

Chapter 4

Layer Growth

In this chapter I will present the study of three growth systems involving stepped metal templates, where flat alkali halide (AH) layer growth occurs. As discussed in section 2.2, due to the Smoluchowski effect [Smo41] an enhanced binding between an ionic adlayer and a stepped metal surface can be expected if the charge modulation of the substrate matches with the characteristic spacing of ions in the film. Previous experiments have shown that such a situation is fulfilled for the system NaCl/Cu(311) [RFMR01]. In the present work, it will be verified if this criterion is of general applicability, i.e. if layer growth can be achieved also for different alkali halide deposit/metal substrate combinations. The goal for the selected systems is the creation of perfect, flat, and insulating layers.

The investigated systems are **NaCl/Cu(311)**, **KCl/Cu(311)**, and **NaCl/Cu(221)**. According to the directional anisotropy of the surface free energy of alkali halides [Ben61, Wol92] and the charge modulation of a stepped metal surface, the preferred orientation for the alkali halide film is expected to correspond to a (100)-termination with the polar $\langle 110 \rangle$ in-plane directions parallel and perpendicular to the intrinsic steps of the metal substrate. Consequently, important geometrical quantities of the selected adsorbate/substrate systems are the intrinsic step separation of the template and the distance of equal ions in the polar $\langle 110 \rangle$ in-plane direction. The ratio between $d_{intr. step separ.}$ and $d_{AH\langle 110 \rangle}$ determines the possibility of flat layer growth. For the selected systems the ratios are:

$$\frac{d_{Cu(311),intr. step separ.}}{d_{NaCl\langle 110 \rangle}} = 1.06 \quad \frac{d_{Cu(311),intr. step separ.}}{d_{KCl\langle 110 \rangle}} = 0.95 \quad \frac{d_{Cu(221),intr. step separ.}}{2 \cdot d_{NaCl\langle 110 \rangle}} = 0.96. \quad (4.1)$$

If the adlayer is perfectly pinned by the charge modulation of the substrate, the mismatch between the substrate and the deposit would lead to a tensile strain of 6% for NaCl/Cu(311), a compressive strain of 5% for KCl/Cu(311), and a compressive strain of 4% for NaCl/Cu(221) perpendicular to the intrinsic steps. The investigations in this chapter are therefore also aimed

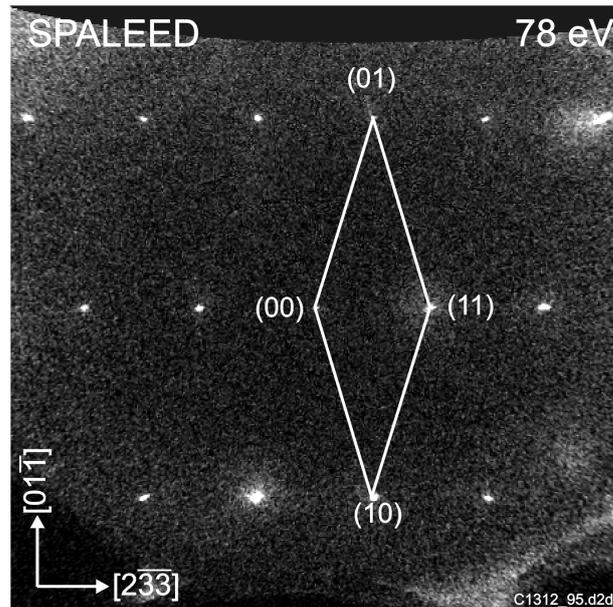


Figure 4.1: LEED pattern of the clean Cu(311) surface taken at 78 eV with the rhombic primitive surface unit cell

at the question, how epitaxial strain in the alkali halide layer is accommodated with increasing film thickness.

The system NaCl on Cu(221) was investigated by SPA-LEED together with supplementary STM studies at submonolayer coverage. The other two systems were studied exclusively by SPA-LEED.

4.1 NaCl on Cu(311)

The Cu(311) surface was prepared according to the procedure described in section 1.3. As a result, a LEED pattern with sharp and bright spots was observed (cf. Figure 4.1). From the half width of the specular spot the average terrace size was estimated to correspond to $\sim 200 \text{ \AA}$ in the $[2\bar{3}\bar{3}]$ direction (i.e. perpendicular to the intrinsic Cu steps) and to $\sim 320 \text{ \AA}$ in the $[01\bar{1}]$ direction (i.e. parallel to the intrinsic steps).

The study of NaCl growth on Cu(311) was carried out by depositing one to three monolayers of NaCl with a rate of 0.6 monolayers per minute at a substrate temperature of 420 K followed by subsequent annealing for ten minutes at this temperature. This procedure was chosen to promote a resulting growth structure close to the thermodynamic equilibrium. The result of the deposition of 1 ML NaCl can be seen in the LEED pattern in Figure 4.2a. The diffraction pattern indicates NaCl layer growth on the Cu(311) template. In Figure 4.2a, the $p(1 \times 1)$ unit

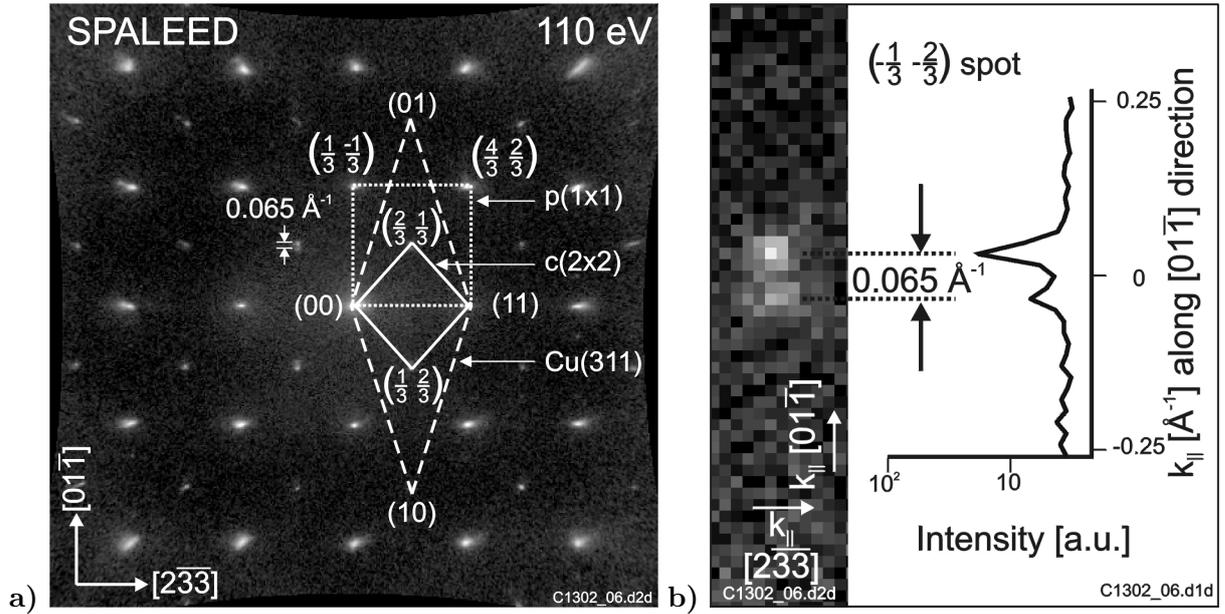


Figure 4.2: LEED pattern and line scan of 1 ML NaCl/Cu(311) deposited at 420 K

- a) diffraction pattern with NaCl(100) bulk-terminated $p(1 \times 1)$ unit cell (dotted line), with the NaCl adlayer-induced $c(2 \times 2)$ unit cell (full line), and with the Cu(311) surface unit cell (dashed line); additional feature: a spot splitting of 0.065 \AA^{-1} in $[01\bar{1}]$ direction, i.e. parallel to the intrinsic steps of the template; the superstructure spots (cf. fractional indices) are indexed with respect to the integral-order spot positions of the Cu(311) substrate
- b) spot at the $(-\frac{1}{3} -\frac{2}{3})$ position taken from diffraction pattern a) with the line scan taken parallel to the intrinsic Cu steps to analyze the spot splitting

cell expected for the bulk termination of NaCl(100) is indicated by the dotted line. The actual situation observed for 1 ML coverage is, however, more complicated: The adlayer induces spots which indicate a superimposed $c(2 \times 2)$ structure whose unit cell is shown by the solid line. Additionally, the Cu(311) unit cell (dashed line) is also drawn into the LEED pattern. Another important feature observed is a spot splitting of 0.065 \AA^{-1} in the $[01\bar{1}]$ direction, i.e. parallel to the intrinsic Cu steps. This splitting is shown in more detail in Figure 4.2b. From the spot splitting a spatial correlation of 97 \AA is derived, whose origin will be explained below.

The essential result from the diffraction data is that NaCl grows in (100) orientation on the Cu(311) surface. The polar $\langle 110 \rangle$ in-plane directions of the adlayer, which span the sides of the $p(1 \times 1)$ unit cell, are parallel and perpendicular to the intrinsic Cu step direction (cf. Figure 4.2a).

In addition to the obtained diffraction data, previous STM results [Rep99, RFMR01] are used in the following to describe the detailed adlayer configuration for one monolayer NaCl. The STM data show that due to the Smoluchowski effect ([Smo41] and section 2.2) the Cl ions

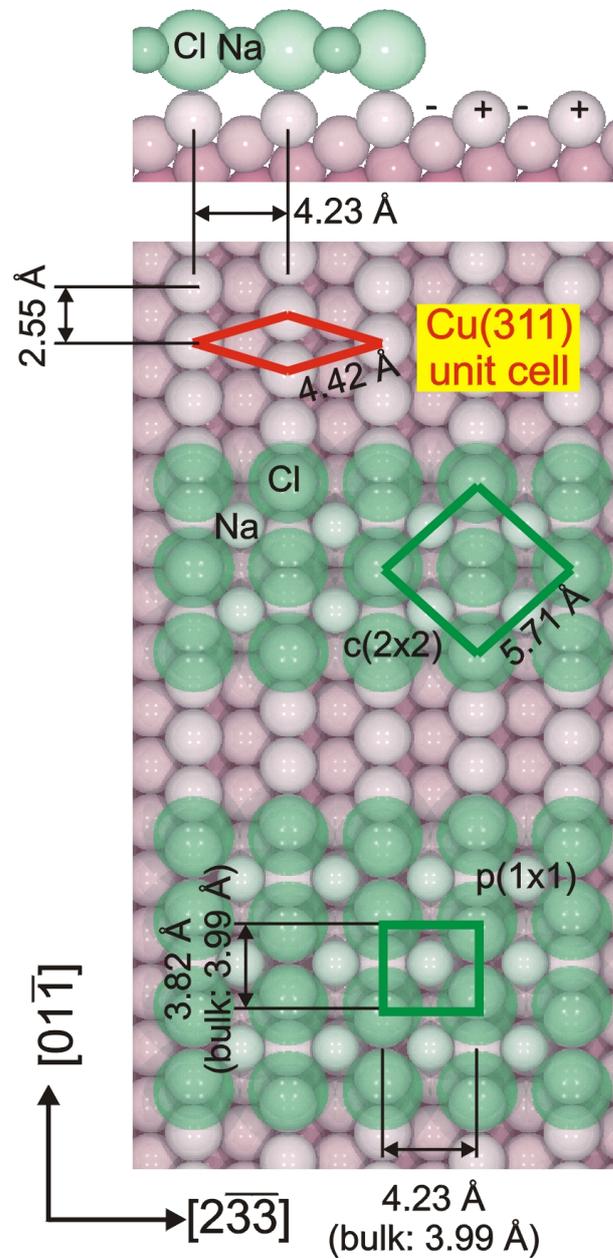


Figure 4.3: Hard-sphere model of NaCl on Cu(311)

top: side view of the Cu(311) surface with indicated charge modulation; the Cl ions are on top of the intrinsic steps

middle: NaCl in $c(2 \times 2)$ configuration with Cl ions in alternating on-top and bridge positions on the close-packed Cu rows

bottom: NaCl in $p(1 \times 1)$ configuration; the Cl ions are shifted by $\frac{1}{4}$ of a Cu-Cu spacing along the intrinsic Cu steps with respect to the $c(2 \times 2)$ structure; consequently, all Cl ions are on equivalent positions with respect to the underlying template

are located on top of the intrinsic steps, whereas the Na ions are located in the troughs. This positioning of the adlayer perpendicular to the intrinsic steps is illustrated in the side view scheme in the top panel of the hard-sphere model in Figure 4.3. The Cl-Cl spacing along the $[2\bar{3}3]$ direction is equal to the step spacing of 4.23 Å.

For the positioning of the Cl ions parallel to the intrinsic steps, two commensurate configurations are possible. The middle and lower part of the hard-sphere model in Figure 4.3 show these configurations of the NaCl adlayer. In the middle of the model, the adlayer is in the $c(2 \times 2)$ configuration, where the Cl ions alternate in on-top and bridge positions with respect to the substrate Cu atoms. The bottom of the figure shows NaCl in $p(1 \times 1)$ configuration. In this case, the Cl ions are shifted by $\frac{1}{4}$ of a Cu-Cu distance with respect to the $c(2 \times 2)$ configuration. As a result, for the $p(1 \times 1)$ structure all Cl ions are in equivalent positions with respect to the underlying template. The diffraction data shown in Figure 4.2a indicate the existence of the $c(2 \times 2)$ configuration and are also consistent with the $p(1 \times 1)$ configuration with the according spots belonging to both configurations. The previous STM data indeed show that both $p(1 \times 1)$ and $c(2 \times 2)$ configurations exist, which occur in a periodic domain structure of alternating configurations along the intrinsic step direction. It was observed that adjacent $c(2 \times 2)$ regions are shifted by half a $c(2 \times 2)$ unit cell along the intrinsic step direction, which corresponds to a shift of half a Cu-Cu distance of the Cl ions with respect to the underlying template. This antiphase domain disorder [Hen77] leads to the spot splitting of 0.065 \AA^{-1} observed in the LEED pattern in Figure 4.2. This corresponds to a periodic length of $L = 97 \text{ \AA}$ in real space, with L as the mean separation of equivalent domains. Regarding the commensurate $c(2 \times 2)$ and $p(1 \times 1)$ configuration shown in the hard-sphere model, the spacing $a_{NaCl,\parallel}$ between two Cl ions along the intrinsic steps would be $3.82 \text{ \AA} = 1.5 \times 2.55 \text{ \AA}$ (Cu-Cu spacing $a_{Cu,\parallel}$). Due to the alternating domain structure with a shift of half a Cu-Cu spacing between adjacent domains, however, the average Cl-Cl spacing is actually $a_{NaCl,\parallel} = 1.5a_{Cu,\parallel} \left[1 \pm \left(\frac{a_{Cu,\parallel}/2}{L} \right) \right]$. For an expansion of the adlayer with respect to the perfectly commensurate structure, the Cl-Cl spacing is determined to 3.88 \AA , whereas a contraction would lead to a Cl-Cl spacing of 3.78 \AA . On the basis of the LEED data, it is not possible to decide whether the film is expanded or contracted with respect to a perfectly commensurate arrangement. However, the state of uniaxial strain perpendicular to the Cu steps and the fact that the layer is obviously free to adjust its lattice constant parallel to the steps may lead to plausible arguments for one or the other case.

The detailed positioning of 1 ML NaCl relative to the Cu(311) substrate can be summarized as follows: Perpendicular to the Cu steps, the Cl ions are localized at the step positions. As a result the Cl-Cl distance along this direction is given by the step spacing of 4.23 Å. Parallel to the steps, on the other hand, the Cl ions are not localized. Along this direction, the Cl-Cl distance adopts a preferred value which is compatible with the uniaxial strain perpendicular to

the steps. The square $p(1 \times 1)$ NaCl unit cell in (100) orientation with a side length according to the bulk value of 3.99 \AA is distorted to a rectangular unit cell with a longer side due to the tensile strain perpendicular to the steps and a shorter side parallel to the intrinsic steps.

Figure 4.4a shows the LEED pattern for a coverage of 3 ML NaCl. As evident, only the $p(1 \times 1)$ overlayer structure indicative for bulk-terminated NaCl(100) prevails at this higher coverage. The corresponding unit cell is shown with the dotted line in Figure 4.4a. The spots connected with the $c(2 \times 2)$ configuration, which is caused by the interfacial adjustment of the NaCl adlayer with respect to the substrate, are not apparent anymore, because the LEED pattern is exclusively determined by the NaCl film for 3 ML. The corresponding gray scale plot in Figure 4.4c shows the intensity $I(k_{\perp}, k_{\parallel})$, where k_{\parallel} is oriented perpendicular to the step direction. It is evident that the modulation of the intensity along the lattice rods corresponds to the NaCl Bragg points. In this figure one can recognize that the lattice rods are split up by 0.14 \AA^{-1} in the direction perpendicular to the intrinsic steps. This spot splitting perpendicular to the intrinsic steps is also observed as a prominent feature of the diffraction pattern in Figure 4.4a (note that for 1 ML coverage the spot splitting was in the direction parallel to the intrinsic steps). The beam profile as shown in detail in Figure 4.4b indicates a spatial correlation of $\frac{2\pi}{\Delta k} = 45 \text{ \AA}$, where $\Delta k = 0.14 \text{ \AA}^{-1}$ is the measured spot splitting. This observation indicates a superimposed periodicity which can be attributed to the formation of a regular Cu defect step structure formed at the film/substrate interface. These monoatomic defect steps are separated by 45 \AA and run parallel to the intrinsic steps. The following consideration shows that such a regular defect step array mediates an effective accommodation of the uniaxial strain in the NaCl film. The defect step periodicity equals the distance of 10 spacings between the intrinsic Cu steps plus the lateral shift connected with a monoatomic defect step in the substrate. The adlayer consists of 11 NaCl units along this direction to match the defect step periodicity in a commensurate manner, which results in an average Cl-Cl spacing of 4.05 \AA close to the bulk value:

$$10 \times 4.23 \text{ \AA} + 2.31 \text{ \AA} \text{ (lateral shift)} = 44.6 \text{ \AA} = 11 \times 4.05 \text{ \AA} \text{ (Cl-Cl bulk spacing: } 3.99 \text{ \AA)}$$

This interfacial matching is illustrated by the hard-sphere model of Figure 4.5. The model illustrates the stepped structure of the Cu(311) surface along the $[\bar{2}\bar{3}\bar{3}]$ direction, i.e. perpendicular to the intrinsic steps. For clarity, only one NaCl monolayer is drawn and only the Cl ions are shown. The model shows that the incorporation of periodic defect steps largely reduces the initial tensile strain while keeping the Cl ions close to the step positions.

To conclude, NaCl is growing in (100) orientation flat on Cu(311). At a coverage of 1 ML NaCl the Cl ions are pinned to the intrinsic steps, whereas they are free to arrange their position parallel to the steps. As a result, there are domains with $p(1 \times 1)$ and $c(2 \times 2)$ configuration,

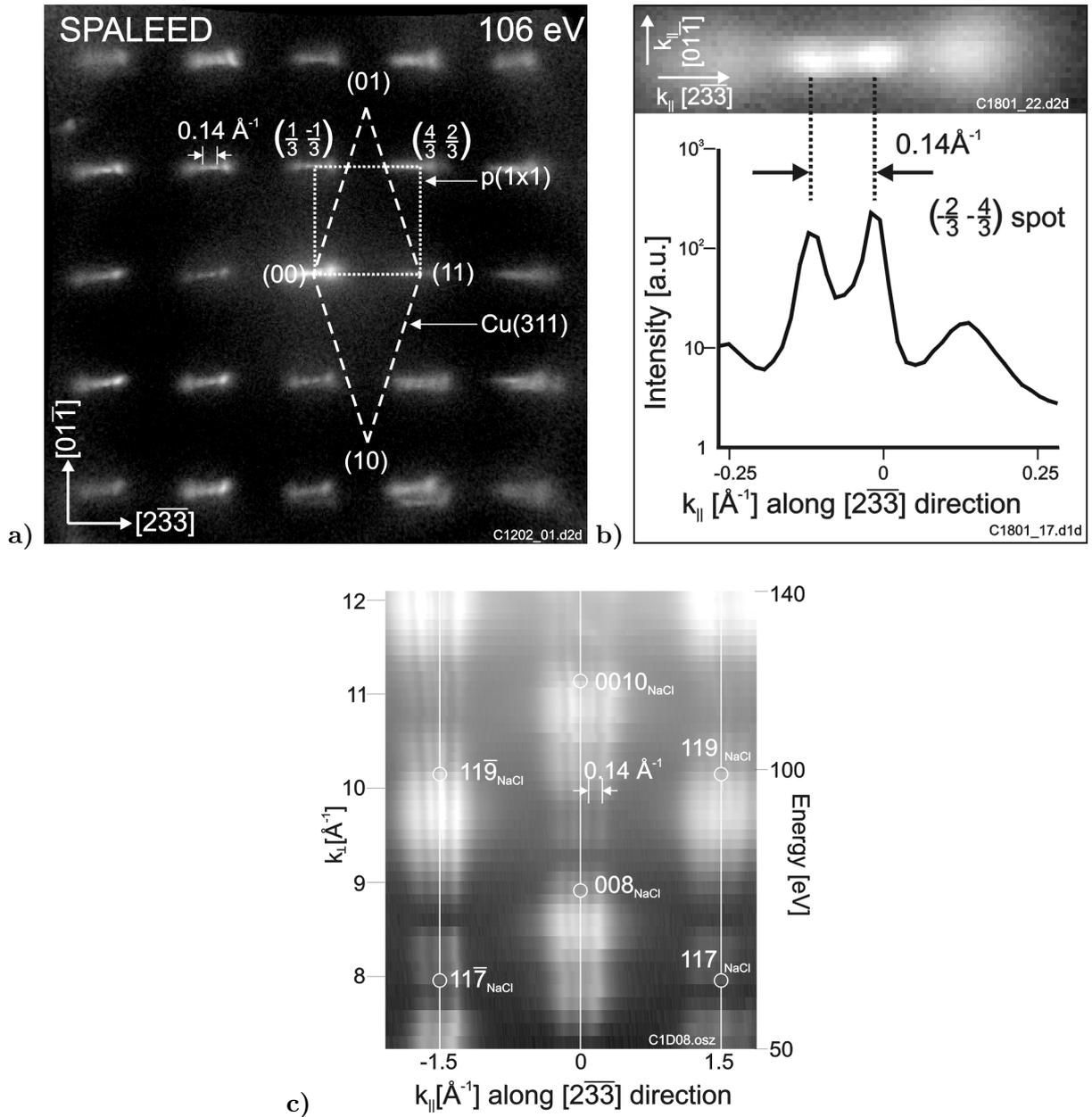


Figure 4.4: LEED pattern, line scan, and gray scale plot of 3 ML NaCl/Cu(311) deposited at 420 K
 a) diffraction pattern with the NaCl(100) bulk-terminated $p(1 \times 1)$ unit cell (dotted line) and with the Cu(311) surface unit cell (dashed line); additional feature: spot splitting of 0.14 \AA^{-1} in $[2\bar{3}3]$ direction, i.e. perpendicular to the intrinsic steps of the template
 b) spot at the $(-\frac{2}{3} - \frac{4}{3})$ position taken from the diffraction pattern in a) with the line scan to emphasize the spot splitting in the direction perpendicular to the intrinsic Cu steps
 c) Gray scale plot $I(k_{\perp}, k_{\parallel})$; the modulation of the intensity along the lattice rods is determined by the NaCl Bragg points; a splitting of the NaCl rods of 0.14 \AA^{-1} is observed along the $[2\bar{3}3]$ direction

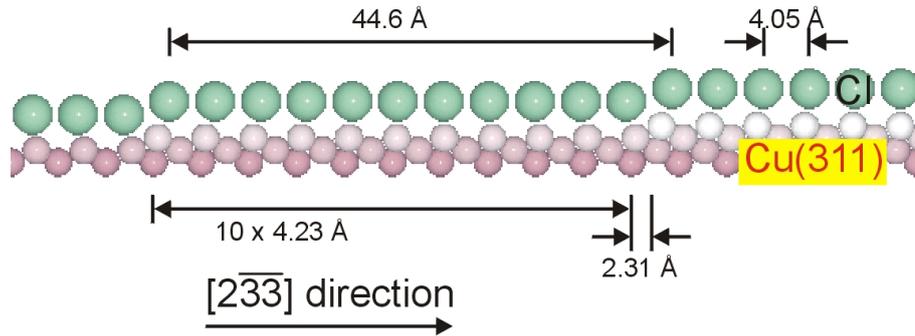


Figure 4.5: Hard-sphere model of NaCl-induced Cu defect steps at the NaCl/Cu(311) interface for simplicity reasons, only 1 ML NaCl is drawn into this graph; only the Cl ions are illustrated in this model, which is developed for the case of 3 ML NaCl/Cu(311); shown is a regular monoatomic defect step structure which is characterized by the incorporation of Cu defect steps after 10 intrinsic step spacings

which alternate along the intrinsic step direction with adjacent domains separated by 97 \AA . This alternation together with a phase shift of the NaCl layer with respect to the underlying Cu template allows the NaCl layer to adjust the Cl-Cl spacing parallel to the intrinsic steps. For 1 ML there is uniaxial strain perpendicular to the intrinsic steps of the template, whereas parallel to the intrinsic steps the preferable Cl-Cl spacing is achieved. The square NaCl surface unit cell is distorted into a rectangular unit cell. For 3 ML NaCl, the initial tensile strain perpendicular to the intrinsic steps of the Cu substrate is reduced by incorporating monoatomic defect steps into the Cu substrate.

4.2 KCl on Cu(311)

The system KCl/Cu(311) was investigated by depositing one to three monolayers of KCl with a rate of 0.25 monolayers per minute at a substrate temperature of 420 K. Also in this case, a subsequent annealing process for ten minutes at this temperature was applied to achieve a growth structure close to thermodynamical equilibrium. The resulting epitaxial overlayer orientation can be inferred from the diffraction patterns in Figures 4.6 (1 ML KCl) and 4.8 (3 ML KCl).

For one monolayer KCl, the diffraction pattern shows a superstructure, whose unit cell is denoted as full line in Figure 4.6a. Additionally, the original Cu(311) primitive unit cell is drawn as the large rhombus (dashed line). In the diffraction pattern a spot splitting of 0.083 \AA^{-1} is observed in the $[01\bar{1}]$ direction, i.e. parallel to the intrinsic steps of the Cu(311) template.

For the interpretation of the adlayer configuration in this system, it is helpful to consider the characteristic features of the system NaCl/Cu(311) discussed in the previous section. Due to

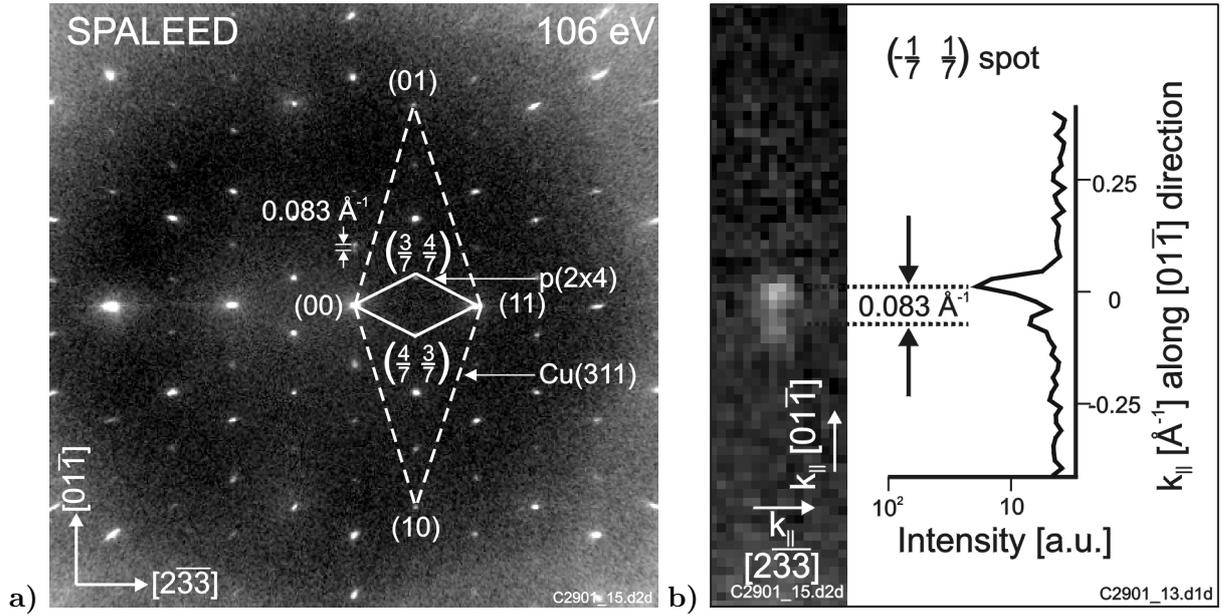


Figure 4.6: LEED pattern and line scan of the $(-\frac{1}{7} \frac{1}{7})$ spot for 1 ML KCl/Cu(311) deposited at 420 K
a) in the diffraction pattern, the Cu(311) unit cell (dashed line) and the KCl superstructure cell (full line) are indicated; a spot splitting of 0.083 \AA^{-1} is observed parallel to the intrinsic Cu steps along the $[01\bar{1}]$ direction
b) line scan of the $(-\frac{1}{7} \frac{1}{7})$ spot parallel to the intrinsic Cu steps to emphasize and quantify the spot splitting of 0.083 \AA^{-1}

the Smoluchowski effect it is suggestive that the Cl ions are located on top of the intrinsic steps, while the K ions are located in the troughs. Hence, the Cl-Cl spacing (4.23 \AA) perpendicular to the intrinsic Cu steps is again identical to the separation of these steps.

The position of the Cl ions in the direction parallel to the intrinsic steps can be determined from the diffraction pattern with the superstructure cell of the adlayer (cf. small rhombus denoted by a full line in Figure 4.6a). This rhombus transforms into a real space unit cell as indicated by the rhombus in the middle of the hard-sphere model in Figure 4.7. This structure may be termed as a $c(2 \times 4)$ structure with respect to the $p(1 \times 1)$ symmetry of bulk-terminated KCl(100). A locally commensurate layer is achieved if four Cl-Cl spacings along the $[01\bar{1}]$ direction match with seven Cu-Cu spacings. The distance between two Cl ions along this direction is determined by $a_{KCl,\parallel} = \frac{1}{4} \cdot 7 \cdot a_{Cu,\parallel}$ and corresponds to 4.47 \AA . Similar to the system NaCl/Cu(311), a spot splitting in the direction parallel to the intrinsic steps is observed, which suggests that a periodic structure with alternating domains along the step direction forms also in the present case. The separation of equivalent domains can be calculated from the spot splitting of 0.083 \AA^{-1} and corresponds to $L=76 \text{ \AA}$. Due to the size of the $c(2 \times 4)$ unit cell the shift between two adjacent

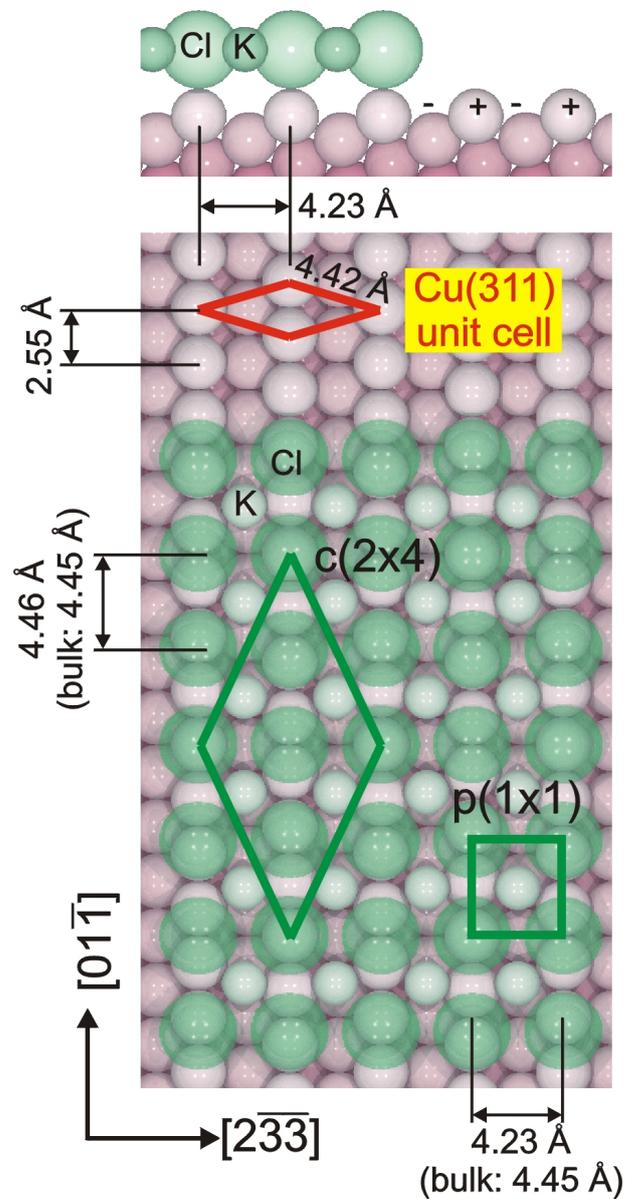


Figure 4.7: Hard-sphere model of the Cu(311) surface with KCl

top: side view of the adlayer configuration with the Cl ions on top of the intrinsic rows and the K ions in the troughs

bottom: locally commensurate KCl configuration with the Cu(311) surface geometry: 4 Cl-Cl spacings match with 7 Cu-Cu spacings along the $[01\bar{1}]$ direction, i.e. along the intrinsic Cu steps; the result is the rhombic $c(2 \times 4)$ cell; for higher coverages, only the intrinsic $p(1 \times 1)$ symmetry of the KCl(100) layer prevails (small square)

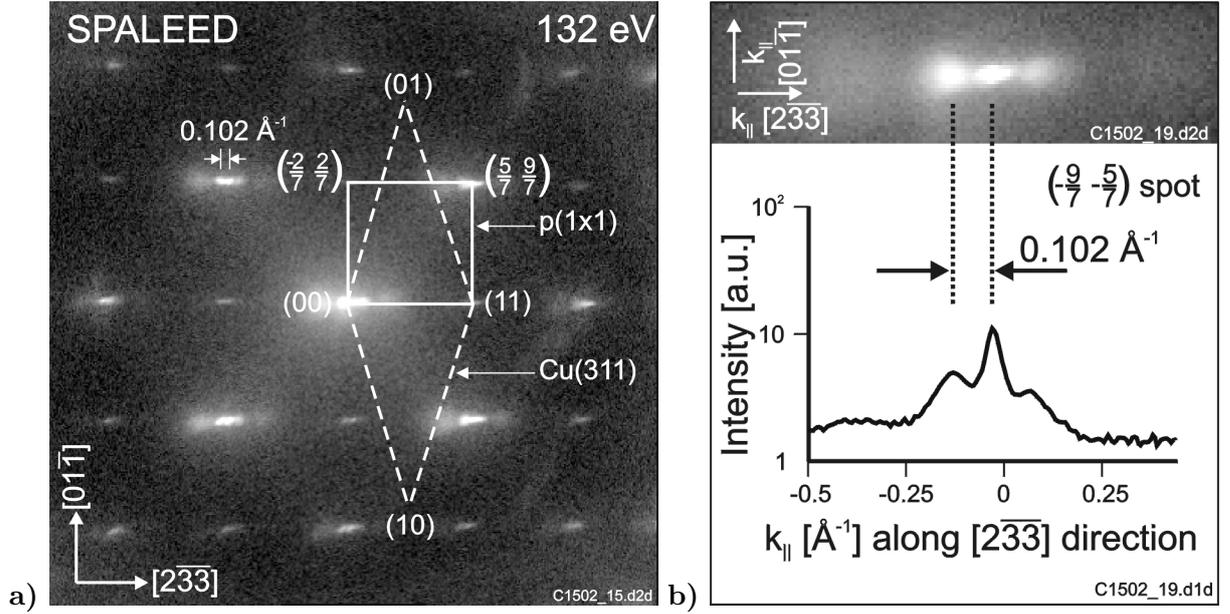


Figure 4.8: LEED pattern and line scan of the $(-\frac{9}{7} - \frac{5}{7})$ spot for 3 ML KCl/Cu(311) deposited at 420 K
a) in the diffraction pattern, the $p(1 \times 1)$ KCl unit cell (full line) as well as the original Cu(311) unit cell (dashed line) are indicated; a spot splitting of 0.102 \AA^{-1} is observed perpendicular to the intrinsic Cu steps in the $[2\bar{3}3]$ direction
b) line scan of the $(-\frac{9}{7} - \frac{5}{7})$ spot perpendicular to the intrinsic Cu steps; spot splitting quantified to 0.102 \AA^{-1}

$c(2 \times 4)$ domains would be $\frac{1}{4}$ of a Cu-Cu spacing and the resulting Cl-Cl spacing would be $a_{KCl, \parallel} = \frac{1}{4} \cdot 7 \cdot a_{Cu, \parallel} \left[1 \pm \left(\frac{a_{Cu, \parallel}}{L} \right)^4 \right]$. An expansion with respect to a perfectly commensurate matching of the adlayer along the steps leads to a Cl-Cl spacing of 4.50 \AA , while a contraction would result in a Cl-Cl spacing of 4.43 \AA . Since the KCl layer is compressed perpendicular to the intrinsic steps (4.23 \AA compared to the bulk value of 4.45 \AA), it is reasonable that the actual Cl-Cl spacing along the steps is larger compared to the bulk equilibrium value and thus corresponds to 4.50 \AA (instead of 4.45 \AA).

For 1 ML KCl, the overall features of the lattice matching between film and substrate are in close correspondence to those found for the system NaCl/Cu(311): Perpendicular to the Cu steps, the Cl ions are pinned by the steps, while the KCl adlayer parallel to the steps is relaxed. The superstructure of the film is described by $c(2 \times 4)$ symmetry in this case. Taking into account that the film is under uniaxial compressive strain perpendicular to the steps, the relaxed Cl-Cl spacing along the steps measures 4.50 \AA .

The LEED pattern for a coverage of 3 ML KCl is shown in Figure 4.8a. Also in this coverage regime, similar structural features are evident from the LEED data compared to those

discussed for NaCl/Cu(311) in the previous section: The $p(1 \times 1)$ diffraction pattern indicates a bulk-terminated KCl(100) film (cf. full line in Figure 4.8a). Also in this case a spot splitting perpendicular to the intrinsic steps of the Cu(311) template develops, which is shown in detail by the line scan in Figure 4.8b. The spot splitting measures 0.102 \AA^{-1} , which corresponds to a periodic correlation of 62 \AA along this direction. This suggests, in analogy to the case of NaCl/Cu(311), the incorporation of a periodic array of Cu defect steps which allows for an optimized interfacial matching. The distance of 62 \AA is represented by 14 spacings between the intrinsic steps plus the lateral shift connected with a monoatomic defect step. The adlayer along this direction consists of 14 KCl unit cells, which results in an average Cl-Cl spacing perpendicular to the intrinsic steps of 4.40 \AA :

$$14 \times 4.23 \text{ \AA} + 2.31 \text{ \AA} \text{ (lateral shift)} = 61.5 \text{ \AA} = 14 \times 4.40 \text{ \AA} \text{ (Cl-Cl bulk spacing: } 4.45 \text{ \AA)}$$

Thus, by incorporating the defect steps into the Cu template, the initial compressive strain perpendicular to the steps is reduced from 5% for 1 ML to $\sim 1\%$ for 3 ML KCl.

4.3 NaCl on Cu(221)

The Cu(221) surface was prepared according to the method described in section 1.3. After several preparation cycles the diffraction pattern in Figure 4.9a was observed. The average terrace width was estimated to be $\sim 70 \text{ \AA}$ along the $[\bar{1}\bar{1}4]$ direction, which is perpendicular to the intrinsic Cu steps, and $\sim 85 \text{ \AA}$ along the $[\bar{1}10]$ direction, i.e. parallel to the intrinsic steps. The STM image in Figure 4.9b shows the Cu(221) sample covered by a submonolayer amount of NaCl. The bright area in the lower center of the image corresponds to a compact monomolecular NaCl island. In the bare Cu area surrounding the NaCl island the corrugation of the intrinsic Cu steps and a considerable atomic roughness of the substrate is observed. The STM image confirms the limited terrace size estimated from the half width of the specular LEED spot.

The investigation of the NaCl growth mode on Cu(221) was performed by depositing one to six monolayers with a rate of 1 monolayer per minute at a substrate temperature of 470 K. The resulting diffraction pattern for 3 ML coverage in Figure 4.9c indicates layer growth on Cu(221) and shows that the adlayer is characterized by a (1×3) superstructure (full line) with respect to the Cu(221) periodicity. With respect to the bulk-terminated $p(1 \times 1)$ symmetry of NaCl, on the other hand, this superstructure can be denoted as a $c(2 \times 2)$ structure (as will be discussed in detail below). As another feature, a spot splitting of 0.15 \AA^{-1} can be observed in the $[\bar{1}10]$ direction, i.e. parallel to the intrinsic Cu steps, as shown in detail in the line scan in Figure 4.9d.

With respect to the orientational properties, the diffraction data show also for this system that the polar $\langle 110 \rangle$ in-plane directions of the NaCl(100) film are parallel and perpendicular to

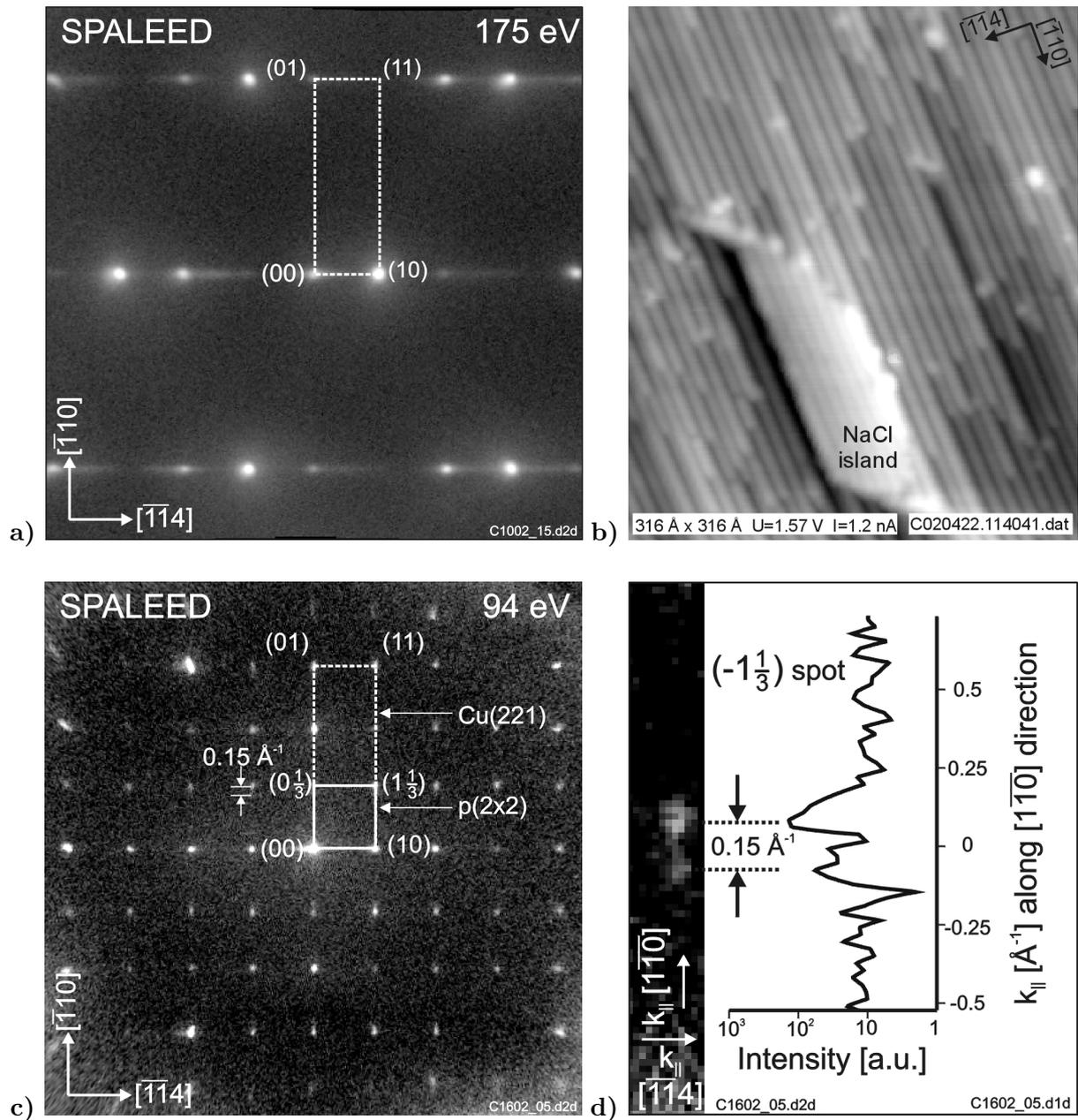


Figure 4.9: a) LEED pattern of the clean Cu(221) surface with the rectangular surface unit cell (dashed line)
 b) STM image of the Cu(221) surface with a small NaCl island in the lower center
 c) LEED pattern for 3 ML NaCl/Cu(221) deposited at 400 K; plotted into the LEED pattern are the NaCl(100) $p(2 \times 2)$ unit cell (full line) and the original Cu(221) unit cell (dashed line)
 d) analysis of the $(-1 \frac{1}{3})$ spot; a line scan taken parallel to the intrinsic steps quantifies the spot splitting to be 0.15 \AA^{-1}

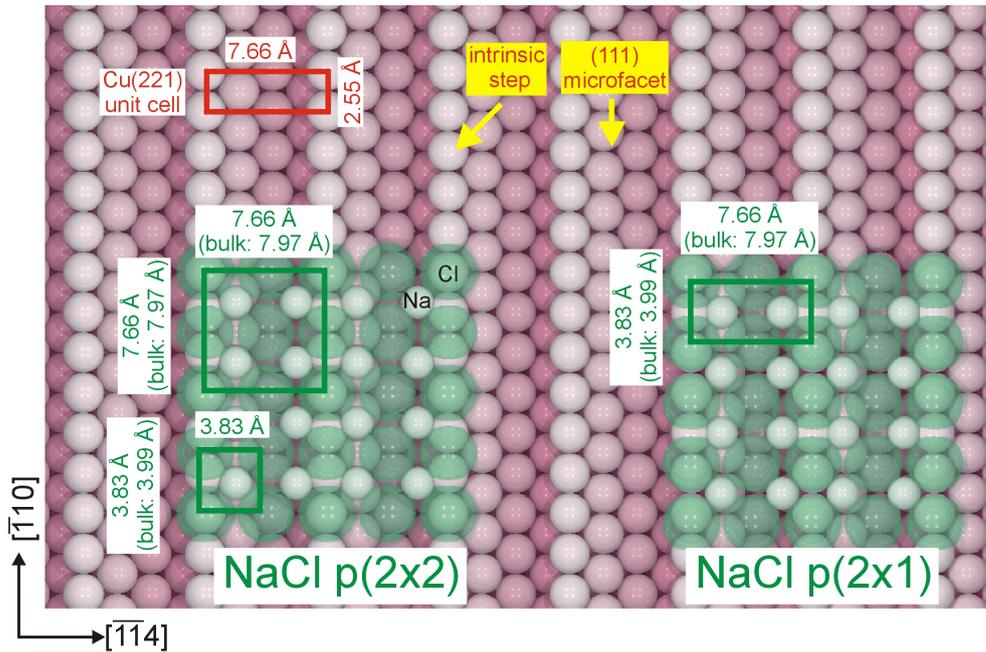


Figure 4.10: Hard-sphere model of the NaCl configuration on Cu(221)

top: primitive unit cell of the Cu(221) surface

left: NaCl in $p(2 \times 2)$ configuration (large square); the Cl ions are located on top of the intrinsic steps and in the middle of the (111) microfacets of the Cu(221) surface in the direction perpendicular to the intrinsic Cu steps; parallel to the intrinsic steps, the Cl ions are alternating in on-top and bridge positions on top of the close-packed Cu rows; small square: primitive NaCl(100) unit cell in $p(1 \times 1)$ configuration

right: NaCl in $p(2 \times 1)$ configuration, which is shifted by $\frac{1}{4}$ of a Cu-Cu spacing parallel to the intrinsic steps with respect to the $p(2 \times 2)$ configuration

the intrinsic steps of the Cu(221) template.

The initial adlayer superstructure evident from Figure 4.9c is observable up to NaCl coverages of ~ 3 ML. The model for the configuration of the NaCl film will be explained for a coverage of one monolayer NaCl as shown in Figure 4.10. The position of the Cl ions (and respectively of the Na ions) in the direction perpendicular to the intrinsic Cu steps can be deduced from the Smoluchowski effect (section 2.2 and [Smo41]) and from the previously investigated systems, NaCl/Cu(311) and KCl/Cu(311). It can be assumed that the Cl ions are located on top of the intrinsic Cu steps and in the center of the (111) microfacets of the Cu(221) surface (see hard-sphere model in Figure 4.10) with a Cl-Cl spacing of 3.83 Å along this direction. The fact that only every second Cl ion row is located on top of the steps obviously leads to an enhanced corrugation of the adlayer in the initial growth stage. Hence, the superstructure indicative for the interfacial arrangement is observable up to 3 ML in this case. In the direction parallel

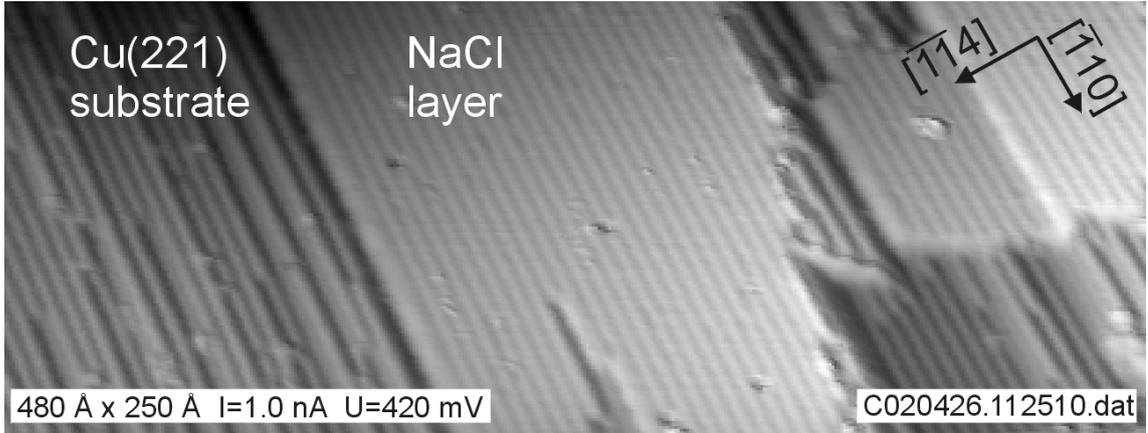


Figure 4.11: STM image of the Cu(221) surface with submonolayer coverage of NaCl
the NaCl film is flattening the former rough Cu(221) template

to the intrinsic steps the Cl ions are free to adjust their interatomic spacing. Two locally commensurate configurations are possible: A $p(2 \times 2)$ configuration, where the Cl ions on top of the steps alternate in on-top and bridge Cu positions. Secondly, a $p(2 \times 1)$ configuration is obtained if the NaCl adlayer is shifted by $\frac{1}{4}$ of a Cu-Cu spacing along the intrinsic Cu steps with respect to the $p(2 \times 2)$ configuration. Both configurations can be seen in the hard-sphere model of Figure 4.10. These domains are alternating along the intrinsic Cu steps to allow for an adjustment of the Cl-Cl spacing, which can be inferred from the observed spot splitting in this direction (cf. Figure 4.9d). This behavior is in analogy to the effect found for the previously investigated systems of NaCl/Cu(311) and KCl/Cu(311). Again, the separation of equivalent domains can be obtained from the spot splitting of 0.15 \AA^{-1} which corresponds to $L=42 \text{ \AA}$ in real space. With the phase shift of half a Cu-Cu spacing between equivalent domains [in analogy to the system NaCl/Cu(311)], the average Cl-Cl spacing can be calculated as $a_{NaCl,\parallel} = 1.5a_{Cu,\parallel} \left[1 \pm \left(\frac{a_{Cu,\parallel}/2}{L} \right)^2 \right]$. If the adlayer is contracted with respect to a perfectly commensurate matching parallel to the steps, a Cl-Cl spacing of 3.71 \AA is obtained. An expansion would lead to a Cl-Cl spacing of 3.94 \AA . Since the layer is under a compressive strain of 4% perpendicular to the steps, it is likely that the relaxed Cl-Cl spacing along the steps corresponds to 3.94 \AA .

To verify these findings, additional STM measurements with submonolayer coverage were carried out. In Figure 4.11 an STM image can be seen with a monomolecular NaCl island in the middle and a bare Cu(221) terrace on the left. It can be observed that the NaCl adlayer is flattening the rough Cu(221) surface. The same effect was found for NaCl/Cu(311) [RFMR01] and can be attributed to a high energetic stability of the interface.

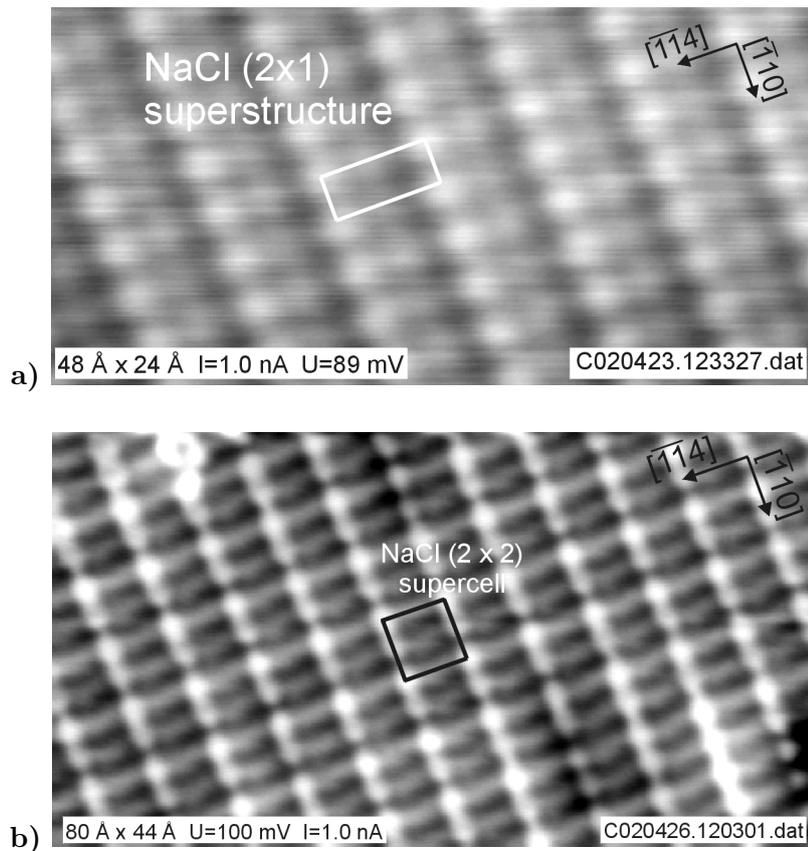


Figure 4.12: Atomically resolved STM images of monomolecular NaCl islands on the Cu(221) surface
 a) NaCl in $p(2 \times 1)$ configuration; mapped are only the Cl ions [HRH⁺99]
 b) NaCl in $p(2 \times 2)$ configuration; unknown adsorbate at the tip apex maps the geometry of the surface, but does not allow to identify the protrusions as one of the species of the NaCl adlayer

Figure 4.12 shows two atomically resolved images of monomolecular NaCl islands. Hebenstreit et al. [HRH⁺99] showed that STM images only one species of the NaCl layer as a protrusions and identified these protrusions as the Cl ions by comparing experimental data with calculations of the local density of states. The two configurations for the NaCl adlayer which are formed on the Cu(221) substrate for coverages up to 3ML, $p(2 \times 1)$ and $p(2 \times 2)$, are apparent from the STM images in Figure 4.12. The upper image shows the Cl ions arranged in the $p(2 \times 1)$ configuration with the Cl ions parallel to the intrinsic Cu steps showing the same corrugation. A modified tip with an unknown adsorbate at the tip apex was used to record the lower STM image. For such a modified tip, it is not clear, which species is imaged as protrusions by the STM. Nonetheless, the surface geometry of the $p(2 \times 2)$ configuration can be verified in this way.

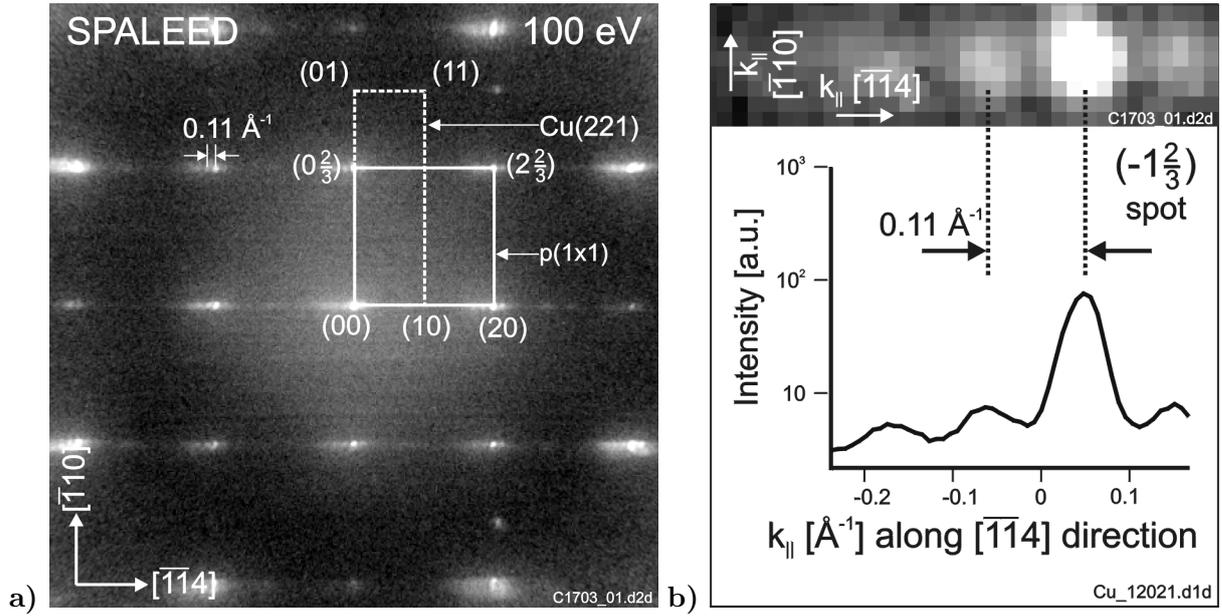


Figure 4.13: LEED pattern and line scan of 6 ML NaCl/Cu(221) deposited at 470 K

- a) LEED pattern with NaCl(100) unit cell in $p(1 \times 1)$ configuration (full line) and with the original Cu(221) unit cell (dashed line)
- b) $(-1 \frac{2}{3})$ spot with respective line scan perpendicular to the intrinsic Cu steps to analyze the spot splitting of 0.11 \AA^{-1}

Figure 4.13a shows the diffraction pattern for 6 ML coverage with diffraction spot positions described by the bulk-terminated NaCl $p(1 \times 1)$ primitive unit cell (full line). A spot splitting of 0.11 \AA^{-1} (cf. line scan in Figure 4.13b) perpendicular to the intrinsic Cu steps occurs (equivalent to a spatial correlation of 57 \AA) which indicates the formation of periodic defect steps also for this system. The separation of these defect steps corresponds to 7 intrinsic step spacings plus the lateral shift of a monoatomic defect step. This separation is matched by 14 NaCl unit cells. The resulting Cl-Cl spacing in the direction perpendicular to the intrinsic Cu steps is 3.98 \AA :

$$7 \times 7.66 \text{ \AA} + 2.13 \text{ \AA} \text{ (lateral shift)} = 55.75 \text{ \AA} = 14 \times 3.98 \text{ \AA} \text{ (Cl-Cl bulk spacing: } 3.99 \text{ \AA)}$$

The NaCl adlayer is almost completely strain-free with respect to the bulk lattice value perpendicular to the intrinsic steps.

To conclude, layer growth is observed for NaCl on Cu(221) with the polar $\langle 110 \rangle$ in-plane directions of the alkali halide parallel and perpendicular to the intrinsic Cu steps. Also for this growth system, the interfacial arrangement is governed by the Smoluchowski effect in the initial stage of growth. Due to the increased Cu step spacing of 7.66 \AA , however, only every second Cl ion row is located on top of the Cu steps. Parallel to the steps, two alternating

domain configurations with $p(2 \times 2)$ and $p(2 \times 1)$ symmetry are formed to allow for an optimal Cl-Cl spacing in this direction. For higher coverages (≥ 3 ML NaCl), the compressive strain perpendicular to the intrinsic steps is reduced by incorporating monoatomic Cu defect steps at the interface.

4.4 Summary for Layer Growth

All three systems investigated in this section, NaCl/Cu(311), KCl/Cu(311), and NaCl/Cu(221), are characterized by layer growth. Common structural features were observed which are summarized in the following:

- The interfacial arrangement is governed by the Smoluchowski effect leading to an alignment of the Cl ion rows along the $\langle 110 \rangle$ in-plane directions parallel and perpendicular to the intrinsic Cu steps.
- This leads to uniaxial strain perpendicular to the Cu steps in the initial stage of growth.
- Parallel to the intrinsic Cu steps, the Cl ions are free to adjust their optimal Cl-Cl spacing leading to antiphase domain disorder along this direction.
- For higher coverages (≥ 3 ML), the strain perpendicular to the intrinsic Cu steps is compensated by the incorporation of monoatomic Cu defect steps at the interface. In this way, the uniaxial strain is accommodated for higher film thickness.