effects of both temperature and velocity are incorporated.

Measurements of the charge states of alkali ions scattered from metal surfaces at hyperthermal energies (≈ 1 eV to 1 keV) have achieved remarkable success in isolating factors that govern neutralization at surfaces [1]. From these studies, it is well known that the magnitude of the neutralization probability, P_0, depends strongly on the value of the projectile ionization potential, I_0, and the surface work function, Φ, while the rate of charge transfer is determined by the projectile-surface coupling [2]. The effects of surface temperature or T_S on neutralization at a surface, however, have typically been ignored experimentally. In fact, few quantitative measurements [3,4] have explored the role of T_S in determining P_0, despite the many theoretical studies [5–13] that have been devoted to the subject.

In this Letter, we present quantitative results which show that T_S has significant effects on the neutralization probability. Our measurements involve scattering Na^+ ions from a Cu(001) surface as a function of incident energy and T_S. The Na-Cu(001) scattering system is interesting because both *energy-dominated* and *coupling-dominated* charge transfer regimes are accessible and can be probed by varying the incident energy or scattered velocity [14]. In the energy-dominated regime, the change in P_0 with scattered velocity is governed primarily by the relative values of I_0 and Φ. In the coupling-dominated regime, the tunneling of electrons between the projectile and surface or equivalently, the projectile-surface coupling, governs the velocity dependence [14]. Our results show that increasing T_S can change P_0 in both of these regimes, enhancing it by as much as a factor of 3 at the lowest incident energies. The effects of T_S and scattered velocity on P_0 have been incorporated into a quantum-mechanical model that treats the electrons involved in the charge transfer as independent particles. Results obtained from this model compare well with the trends seen in our experimental data.

Our measurements were performed in an ultrahigh vacuum chamber and beam line that are described in detail elsewhere [15,16]. All of the ion beams were produced in a Colutron ion source that has been modified to allow highly efficient alkali ion beam production from a solid state source [17]. The beams were scattered along the $\langle 100 \rangle$ azimuth of a Cu(001) single crystal sample. Surface cleanliness and long range order were monitored using Auger electron spectroscopy and low energy electron diffraction, respectively. The sample temperature was varied between 200 and 1100 K during scattering using a combination of cooling from a liquid nitrogen reservoir connected by copper braids and heating from an electron-beam heater mounted behind the sample.

Velocity-resolved charge state fractions were obtained for particles scattered from the sample using time-of-flight techniques along with a neutral particle detector (NPD) [18]. All measurements were made at incident and final angles of 45° in the plane defined by the incident beam direction and the surface normal. A typical time-of-arrival spectrum obtained using the NPD is shown in Fig. 1 for 250 eV Na^+ scattered from the Cu(001) crystal at a temperature of 328 K. The dashed line shows the signal due to both the neutral atoms and ions, the total flux, and the solid line shows the signal coming from the neutrals only. P_0 was obtained by integrating the intensity of the total and neutral spectra and taking a ratio of the results [19].

To illustrate the dependence of P_0 on T_S, typical results obtained for incident Na^+ projectiles at energies of 22, 152, and 640 eV are shown in Fig. 2. There is a significant increase in P_0 at all incident energies as T_S is increased. At each incident energy, the neutralization probability is strongly dependent on T_S, with the largest change occurring at the lowest incident energy.

The dependence of P_0 on incident energy can also be observed from the data presented in Fig. 2. Above 750 K, P_0 decreases monotonically as the incident energy is increased. However, below 750 K, the incident energy dependence is nonmonotonic. This can be seen more clearly in Fig. 3, where P_0 has been plotted as a function
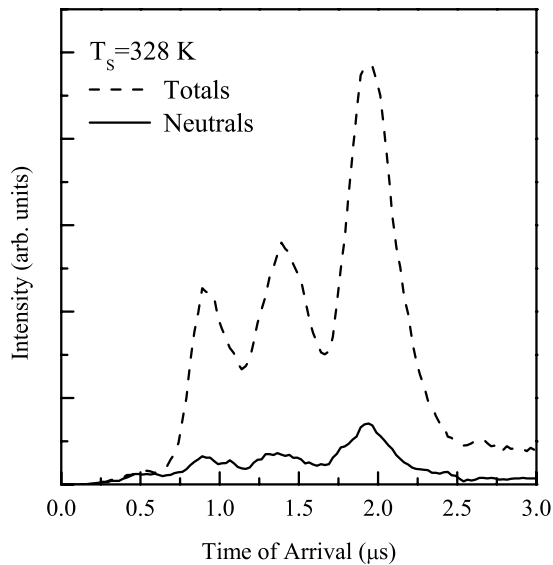
FIG. 1. Time-of-arrival spectra obtained with the NPD for 250 eV Na^+ ions scattered from a Cu(001) crystal. The surface temperature was held at 328 ± 5 K during this measurement. The three peaks present in these spectra are due to trajectory types that involve scattering from one or more individual atoms at the surface [1].

of the inverse perpendicular velocity of the scattered projectiles at three different T_S values. The nonmonotonic change in neutralization is very apparent at 350 K, the lowest temperature shown.

To understand the velocity- and temperature-dependent results shown in Figs. 2 and 3 we first focus on the energy and time dependence of charge transfer for this system at a fixed temperature. We show that the data collected at
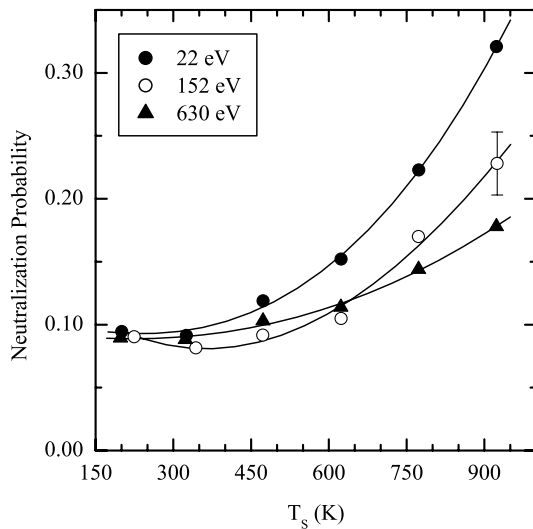
350 K exhibit aspects of both energy- and coupling-dominated charge transfer. Then we examine the effects of increased temperature and discuss why the effects are so large at the lowest incident energies. Finally, we compare our measurements to the results of a theoretical model that incorporates the effects of velocity and temperature.

The energetics of neutralization in ion-surface scattering experiments are typically described using an ionization level diagram. The ionization level, $I(z) = I_0 - 1/4z$, represents both the bare ionization potential of the projectile and the distance dependence induced by the presence of an image charge in the metal [20]. A level diagram for Na(3s) ($I_0 = 5.14$ eV) outside of a Cu(001) surface is shown in Fig. 4. At any distance z the energetically favored charge state of the Na is given by the position of $I(z)$ relative to the Cu(001) Fermi level, E_F. At large distances ($z > 13$ a.u.) the ionization level is below E_F, and the energetically favored charge state is neutral. Closer to the surface, the positive ion is the energetically favored charge state, as the ionization level is shifted above E_F. The level diagram illustrates that different charge states are energetically favored at different z values. This description is incomplete, however, as the projectile-surface coupling must also be considered.

The projectile-surface coupling introduces dynamical and charge state mixing effects that play an important role in determining the final charge state measured in a
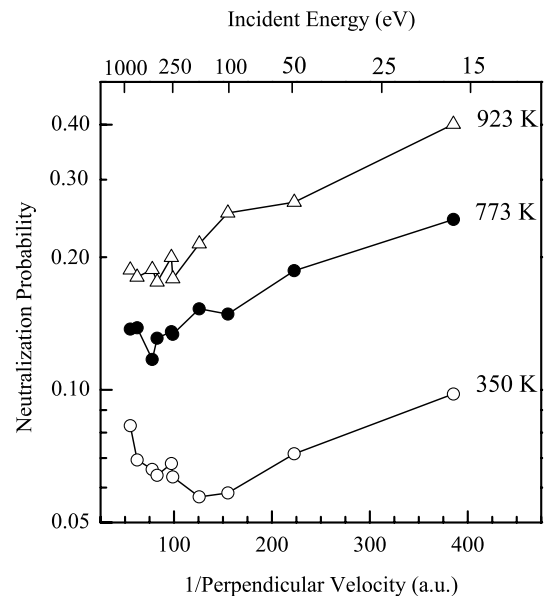

FIG. 2. Temperature-dependent neutralization results for 22, 152, and 630 eV Na^+ ions scattered from a Cu(001) crystal. The lines are drawn to guide the eye, and a typical error bar is shown.

FIG. 3. The neutralization probability, P_0, for Na^+ ions scattered from a Cu(001) crystal at surface temperatures of 350, 773, and 923 K. P_0 is plotted on a logarithmic scale versus the inverse scattered perpendicular velocity to show the exponential dependence present at low energies and high temperatures. The velocity is shown in atomic units (a.u.), where 1 a.u. is approximately 2.2×10^8 cm/sec. The corresponding incident energy scale is noted along the top axis.
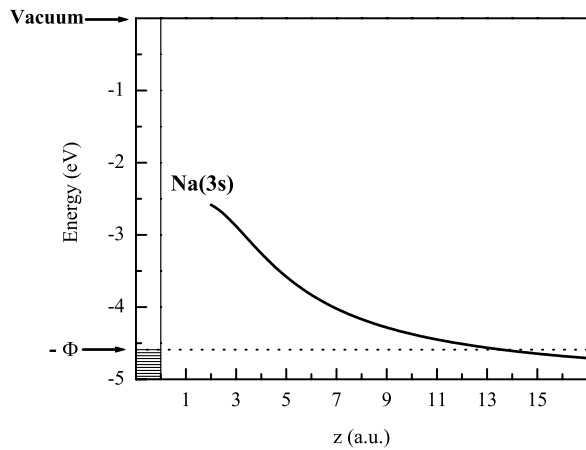
FIG. 4. An ionization level diagram for Na outside of a Cu(001) surface. The Fermi level lies at an energy Φ below the vacuum level, where $\Phi = 4.59$ eV for Cu(001). Filled electron levels in the metal are indicated by the lines drawn on the far left. The distance, z, is plotted in atomic units (a.u.), where 1 a.u. is 0.529 Å.

neutralization experiment. The dynamical effect refers to the competition that arises between the rate of electron tunneling and the finite velocity of the scattered projectile. Put simply, as a projectile leaves the surface, electrons tunnel between the projectile and surface, tracking the energetically favored charge state described above. However, the exponential decay of the coupling with distance implies that at some distance z the charge state is "frozen in" and the projectile is left as either neutral or positive. Quantum-mechanical mixing of projectile charge states outside the surface, however, makes this picture more complex as it implies that there is a nonzero probability of obtaining any allowed charge state at a distance z.

For the Na-Cu(001) system, only the two charge states, neutral and positive, need to be considered. The probability of obtaining either charge state at a distance z is determined primarily by the energetically favored charge state at that distance. Looking at Fig. 4, we see that this implies that the positive ion will dominate at most z values. The velocity dependence at any z, however, is determined, to lowest order, by the relative magnitude of the projectile-surface coupling and the absolute energy difference between $I(z)$ and E_F. Regions where either the coupling or this energy difference are largest determine the energy- and coupling-dominated charge transfer regimes, respectively. If a projectile leaves the surface slowly, the energetically favored charge state can be tracked to large distances, where the coupling is very small. In this case, the velocity dependence is classified as energy-dominated, and an exponential dependence of P_0 on the inverse perpendicular velocity is obtained [14]. Conversely, higher velocity projectiles only track the energetically favored charge state near the surface where the coupling is large. This is the coupling-dominated

regime where the simple exponential dependence of P_0 on inverse perpendicular velocity is no longer valid.

Focusing on the data taken at 350 K in Fig. 3, one can see evidence for both charge transfer regimes as a function of the inverse perpendicular velocity. Energy-dominated charge transfer occurs at the lowest velocities, giving P_0 an exponential dependence for incident energies less than 100 eV. Above 100 eV, the exponential dependence is no longer present, and P_0 increases. The strong projectile-surface interaction dominates at these higher velocities, giving an increased neutral occupancy, or as we measure it, a larger P_0 value [14]. Therefore, the nonmonotonic change observed for P_0 indicates that both energy- and coupling-dominated charge transfer occur in this system at 350 K.

The data in Fig. 3 also show that the magnitude of P_0 and its dependence on inverse perpendicular velocity change dramatically with T_S. Generally, an increase in T_S should alter the electron occupancy in the metal, populating metal levels above E_F according to the Fermi-Dirac distribution. If $|I(z) - E_F| \lesssim k_B T_S$, thermal effects will become significant and lead to a larger P_0 value. Looking at Fig. 4, we see that this condition is met at large distances, where $I(z)$ crosses E_F. This is the energy-dominated regime that is probed at low velocities, and it explains why the measured P_0 values are very sensitive to T_S as the scattered perpendicular velocity is decreased. At higher velocities, $I(z)$ is well above E_F, the charge transfer is coupling dominated, and consequently, the effects of T_S are reduced.

We have compared our measured temperature-dependent P_0 data to results obtained with an independent particle calculation [21]. This calculation is based on the spinless one-level Newns-Anderson Hamiltonian and allows for a determination of the occupancy of the Na atomic level after scattering from the Cu surface. It is a quantum-mechanical treatment that correctly models both of the charge transfer regimes that are probed in our results. This is important because semiclassical treatments, such as the rate equations, do not reproduce the phenomena of coupling-dominated charge transfer that lead to the nonmonotonic P_0 dependence observed in Fig. 3. A modified Fermi-Dirac distribution that incorporates both thermal and velocity-smearing effects was included in the calculation. The distribution was obtained by performing an angular average of a velocity-shifted Fermi-Dirac distribution over a spherical Fermi surface and is written as

$$f^*(\epsilon) = \frac{\ln(1 + e^{-\beta(\epsilon - e)}) - \ln(1 + e^{-\beta(\epsilon + e)})}{2\beta e}, \quad (1)$$

where $\beta = 1/k_B T_S$ and ϵ is the energy of a metallic level relative to E_F. The term e is equal to $k_F v_{proj}$, where k_F and v_{proj} are the Fermi wave vector and the projectile velocity, respectively. The projectile-surface coupling used in the calculation was based on a fit to the theoretical results of Nordlander and Tully [22].
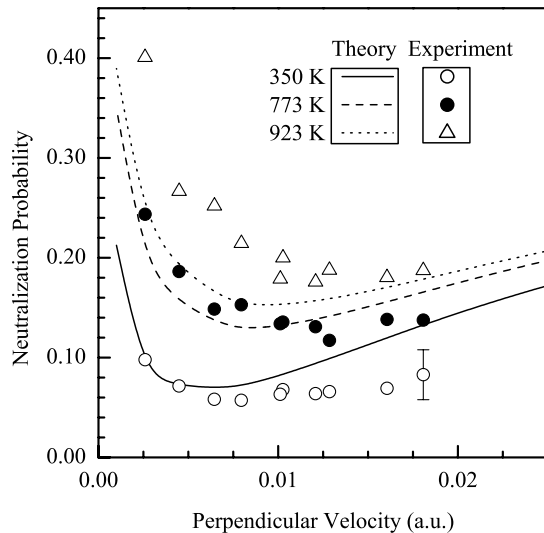
FIG. 5. Comparison of the experimental neutralization probability (symbols) to the results of the independent-particle calculation (lines) for Na^+ scattering from Cu(001). A typical error bar is shown.

A comparison of our theoretical and experimental results for P_0 as a function of the perpendicular velocity at three different T_S values is shown in Fig. 5. The calculation reproduces the increase observed in P_0 with T_S as well as the nonmonotonic change seen in P_0 with perpendicular velocity. Also, the large increase in P_0 observed at the lowest velocity values is reproduced. The quantitative differences evident between the experimental and calculation results shown in this figure vary with velocity and are very sensitive to the coupling and the inclusion of parallel velocity effects [23]. Although a more complex neutralization model may be required to correctly deal with this interplay between T_S, parallel velocity, and the projectile-surface coupling, it is remarkable that such a simple calculation can reproduce the observed trends.

In this Letter, we have shown that T_S can have significant effects on the P_0 values measured in hyperthermal energy ion-surface scattering experiments. By using Na-Cu(001) as the experimental system, our results reveal that these thermal effects are present for both energy- and coupling-dominated charge transfer. The sensitivity of these alkali ion measurements to T_S in the energy-dominated regime demonstrate that the failure to include T_S in the analysis or modeling of neutralization experiments performed at finite temperatures could lead to large errors. Furthermore, in light of these results, future experiments aimed at measuring thermal effects due to many-body or Kondo effects for alkaline-earth projectiles [5,6], must be carefully interpreted.

*Corresponding author: sosolik@nist.gov
Present Address: National Institute of Standards and Technology, Gaithersburg, MD 20899-8412.
†Present Address: Dept. of Chemistry, Penn State University, University Park, PA 16802.
‡Present Address: Woods Hole Oceanographic Institution, Woods Hole, MA 02543.
§Deceased.

[1] B. H. Cooper and E. R. Behringer, in *Low Energy Ion-Surface Interactions*, edited by J. W. Rabalais (J. Wiley & Sons, New York, 1994).

[2] Here we refer to "charge transfer" as meaning the *resonant* transfer of charge between projectile and metal levels at the same energy.

[3] E. G. Overbosch, B. Rasser, A. D. Tenner, and J. Los, Surf. Sci. **92**, 310 (1980).

[4] Y. Bu, E. F. Greene, and D. K. Stewart, J. Chem. Phys. **92**, 3899 (1990).

[5] H. Shao, P. Nordlander, and D. C. Langreth, Phys. Rev. B **52**, 2988 (1995); Phys. Rev. Lett. **77**, 948 (1996).

[6] J. Merino and J. B. Marston, Phys. Rev. B **58**, 6982 (1998).

[7] B. Rasser and M. Remy, Surf. Sci. **93**, 223 (1980).

[8] R. Brako and D. M. Newns, Surf. Sci. **108**, 253 (1981); Vacuum **32**, 39 (1982).

[9] K. C. Liu, T. F. George, and K.-S. Lam, Solid State Commun. **53**, 67 (1985).

[10] F. Battaglia, K. C. Liu, and T. F. George, Int. J. Quantum Chem. Suppl. **19**, 477 (1986).

[11] S. I. Easa and A. Modinos, Surf. Sci. **183**, 531 (1987).

[12] H. Nakanishi, H. Kasai, and A. Okiji, Surf. Sci. **197**, 515 (1988).

[13] K. W. Sulston and F. O. Goodman, J. Chem. Phys. **112**, 2486 (2000); F. O. Goodman and K. W. Sulston, J. Chem. Phys. **114**, 3265 (2001).

[14] G. A. Kimmel and B. H. Cooper, Phys. Rev. B **48**, 12 164 (1993).

[15] R. L. McEachern *et al.*, Rev. Sci. Instrum. **59**, 2560 (1988).

[16] D. L. Adler and B. H. Cooper, Rev. Sci. Instrum. **59**, 137 (1988).

[17] D. R. Peale, D. L. Adler, B. R. Litt, and B. H. Cooper, Rev. Sci. Instrum. **60**, 730 (1989).

[18] G. A. Kimmel and B. H. Cooper, Rev. Sci. Instrum. **64**, 672 (1993).

[19] All three peaks were used to determine P_0 as little variation was observed for the different trajectory types represented. The assigned velocity value was obtained by averaging over the velocities present in each spectrum.

[20] $I(z)$, I_0, and z are expressed here in atomic units.

[21] A. V. Onufriev and J. B. Marston, Phys. Rev. B **53**, 13 340 (1996).

[22] P. Nordlander and J. C. Tully, Surf. Sci. **211/212**, 207 (1989).

[23] C. E. Sosolik, Ph.D. thesis, Cornell University, 2001.