Do Hollow Atoms Exist in Front of an Insulating LiF(100) Surface?

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First measurements of *KLL* Auger spectra arising from collisions of N^{6+} ions on an *insulating* LiF(100) surface are presented. The beam energy is varied from 0.08 up to 16 keV. The incident angle is chosen such that the perpendicular velocity component is constant over the indicated energy range. Spectral features arising from above surface *KLL* emission, observed during interaction of N^{6+} with a *conducting* Si(100) surface, are absent for LiF, implying pronounced differences in the dynamics governing the above-surface neutralization and deexcitation of the highly charged projectiles.

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One of the main goals for the study of the interaction of highly charged ions with surfaces is to find out which electronic processes are induced by the highly charged projectiles, and to what extent this can give rise to sputtering or surface modification [1–5]. For metallic targets reasonable agreement has been obtained regarding the first steps in the ion surface interaction. First the ion is attracted towards the surface by its own image charge; at a reasonably well-defined distance in front of the surface, electrons are transferred from the solid into excited orbits of the projectile, leading to a neutralized, multiply excited "hollow atom" with empty or sparsely filled inner orbits. However, a lot of discussion is still going on regarding the next steps: the decay of these hollow atoms.

Clearly, one observes *KLL* Auger processes. But it is by no means clear whether this represents the last step of an Auger cascade from higher projectile shells or whether electrons are directly captured into the *L* shell from inner shell target orbitals. Also it is still a point of discussion to what extent the *KLL* decay takes place above or below the surface. In view of possible implications for surface modifications it is important to localize where electrons are emitted, i.e., where the potential energy carried by the projectiles is deposited.

For an insulator, already the first steps of ion surface interaction might be quite different, as compared to a conducting surface. Delocalized electrons are not as abundantly available as in a metal, and therefore it is questionable whether hollow atoms will be formed in the same way as in front of a metal surface. This in turn may have a large influence on the impact energy of the originally slow projectiles: Without hollow atom formation the projectile's image charge would not be "switched off" at relatively large distances as for metal surfaces, and therefore the ion would be accelerated by its image charge up to very close distances from the surface. This would impose a lower limit to the kinetic impact energy significantly higher than for metal surfaces. The absence of hollow atom formation would also imply that a considerably smaller amount of the projectile's potential energy is released above the surface, leading to a much more violent interaction.

In order to investigate highly charged ion interaction with an insulating surface we have measured energy spectra of *KLL* Auger electrons resulting from collisions of hydrogenlike N^{6+} ions on a LiF surface. LiF is an insulator, however, at elevated temperatures it exhibits an ionic conductivity, which is sufficient to avoid charging induced by impact of low intensity ion beams (several tens of nA). We use a LiF(100) crystal, which is mounted in a UHV chamber (base pressure 2×10^{-8} Pa) on a manipulator, allowing crystal rotations such that measurements are possible at various polar and azimuthal angles with respect to the ion beam. The crystal is sputter cleaned by a Ne^{+3} beam. Cleanliness is checked by observing recoil particles and by analyzing energy losses of scattered ions. During both sputtering and experimental runs, the target was kept at a temperature of 400 °C. Electrons are analyzed in a 180° hemispherical analyzer, which is rotatable about the scattering center. The energy resolution is $\Delta E/E = 0.5\%$. The ion beam is provided by an electron-cyclotron-resonance ion source and can be decelerated to low kinetic energies (a few tens of eV) by floating the whole apparatus nearly on source potential.

Figure 1 shows energy spectra resulting from collisions of N^{6+} ions on the LiF surface. Electrons in the energy range between 320 and 400 eV are due to *KLL* Auger processes. For comparison, spectra taken at the same conditions, but with a *p*-doped Si(100) surface as a target, are shown in Fig. 2; it should be noted here that the latter spectra closely resemble spectra taken on metallic targets [6]. For obtaining the various spectra the collision energy and the angle of incidence have been varied simultaneously such that the velocity towards the surface $v_\perp$, and thereby the time scales governing

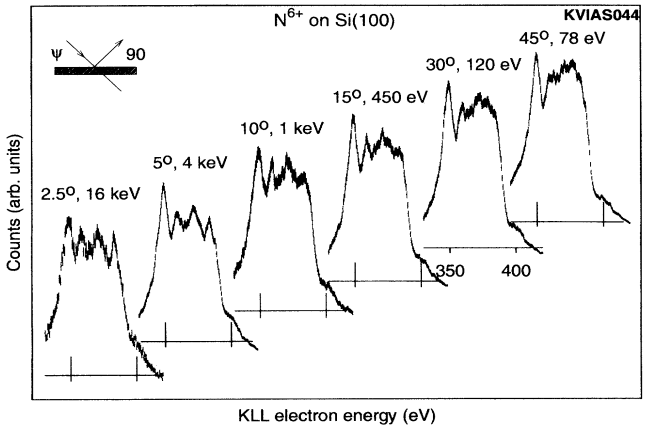

FIG. 1. *KLL* Auger spectra of N^{6+} on LiF(100). The beam energy E_0 and incident angle ψ have been changed in order to keep $v_\perp$ constant. The ordinate is linear.

above surface neutralization and deexcitation, remained constant for all measurements. In order to maximize the time spent by the projectiles in front of the surface, the projectile energy towards the surface was taken as small as possible, without losing too much beam intensity. At these experimental conditions the vertical velocity is close to its principal lower limit, given by the image charge acceleration, which is also active for LiF [7]. Galilei shifts [8] due to the projectile's parallel velocity do not have to be taken into account since $v_\parallel \ll 1$ a.u. for all energies used. However, for metallic targets it has been shown that processes taking place during close collisions at or below the surface can depend on the different projectile velocities [6,9–12].

In comparing the two series of measurements, two striking features are observed: Firstly, the prominent

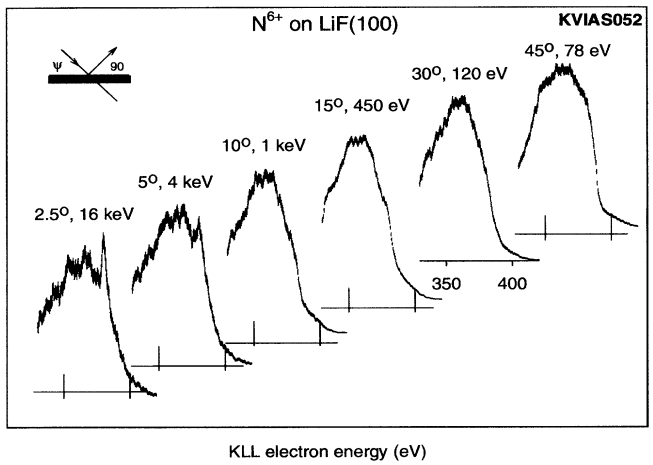

FIG. 2. *KLL* Auger spectra of N^{6+} on Si(100), with the same conditions as in Fig. 1.

peak, which for the Si(100) target shows up on the low energy side of the *KLL* distribution, is missing for the LiF(100) target, whereas the sharp peak ($\Delta E \leq 2$ eV FWHM) on the high energy side of the distribution comes up for both targets with increasing collision energy. On the basis of Hartree-Fock atomic structure calculations the two peaks at the low and high energy sides of the spectra were previously identified as being due to KL_1L_1 decay of a $N(1s2s^23l^4)$ configuration [13] and $KL_{2,3}L_{2,3}$ decay of a $N(1s2s^22p^4)$ configuration, respectively [10]. Secondly, the low energy slope of all *KLL* Auger peaks measured on the LiF target exhibits a remarkable shift by 10–15 eV towards lower energies, as compared to the Si (and metal [6,10]) targets, whereas the high energy peak is practically at the same energy (382 eV) for all targets.

The experimental results can be interpreted in a straightforward way by assuming that two mechanisms contribute to the filling of the projectile L shell [9–11]. A first, slow, mechanism starts at large distances from the surface as soon as electrons are captured into exited projectile states and proceeds via Auger cascades together with resonant electron capture from and electron loss to the target [3]. Initially, for small numbers of L electrons r, the L-shell filling rate $\Gamma_L^{\text{slow}}(r)$ is much smaller than the *KLL* Auger rate Γ_K. Consequently, as soon as two electrons have cascaded into the L shell, *KLL* decay is much more likely than a further accumulation of L electrons via cascade processes. Therefore this mechanism predominantly gives rise to *KLL* processes with a doubly filled L shell, resulting in the low energy part of the measured spectra. Apparently this mechanism is active for the Si(100) target—just as for various metal targets [6,10]—and gives rise to the sharp peak at 350 eV. For LiF, however, this mechanism contributes only weakly. Moreover, the projectiles seem to be incompletely screened in front of the LiF surface. The broadening of the low energy slope in the spectra and the shift towards lower energies can be ascribed to *KLL* electron emission from such differently screened projectiles [13].

A second, fast, mechanism for L-shell population—earlier characterized in a general way as "sidefeeding" [14]—becomes active at small internuclear distances and is caused by a direct electron transfer from inner shell target orbits into the projectile L shell. Based on the fast projectile neutralization and deexcitation observed by Folkerts *et al.* [15], Burgdörfer, Reinhold, and Meyer [16] have recently described in more detail how such a mechanism comes about and why it is to a large extent independent of the orbital energies within the target atom. The localized nature of this type of vacancy exchange leads to a filling rate $\Gamma_L^{\text{fast}}(v)$, which is proportional to the "collision frequency," i.e., to the projectile velocity divided by the path length between sucessive collisions [9–11]. For sufficiently high collision frequencies (i.e., of the order of 10^{15}/s) a further accumulation of electrons

in the L shell up to the maximum is then always more likely than a KLL decay from an incompletely filled L shell. The rise of the sharp $KL_{2,3}L_{2,3}$ peak at 382 eV corresponding to decay from a filled L shell, with increasing velocity, is observed for both the Si(100) and LiF(100) targets. This can be taken as clear evidence for such a fast filling mechanism to be active in the collisions considered here.

The most remarkable features of the LiF spectra, i.e., the absence of the KLL peak belonging to decay of a hollow atom with only two L electrons, and the shift of the low energy slope, can, in principle, be explained by assuming that for LiF a hollow atom in front of the surface is simply not formed. This is just as one would expect from the fact that LiF is an insulator. Even if a complete neutralization takes place, it is to be expected that the two-electron $1s\ 2s^2$ peak would not show up in the Auger spectra, since a "demotion" of electrons (i.e., a transfer of electrons from excited orbits to lower levels) from their primary capture level to the $2s$ orbit cannot proceed as in a metal, where—in addition to Auger cascades—resonant electron capture from and loss to the target do occur [3–5]. In LiF, valence electrons are strongly bound, and therefore resonant capture rates are small before close collisions occur. At the same time resonant loss processes are blocked for the projectiles' deexcitation because of the absence of empty target states in the large band gap (12 eV). Slow projectile deexcitation in front of LiF surfaces has also been inferred from total electron yield measurements [17].

The comparison between spectra of LiF and those of Si and of various metal targets sheds new light on the question of to what extent KLL electron emission really takes place above the surface for conducting targets. The hypothesis of L-shell filling by close ion-atom collisions implies that for high collision energies this mechanism is fast as compared to KLL decay, and therefore Auger processes from a doubly filled L shell become unlikely as soon as the projectile suffers close collisions. At least for the 16 keV spectra one can therefore state that such contributions to the low energy peak will be negligible after the "close collision" range has been entered. The observed peak intensity in the case of 16 keV N^{6+}-Si collisions can therefore completely be ascribed to above-surface emission. The fact that the peak intensity is practically constant for all the spectra taken at the same *vertical* velocity but for *parallel* velocities differing by a factor of 10 supports the view that the peak is always due to emission before close collisions occur. Finally, the absence of this signature of above-surface emission in the LiF spectra leads us to the conclusion that formation of highly excited, hollow atoms in front of an insulating LiF target is much less probable than in front of metal and semiconductor targets.

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