

## Surface Miller Index Dependence of Auger Neutralization of Ions on Surfaces

Yu. Bandurin,<sup>1</sup> V. A. Esaulov,<sup>2,\*</sup> L. Guillemot,<sup>2</sup> and R. C. Monreal<sup>3</sup>

<sup>1</sup>*Department of Physics, University of Uzhgorod, Uzhgorod, Ukraine*

<sup>2</sup>*Laboratoire des Collisions Atomiques et Moléculaires (Unité Mixte de Recherche No. 8625), Batiment 351, Université de Paris-Sud, Orsay, France*

<sup>3</sup>*Departamento de Física Teórica de la Materia Condensada C-V, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

(Received 27 June 2003; published 6 January 2004)

Neutralization of He<sup>+</sup> ions in grazing incidence scattering on Ag(111) and Ag(110) surfaces is studied. These measurements reveal the existence of an order of magnitude difference in the probability of ion survival on Ag(110) and Ag(111). The experimental results are discussed in terms of survival from Auger neutralization, whose rates are derived theoretically. Molecular dynamics simulation of scattered ion trajectories is performed and the surviving ion fractions are then calculated using the theoretical Auger neutralization rates, without adjustable parameters. The calculations agree quite well with the experimental data and show that the observed differences in the neutralization probabilities on these surfaces are related to different extensions of the electron density beyond the surface, resulting from different atomic packing.

DOI: 10.1103/PhysRevLett.92.017601

PACS numbers: 79.20.Rf, 61.85.+p, 79.60.Bm

Electron transfer processes between an atom or a molecule and a surface play an important role in gas surface interactions and are of interest in various branches of physics and chemistry. Electron transfer occurs usually either by one electron processes, such as in resonant electron tunneling, or by two electron processes in Auger neutralization. In recent years, considerable progress has been achieved in the theoretical description of resonant electron transfer processes for which nonperturbative theoretical descriptions have been developed [1,2] and applied to the description of this process on simple metallic surfaces generally using a jellium model. Excellent agreement with experiments on negative ion formation on various surfaces was achieved (see, e.g., [3,4]). Auger neutralization of positive ions in front of metal surfaces has attracted much attention starting from the seminal works of Hagstrum [5], and recently a number of theoretical treatments were developed for free-electron-like metals [6–8] including collective electronic excitations [9] and ion induced effects [10]. These have been applied to the description of electron emission following Auger neutralization [8,9,11] and to the calculation of ion fractions in low energy scattering [12–15]. Fair agreement with recent experiment is now achieved [13,15].

In gas surface interactions and, in particular, in the case of typical catalysts, an important aspect is related to possible differences in reactivity and in electron transfer on different types of surfaces of a given metal. Indeed a supported metal cluster presents different facets, and hence differences in the characteristics of various processes on these facets plays an important role and must be investigated in order to understand the reactivity of the nanoparticle. Recently, attempts have been made to clarify the dynamics of resonant electron transfer on various

Ag surfaces. Experiments [16] revealed significant differences in resonant transfer rates, which were in agreement with predictions [17] of time dependent wave packet calculations [18] of these processes. Such information is unavailable for Auger-type processes. Comparative studies have not been performed since these require precise measurements of very small surviving scattered ion fractions, with accuracies attained only recently [13,19]. The investigation of Auger processes has considerable general importance in view of its role in certain reactions on surfaces (see, e.g., [20]), ion neutralization, metastable deexcitation spectroscopy [1], and, in particular, because of the applications of the latter two in the study of the electronic structure of surfaces and in the analysis of surface composition. In this Letter, we therefore present results of a comparative study of Auger neutralization of He<sup>+</sup> ions on Ag(111) and Ag(110) surfaces.

The remarkable and important feature of our experimental results, which we wish to emphasize in this Letter, is that *we find an order of magnitude difference in the number of ions surviving Auger neutralization on Ag(110) as compared to Ag(111)*. This difference is even greater than the one observed [16] in resonant neutralization for these surfaces. At first glance, this is surprising from the point of view of Auger neutralization, since the electronic structure of these surfaces would not appear to present major differences. In order to comprehend this difference, we performed molecular dynamics simulation of scattered ion trajectories and then calculated the neutralization probability of scattered ions using theoretically derived Auger neutralization rates. These calculations reproduce the important differences that are observed and give clear insight into their nature. These are related to different extensions of the electron density beyond the

surface, resulting from different atomic packing. Because this is a common feature which strongly distinguishes the, e.g., (110) and (111) surfaces in the case of fcc metals, it should be taken into account in general when analyzing information about processes when Auger neutralization are important.

The experiments were performed on the ultrahigh vacuum setup described in detail elsewhere [21] using a standard experimental procedure [2,3,13,16].  $\text{He}^+$  ion fraction measurements were made for a fixed scattering angle of  $7^\circ$  using a position sensitive channelplate detector equipped with three discrete anodes, which simultaneously counts particles of different charge states [21]. The positive ion fractions are defined as the ratio of the scattered  $\text{He}^+$  flux to the total scattered flux into a given angle with respect to the surface plane. Measurements were performed for specular scattering conditions. The Ag surface preparation included multiple cycles of grazing incidence ion beam sputtering and annealing, and time of flight recoil spectroscopy was used to check for absence of contaminants such as H, C, and O [16,19,21]. Note here that the clean surface work function was found to be 4.5 eV for Ag(111) and 4.3 eV for Ag(110) [16]. The crystal azimuthal setting is determined by measuring the scattered intensity of the ion beam in the forward direction during an azimuthal scan. This allows a precision better than  $0.2^\circ$ . In this Letter, for brevity, we will discuss only results for a random scattering direction, which does not correspond to one of the main axes [[001],  $[1\bar{1}0]$  for Ag(110)].

The measured ion fractions are shown in Fig. 1 for the Ag(111) and Ag(110) targets for various incident ion energies. The error bars represent typical statistical scatter in the series of ion fraction measurements. The first important feature that one has to delineate is that the *ion fractions for Ag(110) are an order of magnitude higher than for Ag(111)*. A general feature in both cases is that the ion fractions are small and the highest fraction is obtained at low energies. This result is surprising since, according to Hagstrum's law [9], one would expect the ion fraction to decrease exponentially with decreasing velocity.

In order to analyze these results, we performed calculations of the scattered ion trajectories. Since we deal with grazing ion scattering, we performed classical molecular dynamics calculations which are known to be more accurate in these conditions than simple binary collision codes which include only the interaction with a single surface atom and, hence, can be reasonable only for large angle impact. We used the program KALYPSO [22] in which Ziegler-Biersack-Littmark (ZBL) potentials (see, e.g., [23]) are used. Here we shall discuss only calculations for the random scattering directions. Note here that the calculated trajectories do not vary significantly for different "random" angles for a given surface.

An important source of uncertainty for studies of ion survival probabilities is introduced by the effect of image

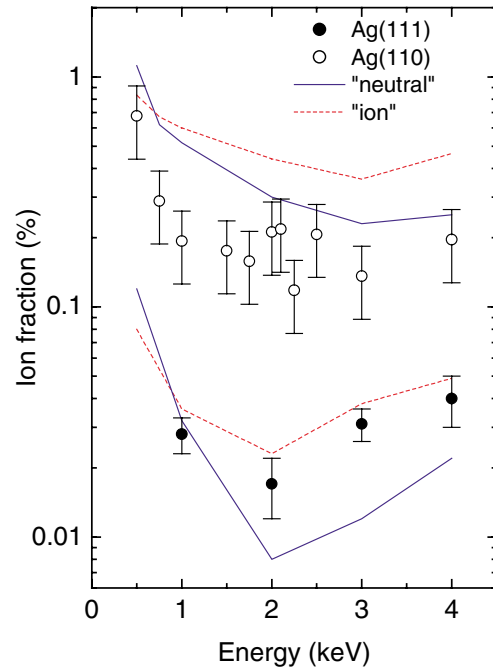


FIG. 1 (color online). Ion fractions for random scattering direction for the Ag(110) and Ag(111). The lines labeled ion and neutral correspond to the two types of calculations that were performed. The top and bottom sets correspond to Ag(110) and Ag(111), respectively.

charge acceleration on the trajectory. To investigate how these effects may influence the analysis of the present experimental results, two sets of simulations are performed. The first set of trajectories is run for neutral conditions, that is, the incident particles are scattered by the repulsive ZBL potential. However, before the repulsive potential sets in, the incident ions are first accelerated by the attractive image potential in their way towards the surface and the surviving ions finally decelerated in the way out so that their trajectories near the surface will be affected by this change of kinetic energy. We take into account this effect approximately by running a second set of trajectories in which the perpendicular energy ( $E_p$ , obtained from the perpendicular component of the ion velocity) has been increased by 2 eV (ion conditions). Although the actual value of the ion energy near the surface could depend on the specific ion-solid combination, 2 eV has turned out to be a remarkable universal figure for low energy  $\text{He}^+$  on a variety of solid surfaces [5].

Figure 2 shows the trajectories calculated for neutral conditions for scattering on Ag(110) and Ag(111) for some incident ion energies. The graphs represent the ion surface distance as a function of time in atomic units. As may be seen with increasing energy, the ion approaches closer to the surface and at the same time the trajectories become narrower in the time scale. It may be seen in the figure that for the same ion energy the trajectories on the two surfaces do not differ strongly and the atoms pass at

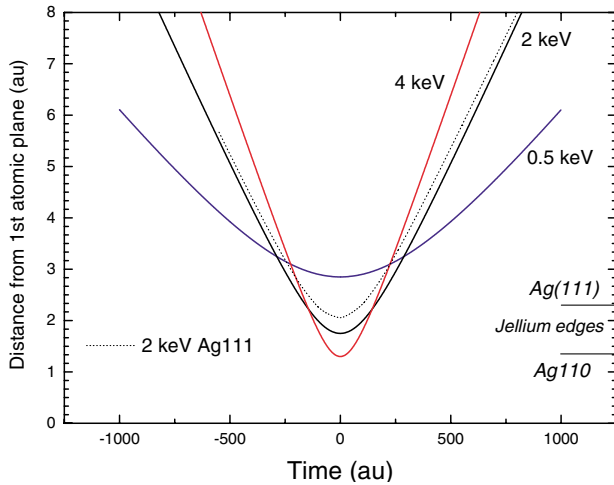


FIG. 2 (color online). Trajectories calculated for the neutral (see text) scattering conditions of He on Ag(110) and Ag(111). The jellium edge positions for both surfaces are indicated by the lines at the right and set as usual above the topmost atomic layer at half the atomic interlayer spacing [24].

roughly the same distance above the outermost atomic layer. The same trends are obtained for ion conditions. Note that in our case of a  $3.5^\circ$  incidence angle, the effect of increasing  $E_p$  by 2 eV is not very large. Thus,  $E_p$  is 3.7 eV at 1 keV, and for the ion trajectories we consider an incident angles of  $4.3^\circ$  at 1 keV. This leads to somewhat closer distances of approach; e.g., from 2.78 to 2.43 a.u. at 1 keV.

These trajectories are used to calculate the  $\text{He}^+$  ion survival probability using a rate equation approach, where we include only Auger capture processes. Other charge exchange processes are ruled out in the present experiment. Resonant capture and loss to excited states of He have been proven to be negligible both theoretically [25] and experimentally [27] for the grazing incidence of  $\text{He}^+$  on Al, and this should also be the case for Ag with a similar or higher work function. On the basis of earlier studies [26,27], we exclude collision-induced neutralization and reionization of He.

Realistic calculations of the Auger neutralization rate of  $\text{He}^+$  on free-electron metal surfaces have been performed in [7,10,12], and good agreement between theory and experiment was obtained in [11,22]. A similar calculation for noble metals is too demanding because it is necessary to account for the  $d$ -band structure at the surface. Therefore in this work we treat Ag within the jellium model but with suitable modifications to describe appropriately both electrons participating in the Auger process, as explained in the following.

As suggested by the self-consistent calculations of [7], the rate for Auger capture is assumed to decay exponentially away from the jellium edge and to saturate inside the jellium edge according to

$$\Gamma(z) = A e^{-(z-z_j)/d_A}, \quad (1)$$

if  $z \geq z_j$ , and  $\Gamma(z) = A$  if  $z < z_j$ , where  $z_j$  is the position of the jellium edge.  $A$  is the bulk value of the Auger neutralization rate and  $d_A$  is the decay length, which determines the decrease of the neutralization rate as a function of ion-surface distance.  $A$  is given by [28]

$$A = 2 \sum_{\vec{k} < k_f} \int_0^\infty d\omega \int \frac{d^3 \vec{q}}{(2\pi)^3} \text{Im} \frac{-1}{\varepsilon(q, \omega)} \times \left| \int d^3 \vec{r} \psi_a^* \psi_{\vec{k}} e^{-i\vec{q} \cdot \vec{r}} \right|^2 \times \delta(E_k - E_a - \omega). \quad (2)$$

In Eq. (2),  $\Psi_{\vec{k}}$  is a metal wave function of energy  $E_{\vec{k}}$  orthogonalized to the Hartree-Fock wave function  $\Psi_a$  of He [6] of energy  $E_a$ ,  $k_f$  is the Fermi wave vector, and  $\varepsilon(q, \omega)$  is the dielectric function of Ag. In our approximation, we consider that only the  $s$  electrons of Ag neutralize the ion and are described by a free-electron gas of  $r_s = 3.02$  a.u., corresponding to one electron per Ag atom. This is because  $d$  electrons are very localized around Ag atoms, with typical decay lengths of 0.25 a.u., and in our calculated trajectories He never gets that close to the surface. On the other hand, the possibility that either an  $s$  electron or a  $d$  electron is ejected in the Auger process is taken into account via the dielectric function. Here, we will consider this possibility by defining the number of effective electrons that can be excited with a given amount of energy  $\omega$ . Optical properties of noble metals have been investigated for a long time [29–31]. In [29] it is shown experimentally that the effective number of electrons per atom contributing to the optical properties of Ag depends strongly on the range of incident energies. Thus, we take an effective number of electrons as a function of  $\omega$  from [29] and define an energy depending effective  $r_s$ . Then  $\varepsilon(q, \omega)$  is the Lindhard dielectric function for the effective  $r_s$ . Moreover, the value of  $E_a$  should be taken consistently with ion or neutral conditions. For ion conditions, an increase in the perpendicular kinetic energy of 2 eV should be accompanied by a decrease in the potential energy by the same amount; we then take  $E_a = -22.6$  eV with respect to the vacuum level. In the opposite case of neutral conditions, the attractive interaction between He and metal is neglected and  $E_a = -24.6$  eV, corresponding to the ionization potential of He in vacuum. The values of  $A$  we obtain in this way are  $A = 0.0186$  a.u. for neutral conditions and  $A = 0.0169$  a.u. for ion conditions. With respect to the decay length  $d_A$ , it should not be very different from the value  $d_A = 1.1$  a.u. found for Al [7,10]. This is because only  $s$  electrons of Ag neutralize  $\text{He}^+$  and the decay length is mainly controlled by the overlap between metal wave functions near the Fermi level, and the wave function of He and work functions of Ag and Al differ by only 0.25 eV.

In Fig. 1, we compare the results of our calculation for the ion survival probability for neutral and ion conditions with experimental data. The ion survival probability is

obtained as

$$P_+ = \exp\left[-\int_{-\infty}^{+\infty} dt \Gamma(z(t))\right], \quad (3)$$

where  $z(t)$  is the trajectory of the ion obtained from the molecular dynamics simulation. We see that the magnitude and the general trend is correctly reproduced by the theory. In particular, the calculated survival probability is an order of magnitude higher for Ag (110) than for Ag(111).

The key feature in explaining this effect relies on the fact that the electronic density of the jellium model is a good approximation to the true electronic density for most metal surfaces [24] as long as the jellium edge is placed at half the atomic interlayer spacing above the first atomic layer. Indeed the jellium edge is located closer to the topmost layer of atoms for Ag (110) than for Ag (111) (see Fig. 2). This leads to a larger extension of the electronic density into vacuum beyond the first atomic layer for Ag(111) and, consequently, to a larger neutralization probability at a given distance from the first atomic layer. This simple fact accounts for the order of magnitude difference between both surfaces since, as noted before, the trajectories of He above the two surfaces are similar for the same ion energy.

The increase of the ion fraction at low energies and the minimum in ion survival probability in the vicinity of 2 keV is the result of the competition between surface approach and available time for neutralization. In particular, at low energies, although the ions have a shallow trajectory and spend more time in the surface region, this occurs for relatively large ion-surface distances and therefore the neutralization probability is low.

In conclusion, we report ion fractions in He<sup>+</sup> scattering on a Ag(111) and Ag(110) surface. These measurements revealed dramatic differences in the values of the surviving ion fractions. We discuss this in terms of theoretical calculation of Auger neutralization rates along with classical molecular dynamics trajectory simulations of ion scattering. Good agreement between the theory and the experimental data is found, without any adjustable parameters. The strong difference in ion survival is related to changes in atomic interlayer spacing, which leads to a different spill out of the electron density beyond the surface and, hence, strong differences in the ion-surface coupling. This effect is quite general and should play a role in surface reactivity and electron emission including exoemission of electrons. It must be taken into account when interpreting data on ion scattering and metastable deexcitation spectroscopies.

---

\*Corresponding author.

Electronic address: esaulov@veof1.lcam.u-psud.fr

- [1] H. Shao, D. C. Langreth, and P. Nordlander, *Phys. Rev. B* **49**, 13 929 (1994).
- [2] A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, *Phys. Rev. Lett.* **68**, 2842 (1992).
- [3] M. Maazouz *et al.*, *Phys. Rev. B* **55**, 13 869 (1997).
- [4] N. Lorente, A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, *Surf. Sci.* **429**, 46 (1999).
- [5] H. D. Hagstrum, *Phys. Rev.* **96**, 336 (1954).
- [6] T. Fonden and A. Zwartkruis, *Phys. Rev. B* **48**, 15 603 (1993).
- [7] N. Lorente and R. Monreal, *Surf. Sci.* **370**, 324 (1997).
- [8] R. Monreal, *Surf. Sci.* **388**, 231 (1997).
- [9] S. M. Ritzau, R. Baragiola, and R. C. Monreal, *Phys. Rev. B* **59**, 15 506 (1999).
- [10] M. A. Cazalilla *et al.*, *Phys. Rev. B* **58**, 13 991 (1998).
- [11] B. van Someren, P. A. Zeijlmans van Emmichoven, and A. Niehaus, *Phys. Rev. A* **61**, 22902 (2000).
- [12] N. P. Wang *et al.*, *Phys. Rev. A* **64**, 012901 (2001).
- [13] R. C. Monreal, L. Guillemot, and V. A. Esaulov, *J. Phys. Condens. Matter* **15**, 1165 (2003).
- [14] T. Hecht, H. Winter, and A. G. Borisov, *Surf. Sci. Lett.* **406**, L607 (1998).
- [15] S. Wethekam, A. Mertens, and H. Winter, *Phys. Rev. Lett.* **90**, 37602 (2003).
- [16] L. Guillemot and V. A. Esaulov, *Phys. Rev. Lett.* **82**, 4552 (1999).
- [17] A. G. Borisov, A. K. Kazanskii, and J. P. Gauyacq, *Phys. Rev. Lett.* **80**, 1996 (1998).
- [18] V. A. Ermoshin and A. K. Kazanskii, *Phys. Lett. A* **218**, 99 (1996).
- [19] M. Casagrande, S. Lacombe, L. Guillemot, and V. A. Esaulov, *Surf. Sci. Lett.* **44**, L36 (2000).
- [20] T. Greber, *Surf. Sci. Rep.* **28**, 3 (1997).
- [21] V. Esaulov, L. Guillemot, O. Grizzi, M. Huels, S. Lacombe, and Vu Ngoc Tuan, *Rev. Sci. Instrum.* **67**, 1 (1996).
- [22] M. Karolewski, KALYPSO v1.0 and Simulation kit v2.4 (private communication).
- [23] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter* (Pergamon, New York, 1985), Vol. 1.
- [24] N. D. Lang and W. Kohn, *Phys. Rev. B* **1**, 4555 (1970).
- [25] W. More *et al.*, *Phys. Rev. B* **58**, 7385 (1998).
- [26] H. H. Brongersma, P. A. C. Groenen, and J. P. Jacobs, *Application of Low-Energy Ion Scattering to Oxidic Surfaces, in Science of Ceramics Interfaces*, edited by J. Nowotny (Elsevier, Amsterdam, 1994), Vol. 81, p. 113.
- [27] H. Winter, *Nucl. Instrum. Methods Phys. Res., Sect. B* **78**, 38 (1993).
- [28] P. M. Echenique, F. Flores, and R. H. Ritchie, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1990), Vol. 43, p. 229.
- [29] H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).
- [30] G. B. Irani, T. Huen, and F. Wooten, *Phys. Rev. B* **3**, 2385 (1971).
- [31] P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**, 4370 (1972).