

Hollow Atom Dynamics on LiF Covered Au(111): Role of the Surface Electronic Structure

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We report on measurements of the hollow atom dynamics on a clean and LiF covered Au(111) surface. The *KLL*-Auger spectrum arising from grazing incidence 6 keV O^{7+} projectiles is monitored as a function of the LiF coverage up to 1 monolayer. As the coverage increases, we observe a strong reduction in the above-surface component of the *KLL*-Auger emission. The astonishing similarity, with respect to *KLL*-Auger emission, between a single LiF monolayer on Au(111) and a LiF bulk surface, indicates that the large band gap of the latter is not the limiting factor in the neutralization of highly charged ions. [S0031-9007(98)06822-7]

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One of the most exciting aspects of the interaction of multiply charged ions (MCI) with surfaces is the formation of the exotic species called hollow atom [1–7]. During the approach of a MCI to a surface, conduction or valence electrons are captured at large distances into excited states of the projectile, thus leading rapidly to full neutralization of the MCI with a highly inverted population. It was observed that for low normal velocities, the time between the first capture and the impact on the surface is long enough for the relaxation to sparsely fill the inner shells. The interaction of MCI with metals has been studied extensively (for a review, see [8]) and a scenario based on the classical over-the-barrier (COB) model reproduced rather well several observed features of the formation and decay of the hollow atom above the surface [5,9]. In particular, the stepwise electron capture is such that already captured electrons can be lost into the empty states of the solid (if any) and to the vacuum due to the image charge upshift of the projectile levels as the distance to the surface decreases. Simultaneously, lower projectile levels can be populated by either Auger transitions from upper configurations or from resonant capture of valence electrons at shorter distances. The resonant electron loss mechanism was meant to account for the fast relaxation degree observed experimentally [9]. By using a cesiated Au surface, Meyer *et al.* [10] confirmed the key role played by the work function in the efficient neutralization of the impinging ion above a metal surface since the first capture distance and the capture levels depend only on the work function and the projectile charge state.

Hydrogenlike ions are often used so that *KLL*-Auger or *K* x-ray emission allows one to probe the projectile neutralization. Our group has concentrated on the study of Auger electron emission during the relaxation of the hollow atom. In the last phase of decay to the ground state, *KLL*-Auger electrons are emitted with energies characteristic of the initial electron configuration. The measured spectra reflect emission from neutral projectiles where all

captured electrons ($Z - 1$) are distributed over the *L* and *M* shells. For a highly inverted population (only two electrons in the *L* shell), a sharp peak is observed on the low-energy side of the spectrum (see top spectrum of Fig. 1). It was demonstrated that this structure is induced by a slow *L*-shell filling process above the surface [7,11]; its intensity is then a direct signature for the efficiency of above-surface neutralization.

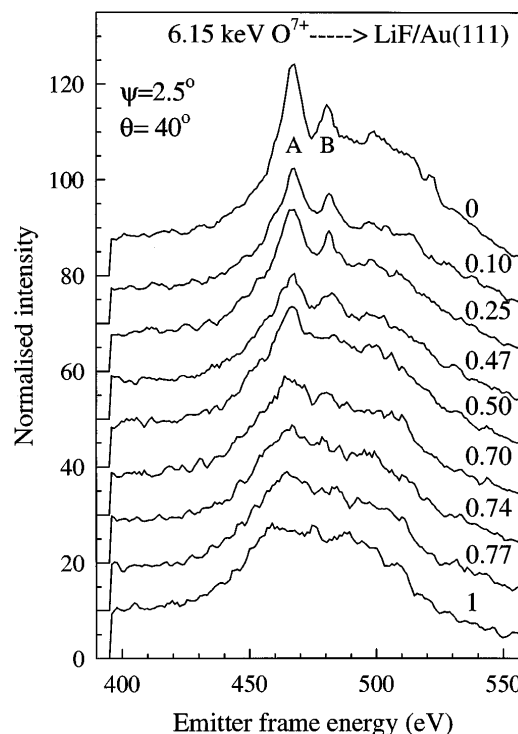


FIG. 1. *KLL* spectra from 6.15 keV O^{7+} on LiF/Au(111). The coverage is indicated on the right. The incidence and observation angles are 2.5° and 40° , respectively. Peaks A and B correspond to configurations $1s2s^23l^5$ and $1s2s2p3l^5$. The electron energy is converted to the projectile frame assuming emission on the incident path.

The interaction of highly charged ions with insulators (LiF) leads to drastically different *KLL*-Auger spectra. The low-energy peak is missing and the whole spectrum appears shifted by a few eV to lower energies [12]. It was then argued that the large electron binding energy (12 eV) and the wide band gap (14 eV) of LiF were responsible for this behavior [8,12]. In the framework of the well accepted COB description, the former delays the onset of first capture and the latter prevents already captured electrons from being lost into the target empty states [13,14], thus suppressing the *L*-shell filling above the surface. In a recent study, Hägg *et al.* [15] have shown that indeed a substantial fraction of electrons captured from LiF is lost if no restriction due to the band gap is imposed.

A satisfactory understanding of the large differences could not be achieved since many parameters are changed simultaneously when one goes from a metal to an insulator such as LiF. Which of these parameters (e.g., electron binding energy, band gap) are the most critical for describing the hollow atom formation and deexcitation on insulator surfaces? In order to decouple the role of the binding energy from that of the band gap, we have carried out an experiment in which the projectile neutralization on a LiF covered Au(111) surface was studied through *KLL*-Auger spectroscopy as a function of LiF coverage up to one monolayer (ML). Such thin films do not exhibit a large band gap and moreover have the advantage of being conducting.

The LiF films were produced by evaporating LiF molecules from an Omicron commercial electron heated evaporator with an integral flux monitor. The evaporator was water cooled so that the base pressure in the chamber could be kept in the low 10^{-8} Pa range. Before each deposition cycle, the Au(111) surface was sputter cleaned with 1 keV Ar^+ and annealed at 400 °C. The surface cleanness and morphology was checked by low energy ion scattering (LEIS). To determine the film growth we also used LEIS, which has been proven to be a powerful technique for studying growth modes of thin films [16–18]. The coverage was also monitored following the deposition of a closed layer (no Au component present in the LEIS spectrum), i.e., during sputtering of the film by the probing beam (the sputtering rate of LiF is relatively high even by He ions [19]). The subsequent relative LEIS signals of Li, F, and Au showed a linear behavior with time, indicating the single layer character of the LiF, as was observed too for other surfaces of Au [20].

A drawback of the large sputtering rate of LiF is the difficulty to maintain a steady coverage while a MCI beam impinges on the film. In the experiments we have used low beam intensities and short scanning times to minimize this limitation. After each deposition procedure, successive spectra are recorded, switching between *KLL* electron and reflected ion spectra. The latter are used for the LiF coverage determination. During all the measurements, the target current was recorded; it was thus possible to correlate this quantity to the LiF coverage. For a constant beam

current, the measured target current increases linearly with coverage, at a rate of 50% per ML up to 1 ML. Low-energy electron spectra show that this additional current is due to a substantial increase of low-energy electron emission, in agreement with the high yields of secondary electrons measured from ion impact on LiF [21,22].

A series of *KLL*-Auger spectra is shown in Fig. 1 as a function of LiF coverage. The 6.15 keV O^{7+} beam is incident at $\psi = 2.5^\circ$ with respect to the surface and electrons are detected at an angle $\theta = 40^\circ$ with respect to the beam direction. The coverage varies between 0 and 1 ML and is determined with an estimated error of approximately ± 0.1 ML. The evolution of the spectrum with LiF coverage can be divided in two parts: first the peaks at 467 and 481 eV (peaks labeled A and B in Fig. 1) slowly loose intensity and become broader. They correspond to the decay of $1s2s^23l^5$ and $1s2s2p3l^5$ configurations, respectively [6]. Simultaneously, we observe a drop of the overall intensity between the top spectrum and the others. Second, around 1 ML coverage, we observe a distinct shift of the spectrum by ≈ -10 eV, with a small structure appearing at 457 eV. Figure 2 shows spectra arising for 6.15 keV O^{7+} impinging at $\psi = 10^\circ$, i.e., at much higher normal velocity. The evolution of the *KLL* intensity distribution with LiF coverage is similar to that of Fig. 1, though the peaks disappear faster due to the shorter time available for above-surface processes.

For a reliable interpretation of the results, one needs information on (i) the emission depth of the low-energy *KLL* electrons observed from a clean gold and (ii) the electronic structure of the thin LiF films on metals. The θ angular dependence of the *KLL*-Auger spectra from

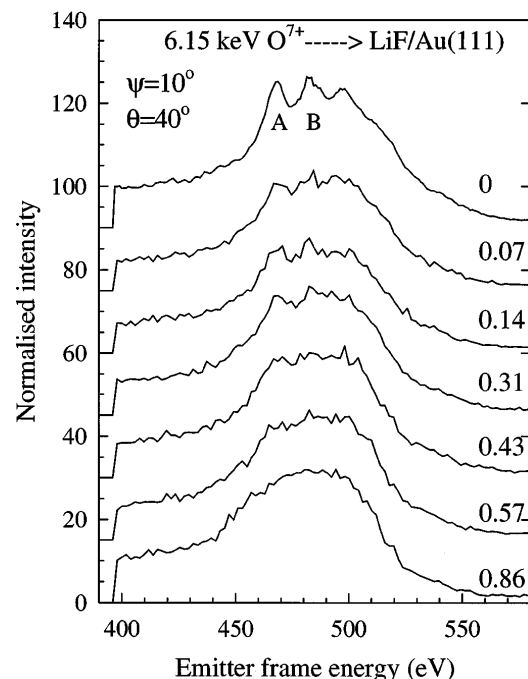


FIG. 2. As in Fig. 1, for an incidence angle of 10° .

the clean Au target [23] demonstrates unambiguously that peak *A* and to a lesser extent peak *B* originate from emission above the surface (here defined by the jellium edge). This is surprising in view of the calculated lifetimes of the corresponding configurations (10 and 120 fs, respectively [6]) and the time available between the first capture at 10 Å, as derived from the COB model, and impact on the surface (≈ 60 fs). Even at the relatively high normal velocity used in Fig. 2, the *KLL* angular distribution indicates that a major fraction of the low-energy peak corresponds to emission above the surface. This is consistent with Marlowe [24] simulations of the projectile trajectories which indicate that for a clean Au(111) surface, nearly all particles are reflected between the jellium edge and the first atomic row. This holds for both impact angles, i.e., 2.5° and 10° . Similar simulations on 1 ML LiF/Au(111) indicate that for 2.5° nearly all particles are reflected from the LiF layer. For $\psi = 10^\circ$ only 15% is reflected from the LiF layer, the majority of the particles (60%) is reflected off the upper Au layer, and the remaining 25% penetrates deeper into the target. Although the simulations show that in close vicinity of the target the trajectories are very different for 2.5° and 10° , the evolution of the *KLL* spectra (cf. Figs. 1 and 2) is similar. This supports the conclusion that the low-energy peaks are due to processes occurring above the surface.

For thin (sub-)monolayer films of insulators on metals, the band gap disappears or is at least strongly reduced. Qualitative insight in the electronic structure of LiF/Au(111) can be gained from the experimental and theoretical investigations on the growth of LiF on W(110) [25,26]. The electronic structure of a thin LiF film resembles that of bulk LiF only for coverage above 5 ML, and even then the band gap is still narrower than that of bulk LiF. Consequently one monolayer of LiF on Au(111) possesses only part of the properties of a LiF bulk surface, namely, the high electron binding energy and not the large band gap. The absence of a large band gap could be verified by He^+ scattering and measuring the survival probability of incident He^+ ions. The survival probability remained on the few percent level when going from clean Au to 1 ML LiF on Au, whereas the existence of a large band gap would lead to an order of magnitude increase in the survival probability through the suppression of Auger neutralization, as shown by Hecht *et al.* [27].

To get some information on the work function or in this case the binding energy of the surface electrons we measured negative ion yields. The yield of scattered O^- following impact of O^{7+} on submonolayer LiF coverages was found to decrease with coverage. Owing to the mechanism of negative ion formation on metals [28–30], this implies an increase of the “work function,” at least for low coverage. The disappearance of the low-energy peaks in our spectra is also a sign of the increase of the binding energy, since the opposite trend was observed by Meyer *et al.* [10], who reduced the work function by evaporating Cs on Au.

Our results can now be interpreted in the following way. During the growth, the Au substrate becomes increasingly shielded by the developing LiF overlayer. This results in an increase of the fraction of surface electrons with higher binding energies [F(2*p*) electrons], leading to a delayed capture onset and a slowdown of the neutralization rate due to the lower electron densities at F sites. For the grazing incidence considered here, the projectiles scan a large area of the surface before impact; thus they are able to efficiently capture Au electrons through any hole in the overlayer. This first phase results in the loss of intensity in the above-surface emission. Finally, at 1 ML coverage, a complete neutralization above the surface is no longer possible, causing the incremental shift of the *KLL*-Auger peak *A* from 467 to 457 eV. The position of the new low-energy peak is consistent with the calculated energy of configurations $1s2s^23l^4$, i.e., for which an electron is missing in the *M* shell. This sudden change in the spectrum is an indication that a closed layer has been reached, and corresponds to the disappearance of the Au component in the reflected ion spectrum.

The main features of the *KLL* spectra from a single LiF monolayer on Au are very similar to those from a LiF bulk surface [12], i.e., there are no sharp structures and the spectrum is shifted to lower energies. We therefore conclude that the large band gap of a LiF surface is not the limiting factor in the neutralization of the MCI above the surface, thus raising a question on the effectiveness of the resonant electron loss mechanism as a speeding-up process in the filling of inner shells. It is worth noting that in both cases this does not exclude that initially a hollow atom might be formed [13,14,31].

A more detailed analysis of the spectra of Fig. 2 reveals that the integrated *KLL*-Auger intensity, starting from a clean gold surface first decreases and then increases to finally nearly recover around 1 ML as is shown in Fig. 3. Similar measurements [23] for N^{6+} show

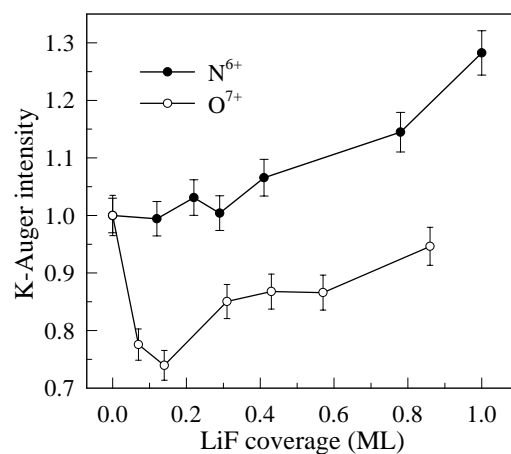


FIG. 3. Integrated *K*-Auger intensity from the O^{7+} spectra of Fig. 2. Data for N^{6+} [23] are also shown for comparison. The error bars result from a pessimistic estimation of beam current variation during acquisition.

a different behavior; the total *KLL* intensity increases monotonically with increasing LiF coverages. Marlowe simulations show that penetration depths and trajectories are basically equal for N and O projectiles. This implies that the different behavior of the *KLL* intensities of N^{6+} and O^{7+} and thus also the initial decrease of the *KLL* intensity for O^{7+} cannot be ascribed to trajectory effects. The change of the intensity must be due to the change in the electronic structure of the surface. The increase of the average binding energy of the surface electrons alone can not account for the observed decrease followed by the increase of the intensity when approaching a monolayer coverage. Therefore the actual balance between the electronic structure of the target and projectile seems to play a key role.

In conclusion, we have shown that a single monolayer of LiF on Au(111) completely shields the gold substrate with respect to the neutralization of slow highly charged ions impinging on the surface. The striking similarities of the *K*-Auger spectra obtained with such a surface with those from a LiF bulk surface indicate that the band gap in LiF does not play any role in the suppression of the projectile inner-shell filling above the surface. Thus the binding energy of the valence/conduction electrons is the most pertinent quantity for the hollow atom dynamics. We believe that a more refined understanding of the neutralization and relaxation processes of multiply charged ions on surfaces can be achieved by the use of thin films for a controlled modification of selected physical quantities of the surface. For instance, the role of the density of occupied states would be of particular interest. Additionally, a substantial effort on the theoretical side is needed for a more refined description of the dynamics of the system surface-hollow atom.

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