Hollow-atom probing of surfaces
Limburg, Johannes

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An L-shell filling model

This chapter presents a detailed description of KLL Auger spectra arising from collisions of hydrogenic N\textsuperscript{6+} on clean Si(100) and Al(110) surfaces at energies ranging from 78 eV up to 60 keV and at incident angles from 2.5\degree up to 45\degree. Atomic structure calculations of KLL Auger energies and decay rates for hollow atoms, together with simulations of the projectile trajectories support a model in which the deexcitation of the ions proceeds essentially via two mechanisms. Before the ion enters the “close collision range”, a few of its L-shell vacancies are filled by Auger cascades involving outer shell electrons. But as soon as the projectile suffers close collisions, L-shell vacancies are rapidly filled by direct capture of target core electrons. The time scale of the latter mechanism is determined by the collision frequency.
7.1 Introduction

The previous chapters thoroughly discussed the influence of the velocity towards the target ($v_\perp$) on the degree of deexcitation the hollow atoms achieve before surface impact. It was shown that due to the image acceleration imposed lower limit on $v_\perp$ only fractions up to about 25% of the projectiles emit a KLL Auger electron before the projectiles and/or the emitted electrons are significantly scattered by the solid. A model capable of reproducing the intensities and energy positions of peaks at the low energy side of the KLL Auger peak was presented. This model explained the quenching of a variety of states with only two L-electrons into the two final states observed in the spectra. However, in the discussions in the previous chapters it was noted already that $(i)$ the observed quenching does not stem solely from Coster-Kronig transitions but also from capture of additional L-electrons (see section 6.4), and $(ii)$ additional peaks are present in the Auger spectra arising from states with different numbers of L-electrons (see chapter 4). Also the question how the component of the projectile velocity parallel ($v_\parallel$) to the surface affects the electron emission dynamics has not been discussed yet. Both $v_\perp$ and $v_\parallel$ determine whether the projectile enters the surface or is reflected. The relaxation of reflected hollow atoms can be observed for periods of time orders of magnitude larger than for atoms entering the target since projectile electrons and photons cannot escape the solid beyond a certain escape depth.

In this chapter the general concepts which allow for an explanation of the main features of the KLL Auger spectra obtained from the neutralization of hydrogenic ions at various solid surfaces are presented. Using these concepts KLL-Auger spectra resulting from collisions of N$^6^+$ on Al(110) and Si(100), taken at different projectile energies $E_0$ and incident angles $\psi$, are discussed.

7.2 Experiment

Figures 7.1 and 7.2 show KLL Auger spectra arising from the interaction of N$^6^+$ with the Si(100) and Al(110) surfaces described in chapter 3. A random azimuthal angle and the $<110>$ surface direction have been chosen respectively. The spectra in figures 7.1 and 7.2 have been corrected for analyzer transmission. No background subtraction has been applied. Incident angle $\psi$ and primary beam energy $E_0$ have been varied simultaneously such that $v_\perp$ was kept constant. First of all it should be noted that in the spectra obtained from both the Al(110) and Si(100) targets with increasing $v_\perp$ a very sharp peak shows up at the high energy side (383 eV) of the KLL spectrum. Furthermore, in both series, the intensity of the peak at the low energy side (at 347 eV in Si and 350 eV in Al) does not change considerably
Figure 7.1: KLL Auger spectra of $N^{6+}$ on Si(100). The beam energy $E_0$ and incident angle $\psi$ have been varied such that $v_{\perp}$ is kept constant.

Figure 7.2: KLL Auger spectra of $N^{6+}$ on Al(110). $E_0$ and $\psi$ same as in figure 7.1.
over the indicated \((\psi, E_\theta)\) range. But the intensity of this peak is target dependent – being pronounced for the Si target.

Figure 7.3 presents spectra taken under specular reflection conditions, varying the parallel velocity \(v_p\) by a factor of 20. These velocities correspond to average interatomic \(<110>\) travelling times, i.e. the time needed to travel along the \(<110>\) direction between adjacent target atoms, ranging from 0.3 fs (60 keV) to 7 fs (150 eV). The velocity component perpendicular to the surface \(v_\perp\) varies by a factor of 3 since this velocity is determined by the sum of the beam energy perpendicular to the surface (30 eV at 16 keV) plus the energy gain due to image charge acceleration (\(\sim 15 \text{ eV}\)).

This series shows a shift of intensity towards higher electron energies for increasing projectile energy.

In figure 7.4, a and b, we plotted the measured Doppler shift of the two sharp peaks for the Al target. The plotted points are measurements, the lines are calculated assuming electron emission on the ingoing path (solid line) and on the reflected path (dotted line). The Doppler shifts were measured with \(\psi = 2.5^\circ\) and \(E_\theta = 16 \text{ keV}\).

### 7.3 Ion trajectory simulations

In order to get an insight into the in-depth ion distribution at the instant of KLL electron emission and into the traveling paths of the projectiles during their interaction with the solid, we performed Monte Carlo ion trajectory simulations using the marlowe computer code. Using this code and additional routines we are able to simulate and visualize the trajectories followed by the projectiles for the \(\psi, E_\theta\) combinations as depicted in figures 7.2 and 7.3. The marlowe program simulates the trajectories followed by the projectiles in a binary collision approximation; between collisions, particles move in straight lines. The interatomic potential is modelled according to Ziegler et al. The surface is implemented as a perfect Al(110) surface, oriented in the \(<110>\) channeling direction. Thermal lattice vibrations are accounted for by the Debye model with a Debye temperature of 400 K. A kinetic energy gain perpendicular to the surface of 15 eV due to image charge acceleration is also accounted for.

The results of the simulations are shown in figures 7.5 and 7.6. In figure 7.5 collision conditions as in the spectra of figure 7.2 were chosen, i.e. varying \(\psi\) and \(E_\theta\) such that \(v_\perp\) is constant. The simulations show that nearly all primary particles are reflected from the first few target layers for incident energies from 4 keV down to 450 eV. For even lower energies like 120 and 78 eV, a large part of the beam will be stopped in the first few layers of the target. Secondly, the number of close collisions with target atoms varies significantly over the indicated \(\psi, E_\theta\) range. In the present context
7.3 Ion trajectory simulations

**Figure 7.3:** Auger spectra of N\(^{6+}\) on Al(110). All spectra are taken under specular reflection conditions, the velocity parallel to the surface \((v_\parallel)\) changes by a factor of 20. The lines are simulated spectra, in the 150 eV spectrum 1s 2s\(^2\)/2s2p3\(^t\)\(^4\) states are assumed, in the 16 KeV spectrum a 1s(2s\(^2\)2p\(^4\))^3P state has been taken. The spectra are calculated according to algorithms described by Schippers.\(^{120}\) KL\(_1\), L\(_1\), KL\(_1\)L\(_2\), KL\(_2\)L\(_2\) and KL\(_2\)L\(_2\)\(_3\) decay is depicted by straight, dotted and straight-dot-dot lines respectively.

**Figure 7.4:** Doppler shifts of 350 eV and 383 eV peaks and of FWHM, measured for different angles of observation \((\theta)\) using 16 keV N\(^{6+}\), \(\psi = 2.5\) on Al(110). Solid lines are calculated shifts assuming emission on the ingoing path, dotted line on the reflected path.
close collisions are defined as collisions with impact parameter smaller than the projectile L-shell radius (see below). In case of 16 keV projectiles, a few tens of close collisions occur per incident ion, whereas in case of low energies like 120 and 78 eV only one or two close collisions per incident ion are encountered. Furthermore it is seen that high energy projectiles travel for a relatively long time (10-100 fs) on their incident trajectory or parallel to the target surface.

In figure 7.6 we show the trajectories calculated using the same $\psi$, $E_0$ as in figure 7.3. Now only for 16 and 60 keV beams some penetration into the bulk material occurs. In this case the incident ions are seen to travel parallel to the surface, sometimes several layers deep inside the solid. At all other energies, the projectiles are reflected by the first or second layer of the target surface. Therefore energy losses due to inelastic scattering of electrons emitted inside the solid will be minimal in all KLL Auger spectra presented in this article, except for the 2.5$^\circ$, 60 keV spectrum. Furthermore it is seen that again the average number of close collisions undergone by the projectiles dramatically decreases with decreasing energy. For low projectile energies, the image charge acceleration of the projectiles towards the target significantly increases the incident angle $\psi$ (even up to 20$^\circ$ for a 2.5$^\circ$, 150
Table 7.1 lists the percentage of reflected projectiles, their flight time along the surface, the average number of collisions undergone and the percentage of collisions with impact parameters smaller than 2 a.u. These numbers result from simulations of trajectories of 50,000 projectiles incident on the Al(110) surface using \( \psi = 2.5 \) and various energies. The large uncertainties in the average numbers of collisions are due to the particles which channel along the \([<1\overline{1}0>]\) surface directions. After listed flight times 95% of the reflected projectiles have left the surface. Conclusively the simulations show that under the present experimental conditions no significant bulk penetration occurs. Consequently the electron spectra are merely disturbed by solid state effects.

### 7.4 Modelling KLL Auger emission

In the previous section the effects of the projectile trajectories at or inside the solid on the KLL Auger electron emission distribution are discussed. It is clear that the point of emission, at or inside the solid, determines the elastic
An L-shell filling model

Table 7.1: Reflected projectiles, flight times, mean number of collisions and the percentage of these collisions with impact parameters smaller than 2 a.u. for different energies. The flight time of the projectiles is the time after which 95% of the reflected particles have left the surface. The large uncertainties in the numbers of collisions is due to particle channeling along <110> channels.

<table>
<thead>
<tr>
<th>$E_0$ (keV)</th>
<th>Refl. (%)</th>
<th>$T$ (fs)</th>
<th>no. coll.</th>
<th>% coll. ($d &lt; 2$ a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>99.9</td>
<td>40</td>
<td>10±4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>1.0</td>
<td>99.8</td>
<td>50</td>
<td>30±10</td>
<td>5</td>
</tr>
<tr>
<td>8.0</td>
<td>99.7</td>
<td>60</td>
<td>80±20</td>
<td>11</td>
</tr>
<tr>
<td>16.0</td>
<td>95.0</td>
<td>200</td>
<td>500±100</td>
<td>13</td>
</tr>
<tr>
<td>64.0</td>
<td>79.0</td>
<td>40</td>
<td>1400±300</td>
<td>50</td>
</tr>
</tbody>
</table>

and inelastic electron energy losses and thereby part of the shape of the KLL Auger structure. But the typical electron emission time scales, determined by both the KLL Auger decay rates and the L-shell filling rates, not only give the in-depth emission distribution but also the distribution of configurations present at the moment of KLL decay. It is evident that the ratio of the KLL decay rate, $\Gamma_K$, and the L-shell filling rate $\Gamma_L$ determines whether KLL decay occurs preferably with a small or large number of L-electrons present. It has been shown by means of atomic structure calculations that with increasing number of L-electrons KLL Auger energies shift to higher values. Accordingly an analysis of the measured K-Auger energy distribution allows a determination of the projectile state at the instant of K-Auger emission.

In this section a simple model will be presented in which the probability that a certain number of L-electrons is captured before KLL decay occurs is calculated. The KLL Auger line intensity $I_{ij}(r)$ resulting from a transition from an initial state $i$ with $r$ L-electrons to a final state $f$ with $r-2$ electrons is given by its initial population $n_i$ times the branching ratio $\Gamma_{ij}(r)/\sum_f \Gamma_{ij}(r)$. However, to arrive at the experimentally observed intensity, we have to incorporate (i) the probability $P_K^r(r)$ that $r$ L-electrons are actually present and (ii) a time window $P_T$ as discussed in chapter 5, reflecting the limited observation time for projectiles penetrating into the solid from where electrons cannot be observed beyond a certain escape depth. Therefore we have

$$I_{ij}(r) = C n_i \frac{\Gamma_{ij}(r)}{\sum_f \Gamma_{ij}(r)} P_K^r(r) P_T$$

(7.1)
in which $C$ is a calibration constant.

In the experiments under consideration here, no significant penetration of the solid occurs. Therefore the timewindow is roughly given by the width of the spectrometer spot on target divided by the parallel velocity of the projectiles, a number in the order of nanoseconds for the fastest (60 keV) projectiles. Since most Auger transitions are much faster than that, the timewindow factor $P_T$ in practice equals 1.

**Atomic structure calculations**

In order to identify the transitions that contribute to the sharp peaks we observe in the nitrogen KLL Auger spectra we calculated the energies and rates for all states present within the configurations $1s^2 2^r 3^{16-r}$ with $2 \leq r \leq 6$ using the Hartree-Fock atomic structure code by Cowan.\textsuperscript{119} It should be noted here that similar calculations have been presented earlier by Hansen et al.\textsuperscript{118} Our calculations are similar to theirs but do distinguish decay towards distinct final states which are actually resolved in the spectra as is shown in chapters 5 and 6.

Table 7.2 lists the rates and Auger energies of all states remaining after Coster-Kronig redistribution, decaying via $KL_1L_1$, $KL_1L_{2,3}$, or $KL_{2,3}L_{2,3}$ Auger transitions for different numbers of L-electrons $r$. In this notation $L_1$ stands for a $2s$ electron and $L_{2,3}$ for $2p$ electrons participating in the Auger transition.\textsuperscript{128} The various decay channels in general have different rates and Auger energies. For a given $r$, the $KL_1L_1$, $KL_1L_{2,3}$ and $KL_{2,3}L_{2,3}$ subgroups are well separated in energy and lead to different peaks which can

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**Figure 7.7:** Calculated sublevel specific Auger energies (a) and lifetimes (b) of hollow atom states present at the moment of KLL decay, as a function of the number of L-electrons.
An L-shell filling model

Table 7.2: $N^+$ hollow atom configurations, transition rates and energies for 2 up to 6 L-electrons (r). The remaining electrons are taken in the M-shell. The energies $E_{KL, L_{2,3}}$ are averages for 4, 5, and 6 L-electrons; see text.

<table>
<thead>
<tr>
<th>r</th>
<th>State</th>
<th>$\Gamma_{KL_1 L_1}$</th>
<th>$E_{KL_1 L_1}$</th>
<th>$\Gamma_{KL_1 L_{2,3}}$</th>
<th>$E_{KL_1 L_{2,3}}$</th>
<th>$\Gamma_{KL_{2,3} L_{2,3}}$</th>
<th>$E_{KL_{2,3} L_{2,3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1s (2s^2 1S)^2S$</td>
<td>9.6 (13)</td>
<td>347</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^3 P)^4P$</td>
<td>—</td>
<td>—</td>
<td>1 (8)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^3 P)^2P$</td>
<td>—</td>
<td>—</td>
<td>8.8 (12)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>$1s (2s^2 2p^2 P)^3P$</td>
<td>7.4 (13)</td>
<td>347</td>
<td>3.6 (13)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$1s (2s^2 2p^2 P)^1P$</td>
<td>7.4 (13)</td>
<td>350</td>
<td>1.2 (11)</td>
<td>—</td>
<td>1 (9)</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^4 P)^5P$</td>
<td>—</td>
<td>349</td>
<td>1 (7)</td>
<td>—</td>
<td>1 (9)</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^4 P)^3P$</td>
<td>—</td>
<td>358</td>
<td>1.9 (13)</td>
<td>368</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>$1s (2s^2 2p^2 1S)^2S$</td>
<td>7.7 (13)</td>
<td>346</td>
<td>4.2 (13)</td>
<td>2.7 (13)</td>
<td>362</td>
<td>377</td>
</tr>
<tr>
<td></td>
<td>$1s (2s^2 2p^2 1D)^2D$</td>
<td>5.5 (13)</td>
<td>349</td>
<td>4.5 (13)</td>
<td>—</td>
<td>6.8 (13)</td>
<td>377</td>
</tr>
<tr>
<td></td>
<td>$1s (2s^2 2p^3 P)^4P$</td>
<td>5.3 (13)</td>
<td>347</td>
<td>6.0 (13)</td>
<td>—</td>
<td>6.3 (8)</td>
<td>371</td>
</tr>
<tr>
<td></td>
<td>$1s (2s^2 2p^3 P)^3P$</td>
<td>5.3 (13)</td>
<td>352</td>
<td>6.0 (13)</td>
<td>—</td>
<td>4 (9)</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^5 S)^6S$</td>
<td>—</td>
<td>357</td>
<td>3 (7)</td>
<td>3 (8)</td>
<td>370</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$1s (2s2p^5 S)^4S$</td>
<td>—</td>
<td>357</td>
<td>2 (13)</td>
<td>1 (9)</td>
<td>371</td>
<td>—</td>
</tr>
</tbody>
</table>
be well resolved by our spectrometer. A more detailed assignment of peaks, as in chapter 5 for the case \( r = 2 \), is prohibitive in general because of the large number of transitions involved for \( r \geq 3 \). Therefore the energies and rates given in table II are mean values averaged over all transitions within a given subgroup \( \gamma \in \{ K_{L_1} L_1, K_{L_2,3}, K_{L_2,3} L_{2,3} \} \):

\[
E'(r) = \frac{\sum n_i E_i'(r)}{\sum n_i}
\]

(7.2)

and:

\[
\Gamma'(r) = \frac{\sum n_i \Gamma_i'(r)}{\sum n_i}
\]

(7.3)

A statistical population \( n_i = 2J_i + 1 \) of all states has been assumed throughout, with \( J_i \) being the total angular momentum of state \( i \). Coster-Kronig redistribution has been accounted for.

In figure 7.7(a) the calculated subgroup specific average energies are plotted as a function of the number \( r \) of L-electrons. Evidently \( E'(r) \) increases with increasing \( r \). Moreover we find that both \( K_{L_1} L_1 \) and \( K_{L_2,3} L_{2,3} \) subgroups are rather sharply peaked in contrast to the \( K_{L_1} L_2 \) subgroup which for \( r > 3 \) covers a broad range of Auger energies in between the \( K_{L_1} L_1 \) and the \( K_{L_2,3} L_{2,3} \) peaks.

Figure 7.7(b) displays the behavior of \( \Gamma'(r) \) versus \( r \). For the cases \( r = 2, 3 \), \( K_{L_2,3} L_{2,3} \) rates have been omitted since the corresponding 1s 2p\(^3\) 3l\(^3\) and 1s 2s 2p\(^2\) 3l\(^3\) configurations primarily decay by Coster-Kronig transitions (the aluminum target has a work function of only 4.3 eV allowing effective Coster-Kronig quenching even for N 1s 2l\(^2\) 3l\(^3\) states). Figure 7.7(b) shows that \( \Gamma^{KL_{1}L_{1}} \) rapidly decreases with \( r \) while \( \Gamma^{KL_{1}L_{2,3}} \) and \( \Gamma^{KL_{2,3}L_{2,3}} \) significantly increase. Furthermore for small \( r \) \( K_{L_1} L_1 \) decay dominates but for larger \( r \) \( K_{L_1} L_{2,3} \) and \( K_{L_2,3} L_{2,3} \) transitions are faster.

### A stepwise L-shell filling model

The number of L-electrons present before KLL decay occurs depends on the outcome of the competition between KLL decay (rate \( \Gamma_K \)) and L-shell filling (rate \( \Gamma_L \)). For a rapid L-shell filling (\( \Gamma_L >> \Gamma_K \)) KLL decay will predominantly occur after the L-shell is filled up to its maximum. For slow L-shell filling, KLL Auger decay occurs mainly as soon as a second L-electron is present.

In order to quantify the competition between KLL-Auger processes and L-shell filling we calculate the probability of KLL-Auger emission from a configuration containing \( r \) L-electrons as:
Table 7.2 continued.

<table>
<thead>
<tr>
<th>$r$</th>
<th>State</th>
<th>$\Gamma_{KL,L_1}$</th>
<th>$E_{KL,L_1}$</th>
<th>$\Gamma_{KL,L_{2,3}}$</th>
<th>$E_{KL,L_{2,3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$1s,(2s^22p^3,^4S)^5S$</td>
<td>3.6 (13)</td>
<td>352</td>
<td>4.2 (13)</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6 (13)</td>
<td>354</td>
<td>5.1 (13)</td>
<td>366</td>
</tr>
<tr>
<td></td>
<td>$1s,(2s^22p^3,^4S)^3S$</td>
<td>5.0 (13)</td>
<td>350</td>
<td>7.5 (13)</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2 (13)</td>
<td>353</td>
<td>5.8 (13)</td>
<td>367</td>
</tr>
<tr>
<td></td>
<td>$1s,(2s^22p^3,^2P)^3P$</td>
<td>3.6 (13)</td>
<td>352</td>
<td>7.6 (13)</td>
<td>365</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6 (13)</td>
<td>352</td>
<td>5.1 (13)</td>
<td>368</td>
</tr>
<tr>
<td>6</td>
<td>$1s,(2s^22p^4,^1S)^2S$</td>
<td>5.0 (13)</td>
<td>353</td>
<td>9.9 (13)</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0 (13)</td>
<td>354</td>
<td>8.8 (13)</td>
<td>369</td>
</tr>
<tr>
<td></td>
<td>$1s,(2s^22p^4,^3P)^4P$</td>
<td>3.0 (13)</td>
<td>357</td>
<td>5.8 (13)</td>
<td>369</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.0 (13)</td>
<td>357</td>
<td>5.3 (13)</td>
<td>367</td>
</tr>
<tr>
<td></td>
<td>$1s,(2s^22p^4,^1D)^2D$</td>
<td>3.0 (13)</td>
<td>357</td>
<td>6.5 (13)</td>
<td>386</td>
</tr>
</tbody>
</table>
7.4 Modelling KLL Auger emission

\[ P_K(r) = \frac{\Gamma_K(r)}{\Gamma_L(r) + \Gamma_K(r)} \prod_{i=1}^{r-1} \frac{\Gamma_L(i)}{\Gamma_L(i) + \Gamma_K(i)} \]  

(7.4)

where the first factor is the branching ratio for KLL-Auger decay of a configuration containing \( r \) L-electrons and the product is the probability that \( r \)-electrons are present before KLL-Auger decay occurs. From \( P_K(r) \) a subgroup specific probability is calculated by multiplying with the corresponding branching ratio, i.e.

\[ P_{K,\gamma}^\gamma(r) = P_K(r) \frac{\Gamma_L^\gamma(r)}{\Gamma_K(r)} \]  

(7.5)

For \( r \geq 2 \), the mean KLL-Auger rate for initial configurations containing \( r \) electrons \( \Gamma_K(r) \), is calculated as the sum of the subgroup specific KLL Auger rates plotted in Fig. 7b. For \( r < 2 \) this rate is taken to be zero. \( \Gamma_L(r) \) denotes the rate for adding an L-electron when \( r \) electrons are already present. We distinguish two mechanisms filling the projectile L-shell, namely L-Auger processes and direct capture of target electrons. While the former is taken to be velocity independent the latter is taken to be proportional to the number of close collisions with target electrons. Therefore we write

\[ \Gamma_L(r) = \Gamma_L^A(r) + P_L(r) \frac{v}{d} \]  

(7.6)

where \( \Gamma_L^A(r) \) denotes the rate for L-Auger processes and \( d \) is the distance between neighboring target atoms in direction of the projectile velocity \( v \). \( P_L(r) \) denotes the probability of actually transferring an electron from a target atom to the projectile L-shell during a close collision event. It should be noted that, based on the same ansatz by Köhrbrück,\textsuperscript{121} and Page,\textsuperscript{122} Stolterfoht\textsuperscript{123} and Arnau and coworkers\textsuperscript{124} developed a similar “cascading model” in their case for the filling of the L-shell of hollow Ne atoms moving inside an Al target. In their treatments, detailed estimates of the direct capture cross sections are taken in the filling rate of equation 7.6.

Figure 7.8 shows plots of \( P_K^\gamma(r) \) for projectile energies of 150 eV, 8 keV and 60 keV respectively. This figure reveals that for high energies nearly all KLL emission occurs after the L-shell has been filled up to its maximum and mainly involves KL\(_1\)L\(_{2,3}\) and KL\(_{2,3}\)L\(_{2,3}\) combinations. This results in contributions to the high energy side of the spectrum, and, most prominently, to the 383 eV peak (see table II). For low energies a major fraction of the emission is from a 1s 2s\(^2\) 3l\(^4\) state contributing to the low-energy peak at 350 eV. For projectile energies between 150 eV and 60 keV a fraction of 70 up to 80 percent of the KLL emission occurs from the “extreme” configurations with \( r = 2 \) and \( r = 6 \). The emission from the “in
between \( r \) configurations with \( 3 \leq r \leq 5 \) plays a minor role; at all energies used the KLL spectrum mainly consists of a mixture of electrons emitted from configurations with \( r = 2 \) and \( r = 6 \).

In the simulations depicted in figure 7.8, the capture probability \( P_L \) has been taken equal to \((8 - r)/16\), i.e. to at most 1/2 when the L-shell is still empty. Values for the L-Auger filling rate \( \Gamma_L^A(r) \) have been taken from recent work by Diez Muñoz et al.\(^{125}\) who calculated IVV Auger rates for projectiles located inside an electron gas with an Al electronic density. Since under the experimental conditions here, all processes occur very close to the target surface, i.e. at distances at which the electronic density approaches the bulk values, the use of the calculated rates\(^{125}\) is justified. These calculations show a strong, almost exponential increase in IVV rates with decreasing effective charge (i.e. increasing \( r \)), from about \( 5 \times 10^{13}/s \) for \( r = 0 \) to about \( 1.5 \times 10^{15}/s \) for \( r = 5 \). This implies that even for 60 keV projectiles \((v/d \approx 3 \times 10^{15}/s)\), both direct filling and Auger filling play an important role for large \( r \). On the other hand, for small \( r \), \( \Gamma_L(r) \) is mainly given by the second, projectile velocity dependent term in equation 7.6.

The exact nature of the L-shell filling during binary collisions is not well known. An efficient Landau-Zener type of quasi resonant charge transfer between the projectile K-shell and inner target shells during close collisions with target atoms has been reported earlier by Schippers et al.\(^{126}\) A comparable type of transfer between the Al and Si 2p core levels (binding energies 80 eV and 100 eV respectively) and the nitrogen L-levels (ranging in binding energy from about 80 eV for a \( 1s \ 3l^6 \) configuration to about 20 eV for a \( 1s \ 2l^5 \ 3l \) configuration) might be responsible for the direct filling described above. A straightforward application of the mentioned Landau-Zener model results in a decreasing exchange probability with increasing separation of projectile and target levels, i.e. with increasing L-occupancy. Moreover, projectile-target distances at which level crossings occur are smaller than 1 a.u. Our trajectory simulations indicate however that such close collisions are rare for grazingly incident keV projectiles.

Recently, Burgdörfer et al.\(^{127}\) presented simulations of the neutralization and deexcitation of O\(^{++}\) ions in grazing incidence with a Au(110) surface as observed by Folkerts et al.\(^{128}\) Based on a modified version of the "over-barrier" model\(^{111}\) including dynamical screening of the projectile levels by target electrons, a very efficient filling of L-vacancies by quasi-resonant target core electrons is found. The distances at which this type of exchange occurs are in the order of one to few a.u. In our experiments discussed here, this condition is fulfilled for a few (150 eV projectiles) up to tens (16 keV projectiles) of consecutive collisions, as can be inferred from table II and figure 7.6.

However, up to now it is not clear how many electrons are actually
captured during a single binary collision event. In case of high-Z materials like Au there are many core electrons available with binding energies in the order of some 10 eV allowing for capture of several electrons during a single binary collision. This is not the case in Al and Si; the gap between the bottom of the conduction band and the least bound core electrons is 60 eV (Al) and 80 eV (Si) respectively. Therefore, the exchange mechanism proposed by Burgdörfer is less effective in case of these materials.

7.5 Discussion

In the previous sections we have tried to indicate the key factors which determine the overall shape of the KLL Auger spectra obtained from the interaction of hydrogenic nitrogen ions with solid surfaces. In the following we will discuss the features observed in the measured spectra using these general concepts.

The differences between the spectra arising from the Si(100) and the Al(110) target can be explained by two distinct L-shell filling mechanisms, via L-Auger decay and by direct capture of target core electrons. The former process leads to L-shell filling rates in the order of \(10^{15}/s\) up to \(10^{15}/s\) with increasing number of L-electrons \(r\). This implies that for small \(r\), i.e. at an early stage of the deexcitation when the projectile has not yet entered the close collision range, the KLL decay rate is much higher than the L-Auger rate. This gives preferred decay as soon as the second L-electron is present, yielding contributions to the low energy side of the spectrum. The large L-Auger rates only become effective when the projectile moves
into the close collision range at or below the surface. The L-Auger rates are independent of the projectile velocities used in the experiments under consideration here. However, they are dependent on the target specific electronic density as shown in the chapter 4. According to our model described above, the differences in peak intensities at the low energy side of the spectra from Si and Al (figures 7.1 and 7.2) can be ascribed to different LVV filling rates. The electron density at the (p-doped) Si surface is orders of magnitude smaller than in case of the Al target, therefore the associated Si L-Auger rate is smaller than the Al counterpart, yielding a larger \( P_{K}^{r} (r = 2) \) for Si compared to Al.

The second L-shell filling mechanism, direct capture of target core electrons, is localized and therefore dependent on the collision frequency, i.e. on the projectile velocity. As soon as the associated rate is larger than the KLL Auger rate, the L shell is rapidly filled up to its maximum shifting KLL energies to higher values. The L-shell filling probability \( P_{L} (r) \) (see eq.7.6) might vary for different targets. But for large velocities \((v/d \gg \Gamma_{K})\) this variation will not be noticeable since the L-shell is filled up to its maximum before KLL decay occurs anyway. This explains why for large \((16 \text{ keV})\) energies the high energy side of the Si and Al spectra look alike (see figs. 7.1 and 7.2).

The model presented in this chapter allows to estimate the spatial range \( s \) over which the initial potential energy of the projectile is released. According to this model, the largest part of this energy release, by emission of an energetic KLL Auger electron, takes place between the second and the \( n \)-th binary collision in which \( n \) is the number of initial projectile L-shell vacancies. In practice this range is likely to be somewhat larger, depending on the probability \( P_{L} (r) \) of the proposed capture process. Folkerts et al.\(^{128}\) found an upper limit of 25 fs for the deexcitation of \( 60 \text{ keV} \) O\(^{7+}\) on Au(110). Applying the L-filling model on this collision system gives a lower limit to the average probability to capture an L-electron, \( \mathcal{P}_{L} \) as follows: \( 7 \times \mathcal{P}_{L} \times d/v \leq 25 \text{ fs} \Rightarrow \mathcal{P}_{L} \geq 0.1 \) \((d/v \text{ equals the collision frequency mentioned before})\). A similar limit can be found using our data: for 16 keV N\(^{6+}\) at 2.5° incidence about 50 close collisions occur. Assuming complete neutralization (capture of 6-L electrons) afterwards this again gives a lower limit: \( \mathcal{P}_{L} \geq 6/50 = 0.12 \). So the proposed model nicely fits within the experimental boundary conditions.

An interesting test for the model can be found using a properly chosen insulating target in a comparable set of experiments. An insulator has no free electrons, leading to a strong reduction in the LVV filling rate. If properly chosen however, such a target should have a core level structure allowing for direct capture of electrons into the L-shell of the impinging ions. Such an experiment will be discussed in the next chapter.