Auger Neutralization of He Ions at an Al(100) Surface Using Isotope Effect

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He atoms and ions of the isotopes ^{3}He and ^{4}He are scattered with keV energies under a grazing angle of incidence from a flat and clean Al(100) surface. For the two isotopes we investigate Auger neutralization of incident He$^+$ and He^{2+} ions via fractions of surviving ions. Pronounced effects for the different isotopes are observed which can be attributed to different time scales concerning the neutralization process of He ions in front of a metal surface. From the analysis of the data obtained for singly and doubly charged ions we find evidence that charge fractions for scattering of He$^+$ ions from an Al surface result predominantly from a *direct* (Auger) electron capture event.

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Electronic transfer processes during the interaction of atomic particles with solid surfaces play an important role for a variety of phenomena and applications. Therefore, substantial efforts have been invested over the last decades to provide a fundamental understanding for the relevant microscopic interaction mechanisms. It turns out that the binding energy of the atoms, the electronic structure of the surface, as well as the dynamic regime, determine the outcome of atom-surface collisions in a decisive manner. Collisions with energies in the hyperthermal regime (energies of up to some 10 eV) are specifically sensitive to properties of surfaces, since projectiles do not penetrate the vacuum-solid interface and electronic interactions and charge transfer take place in front of the topmost layer of surface atoms [1].

Two basic mechanisms for the neutralization of ions at metal surfaces have been identified: (1) resonant neutralization (RN) where the energy of the electron active in charge transfer is conserved during a one-electron transition, and (2) Auger neutralization (AN) where electronic energies are shared in a two-electron transition. For the neutralization of atoms with high binding energies, i.e., noble gas atoms, AN dominates charge transfer. A microscopic understanding of basic features of these two fundamental interaction mechanisms was already provided in the pioneering work of Hagstrum [2] in the 1950s. In these studies, the (Auger) neutralization of noble gas ions in front of metal surfaces was analyzed in terms of Auger transition rates and shifted atomic levels (owing to response of electron gas to presence of atom). By approximating the level shifts using the concept of classical image charges, Hagstrum deduced from energy shifts in electron spectra effective distances for charge transfer and Auger transition rates for the neutralization of various noble gas ion metal combinations. Later studies on this problem [3–5] were in accord with this work.

However, until recently the experimentally derived AN rates showed substantial discrepancies of up to several orders of magnitude compared to calculations [6–8]. The poor agreement between experiment and theory was attributed to the complexity of the problem, but also more recent and sophisticated calculations could not remove the discrepancy [8]. For theoretical transition rates, one has small effective distances for charge transfer, where level shifts derived from the approximation of classical image charges are too large compared to experiments.

In work performed by various groups in recent years, this puzzle concerning a microscopic understanding for AN of noble gas atoms at metal surfaces could be resolved [6,9–18]. It turns out that the energy shift of the atomic level during the interaction plays a key role. AN of He$^+$ is of particular interest here, since the binding energy of unperturbed He atoms is sufficiently large to exclude contributions from RN of the ground state. Aside from effects of excited levels, neutralization of He$^+$ in front of an Al surface (prototype of free-electron metal) can be considered as a model system for studies of AN of ions at surfaces [5–10,17,19].

van Someren *et al.* [11], Merino *et al.* [9], and More *et al.* [10] argued for AN of He$^+$ ions in front of an Al surface that the approximation using classical image charges for the dielectric response and level shift of the He ground state energy breaks down at several a.u. (atomic unit of length) from the topmost surface layer. Then the level shift close to the surface is clearly modified, and experimentally observed response effects are consistent with effective charge exchange closer to the surface caused by small AN transition rates. Important support for this interpretation came from the observation of fractions of surviving incident ions for grazing scattering from the target surface [12–15,17], where projectiles are specularly reflected with well-defined trajectories in front of the topmost surface layer (surface channeling) [20,21]. The survival of ions over complete trajectories can only be understood by sufficiently small AN transition rates as predicted by theory.

Recently, it could be shown for Ag(111) and Ag(110) that the fractions of surviving He$^+$ ions depend strongly on the orientation of the crystal surface, i.e., the position of the electronic reference plane (e.g., "jellium edge") [6,14]. From comparison of angular distributions for incident atoms and ions or from electron spectra, the energy shift of the ground state of the He atom close to the surface was measured and shows a change in sign from the (positive) image charge limit to negative values for sufficiently close distances (about 3 a.u. from topmost surface layer) [16,17]. As a result, substantial details on the interaction scenario of He^+ ions in front of metal surfaces are currently available.

Despite this considerable recent progress, however, it is so far an unsolved question to what extent transient populations of excited levels in He atoms and other mechanisms may affect final charge state distributions. This would considerably modify the analysis and interpretation of measured charge fractions. From the work function of an Al surface (about 4.3 eV), effects involving, e.g., the metastable He $2s$ levels, cannot be excluded [22]. In this Letter we present experiments performed with two different He isotopes ($^3\mathrm{He}^+$ and $^4\mathrm{He}^+$) which provide in a straightforward manner evidence for the dominance of one specific charge transfer process, i.e., AN.

The concept of our study is based on the feature that trajectories of fast atoms and ions during surface scattering result from the effective interaction potential and the kinetic energy of the projectiles. Since the interaction potential is determined by the electronic structure and charge of the projectile, different isotopes of the same sort of atom follow identical trajectories for the same scattering conditions with respect to projectile energy and angle of incidence. Key issues in using different isotopes are the different velocities at the same kinetic energy and the resulting different interaction times with the solid. For a given projectile energy $E = Mv^2/2$, interaction times scale as $t_{\mathrm{int}} \sim (M)^{-1/2}$. As a consequence, the time scales for collisions of ^{3}He and ^{4}He projectiles with the surface differ by a factor of $(3/4)^{1/2} = 0.866$.

The description of the dynamics in charge transfer of He^+ ions in front of a metal surface via AN as dominant channel can be performed with a simple rate equation approach based on an AN rate $\Gamma_A(z)$ with z being a coordinate normal to the surface referred to the topmost atomic layer. Following the neutralization over the complete trajectory gives for the probability for survival in the charge state of the incident ion

$$P_{\mathrm{surv}} = \exp\left[-\int_{\mathrm{traj}} \Gamma_A(z)\frac{dz}{v_z}\right], \qquad (1)$$

where v_z is the projectile velocity component along z which governs the interaction time with the surface. For surface scattering under a glancing angle Φ_{in} and a scattering potential $V(z)$, the energy of motion along the surface normal (z axis) is $E_z = E\sin^2\Phi_{\mathrm{in}} + V(z)$, with $v_z = (2E_z/M)^{1/2}$ we obtain from Eq. (1)

$$\log_e(P_{\mathrm{surv}})/M^{1/2} = -\int_{\mathrm{traj}} \Gamma_A(z)\frac{dz}{(2E_z)^{1/2}}. \qquad (2)$$

For a scenario described by a single transition rate, ion fractions for different isotopes scale according to $\log_e(P_{\mathrm{surv}})/(M)^{1/2}$. On the other hand, for a more complex scenario we expect deviations from this scaling of data.

In our experiments we have scattered the two stable isotopes (mass $M = 3$ amu and 4 amu) of He^+ and He^{2+} ions as well as He^0 atoms with keV energies from a clean and flat Al(100) surface under a grazing angle of incidence of typically $\Phi_{\mathrm{in}} = 1°$ and observed charge fractions of reflected projectiles. The target surface was prepared by cycles of grazing sputtering with 25 keV Ar^+ ions and subsequent annealing. The direction of the incident beam was aligned along a high index crystallographic direction in the surface plane of the target (''random orientation''), in order to avoid effects on the ion fractions owing to different trajectories under axial surface channeling [18]. Scattered projectiles are recorded at a distance of 66 cm behind the target by means of a position sensitive channel plate detector where charged fractions of the beams were separated by biasing a pair of electric field plates.

In Fig. 1 we show ion fractions after scattering of $^3\mathrm{He}^+$ and $^4\mathrm{He}^+$ ions with energies ranging from $E = 1.5$ to 3 keV from Al(100) as function of the (initial) normal energy $E_{oz} = E\sin^2\Phi_{\mathrm{in}}$ (tuned via adjustment of incidence angle). The small ion fractions for impact of ions are attributed to survival of projectiles in the initial charge state [12–14,17,18]. For neutral projectiles the observed ion fractions are more than 1 order of magnitude smaller so that reionization processes can be neglected here. A striking feature of the data is a pronounced isotope effect for the fractions of surviving ions. Since, at given projectile en-

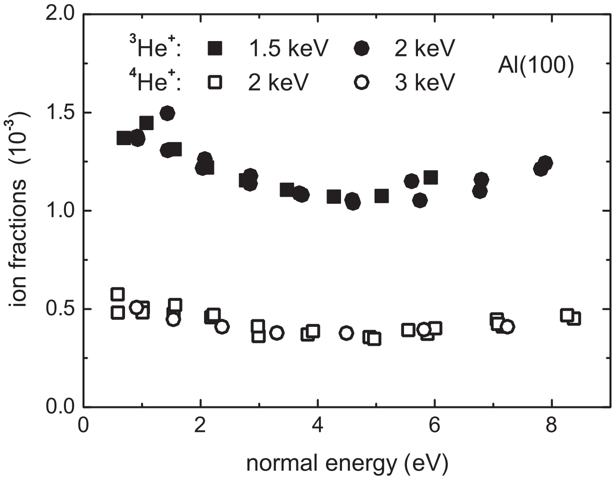

FIG. 1. Ion fractions as function of normal energy for grazing scattering of $^3\mathrm{He}^+$ (full symbols, 1.5 keV and 2 keV) and $^4\mathrm{He}^+$ ions (open symbols, 2 keV and 3 keV) from Al(100).

ergies, interaction times for the lighter isotope ^{3}He are smaller by a factor of 0.866 (see above), less time is available at a given electron transition rate for neutralization of the projectile. This effect enhances the ion fractions by a factor of about three here.

The observed interaction time effects are closely related to different regimes of energy and velocity for the different isotopes. This difference can be illustrated by enhancing E_{oz} for ^{4}He atoms by a factor $4/3$ so that the atoms interact in the same velocity and time regime as ^{3}He atoms. Since for different energies, however, the trajectories for the two isotopes are different, the two cases will not have the same outcome. Our experimental ion fractions show this feature very clearly.

Recently a pronounced effect of the ion fractions on the crystal face was concluded from the comparison of data for Ag(111) and Ag(110) surfaces [14]. This observation might be affected by the rather complex electronic structure, in particular, of the Ag(111) surface (projected band gap within the conduction band, contributions of localized 3*d* electrons). When comparing the ion fractions for ^{4}He$^+$ ions and Al(100) as shown in Fig. 1 with data obtained previously by us for Al(111) [17], we reveal in the present case ion fractions for the more open surface [Al(100)] which exceed those measured for Al(111) by a factor of about four. This provides clear support for the effect reported by Bandurin *et al.* [14].

We have scattered also He^{2+} ions, in order to demonstrate the result of a more complex electron transfer scenario on our evaluation of data. Ion fractions for ^{3}He^{2+} and ^{4}He^{2+} projectiles are displayed in Fig. 2 and show also a pronounced isotope effect. Since the He^{2+} projectiles have two 1*s* vacancies and a higher potential energy, the neutralization scenario is richer than for He$^+$ ions. As outlined by Becker and Hagstrum [23] and in detail by Niehaus *et al.* [24,25], various processes involving ground and excited states contribute to the neutralization of He^{2+} ions. Only after filling of the first 1*s* hole in the projectile ion, AN of the remaining 1*s* vacancy can take place. Therefore, the onset of AN (or other mechanisms of final neutralization) is delayed; the reduced time for AN leads to an enhancement of ion survival compared to singly charged ions. Note that ion fractions for He^{2+} projectiles are almost an order of magnitude larger than for He$^+$ impact. Different interaction times explain also the isotope effect observed for He^{2+} ions, since for ^{3}He^{2+} ions less time is available for filling of the 1*s* vacancies in two consecutive processes.

Based on Eq. (2) we analyze the fractions for ion survival by a plot of $\log_e(P^+)/M^{1/2}$ as function of the normal energy E_{oz} in Fig. 3. The plot reveals that the different ion fractions observed for the two isotopes can be well corrected with respect to effects caused by the interaction time for singly charged ions, whereas for doubly charged projectiles this procedure fails. We conclude from this finding that neutralization of He$^+$ ions is dominated here by a *single* process (AN) with transition rate Γ_A.

In order to demonstrate the additional information obtained by our method, we have investigated possible contributions of the metastable 2*s* levels via computer simulations on level populations based on a rate equation approach. With an adjustment of the AN rate $\Gamma(z) = 0.0196$ a.u. $\exp[-(z - z_o)/1.1$ a.u.$]$ which saturates at $z_o = 1.3$ a.u. and an appropriate scattering potential [9,21], our data are well reproduced, and the different interaction times are perfectly corrected (c.f. dotted curve in inset of Fig. 3). However, for incorporation of resonant

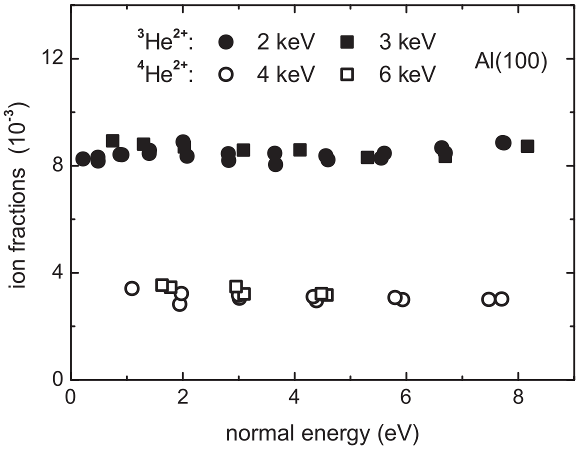

FIG. 2. Ion fractions as function of normal energy for grazing scattering of ^{3}He^{2+} (full symbols, 2 keV and 3 keV) and ^{4}He^{2+} ions (open symbols, 4 keV and 6 keV) from Al(100).

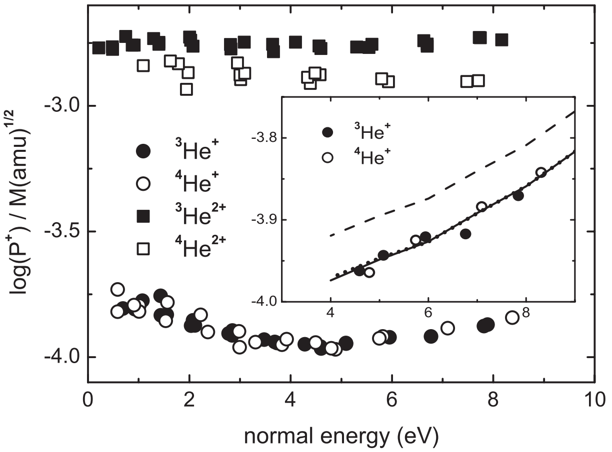

FIG. 3. $\log_e(P^+)/M^{1/2}$ as function of normal energy for scattering of ^{3}He$^+$ (full circles), ^{4}He$^+$ (open circles), ^{3}He^{2+} (full squares), ^{4}He^{2+} ions (open squares) from Al(100). Inset shows part of data for ^{3}He$^+$ and ^{4}He$^+$ ions on enlarged scale; systematic uncertainties of data are estimated to be of same order as scatter of data. Dotted curve: simulation for both isotopes using single AN rate 0.0196 a.u. $\exp[-(z - z_o)/1.1$ a.u.$]$; solid curve: simulation for ^{3}He$^+$ with AN rate 0.01785 a.u. $\exp[-(z - z_o)/1.1$ a.u.$]$ and occupation of 2*s* level; dashed curve: same for ^{4}He$^+$. For details, see text.

neutralization and ionization of $2s$ in the simulations using theoretical transition rates [22,26], we can adjust with a slightly reduced AN rate the calculations to the data for $^3He^+$ (solid curve in inset), but we then find a clear deviation for $^4He^+$ (dashed curve in inset). Since this shift is not found in the data, excited states can have only small contributions to ion survival. A quantitative estimate, however, is beyond the scope of the present Letter.

The plot in Fig. 3 for the He^{2+} data indicates that the description of charge exchange based on a single transition rate is not adequate. This is expected from the neutralization scenario for He^{2+} ions as derived from electron spectroscopy [23,24]. The deviation between the reduced data for the two isotopes provides support for the concept of our method for detailed studies on charge transfer.

In conclusion, we have performed studies on AN at a metal surface by making use of the different time regimes for scattering of the two stable isotopes of He atoms and ions. Since the trajectories for atomic projectiles result from their energy and the scattering geometry, interaction processes at surfaces can be studied for different time regimes in a defined manner. In our work on the neutralization of He^+ ions at Al(100) via AN we observe pronounced differences in the fractions of surviving ions (for neutral projectiles no ions are detected here) for $^3He^+$ and $^4He^+$ ions. We show that this effect is caused by different interaction times for scattering along the same trajectories. The ion fractions observed for the different isotopes can be well referred to each other in terms of a rate equation approach assuming one defined transition rate. We conclude that AN into the $1s^2$ ground state of the He atom is the absolutely dominant process for neutralization of scattered ions and determines the resulting fractions of surviving ions.

For He^{2+} ions we also observe a pronounced isotope effect and clearly larger fractions of surviving ions than for He^+. The reduction of the He^{2+} data in terms of a single process fails owing to the complex scenario involving a sequence of different charge transfer processes. This latter observation supports our interpretation of results for singly charged ions. Thus we have presently arrived at a rather complete conceptual understanding for the Auger process of He^+ ions in front of metal surfaces. The considerable recent progress for this fundamental system in atom-surface interactions provides a profound basis for a detailed microscopic theoretical study.

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[1] J. Los and J. J. C. Geerlings, Phys. Rep. **190**, 133 (1990).
[2] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).
[3] W. Sesselmann, B. Woratschek, J. Kuppers, G. Ertl, and H. Haberland, Phys. Rev. B **35**, 1547 (1987).
[4] P. A. Zeijlmans van Emmichoven, P. A. Wouters, and A. Niehaus, Surf. Sci. **195**, 115 (1988).
[5] T. Hecht, H. Winter, and A. G. Borisov, Surf. Sci. **406**, L607 (1998).
[6] R. C. Monreal and F. Flores, Adv. Quantum Chem. **45**, 175 (2004).
[7] N. Lorente and R. Monreal, Surf. Sci. **370**, 324 (1997).
[8] M. A. Cazalilla, N. Lorente, R. D. Muino, J.-P. Gauyacq, D. Teillet-Billy, and P. M. Echenique, Phys. Rev. B **58**, 13 991 (1998).
[9] J. Merino, N. Lorente, W. More, F. Flores, and M. Yu. Gusev, Nucl. Instrum. Methods Phys. Res., Sect. B **125**, 250 (1997).
[10] W. More, J. Merino, R. Monreal, P. Pou, and F. Flores, Phys. Rev. B **58**, 7385 (1998).
[11] B. van Someren, P. A. Zeijlmans van Emmichoven, and A. Niehaus, Phys. Rev. A **61**, 022902 (2000).
[12] S. Wethekam, A. Mertens, and H. Winter, Phys. Rev. Lett. **90**, 037602 (2003).
[13] S. Wethekam, A. Mertens, and H. Winter, Nucl. Instrum. Methods Phys. Res., Sect. B **212**, 308 (2003).
[14] Yu. Bandurin, V. A. Esaulov, L. Guillemot, and R. C. Monreal, Phys. Rev. Lett. **92**, 017601 (2004).
[15] R. C. Monreal, L. Guillemot, and V. A. Esaulov, J. Phys. Condens. Matter **15**, 1165 (2003).
[16] J. C. Lancaster, F. J. Kontur, G. K. Walters, and F. B. Dunning, Phys. Rev. B **67**, 115413 (2003).
[17] S. Wethekam and H. Winter, Surf. Sci. **596**, L319 (2005).
[18] Yu. Bandurin, V. A. Esaulov, L. Guillemot, and R. C. Monreal, Phys. Status Solidi B **241**, 2367 (2004).
[19] D. Valdés, E. C. Goldberg, J. M. Blanco, and R. C. Monreal, Phys. Rev. B **71**, 245417 (2005).
[20] D. Gemmell, Rev. Mod. Phys. **46**, 129 (1974).
[21] H. Winter, Phys. Rep. **367**, 387 (2002).
[22] S. Jequier, H. Jouin, C. Harel, and F. A. Gutierrez, Surf. Sci. **570**, 189 (2004).
[23] H. D. Hagstrum and G. E. Becker, Phys. Rev. Lett. **26**, 1104 (1971); Phys. Rev. B **8**, 107 (1973).
[24] P. A. Zeijlmans van Emmichoven and A. Niehaus, Comments At. Mol. Phys. **24**, 65 (1990).
[25] P. Eeken, A. Niehaus, and T. Urazgil'din, Vacuum **44**, 907 (1993).
[26] G. E. Makhmetov, A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, Surf. Sci. **339**, 182 (1995).