Bandgaps, surface states and the anomalous neutralization of $\text{Li}^+$ on (111) surfaces of noble metals

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New Journal of Physics 8 (2006) 227
Received 21 June 2006
Published 9 October 2006
Online at http://www.njp.org/
doi:10.1088/1367-2630/8/10/227

Abstract. The effect of progressive changes in the electronic structure of (111) surfaces of noble metals on neutralization of $\text{Li}^+$ ions is studied in relation to recent study on electron transfer on nanoclusters dealing with electronic effects. Strong differences in electron transfer probabilities are revealed and the trends in these changes are related to the progressive changes of the band structure of Ag, Cu and Au surfaces. Experimental data reveal an anomalously high neutralization of ions on these high workfunction surfaces and an unusual ion energy dependence, suggesting a pronounced non-adiabatic character of the electron transfer process, not accountable in a ‘jellium’ model of resonant electron capture. We suggest a mechanism of capture involving non-resonant charge exchange from occupied surface states as well as a strongly reduced loss due to the presence of the L-bandgap.

Resonant electron tunnelling processes in ion/atom surface interactions have been extensively investigated [1]–[3] for the case of simple metal and dielectric surfaces, in relation to their role in gas surface interactions and in relation to application of ion beams in surface analysis. Parameter-free theoretical treatments of resonant charge transfer have been developed in a free-electron model of a metal [4]–[7] and often a satisfactory description of experimental data [8]–[12] has been obtained. In an attempt to develop more realistic models, the role of band structure effects, such as the existence of bandgaps and surface states [13]–[20], have come under scrutiny in the past few years and it has been questioned if knowledge of adiabatic, electronic structure properties of the projectile-target system were enough to predict the outcome of reactive processes. Wave
packet propagation studies [7], [14]–[15] revealed that such adiabatic properties as energies and widths of the states for the fixed atom–surface distance are strongly affected by the projected band gap for (111) surfaces of noble metals. This is in agreement with time-resolved two-photon photoemission measurements [16, 17] for alkali adsorbates. However, when it comes to electron transfer processes in ion/atom-surface interactions involving moving particles, the situation turns out to be more complex [18, 19] and depends on interaction time. Thus on the basis of existing studies involving scattering of hydrogen [18] and Li ions [19, 21] it was concluded, that the band structure effects are washed out for a rapidly moving atom scattering, because of the short interaction time. It thus appeared that while the use of the jellium model, in which band structure effects are neglected, may not be justified, its predictions turn out to be close to those of the wave packet propagation treatments including the effect of particle movement with finite velocities [21].

Very recent study on electron transfer dynamics has focused on interaction with supported nanoclusters in an attempt to understand size specific effects in catalysis and in general quantum confinement effects in clusters and ultra-thin films. Studies of Li⁺ [22] and Na⁺ [23] neutralization in the scattering of these ions at low energies (200 eV to 2 keV) on Ag and Au clusters and thin films supported on TiO₂, showed significant enhancement of neutralization for decreasing cluster size. The results indicate that neutralization is most efficient for very small clusters where a metal to non-metal transition occurs [22]. Neutralization was also found to be significantly larger on large clusters of metallic nature than on bulk metallic films. It was argued [22, 23] that these effects may be related to specific characteristics of the electronic structure of clusters and quantum confinement effects resulting in discretization of electronic energy levels, as illustrated recently [24]–[26] in an elegant series of experiments. It was furthermore suggested [22] that for large metallic clusters some differences in electronic structure with respect to bulk metals could explain higher neutralization.

These explanations in terms of changes in electronic structure would appear to contradict the conclusions [18, 19, 21] that under conditions of short interaction times details of electronic structure would not strongly affect electron transfer dynamics. Indeed the scattering conditions in [21], where the effect of the X bandgap of Ag (100) on Li⁺ neutralization was investigated, were similar to those of the study of neutralization on clusters [22, 23]. One can thus ask whether the proposed interpretation is indeed correct, or if the results on nanoparticles are simply due to some morphological characteristics influencing the efficiency of electron transfer.

In view of the fundamental importance of understanding electron transfer dynamics involving nanoparticles, it is important to model electronic effects. The study of electron transfer processes on a set of well-defined systems showing progressive variations in their electronic structure thus appeared essential. We therefore performed a study of neutralization of Li ions for (111) surfaces of noble metals, under the same scattering conditions as on the clusters. The characteristics of these surfaces are well known and model potentials describing them exist [13], which can serve as a basis for theoretical modelling of electron transfer processes. The choice of the (111) surfaces was dictated by the fact that there are indications that on certain substrates [27, 28] the top facets of Ag and Au clusters and also the Ag and Au films grown on TiO₂ at room temperature [22] exhibit the (111) symmetry.

The results of our study reveal several important features. They show that contrary to any reasonable expectations in terms of standard models, neutralization proceeds very efficiently on these very high workfunction metal surfaces over a wide interaction time range and an anomalous velocity dependence of neutralization is observed for Cu(111) and Au(111). We attribute this to a
highly non-adiabatic electron transfer process involving a dynamical velocity dependent electron pickup (non-resonant charge exchange) from the surface states and a very large survival due to the L-bandgap. Our results illustrate the evolution in neutralization efficiency as a function of changes of the electronic structure of these surfaces.

The experiments are performed in an ultrahigh vacuum (UHV) system described elsewhere [29]. Li+ ions are produced using a Li getter source. Time-of-flight measurements of energy losses of ions and neutrals can also be performed for a 116 cm flight length using a multi-anode channel plate detector, allowing simultaneous separate detection of ions and neutrals in continuous or pulsed beam modes. The crystals are cleaned by multiple cycles of small angle Ar bombardment and annealing. Crystal quality and cleanliness is ascertained by LEED, AES and LEIS (low energy ion scattering, using He ions). Li+ neutralization probabilities are determined by measuring neutral fractions for a scattering configuration where the scattered particles leave normal to the surface. The total scattering angle is 114° and this measurement corresponds to an incident angle with respect to the surface plane of 24°. The final ‘exit’ energy of the backscattered Li projectile can be estimated simply from classical mechanics considering scattering of Li mass M1 off a target atom of mass M2, through the 114° scattering angle.

Energy losses of scattered Li atoms and ions were investigated in LEIS and time of flight measurements. The neutral ion fractions are determined in time of flight measurements in which neutral and ion spectra are recorded simultaneously. Examples of these spectra are shown for Li scattering on Cu(111). The spectra for neutrals and ions are fairly similar. At high energies, one finds a peak related to surface scattered particles and a broad energy loss distribution resulting from particles penetrating into inner atomic layers. The neutral fraction is determined from the Li° and Li+ spectra using the area around the surface peak region as indicated in the figure 1. The neutralization probability is then defined as the ratio:

$$\text{P}_{\text{Cu}} = \frac{\int (C_{\text{neutral}})}{\int (C_{\text{neutral}}) + \int (C_{\text{ions}})}$$

The neutral fractions measured in an incident ion energy range from 200 eV to 1.5 keV are shown in figure 2 for the three surfaces. The neutralization probability on Ag is found to be highest. It decreases as the ion energy increases. The amazing feature of these results, however, is the large value of neutral fractions obtained for Cu and Au. Also the energy dependence is ‘anomalous’: first decreasing with increasing energy and then increasing as opposed to the case of the Ag surface.

Let us first briefly consider the predictions of the ‘standard’ jellium free electron model for neutralization of Li+, which has been frequently used in the description of interaction with metal surfaces [2, 3]. Near the surface the Li level is broadened and shifted by the image potential (see [2, 19, 30] and figure 3). In this ‘standard’ approach alkali ion resonant neutralization would occur if the Li(2s) energy level remained below the Fermi level of the metal at distances, where the interaction is large enough to ensure electron transfer on the collision time-scale. On the right panel of figure 3 we indicate the image potential induced shift of the Li(2s) state. The workfunctions of our surfaces are 4.56, 4.95 and 5.4 eV for Ag(111), Cu(111) and Au(111) and the ionization potential of Li is 5.39 eV. As may be seen when the image potential shift is considered the Li(2s) level crosses above the Fermi level at very large atom surface separations and hence electron capture will be very inefficient for Cu and Au in the jellium model. Neutralization should also be impossible for Na (ionization potential of 5.139 eV) on Au(111) and highly improbable on polycrystalline Au (workfunction about 5 eV) contrarily to the observation of [23] for Au clusters and films. We neglect here the so-called ‘parallel velocity’ effect, which results in a kinematic smearing of the distribution of occupied electronic states of the surface, as ‘seen’ from
the reference frame of a moving atom. This should only be important in fast collisions (for details see [2, 3, 12, 19]), with a large component of velocity parallel to the surface.

Figure 2 gives the expected values of the Li$^+$ neutralization fraction within the above framework. It displays the energetic dependence of the neutral fraction for workfunction values corresponding to Ag and Cu, calculated in a rate equation approach [2], for a jellium surface and assuming that the Li ion leaves the surface along the surface normal direction as in our experiment. The Li level characteristics (position and width) in the jellium model are taken from [21].
Figure 3. Schematic diagram of the electronic structure of (111) surface of noble metals as a function of $k_z$: the shaded area represents the three-dimensional (3D) valence band continuum. The dashed lines labelled SS and IS represent the 2D continuum of the surface state and the first image state, respectively. On the right panel, the Li(2s) energy level is plotted as a function of ion surface distance for a classical image potential shift. The surface model data are from [13].

As expected, the neutralization fraction is larger for the smaller values of the workfunction. The energy trend shows the usual dependence on the perpendicular velocity: slower projectiles are more efficiently neutralized since they spend more time near the surface, in the region where the Li(2s) level lies below the Fermi level. Note that an increase in ion fraction at large energies could be expected if we were to consider ionization of a Li atom leaving the surface. Then we would obviously observe an increase in the neutral fraction because of larger survival. A mixed dependence could be obtained if we consider some neutralization in the incoming path. Note however that on a jellium-like metal surfaces (e.g. Al) resonant ionization is extremely efficient and hence incoming neutralized Li would be reionized. It is in this sense that the observed dependence is ‘anomalous’.

As may be seen in figure 2, the Ag(111) results underestimate the experimental data although the energy trend is similar. In case of Cu(111), however, the prediction of the model turns out to be off by a factor of several hundred and clearly does not reproduce the energy dependence. The Au(111) we would expect essentially no neutralization. We are thus faced with a major failure of the jellium model as opposed to the case of Ag(100) we studied previously [21] for which its predictions turn out to be in agreement with experiment.

Clearly our results could not be accounted for in the jellium description. One could argue that capture occurs at defect sites. To check this we bombarded the Au(111) surface with 1 keV Ar ions for 30 min. The neutral fraction for e.g. 1 keV was then found to be about 7% i.e. lower than that of the just annealed Au(111) surface. Another point which should be considered regards alkali implantation. Our measurements on neutralization probabilities involve low Li$^+$ beam flux, pulsed beam time-of-flight measurements. This precludes implantation effects. This was however regularly checked by performing the same type of measurement (e.g. at a given
energy) in different conditions i.e. at the beginning or end of a series of measurements. We thus exclude that our results are affected by Li implantation.

The general trend of the experimental data follows the trends in electronic structure of the metal surfaces. This is illustrated in figure 3 on the basis of data of Chulkov et al [13]. Figure 3 shows the bandgap region and image and surface states for the three surfaces. At present no high level theoretical calculations, taking these characteristics into account, such as the wave packet propagation treatments [21] or others, exist. We would tentatively account for our observations by considering the effect of the bandgap and surface states on the charge transfer processes, which are not taken into account in the jellium model. We suggest that neutralization involves a dynamical electron capture mechanism involving quasiresonant capture from the surface state. Non-resonant charge exchange has been considered previously in the case of He⁺ collisions with Pb (see e.g. [31]) and this was also proposed for electron transfer on Si surfaces involving surface states [32, 33]. Because of the non-resonant character the process would increase in efficiency with increasing velocity as is observed in e.g. charge transfer in gas phase ion/atom collisions. The presence of the bandgap should lead to a strong decrease in electron loss from the populated Li level to the conduction band. Although for Au the surface state lies lower with respect to the upward shifted Li(2s) state and may thus be populated less efficiently, the Li(2s) lies higher in the bandgap, which may further stabilize it against resonant ionization.

In order to describe the energy dependence of the neutral fraction for Cu and Au we have to assume capture on the ingoing and outgoing paths with varying degrees of survival of the neutralized Li⁺ atoms during the close approach. As mentioned above, this survival here would be mediated by the existence of the bandgap as opposed to the jellium case, where the existence of the L-gap is not taken into account. In case of Ag a somewhat larger ionization of atoms neutralized on the incoming trajectory, could be related to the fact that the Li(2s) state would here lie lower in the bandgap, and this could explain the overall decrease of the neutral fraction.

In conclusion, our experimental results demonstrate a high neutralization of Li ions on the high workfunction (111) surfaces of noble metals and an unexpected energy dependence. A progressive change in neutralization characteristics is observed, which we relate to the progressive changes in electronic structure of these metal surfaces. These results do not follow the trends expected in the ‘standard’ jellium type model of resonant electron capture. We tentatively suggest a mechanism of capture involving non-resonant charge exchange from occupied surface states as well as a strongly reduced resonant electron loss due to the presence of the L-bandgap. This systematic study could help to gain a better understanding of changes in electron transfer probabilities that are observed as a function of size and shape of nanoparticles, which have not yet reached bulk metallic properties. Thus for instance a slight change in electronic structure, when one goes from Au to Cu, leads to a substantially increased neutralization and similar modifications could account for some of the observations on clusters. It is also thought that the finite Na⁺ neutralization on high workfunction polycrystalline Au film reported in [23] could be due to scattering on Au(111) facets. We hope that these results will stimulate an in-depth theoretical study of neutralization for these as yet poorly understood systems.

Acknowledgments

We are grateful to A G Borisov for comments and to M Wiartowsky and L Lavagnino for help with the Ag(111) measurements.

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References

[1] Los J and Geerlings J C 1990 Phys. Rep. 190 133
[2] Borisov A G and Esaulov V A 2000 J. Phys.: Condens Matter 12 R 177
[3] Winter H 2002 Phys. Rep. 367 387
[4] Nordlander P and Tully J C 1988 Phys. Rev. Lett. 61 990
[5] Teillet-Billy D and Gauyacq J P 1990 Surf. Sci. 239 343
[6] Deutscher S A, Yang X and Burgdörfer J 1997 Phys. Rev. A 55 466
[7] Ermoshin V A and Kazansky A K 1997 Phys. Lett. A 218 99
[8] Behringer E R, Andersson D R, Cooper B H and Marston J B 1996 Phys. Rev. B 54 14765
[9] Ustaze S, Guillemot L, Esaulov V A, Nordlander P and Langreth D C 1998 Surf. Sci. 415 L 1027
[10] Borisov A G, Teillet-Billy D, Gauyacq J P, Winter H and Dierkes G 1996 Phys. Rev. B 54 17166
[11] Eeken P, Fluit J M, Niehaus A and Urazgildin I 1992 Surf. Sci. 273 160
[12] Maazouz M, Borisov A G, Esaulov V A, Gauyacq J P, Guillemot L, Lacombe S and Teillet-Billy D 1997 Phys. Rev. B 55 13869–77
[13] Chulkov E V, Silkin V M and Echenique P M 1999 Surf. Sci. 437 330
[14] Borisov A G, Kazansky A K and Gauyacq J P 1998 Phys. Rev. Lett. 80 1996
[15] Borisov A G, Kazansky A K, Gauyacq J P, Chulkov E V, Silkin V M and Echenique P M 2002 Phys. Rev. B 65 235434
[16] Bauer M, Pawlik S and Aeschlimann M 1997 Phys. Rev. B 55 10040
[17] Ogawa S, Nagano H and Petek H 1999 Phys. Rev. Lett. 82 1931
[18] Guillemot L and Esaulov V A 1999 Phys. Rev. Lett. 82 4552–5
[19] Hecht T, Winter H, Borisov A G, Gauyacq J P and Kazansky A K 2000 Phys. Rev. Lett. 84 2517–20
[20] Chakrabarty H, Niederhausen T and Thumm U 2004 Phys. Rev. A 69 052901
[21] Canario A R, Borisov A G, Gauyacq J P and Esaulov V A 2005 Phys. Rev. B 71 121401
[22] Canario A R and Esaulov V A 2006 J. Chem. Phys. 124 224710
[23] Liu G F, Sroubek Z and Yarmoff J A 2004 Phys. Rev. Lett. 92 216801
[24] Hövel H and Barke I 2003 New J. Phys. 5 31
[25] Nilius N, Kulawik M, Rust H-P and Freund H-J 2004 Surf. Sci. 572 347
[26] Valden M, Lai X and Goodman D W 1998 Science 281 1647
[27] Cosandey F, Persaud R, Zhang L and Madey T E 1997 Mat. Res. Soc. Symp. Proc. 440 383
[28] Akita T, Tanaka K, Tsubota S and Haruta M 2000 J. Electron Microsc. 49 657
[29] Canario A R, Sanchez E, Bandourin Yu and Esaulov V A 2003 Surf. Sci. 547 L887
[30] Scheffler M M and Stampfl C 2000 Handbook of Surface Science: Electronic structure vol 2 ed K Horn and M Scheffler (Amsterdam: Elsevier) chapter 5, pp 286–356
[31] Shao H, Langreth D C and Nordlander P 1994 Phys. Rev. B 49 13948–65
[32] Ledyankin D V, Urazgildin I and Yurasova V 1990 Nucl. Instrum. Methods Phys. Res. B 48 585
[33] Maazouz M, Guillemot L and Esaulov V A 1997 Phys. Rev. B 56 9267–70

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