Role of *d* Electrons in Auger Neutralization at Metal Surfaces

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A generalized theory of Auger electron transfer processes in the interaction of ions with metal surfaces, including the previously ignored role of *d* electrons is presented. It is shown that a correct and accurate description of Auger neutralization has to account for the contribution of *d* electrons, as this is illustrated on the case of He^+ ion neutralization on Ag, where the neglect of these leads to a strong overestimation of ion survival probabilities. Crystal lattice site specific rates are calculated and allow for a correct description of crystal azimuthal effects in neutralization.

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Electron and energy transfer processes between an atom or molecule and a surface are extremely important in physics and chemistry for its many applications as well as for being of fundamental interest in understanding the formation of chemical bonds. In the case of molecules, conversion of vibration to electron excitation of the solid has been proved to be a very efficient mechanism for energy transfer [1]. For simple atoms and molecules, electron transfer proceeds via resonant and Auger processes. Resonant electron transfer plays an important role as one of the first steps in molecular adsorption or dissociation processes [2]. Auger neutralization and deexcitation are important processes for neutralization of ions and deexcitation of atoms [3,4] and have also been invoked to explain exoelectron emission in [5]. Since the pioneering work by Hagstrum [4], these processes have been used to extract information about electronic structure and analysis of surfaces and this has become a commonly used tool complementing photoelectron spectroscopy [3].

All these aspects have motivated intensive experimental and theoretical investigation of these processes. Resonant processes are basically one-electron processes that occur when one electron can tunnel to (from) the energy level of the ion from (to) the continuum of states in the solid. In contrast, Auger processes involve at least two electrons: the electron-electron Coulomb interaction causes the scattering of one electron of the solid to the ion while another electron is scattered from an occupied to an unoccupied state of the solid. The difficulty of dealing with electron-electron interaction in a many-electron system has been the main cause why realistic theoretical calculations of the Auger neutralization rate of an ion in front of a metal surface have not been possible until recently. To our knowledge, all of these calculations have been performed by describing the metal surface within the jellium model [6–11], and the role played by *d* electrons has been neglected [12]. Very recently, precise measurements of the very small surviving scattered ion fractions of the He^+ in grazing collisions with various types of Ag [13,14] and Al [15] surfaces have been performed revealing in particular strong differences in the Auger neutralization probability of He^+ at different crystallographic faces of a given element [14] and also a strong dependence on the azimuthal orientation [16] with respect to the initial beam direction. While some of these features could be described fairly well in the jellium model, the azimuthal orientation characteristics could not be accounted for in the absence of knowledge of corrugated Auger rates. Furthermore, electron spectroscopy studies of He^+ neutralization [17] and He metastable atom deexcitation [3,18] do show some structures which could be attributed to neutralization involving *d* electrons. However, these processes manifest themselves at low electron energy on top of a significant secondary electron background that has to be substracted. Thus, while a jelliumlike description of the Auger neutralization process has the appealing property of self-consistency, a theory taking proper account of crystal effects and the existence of *d* electrons has to be developed. The analysis of slow He^+ ion neutralization on Ag is an ideal test for the theory for two reasons. Firstly, Auger processes are the only ones leading to charge transfer since neither the ground state nor the excited states of He are in resonance with occupied metal states to allow for resonant electron transfer, at the distances between ion and surface where these processes can occur. Second, the dielectric properties of Ag exhibit still some characteristics of free-electron-like metals, i.e., the existence of well-defined surface and bulk plasmons, this allowing to make the connection with previous theories.

In this work we calculate for the first time to our knowledge, the corrugated Auger neutralization rate of He^+ on Ag(110) including the contribution of *d* electrons. This rate used in conjunction with molecular dynamics simulation of He trajectories on the surface yields the azimuthal dependence of the ion survival probability in excellent agreement with experiment. Such a good agreement cannot be attained by a jelliumlike calculation. This parameter-free theory provides a benchmark for showing that Auger neu-

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tralization of slow ions by d electrons at a surface is a process that in general cannot be neglected.

Here we generalize the theory developed in [19]. The physical idea is to describe appropriately the local environment seen by the ion when it is neutralized while leaving aside band structure effects in the description of the metal excitations accompanying the Auger neutralization event. To this end, we write down the Bloch wave function of the electron that neutralizes the ion in a linear combination of atomic orbitals (LCAO) basis while the excited metallic electrons and the effective Coulomb electron-electron interaction are treated in a jelliumlike manner. This approximation allows us to Fourier transform in the electron coordinates parallel to the surface and to sum up all the possible metal excitations yielding the imaginary part of the surface dielectric susceptibility which factors out. Proceeding in this way, the corrugated Auger neutralization rate can be written down as (atomic units $e = m = \hbar = 1$ are used throughout this Letter)

$$\begin{aligned}\frac{1}{\tau}(\vec{R}_a) = 2\sum_{\alpha,\vec{R}}\sum_{\alpha',\vec{R}'}\int_0^\infty d\omega\,\delta(\omega + E_a - \epsilon) \times \rho_{\alpha\vec{R};\alpha'\vec{R}'}(\epsilon)\\ \times \int \frac{d^2\vec{q}_\parallel}{(2\pi)^2}\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2\\ \times -\mathrm{Im}\chi(\vec{q}_\parallel, \omega; z_1, z_2) V_{\alpha,\vec{R}}(\vec{q}_\parallel, z_1) V^*_{\alpha',\vec{R}'}(\vec{q}_\parallel, z_2),\end{aligned} \tag{1}$$

with the matrix elements given by

$$V_{\alpha,\vec{R}}(\vec{q}_\parallel, z) = \frac{2\pi}{q_\parallel}\langle\varphi_a(\vec{r}' - \vec{R}_a)|e^{i\vec{q}_\parallel\cdot\vec{\rho}'}e^{-q_\parallel|z-z'|}|\varphi_\alpha(\vec{r}' - \vec{R})\rangle. \tag{2}$$

In Eqs. (1) and (2) $\varphi_a(\vec{r} - \vec{R}_a)$ and $\varphi_\alpha(\vec{r} - \vec{R})$ are localized orbitals representing the $1s$ orbital of a He atom placed at a position $\vec{R}_a$ with respect to the surface unit cell and the α orbital of the Ag atom placed at the lattice point $\vec{R}$, respectively, E_a is the energy of the $1s$ level of He, $\rho_{\alpha\vec{R};\alpha'\vec{R}'}(\epsilon)$ are densities of states of the Ag surface, as a function of energy ϵ, expressed in the basis $\{\alpha\vec{R}\}$ of localized states and $\chi(\vec{q}_\parallel, \omega; z_1, z_2)$ is the surface screened susceptibility depending on the wave vector parallel to the surface $\vec{q}_\parallel$, the electron coordinates perpendicular to the surface z_1 and z_2, and the energy ω. The orthonormal orbitals φ_a and φ_α are constructed from a set of atomic orbitals ψ_ν, obtained from Hartree-Fock calculations for Ag and He atoms, by means of Löwdin's prescription $\varphi_\mu = \sum_\nu (S^{-1/2})_{\mu\nu}\psi_\nu$, where $S_{\mu\nu} = \langle\psi_\mu|\psi_\nu\rangle$ is the overlap integral between the Hartree-Fock orbitals μ and ν. In the present calculation we include the $1s$ orbital of He and the $5s$, $4d$, and $4p$ orbitals of Ag from [20]. Other orbitals of Ag are neglected because their overlap with He is too small to give any appreciable contribution, as was the case for the core orbitals of Al in the He/Al system analyzed in [19]. Densities of states for the unperturbed and unreconstructed Ag(110) surface are calculated *ab initio*, using the FIREBALL code of [21]. These compare qualitatively well with the total ones reported in [18]. In our analysis we neglect surface states because their contribution to the Auger neutralization rate should be minor in comparison with the rest of the states: all the electrons below the Fermi level can participate in the neutralization process. Sums in Eq. (1) are extended to first, second, and third neighbors of He in the first and also in the second atomic layers. Other Ag atoms give negligible contribution. Equation (1) requires the surface susceptibility χ at finite frequencies and wave vectors but to calculate it for real metals is still a very demanding task and to our knowledge only results in the quasistatic limit have been obtained in [22]. Therefore we will use the jellium model, with the jellium edge placed at $\frac{1}{2}d_{110}$ above the first atomic layer, d_{110} being the interplanar spacing of Ag(110), and with suitable modifications to take into account the possibility that either a s or a d electron is excited in the neutralization process. Surface relaxation of Ag(110) amounts to a reduction of layer spacing between top and second atomic layers of ~7%, this change in d_{110} affecting little the results we will present below. In [23] it is shown that the number of electrons per atom that contribute to the optical properties of Ag depends on the excitation energy ω. From these values we define an effective energy dependent electron density $n(\omega)$ and one-electron radius $r_s(\omega)$, according to $r_s(\omega) = [\frac{3}{4\pi n(\omega)}]^{1/3}$. Then $\chi(\vec{q}_\parallel, \omega; z_1, z_2)$ is calculated as the screened susceptibility of a jellium surface described by that $r_s(\omega)$.

An important ingredient to understand the experimental results is provided by the calculation of the scattered ion trajectories. Since we deal with grazing scattering, we perform classical molecular dynamic simulations using the code KALYPSO [24] in which Ziegler-Biersack-Littmark potentials are used. Lattice vibrations at room temperature are included in the code; atoms are assumed to vibrate independently with amplitudes obtained for surface Debye temperatures of 142 and 173 K, for normal and parallel motion, respectively. The effects of an image charge acceleration on the trajectory are included in an average way, by increasing the ion perpendicular energy by 2 eV: this is the typical value of the energy gain of low energy He^+ on a variety of solid surfaces. This leads to an increase in the angle of incidence of the simulated trajectories with respect to the experimental value of 3.5°. Out of all our simulated trajectories, we select those that reach our small detector defined by an aperture of $\Delta\theta = 0.1°$ and $\Delta\psi = 1.0°$ with respect to the specular direction, θ being the scattering angle and ψ the azimuthal angle. Then, for each of them, we calculate the ion survival probability as

$$P_i = \exp\left\{-\int_{t_i}^{t_f}\frac{dt}{\tau_A}[\vec{R}_a(t)]\right\}, \tag{3}$$

t_i and t_f being initial and final times in the simulation. The ion fraction, to be compared with the experiment, is calculated as $I = \frac{\sum_i P_i}{N}$, where N is the total number of trajectories that reach the detector. Inclusion of thermal vibrations is very important for obtaining N [12,16] and thus the theoretical ion fraction.

The experiments were mostly described previously [14,16] and a description of the apparatus and experimental procedure can be found in these papers.

Figure 1 shows the Auger neutralization rate of He^+ on Ag(110) as a function of the distance perpendicular to the surface assuming that He^+ approaches the surface (a) on top of a Ag atom, (b) on the central hollow position. We show the total results of Eq. (1) including s and d electrons and the results of Eq. (1) when considering s electrons only. The contributions of s and d electrons to the total rate of Eq. (1) are nearly additive since crossed terms such as $\alpha = s$, $\alpha' = d$ are very small in general. For comparison, we also show in this figure the jelliumlike Auger rate used in [14]. The relative role of s and d electrons enter in the calculation basically trough two magnitudes: (i) densities of states and (ii) matrix elements for the transition, Eq. (2). Densities of states give the number of electrons in each orbital of Ag and the matrix elements depend on the spatial localization of the orbital and its overlap with He, yielding and exponential decrease with distance. Then, at large distances between He and the surface, only the relatively delocalized s electrons of many atoms of Ag contribute to the rate, similarly to the case of He/Al analyzed in [19]. The on-top calculations of Fig. 1(a) show that neutralization of the He^+ ion by a d electron of Ag starts to be operative at atom-atom distances shorter than 4 a.u. Consequently, we find practically no difference between calculations with and without d electrons if He is in a central hollow position, for the distances shown in Fig. 1(b). However, at the shorter atom-atom distances shown in Fig. 1(a), the Auger neutralization rate is completely dominated by the contribution of d electrons: their matrix elements can be as large as the one of s electrons and they are more numerous. The comparison with the jelliumlike Auger rate yields the interesting observation that the jellium model is very similar to the LCAO calculations when d electrons play essentially no role [Fig. 1(b)], while it is a kind of average between the LCAO calculations with and without d electrons when He^+ is near a Ag atom [Fig. 1(a)]. The jellium model, being translationally invariant with respect to the surface, can at best describe strong corrugation in an average way. Figure 2 shows the experimental ion fraction for a direction of ~15° with respect to the [110] direction, compared with the results of the present calculation for an azimuthal angle of 19.5°, as a function of the incident energy. The excellent agreement between theory and experiment, better than the one obtained in [14] using a jelliumlike description, also shown in this figure, shows the accuracy of our present approach. This good agreement is not a consequence of the choice of azimuthal angles because differences in ion fraction with azimuth are small out of the symmetry directions as can be appreciated in Fig. 3. In this figure we compare theory and experiment for the ion fraction versus azimuth for He^+-incident energies of 1 and 2 keV. We show the theoretical results we obtain for the cases: (i) the LCAO calculation including s and d electrons, (ii) the LCAO calculation that only considers s electrons. The deep minima at 0° and 90° are due to the fact that many incident ions penetrate the first atomic layer [12,16] and they do not survive Auger neutralization: only

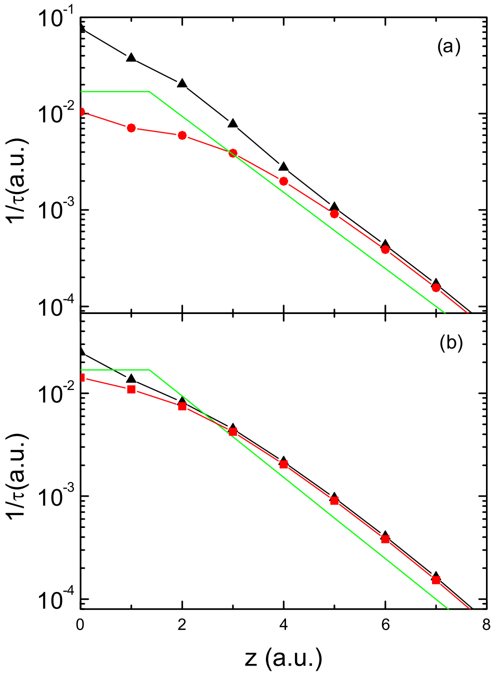

FIG. 1 (color online). The Auger neutralization rate of He^+ approaching the Ag(110) surface (a) on top of an Ag atom and (b) on the center hollow position is plotted as a function of the distance to the first atomic layer. Dots: results of Eq. (1) including s electrons only, triangles: calculation including s and d electrons. The jellium values used in [14] are also shown as a continuous line.

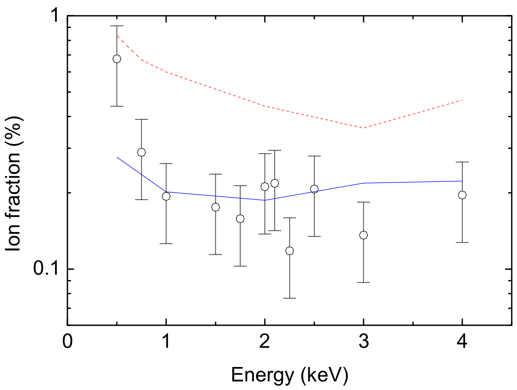

FIG. 2 (color online). The experimental ion fraction versus incident kinetic energy is compared with the present theoretical results (continuous line). Results obtained in [14], using the jellium model, are shown as a dotted line. The experimental angle of incidence in of 3.5° with respect to the surface.

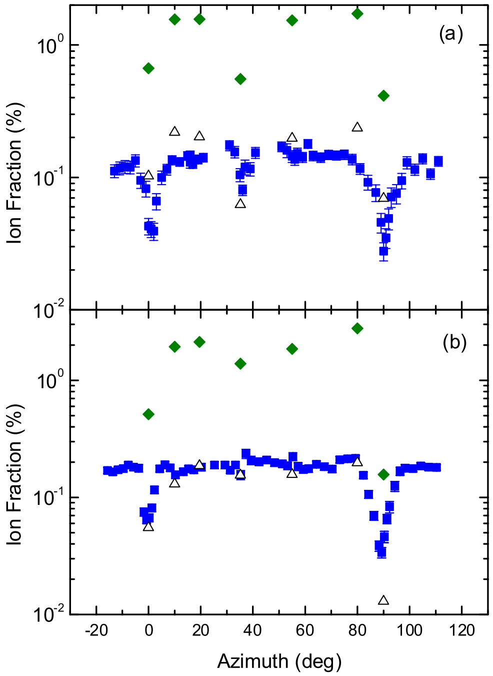

FIG. 3 (color online). The ion fraction versus azimuthal angle for (a) 1 and (b) 2 keV incident energy. The experimental results (squares) are compared with the results of calculations including only *s* electrons (diamonds), *s* and *d* electrons of Ag (triangles).

the few ions that follow trajectories above the surface can survive. At the azimuth of 35.2° (this is the direction along the diagonal of the unit surface cell) ions are scattered off the first atomic layer but with distances of closest approach that are significantly shorter than the ones found for random (out of symmetry) directions. Consequently, the ion fraction tends to develop a minimum at 35.2°. The magnitude of the ion fraction is very dependent on the values of the Auger rate. We are able to reproduce the experimental results only when we include in the calculation the neutralization of He by a *d* electron of Ag. In particular, the importance of the *d* electron contribution is clearly seen at random directions, where penetration effects do not exist and where the best agreement between theory and experiment is obtained for many values of the azimuth. The results of the present calculation, using a corrugated Auger rate that includes neutralization by *s* and *d* electrons in conjunction with a proper simulation of trajectories, are in excellent agreement with experiment for all azimuths, showing the important role played by *d* electrons in the survival of He^+ on Ag.

In conclusion, we have presented a generalized theory of Auger neutralization of ions on arbitrary metal surfaces, including the previously ignored role of *d* electrons, extremely important for, e.g., the case of noble and transition metal surfaces important in surface chemistry. We are thus able to show for the first time that a correct and accurate description of Auger neutralization at noble metal surfaces has to account for the contribution of *d* electrons, as this is illustrated on the case of He^+ ion neutralization on Ag. The up to now used jellium model, being translationally invariant with respect to the surface, represents an average of the contributions due to *s* and *d* electrons. Our treatment can be generalized to the analysis of other charge transfer processes such as resonant neutralization and Auger deexcitation. It is an important step towards an accurate description of molecule interaction with chemically important transition metal surfaces.

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