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Charge exchange in low-energy He$^+$ ion scattering from solid surfaces

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We present a model for neutralization of He$^+$ based on resonant charge transfer from a surface valence band to the He $2s$ level, followed by Auger deexcitation or autoionization, thus creating a He atom in the ground state. If a He$^+$ ion approaches a surface, it is energetically favorable for the He-surface system to screen the $1s$ core hole by putting an electron in the $2s$ level. By taking into account this Coulomb interaction Q we are able to explain the trend in the neutralization behavior of 1–5-keV He$^+$ ions scattered from clean metal surfaces. It is shown that the neutralization probability of He$^+$ is mainly determined by the work function and the surface local density of states.

Low-energy ion scattering, also called ion scattering spectroscopy (ISS), has become an important technique for the characterization of the composition and structure of solid surfaces. The information depth of this surface-sensitive technique is determined by the primary ions and the incident angle conditions. By using alkali ions (such as Li$^+$, Na$^+$, or K$^+$), quantitative information about the first and second layers can be obtained, only for single-crystal surfaces, by a variation of the incident, azimuthal, and total scattering angle.[1] If inert-gas ions (such as He$^+$, Ne$^+$, or Ar$^+$) are used, the information depth is limited to the first layer due to the high neutralization probability of inert-gas ions. Most ions that penetrate through the first layer are neutralized, because of an increased interaction with surface atoms, and are not detected with an electrostatic analyzer. So low-energy inert-gas ion scattering can be used for the study of polycrystalline surfaces, but only if the absolute neutralization probability of the ion is known.

A complication arises from the fact that, at present, there is no model that can predict the absolute neutralization probability on an *ab initio* basis. The intensity of backscattered ions is usually calibrated by samples containing one element with a known surface concentration. This calibration method is based on the assumption that the neutralization probability of an inert-gas ion, scattered by a surface atom, is not influenced by the neighboring surface atoms. Recently, it was shown experimentally that this assumption is not necessarily true.[2]

For a long time, debate went on in the literature about the dominant charge-exchange mechanism in low-energy inert-gas ion scattering. Authors argued whether an Auger mechanism or a resonant charge-exchange mechanism is dominant, and, in the case of resonant charge exchange, which energy level(s) of the inert-gas ion and which energy band(s) of the surface are involved. Up till now, no satisfactory explanation has been given for the experimentally observed charge-exchange behavior of He$^+$.

Several models have been developed to describe charge exchange. These models can be divided into the ones that parametrize the neutralization rate with a functional form, which contains a number of adjustable parameters

that have to be fitted by experimental results,[3,4] and (quasi-) *ab initio* calculations in which a quantum-mechanical description of the charge-exchange process is given.[5,6]

In this paper, we show that the trend in the neutralization behavior of 1–5-keV He$^+$ ions scattered from clean metal surfaces can be explained by resonant charge transfer from a surface valence band to the He $2s$ level, followed by deexcitation. Our model for resonant charge exchange is based on a spinless time-dependent Anderson-Newns Hamiltonian[7,8]

$$H(t) = \varepsilon_a c_a^\dagger c_a + \sum_k \varepsilon_k c_k^\dagger c_k$$

$$+ \sum_k [V_{ak}(t) c_a^\dagger c_k + V_{ka}(t) c_k^\dagger c_a] , \qquad (1)$$

where the first term represents the incident He$^+$ ion (subscript a), and the second term a surface (subscript k). The third term (both subscripts a and k) describes the interaction between the ion and the surface. $c_a^\dagger$, c_a, $c_k^\dagger$, and c_k are the creation and annihilation operators for an electron in the states ϕ_a (ion) and ϕ_k (surface), respectively. ϕ_a and ϕ_k are the eigenstates of the Hamiltonian without interaction between ion and surface, while ε_a and ε_k are the corresponding energy eigenvalues (the continuous energy band of the surface is represented by a great number of discrete energy levels ε_k). The hopping integrals V_{ak}, which lead to an effective broadening of the levels, are a function of the internuclear distance z between the ion and the surface. The time dependence of V_{ak} enters through the ion trajectory $z(t)$. This trajectory is calculated for a scattering angle of 180°, using the Ziegler-Biersack-Littmark (ZBL) potential,[9] which is a screened Coulomb potential.

The ion-surface system is described by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H(t)\psi(t) , \qquad (2)$$

where $H(t)$ is the Hamiltonian given in (1), and $\psi(t)$ is the wave function of the total (ion plus surface) system. The parameter of interest is the electron occupation num-

ber of state ϕ_a,

$$N_{aa}(t) = \langle \psi(t)|c_a^\dagger c_a|\psi(t)\rangle , \tag{3}$$

representing the fraction of He$^+$ that has been neutralized. The electron occupation number $N_{aa}(t)$ is calculated, using a method originally proposed by Muda and Hanawa.[10] Defining the occupation number matrix $N_{ij}(t)$ by the equation

$$N_{ij}(t) \equiv \langle \psi(t)|c_i^\dagger c_j|\psi(t)\rangle , \tag{4}$$

its time derivative is given by

$$i\hbar\frac{dN_{ij}(t)}{dt} = \langle \psi(t)|[c_i^\dagger c_j, H(t)]|\psi(t)\rangle . \tag{5}$$

Substitution of Hamiltonian (1) gives the following set of coupled first-order differential equations for $N_{ij}(t)$:

$$i\hbar\frac{dN_{ij}(t)}{dt} = \sum_n [h_{jn}(t)N_{in}(t) - h_{ni}(t)N_{nj}(t)] , \tag{6}$$

where $h_{ij}(t)$ is a short notation for the matrix elements of Hamiltonian (1). The set of coupled first-order differential equations can be solved numerically, e.g., by the Runge-Kutta-Merson method. The calculation method is described in more detail elsewhere.[11]

As discussed by Marston et al.[5] and Shao, Langreth, and Nordlander,[6] many-body effects can be very important in charge-exchange processes. One of these effects, the Coulomb interaction Q between a He $1s$ core hole and He $2s$ plus a surface valence band, has never been taken into account, as far as we know. If a He$^+$ ion approaches a surface, it is energetically favorable for the He-surface system to screen the $1s$ core hole by putting an electron on the $2s$ level. So during a close encounter He $2s$ is effectively lowered. The Coulomb interaction Q is known in condensed-matter physics, and can be of the order of a few eV.[12] The effect of the Coulomb interaction can be incorporated into Hamiltonian (1): $\varepsilon_a = -4.77$ eV$+Q$. If we assume that Q is about -1.5 eV, we find that $\varepsilon_a = -6.3$ eV. A shift of the $2s$ level for Li$^+$ was proposed very recently by German, Weare, and Yarmoff,[13] who showed that removal of a $1s$ electron shifts the Li electron affinity level down, so that the Li $2s$ level becomes fully occupied via resonant charge transfer from a surface valence band. One may argue that we have not taken into account the image potential of He$^+$ which may lead to an upward shift of He $2s$. Marston et al.[5] estimated the shift for alkali ions to be of the order of 2.6 eV. The shift cannot be very large, since otherwise no alkali ion would be neutralized. For He$^+$, this upward shift can easily be overcome by the Coulomb interaction of a few eV,[12] which is not present for alkali ions without a core hole. In fact, our estimate for Q is already quite low. The importance of He $2s$ is further illustrated by Shao, Langreth, and Nordlander,[6] who show that the oscillations observed in the intensity of backscattered He$^+$ ions as a function of the initial kinetic energy for a few elements (such as Pb) (Ref. 14) can only be explained if not only He $1s$ but also He $2s$ is involved.

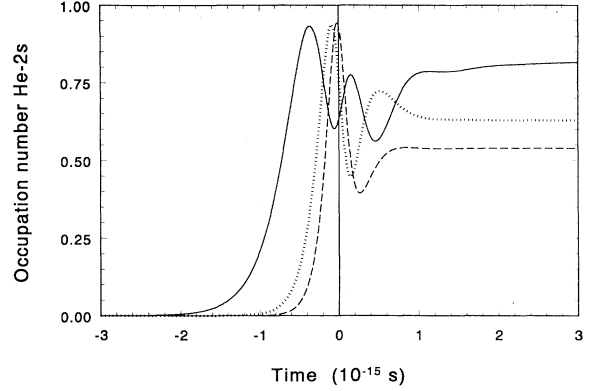We will examine the charge exchange between a He$^+$

FIG. 1. The occupation number of He $2s$ is shown as a function of time for kinetic energies vs of 1 keV (solid line), 3 keV (dotted line), and 5 keV (dashed line).

ion and a Cu surface, since the density of states (DOS) of Cu is very well known. The structure of the valence band of Cu, represented by the discrete ε_k's in Hamiltonian (1), is roughly approximated by the following analytical expression:

$$\varepsilon_k = -6 - 4\frac{(k-1)^2}{(n-1)^2}[\text{eV}], \quad k = 1, 2, \ldots, n . \tag{7}$$

This expression contains the surface state of the Cu valence band, as shown in Ref. 15.

The hopping integrals V_{ak} are calculated with the extended Hückel method between a He $2s$ wave function and a Cu $3d$ wave function, since the valence band of Cu has mainly $3d$ character. At distances smaller than a few Å, electron-electron repulsion terms (which are neglected in the extended Hückel method) become very important, and will distort the wave functions of both He and Cu. The hopping integrals for these distances have been obtained by an exponential extrapolation of the results at larger distances: $V_{ak}(z) = -n^{-1/2}5.07\exp(-z/1.16)$, with V_{ak} in eV, z in Å, and n as defined in expression (7).
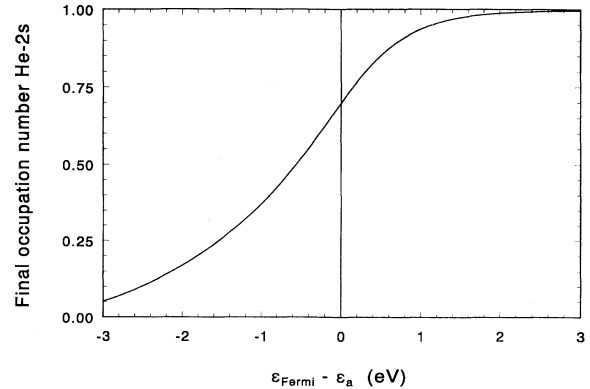

FIG. 2. The occupation number of He $2s$ at $t = \infty$ is shown as a function of the difference between the Fermi level ($\varepsilon_{\text{Fermi}}$) and the He $2s$ level ($\varepsilon_a = -6.3$ eV). The initial kinetic energy is 1 keV.

Using the values for ε_a, ε_k, and V_{ak} as discussed above, we can calculate the electron occupation number $N_{aa}(t)$ [Eq. (3)] of the He $2s$ level as a function of time. The results for $n = 200$ are shown in Fig. 1, for initial kinetic energies of 1, 3, and 5 keV. As He^+ approaches the surface, the He $2s$ level starts to fill by resonant transfer from the Cu valence band. Near the distance of closest approach ($t = 0$ s), the occupation number of He $2s$ starts to oscillate, because the hopping integrals V_{ak} increase very rapidly.[11] Note that the final ion fraction $[= 1 - N_{aa}(t = \infty)]$ becomes larger when the initial kinetic energy of He^+ is increased. This finding is in agreement with experimental results.[16]

We will now examine the effect of the work function of a solid surface on the neutralization probability of a He^+ ion. The effect is studied by changing the number of ε_k's that are initially filled, since the Fermi level of a surface is determined by the highest occupied ε_k. We assume that the structure of a surface valence band can be approximated by an analytical expression of the same form as expression (7). The only change is an increase in the width of the band to 8 eV (from -10 to -2 eV) to create a greater variety in work functions. No changes are made in V_{ak} or ε_a. Figure 2 shows the occupation number of the He $2s$ level at $t = \infty$ as a function of the Fermi level, relative to the He $2s$ level (taken to be -6.3 eV). From this figure, it is clear that the neutralization probability of He^+ strongly depends on the work function, if the He $2s$ level is involved in the neutralization process. Furthermore, we observe a significant neutralization probability, even for $\varepsilon_a > \varepsilon_{\text{Fermi}}$.

In Fig. 3 the Fermi levels of solids, consisting of elements of the second, third, fourth, and fifth rows of the periodic system, are plotted with respect to the vacuum level (taken to be 0 eV). The Fermi levels are obtained from the work function of the elements,[17] since the work function is the minimum energy required to create a free
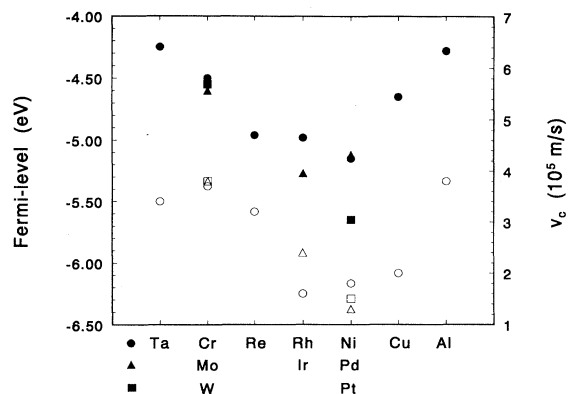

FIG. 3. A comparison of the Fermi levels (left axis, closed symbols) (Ref. 17) and neutralization probabilities of He^+ (right axis, open symbols) (Ref. 16) for several elements. The characteristic velocity v_c is a measure for the neutralization probability, as used in $P^+ = \exp[-v_c(1/v_i + 1/v_f)]$, where P^+, v_i, and v_f are the total final ion fraction, the initial velocity, and the final velocity of the ion, respectively (Ref. 16).

electron. Figure 3 also contains an experimental measure (the characteristic velocity v_c) for the neutralization probability of He^+ scattered from the respective surfaces.[16] It is immediately clear from this figure that the neutralization probability of He^+ scattered from an element is correlated with the work function of the element. This correlation is completely in agreement with our mechanism of resonant transfer of an electron from a surface valence band to the excited He $2s$ level (Fig. 2), assuming a reasonable density of states around the Fermi level. The relation between the neutralization probability and the work function was studied before, but no correlation was found then.[18]

Deviations from the correlation can be explained by taking into account the surface local density of states (SLDOS) of the valence band. Figure 3 shows that the neutralization probability of He^+ scattered by Cu is comparable to the neutralization probability of He^+ scattered by Pt. We also see that the work function of Cu is smaller than the work function of Pt. However, Ref. 15 shows that the Fermi level of Cu is positioned within the part of the valence band that has mainly s character, where the density of states (DOS) is extremely low in comparison with the DOS of Pt and the other elements in Fig. 3. This explains why the neutralization probability of He^+ scattered by Cu is not very much larger than that of Pt.

The behavior of Ta can be explained by Fig. 2, showing that the neutralization probability saturates when the difference between the Fermi level and the He $2s$ level exceeds a value of about 2 eV. Differences in the hopping integral between He $2s$ and the surface valence band, due to a difference in the character of this band (d, s, or p character) may also lead to small deviations from the correlation.

After resonant transfer of an electron to He $2s$, the He particle is left in an excited state. An excited $He^*(1s,2s)$ atom cannot be deexcited into the $He(1s^2)$ ground state by emitting a photon, since this is a forbidden transition: $He^*(1s,2s)$ is a metastable state. A neutral He atom in the ground state can be obtained by Auger deexcitation $[He^*(1s,2s) + M \rightarrow He(1s^2) + M^+ + e^-]$ or autoionization $[He^{-*}(1s,2s^2) \rightarrow He(1s^2) + e^-]$.[19] Autoionization is only possible when two electrons have been transferred to He $2s$ by resonant charge exchange from a surface valence band. However, autoionization can take place far away from the surface, since no electrons of the surface are involved in this process.

The lifetime of resonant charge exchange is of the order of less than 1×10^{-15} s (see Fig. 1), while the lifetimes of Auger deexcitation and autoionization are of the order of a few times 10^{-15} s.[19] Autoionization is generally the slowest process. We see that resonant charge exchange is the fastest process, so, in first order, resonant charge exchange and deexcitation may be treated as two independent processes. Ultimate proof for our model can be obtained by measuring the energy of secondary electrons, as has been done by German, Weare, and Yarmoff[13] for Li^+ scattering. At this point we cannot say which deexcitation process is dominant, since to our knowledge no experiments to measure secondary electrons emitted during autoionization or Auger deexcitation for He^+ scattering

in the range of 1–5 keV have been performed.

We have also tested the possibility of resonant charge exchange between a surface valence band and a promoted (upward shifted) He $1s$ level, as suggested by Verbist, Brongersma, and Devreese.[20] Calculations show that the neutralization probability increases when the initial kinetic energy is increased,[11] in disagreement with experimental results. However, resonant charge exchange between a promoted He $1s$ level and a surface valence band can account for the rise in the reionization probability of neutralized He when the initial kinetic energy is increased.[11] This indicates that neutralization and reionization are two different processes, in contrast to what is stated in Ref. 16. At present, models for direct Auger neutralization of He$^+$ by jelliumlike surfaces are developed, but no reliable predictions for real surfaces can be made yet.[6,21]

In conclusion, we have shown that the trend in the neutralization behavior of 1–5-keV He$^+$ ions scattered from clean metal surfaces can be explained by resonant charge exchange between a surface valence band of the solid and the He $2s$ level. Assuming a reasonable density of states around the Fermi level, our model predicts a correlation between the neutralization probability and the work function (Fig. 2), which has been observed (Fig. 3). Resonant tunneling to He $2s$ will take place when it is energetically favorable for the He surface system to have the He $2s$ level occupied. This occurs either when the work function is sufficiently small, as has been shown for alkali-adsorbed metal surfaces, or when the He $2s$ level is lowered due to the Coulomb interaction Q. We have shown that the high neutralization probability of He$^+$ can be explained by the Coulomb interaction Q due to the He $1s$ core hole, which is absent for alkali ions.

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