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Dynamics of He^+ ion neutralization at clean metal surfaces: Energy- and spin-resolved studies

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Measurements of the energy distributions and energy-resolved polarizations of electrons ejected by incident polarized He^+ ions are used to probe the dynamics of He^+ ion neutralization at clean Al(100), Au(100), and Cu(100) surfaces for incident ion energies in the range 10–500 eV. The results are interpreted using recent theory and suggest that neutralization occurs at typical atom/surface separations of ~2–3 a.u., significantly smaller than those inferred from earlier experimental studies of ion scattering and ion neutralization at surfaces. Close to the surface strong short-range repulsive interactions become important and lead to increases in the maximum energy of the ejected electrons and to a spin-dependent increase in the local density of electronic states near the Fermi energy.

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Ion neutralization at clean metal surfaces has been investigated both by analyzing the energy distributions of electrons ejected from the surface and by examining the number, and charge state distribution, of particles produced by reflection of incident ions.[1–3] Recently, an additional tool for probing the dynamics of ion/surface interactions was introduced that makes use of spin-labeling techniques, specifically the use of incident electron-spin-polarized He^+ ions coupled with energy-resolved measurements of the ejected electron polarization.[4–6] This technique complements the earlier approaches and can provide new insights into the perturbations in surface electronic structure induced by the presence of the ion. Here we combine measurements of the energy distributions and the energy-resolved polarizations of electrons ejected by polarized He^+ ions to probe the dynamics of He^+ ion neutralization at clean Al(100), Au(100), and Cu(100) surfaces for incident ion energies in the range ~10–500 eV. Data recorded with the ion energy and angle of incidence varied so as to maintain an approximately constant component of ion velocity (kinetic energy) parallel or perpendicular to the surface show that the maximum energy of the ejected electrons is determined principally by the component of ion energy perpendicular (rather than parallel) to the surface. In addition, it is observed that the electrons involved in ion neutralization tend to have antiparallel spins leading to the preferential formation of singlet two-hole final states in the surface. These results are interpreted using current theoretical models and suggest that ion neutralization occurs close to the surface, typically ~2–3 a.u. from the outermost atomic layer, where strong localized short-range interactions between the He^+ ion and neighboring metal atoms are important. This distance is significantly smaller than those inferred from earlier experimental studies of ion scattering[2] and ion neutralization[1] at surfaces.

Conventional models[1] suggest that at clean high work function metal surfaces He^+ ions undergo Auger neutralization (AN) in which an electron from the metal tunnels into the He^+ 1*s* core hole. The energy liberated is communicated to a second electron in the metal which, if the energy transfer is sufficient, can be ejected from the surface. This process results in a relatively structureless ejected electron energy distribution that reflects, approximately, a self-convolution of the local density of electronic states at the surface. However, studies have indicated that although (for high work function surfaces such as studied here) the helium $n=2$ atomic levels lie above the Fermi energy ε_F for small atom/surface separations they also broaden to such an extent that they extend below the ε_F allowing each to be partially filled by electrons from the metal, thereby increasing the local density of electronic states in the vicinity of the ion.[4] Because of this partial filling, three basically independent mechanisms have been pictured as leading to ion neutralization: AN (which plays a dominant role), ‘‘direct’’ Auger deexcitation of singlet states in which an electron in the $n=2$ level falls into the helium 1*s* core hole with simultaneous ejection of an electron from the metal, and ‘‘indirect’’ Auger deexcitation of singlet or triplet states in which a metal electron fills the 1*s* core hole with the simultaneous emission of the electron in the $n=2$ level. (Direct Auger deexcitation is forbidden for triplet states because the helium atom ground state is a spin singlet.) Recently it has been suggested[7] that an additional mechanism is also important in which the energy released as a metal electron falls into the He^+ 1*s* core hole is used to excite a surface plasmon, electron ejection occurring as this plasmon subsequently decays.

The present apparatus has been described in detail elsewhere.[4,5,8–10] Briefly, polarized He^+ ions extracted from an optically-pumped rf-excited helium discharge are formed into a beam by a series of electrostatic lenses and directed onto the target surface. The energy distribution of the ejected electrons is measured using a retarding potential energy analyzer; their polarization is determined using a compact Mott polarimeter[10,11] that is equipped with a retarding-potential energy analyzer at its input. The target surfaces are prepared by repeated argon ion bombardment/thermal annealing cycles. Surface cleanness is monitored by Auger analysis and by ion neutralization spectroscopy, i.e., by measuring the energy distribution of electrons ejected from the surface as a result of He^+ ion neutralization, which is very sensitive to surface contamination.

Ejected electron energy distributions observed following He^+ ion neutralization at a clean Au(100) surface are presented in Fig. 1 for ions incident normal to the surface with energies in the range 10 to 500 eV. The distributions are

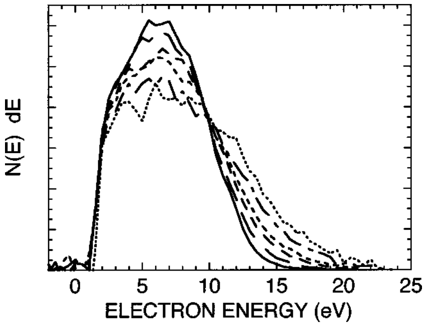

FIG. 1. Energy distribution of electrons ejected from a clean Au(100) target by He^+ ions incident normally with energies of 10 eV. (solid line), 20 eV (long dashed line), 40 eV (medium dashed line), 60 eV (dashed line), 250 eV (dot-dashed line), and 500 eV (dotted line).

normalized to have equal area to reflect the fact that, over the present range of ion energies, the secondary electron ejection coefficient γ is essentially constant.[12] As expected, the energy distributions, which reflect a self-convolution of the local density of states, are broad and relatively featureless. The high energy cutoffs in the distributions, however, increase markedly with increasing ion energy. Similar behavior is observed with the other surfaces studied here. To investigate the origin of this effect, data were recorded in which the ion energy and angle of incidence were varied so as to maintain an approximately constant component of ion energy parallel or perpendicular to the surface. (The angle between the incident ion beam and the axis of the energy analyzer, however, remained fixed at ~45°.) Representative data recorded for each of the present surfaces are shown in Fig. 2. These demonstrate that the broadening of the electron energy distribution is governed principally by the component of ion energy perpendicular to the surface, which suggests that it is related to the distance of closest approach of the ion to the surface.

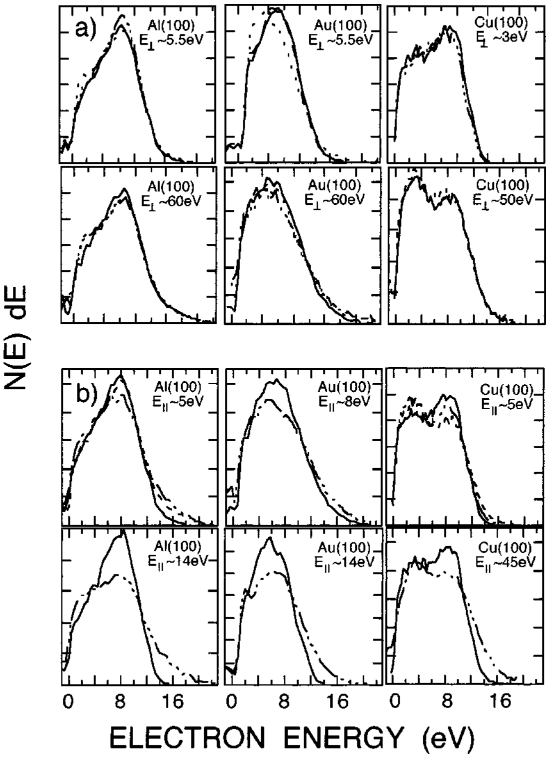

FIG. 2. Energy distribution of electrons ejected from clean Al(100), Au(100), and Cu(100) surfaces by He^+ ions with the ion energy and angle of incidence varied so as to maintain approximately constant components of ion energy (a) perpendicular ($E_\perp$) and (b) parallel ($E_\parallel$) to the surface. These components of energy are indicated in each element of the figure and were obtained using the following combinations of ion energy and angle of incidence: (a) Al(100), $E_\perp \sim 5.5$ eV:-15 eV/32.5°, 60 eV/65°, and 250 eV/78°, $E_\perp \sim 60$ eV:-60 eV/10°, 250 eV/60°, 500 eV/69°; Au(100):- same as for Al(100); Cu(100), $E_\perp \sim 3$ eV:-10 eV/55°, 25 eV/70°, $E_\perp \sim 50$ eV:-60 eV/20°, 250 eV/65°; (b) Al(100), $E_\parallel \sim 5$ eV: -15 eV/32.5°, 60 eV/15°, 250 eV/10°, $E_\parallel \sim 14$ eV:-15 eV/75°, 500 eV/10°; Au(100), $E_\parallel \sim 8$ eV:-60 eV/25°, 250 eV/10°, $E_\parallel \sim 14$ eV:-15 eV/75°, 60 eV/30°; Cu(100), $E_\parallel \sim 5$ eV:-10 eV/45°, 25 eV/25°, 60 eV/15°, $E_\parallel \sim 45$ eV:-60 eV/65°, 250 eV/25°.

Simple arguments suggest that the maximum ejected electron energy should be given by $E_{\max}=\varepsilon_i-2\phi$, where ε_i is the energy liberated by neutralization of the ion and ϕ is the surface work function; 5.5 eV for Au(100), 5.1 eV for Cu(100), and 4.25 eV for Al(100). The available energy ε_i depends critically on ion/surface separation, initially decreasing from the value $\varepsilon_i \sim 24.6$ eV characteristic of an isolated He^+ ion as the surface is approached due to image charge interactions. One possible mechanism that might account for the increase in the high-energy cut off in the energy distribution with increasing ion energy is the excitation of electrons in the solid by the moving ion to create electron/hole pairs. This would produce electrons with energies above ε_F, which, if they participate in the Auger process, could lead to an increase in the ejected electron energy. Fourier analysis suggests that this increase might amount to ~0.5–1.5 eV for the present range of ion energies,[13] which is significantly smaller than that observed. Further, to a first approximation, the energy shifts associated with this effect should be governed simply by the speed of the incident ion rather than, as is observed experimentally, by its component of energy perpendicular to the surface. A smaller increase in the high energy cut off, associated with the component of ion velocity parallel to the surface, arises as a consequence of the reference frame transformation between ion and metal.[2,4]

Recent calculations of the energies of He^+ ions and ground-state He^0 atoms near metal surfaces, however, suggest an alternate explanation for the broadening. These show that, whereas the image potential provides a fair approximation to the He^+ and He^0 level shifts at large separations, close to the surface strong short-range "chemical" interactions with neighboring metal atoms become important and lead to large shifts in the energy levels.[14–16] In particular, the calculations indicate that the energy difference $E[\mathrm{He}^+]-E[\mathrm{He}^0]$, which is equal to the energy release ε_i that occurs when the ion is neutralized, depends critically on the ion/surface separation. This is illustrated in Fig. 3(a) which shows the calculated energy differences[16] for an Al(111) surface as a function of the distance z from the first atomic layer. These calculations, which assume that the ion is inci-

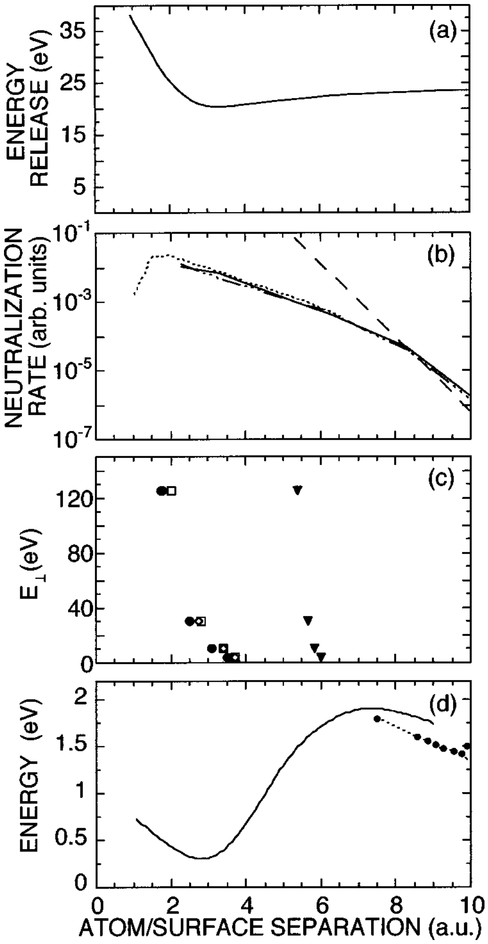

FIG. 3. (a)Calculated energy release ε_i that occurs upon neutralization of a He$^+$ ion as a function of atom/surface separation z (taken from Ref. 16). (b) Ion neutralization rates $R_t(z)$ as calculated in Ref. 16 (dotted line), Ref. 17 (solid line) and Ref. 18 (dot-dashed line), and as inferred from measurements of grazing-incidence ion scattering (dashed line), taken from Ref. 2. (c) Typical neutralization distances predicted using Eq. (3) and the neutralization rates given in Ref. 16 (□), Ref. 17 (◇), Ref. 18 (●), and Ref. 2 (▼) for different initial components of ion energy perpendicular to the surface $E_\perp$. (d) Calculated helium $n=2$ singlet level near an aluminum surface {taken from Ref. 15 (solid line), Ref. 20 (dot-dashed line)}, referenced to the Fermi energy.

dent directly on top of an atom in the surface, predict that the energy release will increase dramatically if the ion is neutralized close to the surface. Similar behavior is also predicted for a Pd(111) surface suggesting that it might be typical of a wide variety of high work function metals. Given that the distance of closest approach to the surface will depend on the component of incident ion energy perpendicular to the surface, such an effect could account in large part for the observed increases in the high energy cutoff in the ejected electron energy distributions. For this to be true, however, ions must be able to approach close to the surface before neutralization takes place.

The distance from the surface at which neutralization occurs can be determined if the transition (neutralization) rate $R_t(z)$ and the perpendicular component of incident ion velocity $v_\perp(z)$ are known as a function of ion/surface separation. The probability that an incoming ion will undergo neutralization at a distance z from the surface in a time interval dt is given by

$$d\mathcal{P}_o(z)=\mathcal{P}_o(z)R_t(z)dt, \tag{1}$$

where $\mathcal{P}_o(z)$ is the probability that the ion has reached z without undergoing neutralization. Since dt is related to the incremental distance dz travelled in this interval by $dt=dz/v_\perp(z)$, then

$$\frac{d\mathcal{P}_o(z)}{\mathcal{P}_o(z)}=R_t(z)\frac{dz}{v_\perp(z)}. \tag{2}$$

when integration yields

$$\mathcal{P}_o(z)=\exp-\left(\int_z^\infty\frac{R_t(z')dz'}{v_\perp(z')}\right). \tag{3}$$

Figure 3(b) shows the results of several recent calculations of $R_t(z)$ for He$^+$ ions incident on an aluminum surface.[16–18] To aid in evaluating the integral in Eq. (3), each was fit by a polynomial. $v_\perp(z)$ was derived from the initial value, $v_{o\perp}(\infty)$, using the potential calculated for the interaction of a He$^+$ ion with an Al(100) surface.[16] This potential rises sharply near the surface due to strong short-range repulsive interactions. Given $R_t(z)$ and $v_\perp(z)$, $\mathcal{P}_o(z)$ was determined by numerical integration. The atom/surface separation z_c at which $\mathcal{P}_o(z)$ falls to 0.5 was then taken as a measure of the typical distance at which neutralization might be expected. Values of z_c obtained using the different theoretical predictions for $R_t(z)$ are presented in Fig. 3(c) for several initial components of ion energy perpendicular to the surface. Although the different theoretical calculations predict somewhat different neutralization rates they, nonetheless, each indicate that, for the present experimental conditions, neutralization should typically occur ~2–3 a.u. from the first atomic layer, i.e., close to the jellium edge which is located at $z\sim2$ a.u. A fraction of the incident ions, however, undergo neutralization at smaller atom/surface separations where, as shown in Fig. 3(a), the energy available upon neutralization is increased. This would then account for the (sizable) increase in the high-energy cutoffs evident in Fig. 1 (and 2) as the component of incident ion energy perpendicular to the surface is increased.

Figure 3(b) also includes neutralization rates $R_t(z)$ inferred from measurements of grazing-incidence He$^+$ ion scattering.[2] These rates, although consistent with earlier experimental estimates,[1] are much higher than those suggested by the recent theory and would lead to ionization at distances of ~5–7 a.u. from the first atomic layer. At these distances the neutralization energy ε_i is too small to account for the high energy components of the ejected electron energy distributions. Recently, however, the initial interpretation of the ion scattering data has been questioned[3,14] and it has been argued that they, in fact, point to neutralization at ion/surface separations similar to those indicated in the present work.

Ionization at small atom/surface separations is also consistent with the measured ejected electron polarizations.[19]

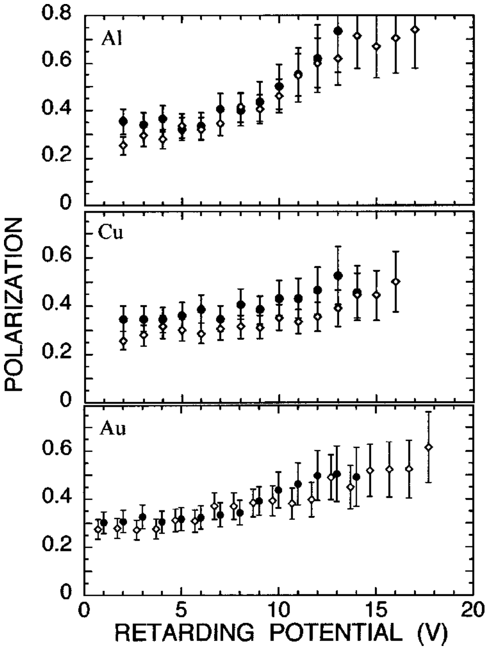

FIG. 4. Ejected electron polarizations as a function of the retarding potential V_R applied to the retarding grids at the input of the Mott polarimeter for Al(100), Au(100), and Cu(100) and incident ion energies of 15 eV (●) and 500 eV (◇). The electron polarization is normalized to that of the incident ions, which are incident at an angle $\theta \sim 50°$ to the surface normal.

These are shown in Fig. 4 as a function of the retarding potential V_R applied to the retarding grids at the input of the Mott polarimeter. The ions are incident at $\theta_i \sim 50°$ to the surface normal and data are included for ion energies of ~ 15 and 500 eV. The ejected electron polarization is normalized to that of the incident ions. For any particular retarding potential V_R, the measured polarization represents the average polarization of all electrons ejected with energies greater than eV_R, where e is the electronic charge. A marked spin correlation is evident indicating that the electrons involved in the Auger process tend to have antiparallel spins. This can be seen, for instance, by considering the specific case where the incident He^+ ions are polarized in the $m_j(m_s) = +1/2$, i.e., spin-up (↑), state. Because the helium ground state is a spin singlet, such ions must be neutralized by spin-down (↓) $m_s = -1/2$ electrons. However, as demonstrated in Fig. 4, this is accompanied by the preferential ejection of spin-up electrons leading to the formation of singlet two-hole final states in the surface.

Similar behavior is observed for each of the present target surfaces. At low-to-intermediate values of retarding potential the measured electron polarizations are essentially constant and independent of incident ion energy. Interestingly, the average polarization $\overline{P}_e$ of the ejected electrons, i.e., that measured with the smallest retarding potential V_R, is similar for each of the present surfaces and has the value $\overline{P}_e \sim \frac{1}{3}$. In each data set, however, the polarizations increase markedly at the highest retarding potentials indicating that those electrons in the high-energy tail of the electron energy distributions have polarizations that are significantly higher than those characteristic of the rest of the distribution. This increase is particularly pronounced in the case of Al(100).

An average polarization $\overline{P}_e \sim \frac{1}{3}$ can be accounted for as follows. Neutralization of a He^+ ion in which the electron is polarized spin up (↑) requires a spin-down (↓) electron. Thus, for neutralization to proceed, at least one of the two participating electrons must be spin down, resulting in the possible spin configurations $\{\uparrow\downarrow\}$, $\{\downarrow\uparrow\}$, and $\{\downarrow\downarrow\}$. Assuming that the available electrons are not strongly spin polarized, it is reasonable to expect that the overall spin configurations $\{\uparrow + \uparrow\downarrow\}$, $\{\uparrow + \downarrow\uparrow\}$, and $\{\uparrow + \downarrow\downarrow\}$ will be equally probable, whereupon twice as many spin-up as spin-down Auger electrons will be produced, resulting in an average ejected electron polarization $\overline{P}_e \sim \frac{1}{3}$ independent of the nature of the surface. This picture is similar to that recently employed to explain data obtained in spin-dependent studies of He^+ neutralization at a solid CO_2 surface where the ejection of electrons with an average polarization $\overline{P}_e \sim \frac{1}{3}$ was also observed.[20] The formation of an autoionizing complex was postulated in which a significant fraction of the kinetic energy of the incident ion is converted to potential energy.

Careful inspection of the data in Fig. 4 reveals that the average electron polarization decreases somewhat as the incident ion energy is increased, this effect being most marked for Cu(100) and Al(100). As evident from the ejected electron energy distributions shown in Figs. 1 and 2, an increase in ion energy can result in an increase in the relative production of low-energy electrons. This effect is most noticeable for Al(100) and for Cu(100). No similar significant increase is observed for Au(100). This suggests that the observed decreases in the average electron polarization can be attributed to an increase in the production of (unpolarized) low-energy secondary electrons. For Al(100) it has been suggested that electron ejection associated with the excitation and subsequent decay of surface plasmons might provide an important contribution to the total secondary electron signal at energies below $\sim$6–7 eV.[7] Since no spin correlation is expected in the decay of such a collective excitation these electrons should also be unpolarized. However, given that the behavior of the polarizations measured for Al(100) and Cu(100) (a transition metal for which no well-defined plasmon features have been observed) are similar, this suggests that plasmon decay provides, at most, only a small contribution to the total electron signal.

A simple model[4–6] which considers the perturbation in surface electronic structure induced by the presence of the (polarized) He^+ ion has been proposed to explain the polarization increases observed at the higher retarding potentials. The induced density of states was evaluated using an Anderson model and exhibited a marked spin dependence that resulted from perturbations in the local densities of states associated with the helium $2s$ orbital. As the surface is approached, the shift and broadening of the 2^1S and 2^3S atomic levels is such that each is partially filled by electrons from the metal which increases the local density of states in the vicinity of ε_F. This increase is markedly spin dependent because the (spin polarized) 2^3S level lies appreciably lower in energy than the 2^1S level and therefore provides a greater contribution to the induced density of states leading to a net electron polarization in the same sense as that of the incident ions. The increase in electron polarization observed at the highest ejected electron energies is then explained because, as the energy increases, the electrons involved in the Auger process must originate from ever higher energy states where the spin dependence in the total density of occupied states is most pronounced.

Although in discussing this mechanism earlier it was assumed that neutralization occurred relatively far from the surface,[4,6] its effects are likely to be more important if neutralization occurs close to the surface. Recent calculations of the helium $n=2$ singlet levels near an aluminum surface are shown in Fig. 3(d),[15,21] referenced to the Fermi energy. These calculations suggest that, whereas these levels initially move up in energy as the surface is approached, close to the surface short-range interactions become important leading to strong mixing between the S and P states and to a lowering of their energies. The calculated energies reach a minimum $\sim$3 a.u. from the outermost atomic layer where the triplet level, which is located $\sim$0.3 eV below the singlet level, is predicted to lie close to ε_F. At smaller atom/surface separations the levels again rise but their widths should be sufficient to ensure that they extend below ε_F resulting in a significant spin-dependent induced density of states in the vicinity of ε_F. As a result, the spin configurations $\{\uparrow + \uparrow\downarrow\}$ and $\{\uparrow + \downarrow\uparrow\}$ are favored leading to an increase in the ejected electron polarization which, as noted above, will again be most pronounced at the highest ejected electron energies. This picture is also consistent with the observation that, of the surfaces studied here, the increase in polarization is most marked for Al(100). This has the smallest work function and its Fermi energy presumably therefore lies closest to the helium $n=2$ atomic levels resulting in the largest induced density of states.

The present work indicates that ion neutralization at clean, high-work-function metal surfaces occurs at much smaller ion/surface separations, typically $\sim$2–3 a.u., than inferred from earlier measurements of ion scattering and ion neutralization. Close to the surface, strong short-range chemical interactions between the incident ion (as well as the product neutral) and neighboring metal atoms are important and lead to pronounced energy level shifts. These make possible increases in the maximum energy of the ejected electrons and result in a spin-dependent increase in the local density of electronic states near the Fermi level. However, further detailed calculations will be required to fully evaluate the role of localized interactions in ion/surface scattering.

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